

Titre: Production and Combustion of Syngas in Biomass Polygeneration
Title: Systems

Auteur: Elie Antar
Author:

Date: 2023

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Antar, E. (2023). Production and Combustion of Syngas in Biomass Polygeneration
Citation: Systems [Thèse de doctorat, Polytechnique Montréal]. PolyPublie.
<https://publications.polymtl.ca/55825/>

 **Document en libre accès dans PolyPublie**
Open Access document in PolyPublie

URL de PolyPublie: <https://publications.polymtl.ca/55825/>
PolyPublie URL:

**Directeurs de
recherche:** Étienne Robert
Advisors:

Programme: Génie mécanique
Program:

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Production and Combustion of Syngas in Biomass Polygeneration Systems

ELIE ANTAR

Département de génie mécanique

Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

Génie mécanique

Septembre 2023

POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Cette thèse intitulée :

Production and Combustion of Syngas in Biomass Polygeneration Systems

présentée par **Elie ANTAR**

en vue de l'obtention du diplôme de *Philosophiæ Doctor*
a été dûment acceptée par le jury d'examen constitué de :

Huu Duc VO, président

Étienne ROBERT, membre et directeur de recherche

Mark LEFSRUD, membre

Ömer L. GÜLDER, membre externe

DEDICATION

*To my beloved mother,
I miss you. . .*

ACKNOWLEDGEMENTS

First and foremost, I would like to sincerely thank my advisor Etienne Robert, whose guidance was essential for the success of this PhD project. The generous support I got goes beyond technical resources, as you always insisted on ensuring a formidable working environment where meaningful friendships were forged. I am also very grateful for the esteemed jury member professors Huu Duc Vo, Mark Lefsrud, Omer Gülder, and Alain Rochefort for their time and comments. I would also like to acknowledge the funders of this work: The Trottier Energy Institute, the Natural Sciences and Engineering Research Council of Canada (NSERC), and the Fonds de Recherche du Québec Nature et technologies (FRQNT).

A big THANK YOU also goes to all my colleagues in the LEMUR group, with whom I shared a couple of unforgettable years. I could write long paragraphs on the wonderful memories with each one of you. *Khaye* Cristian Boanta, I benefited a lot from your expertise in the lab, particularly during my first couple of months, which made my integration process much easier. On behalf of many people in the lab, we are very grateful on how generous you were with your help. Same goes to *Don* Pablo Chavez, Tanja Pelzmann, and Olivier Jobin whose humor, discipline and commitment in lab protocols ensured a safe and pleasant working environment for everyone. I would like to also thank all the staff members and technicians from Polytechnique for helping me process endless purchase requests, and Philippe Massé for taking care of all the gas bottles that I needed and for the help in manufacturing processes.

I am also very fond of the support of my friends, who despite the long distances, were always available. Tareq Hijazi (*mmm*), thank you for the deep discussions on FCBarcelona's on and off the field performances. Jean Paul El *Moodir* Skayem, thank you for always getting it *aal tayir* and for the endless philosophical *sugg* sessions. Ralph Donabedian (Georges), your *tarab* recommendations made life much easier, along with *mjaddra* and cabbage salads. To my maternal family, I am forever in debt for your unlimited support and for tolerating my pro-longed absence. Last, but never the least, this wouldn't have been possible without the unconditional love of Antonella. It is impossible to find the right words that can adequately express my gratitude for every single minute I spent with you. I am the luckiest person, *bhebbik*.

RÉSUMÉ

Il semble paradoxal que malgré la biomasse abondante à leur disposition, les serres agricoles dépendent encore fortement des produits à base de combustibles fossiles pour leurs activités énergivores. Pourtant, la biomasse résiduelle présente dans les zones agricoles comme les copeaux de bois ou la paille de blé, ressources qui ne sont pas en concurrence avec les cultures vivrières, est une ressource d'énergie renouvelable neutre en carbone. En plus d'être simplement brûlée, la biomasse peut être convertie par gazéification en produits à valeur ajoutée pour satisfaire les principaux besoins énergétiques des serres et de plusieurs autres tâches énergivores en milieu agricole. Alors que la littérature sur de tels systèmes de conversion se concentre principalement sur les implémentations à grande échelle, les bioraffineries décentralisées à petite échelle qui pourraient être intégrées dans des serres sont rarement discutées. Par conséquent, le premier objectif de cette thèse est de concevoir et d'analyser les performances de nouvelles conceptions de systèmes de biomasse qui pourraient produire du biocarburant, de l'électricité, de la chaleur et un flux de dioxyde de carbone de haute pureté. Ce dernier, en plus d'être nécessaire dans les atmosphères de serre pour améliorer la croissance des cultures, est facilement séquestrable, permettant ainsi la capture et le stockage du carbone.

Des modèles thermodynamiques sont mis en œuvre en utilisant le simulateur ASPEN Plus pour concevoir quatre nouveaux systèmes de polygénération, qui diffèrent soit par le type de gazéifieur utilisé, soit par le biocarburant synthétisé. Pour ces derniers, le méthanol et le gaz naturel renouvelable sont considérés. Ces biocarburants peuvent être utilisés pour alimenter des machines dans ou autour des serres, et les quantités excédentaires peuvent être vendues par les agriculteurs, fournissant une nouvelle source de revenus. Des piles à combustible réversibles à oxyde solide sont également incorporées dans les systèmes. Ces composants polyvalents peuvent produire de l'électricité de manière efficace et propre lorsqu'ils sont alimentés en gaz de synthèse dérivé de la biomasse, et produisent H_2 et O_2 par l'électrolyse de la vapeur d'eau lorsqu'ils sont alimentés avec une partie de l'électricité générée. Ce H_2 est essentiel pour conditionner le gaz de synthèse avant le réacteur de biocarburant, tandis que le O_2 pur est utilisé dans le gazéifieur pour générer un gaz de synthèse sans N_2 . Les conditions de fonctionnement favorables sont identifiées par une analyse paramétrique, qui a montré que l'efficacité globale du processus de polygénération pourrait atteindre 85%.

Un élément clé pour atteindre ces rendements élevés est le brûleur de gaz de synthèse, qui exploite l'énergie du gaz résiduel après les étapes de production de biocarburant et d'électricité,

et produit de la chaleur qui est localement demandée en grande quantité par les serres. L'énergie chimique du gaz de synthèse restant pourrait atteindre 35% de l'énergie initiale de la biomasse. Cependant, notre modèle révèle également que la concentration d'espèces inertes (CO_2 et H_2O) dans le gaz de synthèse est importante, variant entre 72 et 90%, ce qui augmente considérablement la propension à la formation d'instabilités diffusive-thermiques (DTIs) et le risque d'extinction. Les DTIs ont été fréquemment étudiés dans la littérature, à la fois théoriquement et expérimentalement, où deux principaux modes d'instabilité ont été identifiés. Les instabilités cellulaires sont connues pour apparaître dans les flammes avec de faibles rapports entre la diffusivité thermique et la diffusivité moléculaire (nombre de Lewis < 1), provoquant une combustion incomplète et la formation de polluants. Lorsque le nombre de Lewis est supérieur à un, les flammes peuvent présenter des pulsations dans leur taux de réaction chimique, pouvant complètement éteindre la flamme. Cependant, ces modes d'instabilité ont été observés en utilisant des carburants à une seule espèce combustible tels que H_2 ou CH_4 , avec le mécanisme sous-jacent des DTI dans des mélanges multi-carburants tels que le gaz de synthèse (H_2 , CO et CO_2) restant inconnus.

Le brûleur à diffusion unidimensionnelle et sans étirement offre des flammes idéales pour les études fondamentales sur les limites d'inflammabilité et les DTI. En effet, les effets hydrodynamiques parasites omniprésents dans les brûleurs courants sont essentiellement éliminés. Cependant, même la version la plus avancée de ce brûleur unique ne peut pas fonctionner avec des combustibles à haute teneur en eau tels que le gaz de synthèse. Par conséquent, pour le deuxième objectif de cette thèse, une nouvelle version du brûleur à diffusion unidimensionnelle qui peut fonctionner avec une forte teneur en eau est construite. Le brûleur à contre-diffusion adopte un bouchon poreux en aluminium uniformément chauffé, pour fournir les espèces combustibles humides au fond de la chambre de combustion. Le comburant est alimenté par le haut via un réseau d'aiguilles fines, et contre-diffuse vers la flamme contre les produits qui sont évacués par un autre jeu d'aiguilles entrelacées. En conséquence, contrairement à la configuration classique de flamme de diffusion à contre-courant, dont les flammes planes présentent un écoulement radial contraint, le transport des espèces dans notre brûleur est essentiellement unidimensionnel. Ceci est confirmé en mesurant les principaux profils de concentration des espèces et l'emplacement de la flamme, qui sont en accord avec la solution idéalisée de la flamme de diffusion unidimensionnelle.

Par conséquent, les capacités de la nouvelle installation de recherche sont exploitées dans le troisième et dernier objectif de cette thèse, où les DTIs des mélanges de H_2 - CO - CH_4 diluées avec CO_2 - H_2O sont étudiés. La stabilité des flammes et les limites d'extinction sont présentées pour une large gamme de mélanges. Des expériences systématiques sont menées à partir d'une flamme stable près de la limite Burke-Schumann de combustion intense, après quoi le

nombre de Damköhler est progressivement réduit en passant par l'état de stabilité marginal où les DTI apparaissent pour la première fois et jusqu'à la limite d'extinction. Une dynamique de flamme instable particulière est observée. La présence simultanée de H_2 avec une mobilité élevée et de CO/CH_4 avec une diffusivité beaucoup plus faible conduit à la formation d'instabilités pulsatoires cellulaires superposées. De telles observations sur des flammes de diffusion multi-combustibles sont rapportées pour la première fois dans cette thèse, fournissant des données de référence. Les instabilités sont caractérisées en mesurant le nombre et la taille des cellules, ainsi que l'amplitude et la fréquence des pulsations. La physique sous-jacente est révélée en mettant en évidence la mise à l'échelle entre les caractéristiques des instabilités avec des paramètres de combustion fondamentaux tels que le rapport de mélange, les nombres de Lewis du combustible et du comburant et le nombre de Damköhler.

ABSTRACT

It is paradoxical to realize that despite having abundant biomass at their disposal, agricultural greenhouses are still heavily relying on fossil fuel-based products for their energy-intensive activities. Residual biomass found in agricultural areas such as wood chips or wheat straw, resources that do not compete with food crops, is a carbon-neutral and renewable energy resource. Moreover, in addition to simply being burned, biomass can be converted via gasification into value-added products to satisfy the main energy demands of greenhouses and of several other energy-intensive tasks in agricultural settings. While the main focus in the literature for such conversion systems is large-scale implementations, decentralized small-scale biorefineries that could be integrated in greenhouses are rarely discussed. Therefore, the first objective of this thesis is to design and analyze the performance of novel biomass system designs that could produce biofuel, electricity, heat, and a high-purity carbon dioxide stream. The latter is needed within the greenhouse atmospheres to enhance crop growth, with surplus amounts being readily sequesterable to enable carbon capture and storage.

Thermodynamic models are implemented on the ASPEN Plus process simulator to design four novel polygeneration systems, which either differ in the type of gasifier used or biofuel synthesized. For the latter, methanol and synthetic natural gas are considered. These biofuels can be used to power machinery in or around greenhouse facilities, and the excess amounts can be sold by farmers, providing a new revenue stream. Reversible solid-oxide fuel cells are also incorporated in the systems. These versatile components can produce electricity in an efficient and environmentally friendly manner when supplied with biomass-derived syngas, and produce H_2 and O_2 via steam electrolysis when fed with part of the generated electricity. This H_2 is key for conditioning the syngas before the biofuel reactor, while the pure O_2 is used in the gasifier to generate an energy-dense N_2 -free syngas stream. The favorable operating conditions are identified through parametric analysis, where it is revealed that the overall polygeneration process efficiency could reach 85%.

A key component in attaining such high efficiencies is the syngas burner, which harnesses the energy of the residual gas following the biofuel and electricity production stages, and produces heat that is locally demanded in large quantities by greenhouses. The chemical energy of the leftover syngas could reach 35% of the initial biomass energy. However, our model also reveals that the concentration of inert species (CO_2 and H_2O) in syngas is significant, varying between 72 and 90%, which dramatically increases the propensity of diffusive-thermal instabilities (DTIs) forming and the risk of extinction. DTIs have been frequently investigated

in the literature, both theoretically and experimentally, whereby two main instability modes have been identified. Cellular instabilities are known to onset in flames with low thermal over molecular diffusivity ratios (Lewis number < 1), causing incomplete combustion and pollutant formation. At large Lewis numbers, flames could exhibit pulsations in their chemical reaction rate, which often lead to complete extinction. These instability modes however, were observed using single-species fuel such as H_2 or CH_4 , with the underlying mechanism of DTIs in multi-fuel mixtures such as syngas (H_2 , CO , and CH_4) remaining unknown.

The one-dimensional unstrained diffusion flame burner provides ideal conditions for fundamental studies on DTIs and flammability limits. This is because parasitic hydrodynamic effects that are omnipresent in common burners are essentially eliminated. However, even the most advanced version of this unique burner cannot be operated with fuels containing high water content such as syngas. Therefore, for the second objective of this thesis, a new version of the one-dimensional diffusion flame burner that can be operated with high water content was successfully built. The counter-diffusion burner adopts an evenly heated aluminum porous plug, to uniformly supply the humid fuel species into the bottom of the combustion chamber. The oxidizer is supplied from the top via a thin needles array, and counter-diffuses towards the flame sheet against the products, which are evacuated from the top by another set of interlaced needles array. As a result, unlike the classic counterflow diffusion flame configuration, whose planar flames exhibit strained radial flow, the species transport in our burner is essentially one-dimensional and unstrained. This is confirmed by measuring the major species concentration profiles and flame location, which are in agreement with the one-dimensional chambered diffusion flame solution.

Consequently, the capabilities of the new research facility are exploited in the third and final objective of this thesis, where DTIs in $\text{H}_2\text{-CO-CH}_4\text{-CO}_2\text{-H}_2\text{O}$ mixtures are investigated. Flame stability and extinction limits are presented for a broad range of blends. Systematic experiments are conducted starting from a stable flame near the Burke–Schumann limit of intense combustion, after which the Damköhler number is gradually reduced going through the marginal stability state where DTIs first onset and down to the extinction limit. Peculiar unstable flame dynamics are observed. The simultaneous presence of H_2 with high mobility, and CO/CH_4 with much lower diffusivity leads to the formation of superimposed cellular-pulsating instabilities. Such observations on unstrained multi-fuel diffusion flames are reported for the first time in this thesis, providing benchmark data. The instabilities are characterized by measuring the number and size of the cells, along with the amplitude and frequency of pulsations. The underlying physics is revealed by highlighting the scaling between the characteristics of the instabilities with fundamental combustion parameters such as the mixture strength, fuel and oxidizer Lewis numbers, and the Damköhler number.

TABLE OF CONTENTS

DEDICATION	iii
ACKNOWLEDGEMENTS	iv
RÉSUMÉ	v
ABSTRACT	viii
TABLE OF CONTENTS	x
LIST OF TABLES	xiv
LIST OF FIGURES	xv
LIST OF SYMBOLS AND ACRONYMS	xx
LIST OF APPENDICES	xxii
CHAPTER 1 INTRODUCTION	1
1.1 Biomass	1
1.2 Polygeneration systems	2
1.3 Combustion	3
1.4 Flame instabilities	7
1.5 Scope and thesis outline	10
CHAPTER 2 LITERATURE REVIEW	12
2.1 Modelling of biomass polygeneration systems	12
2.1.1 Synthetic natural gas systems	14
2.1.2 Methanol systems	17
2.1.3 Carbon dioxide capture systems	19
2.2 Diffusive-thermal flame instabilities	23
2.2.1 Experimental studies	28
2.2.2 Theoretical studies	31
2.2.3 Unstrained diffusion flame burner	36
2.3 Syngas diffusion flames	41
2.3.1 Opposed-jet flames	41

2.3.2	Coflow flames	43
CHAPTER 3 RESEARCH OBJECTIVES		45
3.1	Critical assessment of the literature	45
3.1.1	Modelling of polygeneration systems	45
3.1.2	Diffusive-thermal instabilities	46
3.2	Specific objectives	46
3.3	Articles outline	47
CHAPTER 4 ARTICLE 1: THERMODYNAMIC ANALYSIS OF NOVEL METHANOL POLYGENERATION SYSTEMS FOR GREENHOUSES		48
4.1	Introduction	48
4.2	Methodology	50
4.2.1	General design choices	50
4.2.2	Downdraft gasifier-based system	52
4.2.3	Dual fluidized bed gasifier-based system	53
4.2.4	Thermodynamic modelling	54
4.3	Results	57
4.3.1	Downdraft gasifier-based system	58
4.3.2	Dual fluidized bed gasifier-based system	61
4.4	System comparison and discussion	65
4.5	Conclusion	67
CHAPTER 5 ARTICLE 2: THERMODYNAMIC ANALYSIS OF SMALL-SCALE POLYGENERATION SYSTEMS PRODUCING NATURAL GAS, ELECTRIC- ITY, HEAT, AND CARBON DIOXIDE FROM BIOMASS		69
5.1	Introduction	69
5.2	System description	71
5.2.1	Drying and gasification	72
5.2.2	Syngas cleaning	73
5.2.3	Electricity production	74
5.2.4	Methantion	75
5.2.5	Heat and carbon dioxide generation	76
5.2.6	Modelling and operating conditions	76
5.3	Results	77
5.3.1	Dual fluidized bed gasifier-based SNG system	77
5.3.2	Downdraft gasifier-based SNG system	83

5.3.3	System comparison and discussion	88
5.4	Conclusion	90
CHAPTER 6 ARTICLE 3: EXPERIMENTAL CHARACTERIZATION OF DIFFUSIVE-THERMAL INSTABILITIES IN CO ₂ -DILUTED H ₂ -CH ₄ -CO UNSTRAINED DIFFUSION FLAMES		
		92
6.1	Introduction	92
6.2	Methodology	95
6.2.1	Experimental facility	95
6.2.2	Diagnostics	96
6.2.3	Parameters of interest	99
6.3	Results	101
6.3.1	H ₂ -CO ₂ mixtures	101
6.3.2	CH ₄ -CO-CO ₂ mixtures	104
6.3.3	H ₂ -CO-CO ₂ mixtures	105
6.3.4	H ₂ -CO-CH ₄ -CO ₂ mixtures	113
6.4	Conclusion	116
CHAPTER 7 ARTICLE 4: DIFFUSIVE-THERMAL INSTABILITIES IN UNSTRAINED H ₂ O-DILUTED SYNGAS DIFFUSION FLAMES		
		118
7.1	Introduction	118
7.2	Unstrained diffusion flame burner	121
7.2.1	Mark III design	121
7.2.2	Burner characterization - stable flames	123
7.2.3	Burner characterization - stability and extinction limits	125
7.3	Diffusive-thermal instabilities	128
7.3.1	Effect of H ₂ O dilution on the instability type	128
7.3.2	Effect of H ₂ O dilution on the instability size	138
7.4	Conclusion	141
CHAPTER 8 GENERAL DISCUSSION		
		144
8.1	Thermodynamic polygeneration efficiency	144
8.2	Syngas properties	145
8.3	Characterization of diffusive-thermal instabilities	146
8.4	General impact	150
CHAPTER 9 CONCLUSION AND RECOMMENDATIONS		
		151

9.1	Summary	151
9.2	Limitations and recommendations for future work	152
9.2.1	Biomass polygeneration systems	152
9.2.2	Diffusive-thermal instabilities	154
REFERENCES		156
APPENDICES		184

LIST OF TABLES

Table 4.1	Characteristics of wood chips	51
Table 4.2	Different operating conditions of the downdraft gasifier-based system with a MeOH reactor pressure of 30 bar.	66
Table 4.3	Different operating conditions of the DFB gasifier-based system with a MeOH reactor pressure of 30 bar.	68
Table 5.1	Summary of the Aspen Plus models used for each component in the systems.	78
Table 5.2	Description of the different H ₂ recycling modes adopted in this study .	82
Table 6.1	Parameters of the observed pulsating CH ₄ -CO-CO ₂ flames	106
Table 8.1	Properties of the burned syngas as is from the SOFC.	147

LIST OF FIGURES

Figure 1.1	Envisioned decentralized polygeneration system in agricultural green-houses	4
Figure 1.2	Structure of a one-dimensional adiabatic a) premixed and b) purely-diffusive non-premixed flame.	6
Figure 1.3	Mechanisms of cellular and pulsation instabilities in premixed flames. .	8
Figure 1.4	Cellular Bunsen burner butane-air flame	9
Figure 1.5	Pulsating propane-nitrogen jet flame.	10
Figure 2.1	Examples of the different technologies that could be used in each stage of the biomass gasification process.	13
Figure 2.2	Two operating modes of reversible solid oxide cells	16
Figure 2.3	The concept of chemical looping combustion and allothermal dual-fluidized bed gasification.	21
Figure 2.4	Mechanism of the hydrodynamic (Darrieus-Landau) instability.	24
Figure 2.5	Hydrodynamically unstable premixed flame front with suppressed and superimposed DTIs.	25
Figure 2.6	Typical S-shape response curve of diffusion flames	26
Figure 2.7	Mechanistic illustration of a) cellular and b) pulsating instabilities in diffusion flames.	27
Figure 2.8	Schematic representation of the a) Wolfhard–Parker, b) counterflow tubular, and c) opposed-jet counterflow burners.	29
Figure 2.9	Schematic representation of the idealized one-dimensional chambered diffusion flame theoretical construct.	32
Figure 2.10	Map illustrating the various types of instabilities in terms of the fuel and oxidizer Lewis numbers.	35
Figure 2.11	Schematic representations of a) the mark I version of the one-dimensional unstrained diffusion flame burner, b) injection layer, and c) mark II burner design with the extraction needles.	37
Figure 2.12	Stable and cellular flames generated in the mark I and II versions of the unstrained diffusion flame burner.	38
Figure 2.13	Comparison between experimental measurements of H_2 flames ($X_F = 0.35$, $U \approx 20$ mm/s) in the mark II burner and the analytical one-dimensional diffusion flame solution.	40

Figure 4.1	Simplified schematic representation of the downdraft gasifier-based system	53
Figure 4.2	Simplified schematic representation of the DFB gasifier-based system .	54
Figure 4.3	Aspen Plus model of the SOFC. The solid and dashed lines represent material and heat streams, respectively.	57
Figure 4.4	Sankey diagram of the downdraft gasifier-based system	59
Figure 4.5	Variation of the downdraft gasifier-based system efficiencies with a) H_2 recycling fraction at $ER = 0.2$ and b) ER at full H_2 recycling.	60
Figure 4.6	Efficiency of the downdraft gasifier-based system with ER at different MeOH reactor pressures.	61
Figure 4.7	Sankey diagram of the DFB gasifier-based system	63
Figure 4.8	Variation of the DFB gasifier-based system performance as a function of the ratio of the actual over the baseline recycled H_2 flow from the SOEC.	64
Figure 4.9	Variation of the DFB gasifier-based system performance as a function of the unreacted syngas sent to the SOFC.	65
Figure 4.10	Effect of changing the MeOH reactor pressure. The lines with markers represent full depletion of electricity to maximize H_2 enrichment. . . .	66
Figure 4.11	Performances of the downdraft gasifier-based system and the DFB gasifier-based system under different conditions.	67
Figure 5.1	Schematic representation of the dual fluidized bed gasifier-based SNG system	73
Figure 5.2	Schematic representation of the downdraft gasifier-based SNG system .	74
Figure 5.3	Sankey diagram of the dual fluidized bed gasifier-based SNG system. .	79
Figure 5.4	Variation in the output of the dual fluidized bed gasifier-based SNG system as a function of the fraction of syngas sent to the methanation reactor.	81
Figure 5.5	Change in output when electricity from an external source is supplied to the system operating under mode 3.	83
Figure 5.6	Efficiencies at different CO_2 generation rates.	84
Figure 5.7	Sankey diagram of the downdraft gasifier-based SNG system.	85
Figure 5.8	Variation in the output of the downdraft gasifier-based SNG system as a function of the fraction of syngas sent to the methanation reactor. .	86
Figure 5.9	Changes in efficiencies when electricity from an external source is injected into the downdraft gasifier-based system (—) and the DFB gasifier-based configuration (— — —) both operating in mode 3.	87

Figure 5.10	Variation in efficiencies as a function of the quantity of CO_2 produced by the downdraft gasifier-based system, when no H_2 enrichment is adopted (mode 0).	88
Figure 5.11	Comparison of the proposed SNG systems with MeOH-based polygeneration systems.	89
Figure 6.1	Schematic representation of the experimental facility used to create one-dimensional unstrained diffusion flames.	95
Figure 6.2	Flame structure from the idealized one-dimensional diffusion flame model, and experimentally measured light intensity signal.	97
Figure 6.3	Temporal variation of flame position, and maximum light intensity emitted for two pulsating $\text{CH}_4\text{-CO}$ flames.	98
Figure 6.4	H_2 flames with travelling waves, partly cellular flame, and fully cellular flame	99
Figure 6.5	Flame stability limits in terms of the fuel concentration and mixture strength for $\text{H}_2\text{-CO}_2$ mixtures.	102
Figure 6.6	Stability map showing the Lewis numbers of the three fuel species and oxygen, as well as the effective Lewis number of the fuel mixture for the different flames studied in this paper.	103
Figure 6.7	Top branch of the S-shaped response curve for the $\text{H}_2\text{-CO}_2$ flames. . .	104
Figure 6.8	Measured cell size as a function of diffusion length for fully cellular $\text{H}_2\text{-CO}_2$ flames	105
Figure 6.9	Non-dimensional pulsations frequency as a function of Damköhler number for unstable $\text{CH}_4\text{-CO}$ mixtures.	107
Figure 6.10	Flame stability limits for different $\text{H}_2\text{-CO}$ binary fuels with no CH_4 . . .	108
Figure 6.11	Oblique and side views showing the instability cycle of a pulsation-induced cellular flame at $X_F = 22\%$, $\phi = 0.46$, $X_{\text{H}_2,\text{CO}} = 75\%$, and $X_{\text{CH}_4} = 0\%$	109
Figure 6.12	Cell size measured at the lowest intensity point of the pulsation cycle for the fully cellular multi-fuel flames.	110
Figure 6.13	Variation in the amplitude and frequency of the superimposed cellular-pulsations instabilities with Damköhler number.	111
Figure 6.14	Light intensity emitted from pulsating cells at different Damköhler numbers in 75-25% $\text{H}_2\text{-CO}$ mixtures.	112
Figure 6.15	Effect of CH_4 addition on the flame stability limits at $X_{\text{H}_2,\text{CO}} = 75\%$. . .	114

Figure 6.16	Qualitative illustration of the instabilities that onset in unstrained syngas diffusion flames with various fuel mixture Lewis numbers and $Le_o \approx 0.97$	115
Figure 6.17	Flammability limits for different syngas compositions.	116
Figure 7.1	The idealized one-dimensional chambered diffusion flame theoretical construct	120
Figure 7.2	Schematic representation of the mark III unstrained diffusion flame burner.	122
Figure 7.3	Temperature of the fuel injection block holes, and temporal variation of the gasses volume fraction within the mixing chamber.	124
Figure 7.4	Structure of a H_2 flame diluted with 70% CO_2 at $\phi = 0.5$ and $U = 7.6$ mm/s.	125
Figure 7.5	Comparison between experimental and modelled flame positions under different conditions.	126
Figure 7.6	Flame stability and extinction limits as a function of the water dilution fraction for different fuel blends.	127
Figure 7.7	Flame instability patterns of single-fuel H_2 , CO and CH_4 mixtures diluted in H_2O and CO_2	129
Figure 7.8	Travelling waves, partly cellular, and fully cellular H_2 flames at $\phi \approx 0.4$	130
Figure 7.9	Effective fuel blend and oxidizer Lewis numbers for the unstable flames generated in our burner.	131
Figure 7.10	Illustration of the typical planar intensity pulsations for CO and CH_4 .	132
Figure 7.11	Variation in the instability patterns with H_2O fraction relative to CO_2 at different Damköhler numbers for 75-25% H_2 - CO	133
Figure 7.12	Effect of the H_2O dilution fraction on the pulsation-induced instabilities at 75-25% H_2 - CO	134
Figure 7.13	Development of inherently cellular pulsating instabilities at 75-25% H_2 - CO	135
Figure 7.14	Typical variation in the light intensity of a single cell at different water dilution fractions.	136
Figure 7.15	Variation of the instability patterns with H_2O fraction relative to CO_2 for 60-40% H_2 - CO , 75-25% H_2 - CO + 15 % CH_4 , and 75-25% H_2 - CO + 30 % CH_4	137

Figure 7.16	Illustration of the sustained instability patterns observed as a function of the effective fuel Lewis number for $\text{H}_2\text{-CO-CH}_4$ mixtures diluted in H_2O and CO_2 at $\phi \approx 0.6$ and $Le_o \approx 0.95$. The effect of increasing Le_o or ϕ is qualitatively shown by the dashed horizontal axis.	138
Figure 7.17	Variation in the number and size of cells as a function of the water fraction for a) pulsation-induced cells and b) inherently cellular flames.	139
Figure 7.18	Instability wavenumber of inherently cellular flames as a function of the effective fuel Lewis number.	140
Figure 7.19	Frequency as a function of water fraction in the diluting stream for different pulsation-induced unstable flames.	141
Figure 7.20	Non-dimensional frequency as a function of the mixture strength at different effective fuel Lewis numbers.	142
Figure 8.1	The composition of the burned syngas a) as is from the SOFC, and b) after being passed through a 40°C flash separator. Different operating points from the four MeOH and SNG systems are considered.	146
Figure 9.1	Effect of H_2O dilution on soot formation in CH_4 flames with $\phi \approx 2.6$	155
Figure A.1	Schematic representation of the downdraft, updraft, and two-stage Viking gasifiers	185
Figure C.1	Comparison between stable flames, diffusive-thermal instabilities, and bouyancy-driven instabilities, with the inner cylinder removed from the combustion chamber.	198
Figure C.2	Comparison between stable flames, diffusive-thermal instabilities, and bouyancy-driven instabilities. The vertical dashed lines represent the inner quartz cylinder.	199

LIST OF SYMBOLS AND ACRONYMS

ASU	Air separation unit
ASR	Area specific resistance
CHP	Combined heat and power
c_p	Specific heat at constant pressure
D_a	Damköhler number
DFB	Dual-fluidized bed
DME	Dimethyl ether
D_i	Molecular diffusivity of species i
D_{th}	Thermal diffusivity
DTIs	Diffusive-thermal instabilities
ER	Equivalence ratio
FICFB	Fast internally circulating fluidized bed
FC	Fixed carbon
GHG	Greenhouse gas
HHV	Higher heating value
ICE	Internal combustion engine
l_D	Diffusion length
l_f	Flame thickness
$Le_{F,eff}$	Fuel mixture effective Lewis number
Le_F	Fuel Lewis number
Le_i	Lewis number of species i
Le_O	Oxidizer Lewis number
LDA	Laser Doppler anemometry
LHV	Lower heating value
M	Feed gas module
MGT	Micro gas turbine
MeOH	Methanol
V_{op}	Operating voltage
V_N	Nernst voltage
p_o	Ambient pressure
PIV	Particle image velocimetry
PM	Particulate matter
PSA	Pressure swing adsorption

q	Heat release per unit mass of fuel
R	Ideal gas constant
RSOC	Reversible solid oxide cell
R_{meth}	Syngas fraction to methanation reactor
S_L	Laminar flame speed
SNG	Synthetic natural gas
SOEC	Solid oxide electrolysis cell
SOFC	Solid oxide fuel cell
S/B	Steam to biomass ratio
S/C	Steam to carbon ratio
T_a	Adiabatic flame temperature
$\hat{W}$	Mean molecular weight
W_i	Molecular weight of species i
WGS	Water gas shift
VM	Volatile matter
U	Bulk velocity
U_f	Fuel utilization factor
X_{CH_4}	Relative amount of CH_4 to H_2 and CO
$X_{H_2,CO}$	Relative amount of H_2 to CO
X_{H_2O}	Relative amount of H_2O to CO_2
X_F	Total fuel concentration
X_i	Mole fraction of species i
Y_i	Mass fraction of species i
x_f	Flame position
Ze	Zel'dovich number
η_{CG}	Cold gas efficiency
ϕ	Mixture strength
λ	Thermal conductivity
λ_c	Cell size
σ^*	Wavenumber
ω_I^*	Oscillation frequency of the most unstable disturbance at marginal stability
ω_{rxn}	Chemical reaction rate
β	Arrhenius pre-exponential factor
ν_i	Stoichiometric coefficient of species i
ρ	Density

LIST OF APPENDICES

Appendix A	BIOMASS GASIFICATION	184
Appendix B	SYNGAS CLEANING	189
Appendix C	SUPPLEMENTARY MATERIAL OF ARTICLE 3	198

CHAPTER 1 INTRODUCTION

This thesis discusses diffusive-thermal instabilities in syngas diffusion flames, along with the thermodynamic modelling of small-scale biomass polygeneration systems. The latter are well suited to the decentralized nature of biomass resources, however, they have received less attention than large-scale centralized plants. While the efficient and reliable combustion of syngas plays a key role in the overall energy balance of small-scale biorefineries, the low-calorific value flames are prone to the formation of diffusive-thermal combustion instabilities. To obtain fundamental insight into these complex combustion phenomena in the absence of parasitic hydrodynamic effects, a new version of the one-dimensional unstretched diffusion flame burner is introduced.

1.1 Biomass

In its most general definition, biomass is any form of organic non-fossilized matter that is or was at some point in time a living organism, such as wood, food crops, manure, etc. [1]. Ever since the dawn of civilization, biomass has served as a reliable heat source, providing warmth and protection for hundreds of millions of people. In fact, up until the mid 1800s, burning wood represented the largest share of the total energy consumption in the United States, before being taken over by fossil fuels such as coal, petroleum, and natural gas [2]. However, climate change-driven technological advances have been paving the way over the past couple of decades for the resurrection of bioenergy. As demonstrated throughout this thesis, biomass can be converted to different types of storable biofuel, which could be burned for various applications in a carbon neutral cycle as the emitted CO_2 is reabsorbed by growing biomass during photosynthesis in a relatively short period of time, unlike the carbon cycle of fossil fuels that spans millions of years.

Nowadays, the biomass used for energy production mainly comes from the biodegradable fraction of products from forestry, agricultural, industry, and waste sectors [3]. Out of the different types of biomass, lignocellulosic feedstock such as wood chips, wheat straw, or sugarcane bagasse, is the most abundant type on earth [4]. According to a recent report by WSP and Deloitte [5], biomass on its own has the potential to produce an equivalent of 66% of the current natural gas needs of the province of Quebec, with the majority (82%) coming from woody forest waste. In fact, bioenergy from forest residues has a huge potential in Canada, as the nation's forest industry is renowned for having the largest net product trade balance worldwide [6]. Approximately 36% of Canadian land is covered by forest,

contributing to 9% of the total forest land worldwide [7].

The energy of biomass is stored in its chemical bonds, and can be exploited through different thermochemical or biochemical processes, depending on the feedstock type. When it comes to lignocellulosic biomass, the biochemical route requires the incorporation of expensive and time-consuming biomass pretreatment stages using enzymes and acids, essentially for the extraction of sugars that can be fermented or digested [8]. On the other hand, the thermochemical route, in particular gasification, is considered the most cost-effective, practical, and efficient process for the conversion of lignocellulosic biomass [9–11]. Generally in a gasifier, biomass undergoes pyrolysis or devolatilization, whereby moisture and volatile gases are released leaving behind char, a carbonaceous solid that then reacts heterogeneously with the gas phase yielding syngas, a versatile combustible mixture. To sustain these endothermic reactions, the biomass is partially oxidized as oxygen-deficient conditions are maintained in the gasifier by feeding it with only 20-30% of the oxygen needed for stoichiometric combustion.

The resulting crude syngas mixture following biomass gasification is mainly composed of H_2 , CO , CH_4 , CO_2 , and H_2O , along with contaminants such as tar, acid gas, ammonia, particulate matter, and alkali metals. After eliminating these contaminants, various storable biofuels such as methanol, ethanol, or dimethyl ether can be synthesized from the cleaned syngas [12]. This process occurs in catalytic biofuel reactors, which are usually governed by stringent thermodynamic chemical equilibrium laws that restrict the complete conversion of syngas to biofuel. For instance, roughly only 25% of syngas is converted to methanol for every pass through the reactor [13]. While the overall conversion fraction can be significantly enhanced by recycling the product stream back into the reactor after separating methanol from it, and by increasing the operating pressure, the economy of scale plays a significant factor in justifying the increased biofuel equipment size and cost [14]. This is one of the main reasons why the main focus of the gasification-derived biofuel literature has been large-scale implementations.

1.2 Polygeneration systems

Despite generally having a lower biofuel yield, small-scale systems are attributed with several potentially compensating features that could be leveraged over large-scale implementations. Decentralized small-scale systems are more suited to the distributed nature of biomass, whose transportation costs and emissions could be considerably minimized compared to large centralized biorefineries. Wood chips for instance, which usually contain a significant amount of moisture ($\approx 30\%$ by mass), have a relatively low energy density of ≈ 13 MJ/kg [12] compared to globally traded energy commodities such as gasoline with 43 MJ/kg [15], which could ren-

der its transportation costs unjustifiable over long distances [16]. In addition, decentralized systems could readily valorize the huge amounts of excess heat generated throughout the globally exothermic biomass conversion process, as they could be deployed in venues where heat is locally demanded, yielding high overall process efficiencies. On the other hand, utilizing the excess heat of large-scale gasification systems is a challenging task, as the storage and long-distance transportation of heat to consumers is often economically unviable [17]. For instance, a large 300 MW methanol plant produces approximately 90 MW of excess heat [18], which has the potential to provide space heating for 40 to 165 households depending on the geographic location [19], if not vented into the atmosphere/rivers.

In this thesis, we focus on decentralized biomass conversion systems in agricultural greenhouses whose local energy needs are diverse and coincide with the type of products that could be co-produced during biomass gasification, and since the venue is usually surrounded by abundant residual biomass. Greenhouses are distributed users of an enormous amount of heat, which typically represents 70-85% of the total energy expenses [20]. In addition to fuel for transportation and machinery, greenhouse facilities also require a significant amount of electricity, which could be generated from the unconverted syngas of the biofuel reactor in heat engines or fuel cells. Farmers also purchase CO_2 and inject it into the greenhouse atmosphere to enhance crop growth, since CO_2 concentration in ambient air is suboptimal for the crops. Although all of these four products could, in theory, be poly-generated from biomass, which arguably renders agricultural greenhouses one of the most attractive venues for the efficient deployment of decentralized biomass conversion, no such polygeneration system designs have been proposed yet in the literature as schematically shown in figure 1.1. We aim to address this gap in the first part of this thesis.

1.3 Combustion

In biomass conversion systems, particularly small-scale decentralized implementations, a significant fraction of the large amounts of heat produced comes from burning the residual syngas. This takes place after the biofuel and electricity production stages as shown in figure 1.1, during which a significant fraction of the combustible H_2 , CO , CH_4 species gets converted to inert CO_2 and H_2O . The resulting high dilution levels in the leftover syngas narrow its flammability range and promote flame instabilities, which could deteriorate the syngas utilization and hence overall biomass conversion efficiency. Consequently, the second portion of this thesis is dedicated to studying the combustion physics of highly-diluted syngas flames.

Stemming from the Latin word *comburare*: "to burn up", combustion is the study of chemically reacting flows involving rapid and highly exothermic reactions. The latter is usually

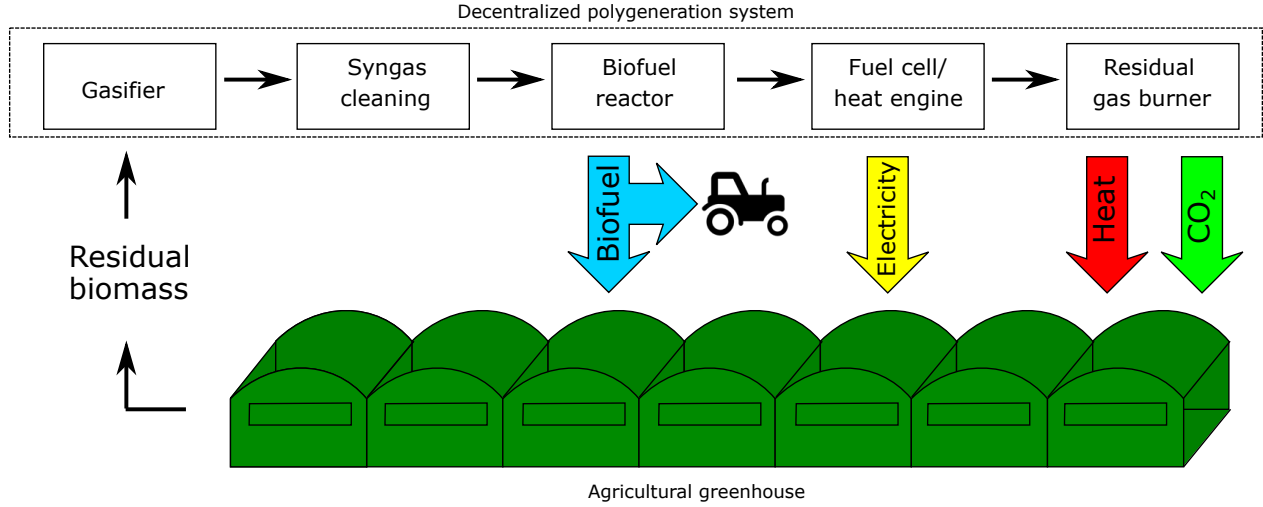


Figure 1.1 Envisioned decentralized polygeneration system in agricultural greenhouses

confined to a highly localized region in the flow that is commonly referred to as the flame, which is characterized by high temperatures and product concentrations, along with depleted reactants. From a global point of view, the reactants are essentially the fuel and oxidizer, which must be mixed together on a molecular level to react and produce heat. The mixing could be done a priori, before initiating the reactions in the combustion chamber using a spark plug for instance, leading to what is formally known as a premixed flame. The reactants could also be supplied separately, whereby they are brought together in the combustion chamber by diffusion and bulk convective flow to produce a non-premixed flame. This is one of the most widely used distinctions to categorize combustion systems, which as illustrated next, behave differently whether the fuel and oxidizer are initially mixed or separated.

When a mixture of fuel and oxidizer is ignited at one point of the domain by a heat source, the resulting premixed flame always has a tendency to propagate in a wave-like fashion to consume the unreacted mixture at a characteristic propagation rate, leaving behind hot combustion products. A schematic of a one-dimensional premixed flame is shown in figure 1.2 a). From the perspective of the large hydrodynamic scale, the flame is essentially a propagating interface separating two non-reacting fluid domains across which the temperature and velocity abruptly increase, with the reactants vanishing. Looking into the structure of the thin flame (figure 1.2 a) inset), we find a preheat zone with a characteristic length l_f in which the concentration of the reactants starts decreasing relative to the freestream, while the mixture temperature begins increasing as heat is conducted away from the narrow downstream reaction zone with length l_R . The large energy barrier that must be crossed by the chemical reactions, also known as the activation energy, renders their rate extremely

sensitive to temperature, which is maximized in the reaction zone yielding $l_R \ll l_f$. This is why the thickness of the flame is usually considered equivalent to l_f . Consequently, the mathematical treatment of the problem reveals [21]:

$$(S_L)^2 \sim \frac{(\lambda/c_p)\omega_{rxn}}{\rho^2 Ze} \quad (1.1)$$

$$l_f^2 \sim \frac{(\lambda/c_p)Ze}{\omega_{rxn}} \quad (1.2)$$

with S_L being the flame speed, ω_{rxn} the reaction rate, and Ze the Zel'dovich number, which is the ratio of the activation and flame temperatures. In the idealized case considered, the flame temperature is also known as the adiabatic flame temperature (T_a) since the heat of combustion is solely used to warm up the unburned mixture with no losses. T_a is given by:

$$T_a = T_u + qY_u/c_p \quad (1.3)$$

with q being the heat released rate per unit mass of fuel, a property that can be readily evaluated from thermodynamic laws, and Y_u being the fuel concentration of the unburned mixture. From relations 1.1 - 1.3, it can be seen that both transport and chemical processes, through the λ/c_p and ω_{rxn} terms, respectively, dictate the behaviour of premixed flames. In addition, the laminar flame speed obtained for this simple one-dimensional configuration is an intrinsic property of the mixture, and is often used to highlight the reactivity and exothermicity of different fuels.

Considering the case where the fuel and oxidizer are initially separated, either by nature or design, a non-premixed flame is established when the chemical reaction initiation time is sufficiently faster than the reactants mixing time. Following ignition, a non-premixed flame situates itself between the separate sources of fuel and oxidizer, which are transported to the reaction zone by diffusion, and possibly convection, at stoichiometric proportions. Therefore, unlike a premixed flame, a non-premixed flame is not attributed with a characteristic flame speed. In addition, since the chemical reactions often occur significantly faster than the diffusion processes, information on the reaction mechanism may not be required to predict the global non-premixed flame properties, as the stoichiometric transport of the fuel and oxidizer could become the limiting mechanism. This is why non-premixed flames are often referred to as diffusion flames. Consequently, the problem could be solved by assuming the flame to be an infinitely thin sheet as shown in figure 1.2 b), where a one-dimensional purely-diffusive (no convective flow) non-premixed flame is considered, with the two boundaries

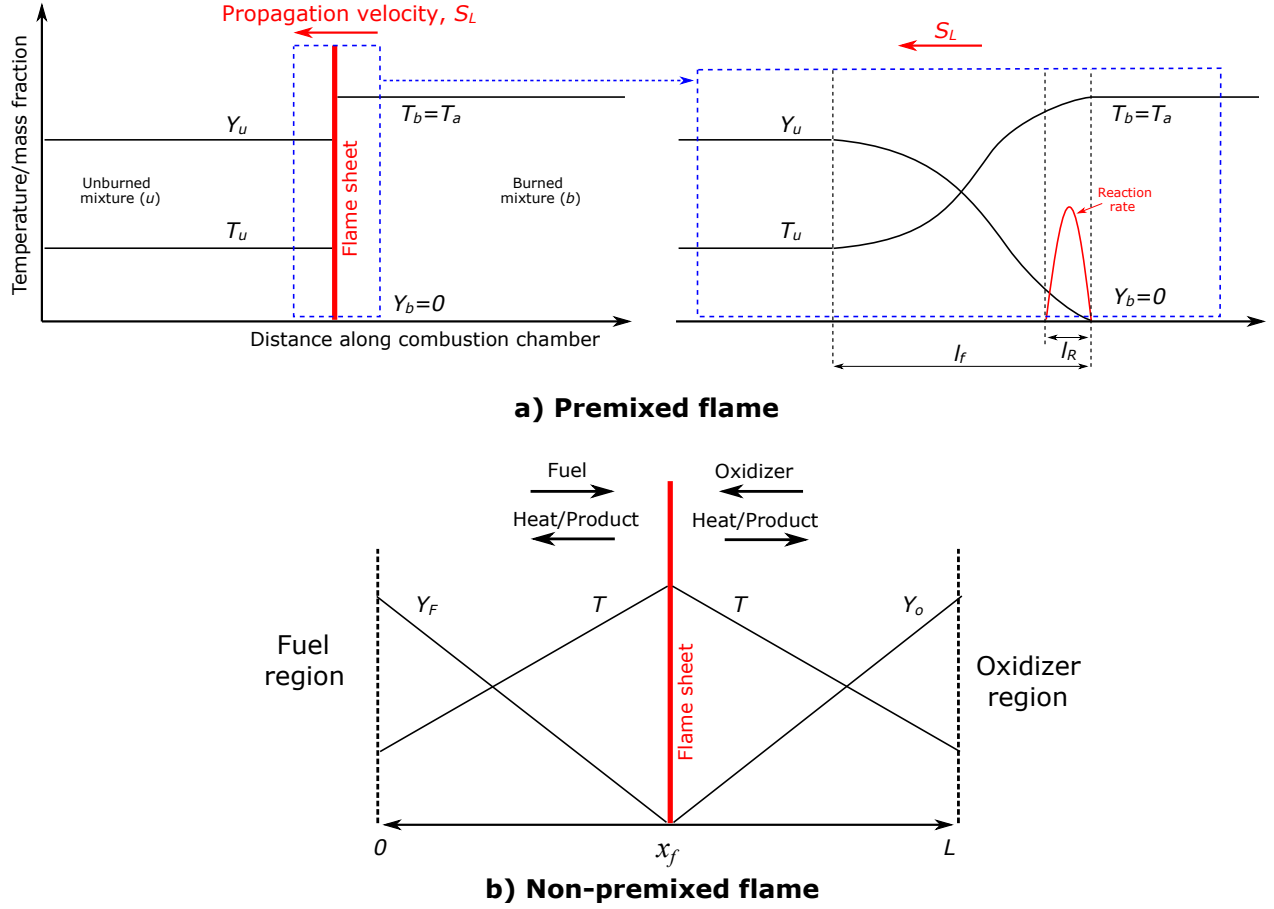


Figure 1.2 Structure of a one-dimensional adiabatic a) premixed and b) purely-diffusive non-premixed flame. Y : Mass fraction, and T : temperature.

separated at a distance L , and which constitute of porous walls that allow the reactants to diffuse into the reaction zone and the products to escape. Solving the governing equations yields the flame position (x_f) and the fuel burning flux (f):

$$x_f \sim \frac{\phi}{1 + \phi} \quad (1.4)$$

$$f \sim \frac{\lambda/c_p Y_{F,0}}{L x_f} \quad (1.5)$$

with ϕ being the mixture strength or the ratio of the fuel to oxygen mass fractions at the boundaries normalized by their stoichiometric proportions, and $Y_{F,0}$ the mass fraction of the fuel at the boundary. The adiabatic flame temperature is given by:

$$T_a = (T_L - T_0 + Y_{O,L}/q c_p) x_f + T_0 \quad (1.6)$$

with the subscripts 0 and L referring to the fuel and oxidizer boundaries, respectively. From these relations, it can be seen that the behaviour of non-premixed flames is dictated by stoichiometrically weighted transport coefficients, and unlike the expressions for premixed flames (Eqs. 1.1 and 1.2), the chemical reaction rate is not needed to predict the global diffusion flame properties. It can also be seen that as the fuel concentration at the boundary decreases, by diluting with an inert gas, the mixture strength and hence, the flame position decreases. The flame responds by positioning itself closer to the fuel boundary in order to compensate for the drop in the gradient of the fuel concentration profile, which is proportional to its diffusion rate.

1.4 Flame instabilities

Albeit very useful in elucidating the fundamental differences between premixed and non-premixed combustion, the idealized conditions assumed in the two aforementioned flames are seldom encountered in practical systems. A small perturbation to the basic states considered in figure 1.2 could significantly grow in amplitude, rendering the one-dimensional stable flames multidimensional and/or unsteady. Besides the significantly added modelling complexity, flame instabilities could have detrimental ramifications in practical combustors as they may lead to extinction, pollutant formation, load variation, pressure fluctuation, or high-amplitude vibrations. The driving mechanism of flame instabilities can be intrinsic to the combustion process itself, and not driven by factors related to the combustor geometry or imposed flow field. With high relevance to biomass-derived syngas, intrinsic flame instabilities can arise from a disparity between the rates of thermal and molecular diffusivities, the ratio of which is known as the Lewis number (Le).

Consider the response of a one-dimensional planar premixed flame to a small spatial perturbation in the reaction zone, as shown in figure 1.3 a). A similar mechanistic description could be given using non-premixed flames since the underlying instability mechanism is the same, as shown in section 2.2. Given that molecular diffusion occurs normal to the reaction zone, the reactants get focused on the convex side of the flame front, and in the situation where the reaction zone gains more reactants from the transport zone than it loses heat to it, or in other words when $Le < 1$, higher flame temperatures ($> T_a$) and stronger local combustion intensities are attained. The inverse argument holds at the concave side of the flame where the reactants get defocused, leading to lower flame temperatures and potentially, local

extinction. Therefore, alternating variations between intensified and weakened/incomplete combustion develop all over the flame, leading to what is formally known as cellular instabilities, as shown in a Bunsen burner flame in figure 1.4. This is one of the two main modes of diffusive-thermal instabilities (DTIs), and is frequently reported in H_2 flames due to their very low Lewis numbers.

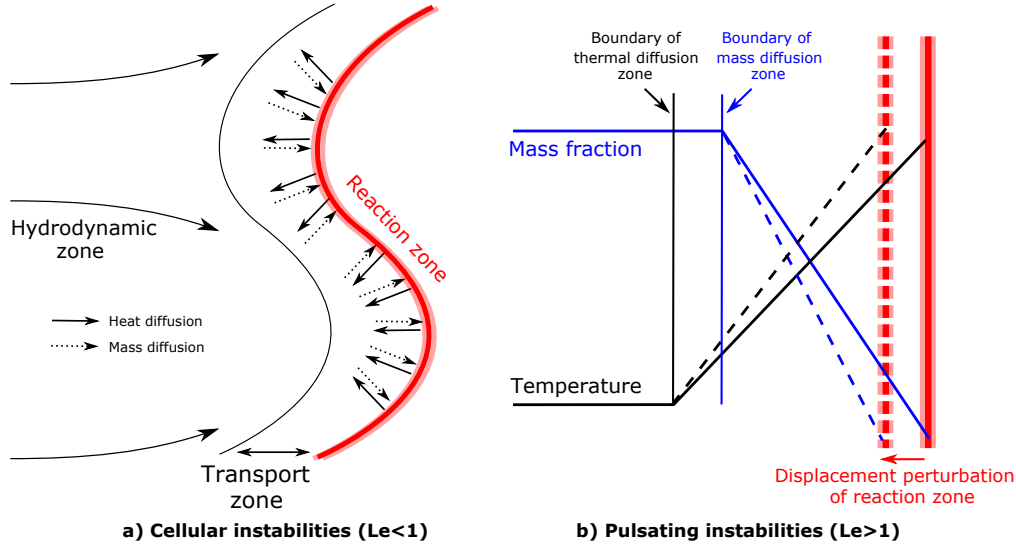


Figure 1.3 Mechanism of a) cellular and b) pulsation instabilities in premixed flames. Reproduced with permission from [21].

For nonequidiffusive fuels with $Le > 1$ such as CO and CH_4 which are also present in syngas, the other major DTI mode is encountered, one that is characterized by periodic temporal variation in the chemical reaction rate. Consider a small planar disturbance applied to the whole reaction zone such that it is displaced towards the unburned reactants side as shown in figure 1.3 b). Both the thermal and mass diffusion zones are narrowed by the same amount, but for $Le > 1$, the gradient of the mass diffusion zone is steeper since it is relatively thinner than the thermal zone as indicated by the Lewis number. Consequently, the rate of reactants supply to the reaction zone is increased relative to the amount of heat it loses to the free stream, and this leads to intensified burning, a higher flame speed, and therefore the forward propagation of the flame. The opposite argument holds when a disturbance is applied in the burned mixture direction, which leads to less intense burning and backward flame propagation. Consequently, fuels with $Le > 1$ are susceptible to temporal oscillations in their combustion intensities, running the risk of extinction at the low-intensity part of the pulsation cycle. Images of a pulsating jet flame are shown in figure 1.5.

The reactive-diffusive nature of DTIs, which as illustrated above, onset following the modification of the chemical reaction rates via the preferential diffusion of heat or mass from the

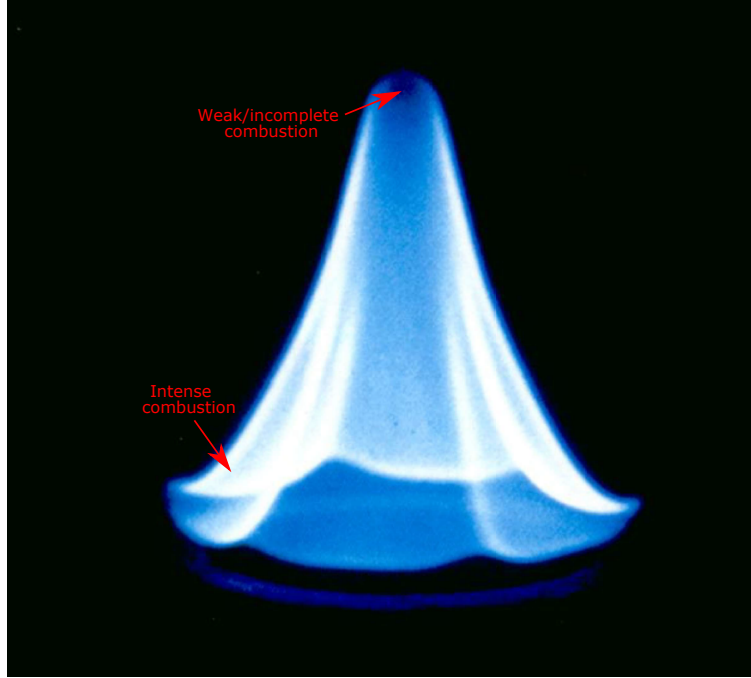


Figure 1.4 Cellular Bunsen burner butane-air flame. Reproduced with permission from [22]

transport zone into the reaction zone, means that the relevance of DTIs increases in thicker flames. Lower chemical reaction rates lead to thicker diffusion zones in premixed flames as seen from equation 1.2, and in non-premixed configurations as shown in section 2.2.2. Given that the reaction rate is inversely proportional to the dilution level, biomass-derived syngas mixtures are therefore, highly prone to DTIs. The simultaneous presence of H_2 , CO and CH_4 means that both the cellular and oscillating instability modes could co-exist and interact. However, this is yet to be formally studied as the literature on the nature of DTIs in multi-fuel mixtures such as syngas is scarce, with single-species fuels being the main focus.

One reason for the scarcity of fundamental experimental studies on intrinsic DTIs is perhaps the inherent difficulty of producing simple flames in the laboratory that are not perturbed by exogenous factors such as aerodynamic effects. A uniform flow field for instance is very challenging to achieve due to the huge thermal expansion that occurs to the flow across the flame. A multidimensional or unsteady flow character is directly reflected on the flame, inducing parasitic effects that significantly complicate obtaining fundamental insight into diffusive-thermal effects. Consequently, to eliminate aerodynamic disturbances, and most importantly to facilitate the mathematical description of the problem, theoretical models often assume a one-dimensional flow field. They subsequently subject the planar flame front to small perturbations, on the order of the flame thickness, and exploit the disparate scales of

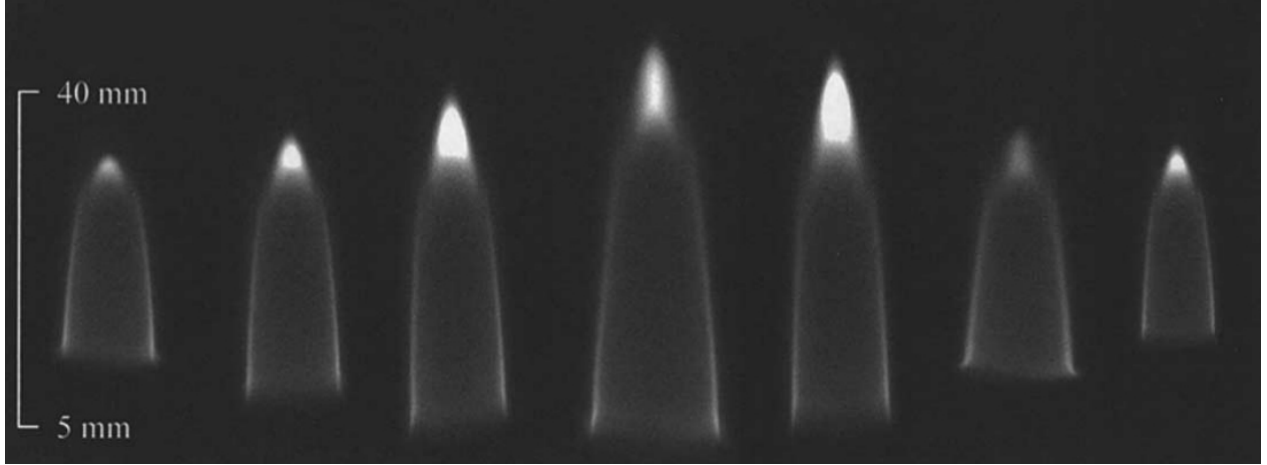


Figure 1.5 Pulsating propane-nitrogen jet flame. Reproduced with permission from [23]

the problem to generate analytical solutions that can approximate the growth or decay rates of the disturbance. Despite the valuable physical insight, the scarcity of an experimental setup capable of producing one-dimensional flames also means that such models often lack quantitative validation. In this thesis, we build on previous successful efforts to produce one-dimensional non-premixed flames, and modify the proposed burner design to be able to accommodate fuels with high water vapor content such as syngas. The new burner is then used to study diffusive-thermal instabilities in these mixtures.

1.5 Scope and thesis outline

The goal of this thesis is twofold, starting with the study and design of decentralized biomass polygeneration systems using thermodynamic modelling. These systems should be able to simultaneously produce a storable biofuel, electricity, heat, and a high-purity CO_2 stream that can be injected into the atmosphere of a greenhouse or readily sequestered. Despite these products being in high demand in agricultural greenhouses, the thermodynamic feasibility of such a process has never been formally investigated. Farmers are still heavily relying on fossil fuels for their energy-intensive activities [24], with biomass being sporadically used in boilers to provide part of the heating load. A decentralized polygeneration system therefore has the potential to promote a sustainable circular economy for the agricultural sector which: 1) diminishes the elevated energy bills incurred by agricultural practices, 2) creates a new income stream for farmers as they market their surplus fuel/electricity, and 3) creates new employment opportunities, which would benefit the rural economy as a whole. Ultimately, the commercialization of this concept could contribute to shift the balance of power in the

agriculture sector, where the role of the farmers could change from energy users to energy providers.

Another fundamental aspect addressed in this thesis is the combustion characteristics of $\text{H}_2\text{-CO-CH}_4$ fuel blends that are highly diluted in CO_2 and H_2O . These mixtures are representative of the leftover syngas in biomass polygeneration systems that must be adequately burned to enhance the overall efficiency of the process. The significant quantities of inert gases promote diffusive-thermal flame instabilities, which could lead to incomplete combustion or extinction, and hence a deteriorated thermal efficiency and enhanced pollutant formation. DTIs have been frequently studied in the literature, from a theoretical perspective, and using advanced experimental approaches. However, the focus was mainly on single-species fuels, with fundamental investigations on mixtures of distinctive combustible species such as syngas being scarce. To address this need, we introduce a new version of the one-dimensional non-premixed burner that can be operated with humid gaseous fuels. This burner produces flames with negligible aerodynamic disturbances, and therefore puts the spotlight on diffusive-thermal effects.

In the next chapter, a literature review on the latest advances in biomass polygeneration systems is given, followed by an exhaustive presentation of DTIs in diffusion flames. Experimental and fundamental theoretical studies are discussed, followed by recent attempts in realizing a truly unstrained diffusion flame burner. In chapter 3, a critical assessment of the literature is presented, leading to the specific objectives of this thesis. The results are then discussed in the next four chapters, each in the form of a journal article. A general discussion of our findings along with their expected impact is presented in chapter 8. The thesis is summarized in chapter 9, which also includes recommendations for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Modelling of biomass polygeneration systems

The term polygeneration refers to chemical processes, including biomass gasification, where at least one chemical or fuel is produced in addition to electricity and heat. The integrated topologies of polygeneration systems allow their output product mix to be readily varied in order to accommodate changes in local energy demands. Consequently, polygeneration systems are more efficient and often more profitable than stand-alone biorefineries of a similar size that convert biomass to a single product only [25, 26]. Polygeneration is an attractive sustainable solution for various applications, going beyond decentralized agricultural greenhouses, whose synergy was illustrated in section 1.2. As frequently discussed nowadays, the flexibility of polygeneration systems could be exploited for managing intermittent energy sources such as wind or solar. For instance, on cloudy or calm days, where renewable power is not abundant, electricity production from biomass could be boosted on the expense of biofuel, and vice versa in the opposite scenario. In fact, as illustrated next, if reversible fuel cells are incorporated, surplus electricity could be injected into the polygeneration system to be stored as biofuel. The European Union Horizon 2020 project Waste2GridS aims at developing such polygeneration systems to offer grid balancing services. The same system could convert waste biomass to either natural gas or power, and utilize its waste heat for district heating [27]. By the same token, biomass polygeneration systems could also serve as back-up power plants in rural areas, whereby if the local electricity consumption increases, biofuel synthesis can be switched for power production.

In the next two sections, we discuss polygeneration systems that produce biofuel, electricity, heat, or high-purity- CO_2 , since these products are generally in high demand, particularly in agricultural greenhouses. We consider two types of biofuel: 1) natural gas, one of the most common energy commodities worldwide, and 2) methanol, a versatile biofuel that can be conveniently stored as a liquid at ambient conditions. The list of studies included are by no means exhaustive, however, they remain fairly representative of the overwhelming number of publications in the literature. For a review on the progress of a wide range of gasification-based biofuels, interested readers are kindly referred to Sikarwar et al. [11].

Typically in biomass conversion systems, the feedstock first undergoes gasification, then the generated syngas is cleaned from contaminants and conditioned, before being converted to the desired value-added products. Given the sheer volume of technologies that could be adopted in each step of the process, the discussion is mainly limited to general layout and outputs

of polygeneration systems, without delving into the working mechanism of each component. For instance, as shown in figure 2.1, several types of fixed or fluidized bed gasifiers could be used with air, O_2 , or steam as gasification agents. For syngas cleaning, various technologies exist for each contaminant, with tar often being the main culprit. For the latter, physical or thermochemical processes such as lipophilic towers and catalytic reformers, respectively, could be adopted. Interested readers are kindly referred to appendix A and B for a review on the gasification and syngas gas cleaning stages, respectively. The cleaned syngas could then be converted to a myriad of products, including 1) various chemicals such as natural gas, methanol, and ethanol, 2) electricity through combustion in heat engines (ex: internal combustion engines or gas turbines) or through electrochemical conversion using fuel cells, and 3) heat. For the latter, a residual gas burner can be used, in addition to recovering the excess heat that is generated by various components such as the gasifier, syngas cleaning units, and biofuel reactor.

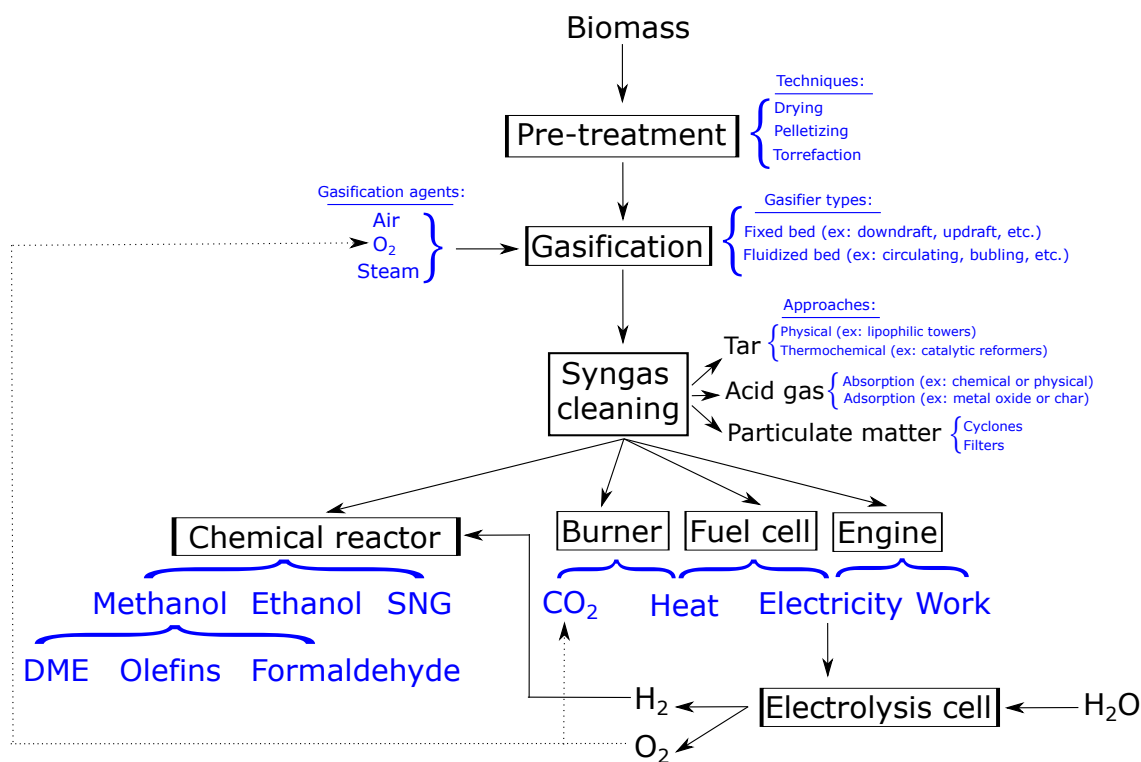


Figure 2.1 Examples of the different technologies that could be used in each stage of the biomass gasification process.

To design biomass gasification systems, researchers typically use thermodynamic equilibrium and/or kinetic models. The former relies on general thermodynamic properties to predict the composition of the outlet gas, which is assumed to attain chemical equilibrium. Consequently,

the outcome is independent of the reactor design, and is useful in identifying the limiting behaviour of novel system designs or ones that may be expensive/dangerous to investigate experimentally [28]. One of the main assumptions in equilibrium models is that the reactants residence time is much longer than the chemical reaction time, which may not be accurate for all reactors, especially ones operating at low temperatures [29].

Kinetic models on the other hand, consider finite residence time, yielding accurate results at low temperatures, while also capturing more details such as temperature distribution, and hydrodynamic effects. To do so, reaction kinetics and transport are considered, along with particle size distribution in some cases [30]. These make the kinetic modelling approach computationally intensive, and limited to specific system designs [31]. Out of the numerous publications reviewed by Safarian et al. [30], 61% used thermodynamic equilibrium modelling, 28% relied on kinetic rate models, and 11% combined both approaches.

ASPEN Plus, a commercial simulation software, is used by various researchers to model different chemical engineering processes, including biomass gasification. A diverse list of thermodynamic properties for solids, liquids, and gasses is offered, in addition to equilibrium and kinetic rate-based reactors that can be combined in a flowsheet, with the option of incorporating user-defined scripts for more flexibility.

2.1.1 Synthetic natural gas systems

Synthetic natural gas is a versatile biofuel that can be used in greenhouses for transportation, power generation, and heating [32]. Engines running on natural gas can reach efficiencies similar to those running on diesel fuel [33]. In addition, the far-reaching distribution network makes natural gas an attractive energy commodity. Being the main constituent of natural gas, methane is generated from syngas along with an abundance of heat according to the following global reactions [34]:



The first reaction is known as CO methanation, and the second one is the well-known water gas shift (WGS) reaction. Ideally, syngas with $M = (\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2) = 3$ molar composition must be fed to the methanation reactor operating between 1-10 bar, and around 250°C with a nickel catalyst. An informative discussion on the reactors design and operation can be found in the review paper of Rönsch et al. [35]. Tremel et al. [32] designed a 500 kW SNG-producing system that fed on spruce wood. Thermodynamic simulations revealed

a biomass-to-SNG efficiency of 74 % (based on the LHV). Pressure swing adsorption (PSA) was used to separate the CO_2 from the crude CH_4 product stream, in a unit that operated near the pressure of the methanation reactor (8 bar) and at a temperature of 30°C . Using this relatively simple approach, refined natural gas with 88.7% CH_4 was obtained. With a Wobbe index of $47.0 \text{ MJ}/\text{NM}^3$, the biomass-derived natural gas was rendered suitable for injection into the natural gas grid. Along with the low operating pressures, such high conversion fractions ($\approx 90\%$) are what make SNG an attractive option for small-scale implementation.

However, from an economic point of view, single-product SNG systems are usually far from competing with conventional natural gas. This is especially the case when talking about systems rated less than 20 MW [36]. Rönsch and Kaltschmitt [37] studied 14 different biomass to SNG configurations using flowsheet analysis. Their results showed that even in optimistic scenarios involving large-scale plants, where process efficiency is maximized and investment cost is minimized, the cost of producing only SNG from biomass was far from the selling price of conventional natural gas.

Consequently, Heyne et al. [38] designed a 90 MW tri-generation biomass system, in which the excess heat from the gasifier was fed to a steam power cycle. Adopting a tri-generation approach allowed for flexible power output, where the fraction of SNG and electricity output could be readily varied. Thermodynamic simulations conducted using ASPEN Plus revealed a maximum SNG efficiency of 69.4% (based on the LHV), and a maximum electrical efficiency of 31.7%. Gassner and Marechal [39–41] conducted multi-variable optimization on the topologies of tri-generation SNG, electricity, and heat systems. Different technologies, market scenarios, and process scales were considered, the latter varying between 5 and 200 MW. The key role played by adequately harnessing the excess heat of the process was highlighted, with the most profitable systems converting wood to SNG at efficiencies ranging between 66 and 75%.

Instead of heat engines, there has been an increasing number of studies focusing on integrating high temperature fuel cells (HTFCs) for more efficient electricity production. HTFCs ($\approx 800^\circ\text{C}$) such as solid oxide fuel cells (SOFCs, figure 2.2) and molten carbonate fuel cells (MCFCs) electrochemically convert the chemical energy of syngas into electricity in an environmental friendly manner [42]. Unlike engines, virtually no particulate matter, NO_x , or SO_x are emitted from fuel cells, whose operation is also devoid from any moving parts [43]. The model developed by Minutillo et al. [44] showed that replacing a micro gas turbine with an SOFC in a small-scale combined heat and (CHP) biomass gasification system has the potential of increasing the process efficiency by at least 7.3%. Compared to low temperature fuel cells (LTFCs), HTFCs are more resistant to syngas contaminants [17]. Electrical

power ranging from 1 kW to 1 MW can be provided by these units [45]. Gadsbøll et al. [46] successfully operated an SOFC that was fed with syngas from biomass gasification, where an electrical efficiency of 36.9% was attained. Similar successful experimental coupling of gasifiers and HTFCs are also reported in these references [47–50].

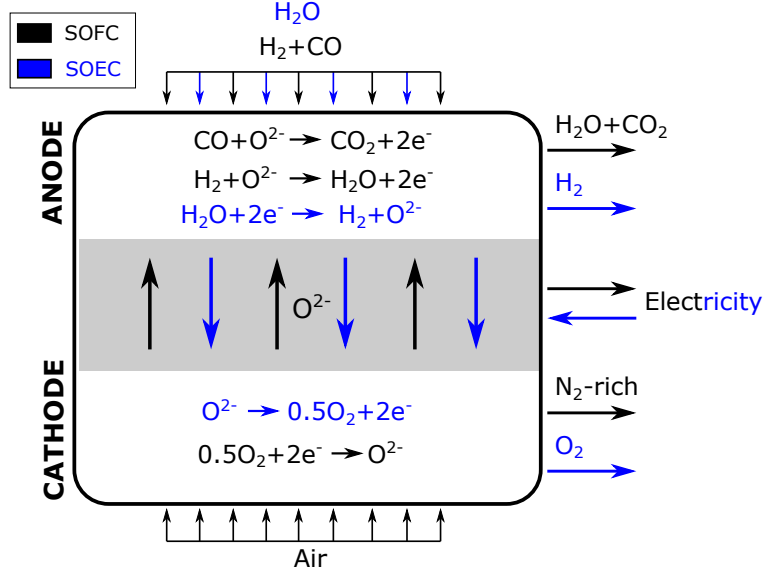


Figure 2.2 Two operating modes of reversible solid oxide cells [43]

Besides efficient electricity production, another major and potentially the most lucrative feature of SOFCs for decentralized polygeneration systems is their ability to operate in reverse mode. As depicted in figure 2.2, when fed with electricity and steam, reversible solid oxide cells (RSOCs) start operating as electrolyzers, producing O₂ and H₂ [51–53]. The former can be fed to the gasifier for the production N₂-free syngas that is crucial for SNG synthesis, replacing expensive and complex air separation units that must be otherwise used. The O₂ can also be exploited for carbon capture via oxy-fuel combustion, as discussed in section 2.1.3. Regarding the second solid oxide electrolysis cell (SOEC) product (H₂), and in addition to being a valuable biofuel by itself, it can be used for conditioning the syngas to $M = 3.0$ for optimal SNG synthesis. The syngas produced by most biomass gasifiers is usually deficient in H₂, even for MeOH synthesis (section 2.1.2), where a significant fraction of the biomass carbon content ends up as CO₂ in the effluent gas from conventional plants. The incorporation of an SOEC therefore provides the double benefit of easing the capture of this carbon emission, while also converting electrical energy to a storable biofuel.

Sigurjonsson and Clausen [54] integrated an RSOC to an SNG-biomass plant. Thermodynamic simulations revealed an overall efficiency of 90%, with SNG and heat generated at 69% and 21%, respectively. The inputs to the system were wood chips and electricity, with

the latter being used for enriching the H_2 content of syngas prior to methanation. Economic analysis was also conducted, putting into spotlight the importance of adequate excess heat integration and flexibly to cope with market fluctuations in energy prices. Clausen [55] investigated an SNG system design where the SOEC was coupled with a steam biomass dryer. The latter provided part of the steam required for electrolysis, instead of using a separate boiler. This novel approach allowed the system to tolerate feedstock such as sewage, sludge, and manure, which are very wet biomass containing up to 70% water content by mass, along with a significant amount of ash.

2.1.2 Methanol systems

The second biofuel considered in this work is methanol. It is a liquid at ambient conditions that can be readily transported, and that can also serve as a building block for the synthesis of other useful chemicals, such as formaldehyde [56]. Compared to gasoline (98), MeOH has a higher octane number (107) and a wider flammability range [57]. Grade AA MeOH (99.8% purity) can substitute gasoline in internal combustion engines (ICEs) with minor modifications [58]. In the context of agricultural greenhouses, biomass-to-MeOH conversion would help farmers reduce their excessive reliance on fossil fuel-based resources for powering their machinery. The overall chemical reactions for the globally exothermic conversion of syngas to MeOH are [56]:



From reaction 2.3, it can be seen that the ideal syngas module is $M = (H_2 - CO_2)/(CO + CO_2) = 2.0$. MeOH synthesis experienced a significant leap during the latest century. In 1923, a $ZnO - Cr_2O_3$ catalyst was used to hydrogenate CO at 240-300 bar and 350-400°C. However, a major improvement took place in the 1960s when Cu/ZnO was first used. This catalyst is more active and allows for much less severe reactor conditions, reducing the ideal operating pressure and temperature to 60-80 bar and 250-280°C, respectively [59]. For more details on the MeOH synthesis process from syngas, please consult the review paper of Bozzano and Manenti [56].

Clausen et al. [60] were amongst the first to study tri-generation MeOH systems rated as low as 5 MW. Despite the relatively small scale, the methanol reactor was operated at 96 bar, a high pressure that could raise safety concerns when implemented in agricultural greenhouses. Thermodynamic simulations using wood chips as feedstock yielded MeOH, heat, and net

electrical efficiencies of 45%, 37%, and 6% respectively. Electricity was generated using a gas engine that harnessed the leftover energy of the unreacted syngas from the once-through MeOH reactor. Recycling part of the unconverted syngas back into the reactor increased the MeOH yield to 56%, however, at the expense of increasing the reactor size by more than 3.5 times. When assessing the possibility of producing DME instead of MeOH, the authors obtained a similar energy conversion efficiency for the two biofuel. However, from a technical point of view, the added complexity of DME synthesis systems make them a potentially inferior option for small-scale applications. For MeOH, a flash separator operating at atmospheric conditions is usually enough to separate the majority of the MeOH from the reactor's product into a storable liquid. This is normally not the case with DME, where a refrigeration system must be incorporated since the partial pressure of DME in the products is considerably low, and significant cooling (to approximately -50°C) is required to condense it [60].

Clausen [61] then investigated the potential of the addition of electrolytic H_2 for maximizing MeOH production. Thermodynamic simulations predicted that this approach could more than double the energy of MeOH produced per unit energy of biomass input. Specifically, an increase from 63% to 136% in the MeOH-to-biomass energy ratio was attained, when additional electrical energy equivalent to 119% of the input biomass energy is also supplied to the system. Most importantly, almost all of the carbon input (96%) ended up in the storable MeOH stream, which is again more than double the amount of carbon recovered from the electrolysis-free system, with 44%.

As discussed earlier, a versatile source of electrolytic H_2 is an SOEC, the effect of which on MeOH production was investigated by Zhang et al. [53]. Besides H_2 supply, the SOEC also provided the gasifier with pure O_2 . Simulations revealed an increase in the total efficiency from 47.9% for a conventional biomass-to-MeOH system to 59.1%, following the incorporation of an SOEC. The biofuel reactor was operated at 56 bar, with unconverted syngas recycling for enhanced MeOH yield. Butera et al. [62] exploited the features of RSOCs for flexible energy management, which could be of paramount importance in future smart-energy systems looking to capitalize on the sporadic nature of intermittent energy sources such as wind or solar. When abundant or cheap, the biomass system was able to convert electricity to MeOH (reactor at 80 bar with product recycling) at an efficiency of 70%. While when in high demand, the same system was able to produce electricity at an efficiency of 37%. This mode had the the RSOC operating as an SOFC by feeding on syngas.

2.1.3 Carbon dioxide capture systems

Studies on carbon capture and storage systems have skyrocketed amid our current battle against climate change, with CO₂ contributing to more than 75% of the total greenhouse gas emissions worldwide [63]. In the context of gasification systems, the most convenient scenario to prevent CO₂ release to the atmosphere is to obtain the biggest fraction of the initial biomass carbon content in a high-purity CO₂ stream that can be readily sequestered. Given that the carbon in biomass comes directly from the atmosphere via photosynthesis over a relatively short time span, compared to fossil fuels such as coal which form over millions of years, an overall carbon-negative biomass conversion process can be achieved.

Instead of long-term storage, for instance in aquifers or former oil and gas reservoirs [64], the captured CO₂ can also be re-used in several applications, such as fire-extinguishers, food beverages, or refrigerants [65]. In agricultural facilities, farmers usually purchase CO₂ and inject it into the greenhouse atmosphere to enhance crop growth, since CO₂ concentration in ambient air is suboptimal for the crops, being particularly low during day time in greenhouses at around 150 ppm [66] relative to the optimal 700-1000 ppm concentration [67]. This represents another cost that could be potentially spared in greenhouses by decentralized biomass polygeneration systems.

There are generally four routes for carbon capture: 1) Post-combustion, 2) pre-combustion, 3) oxy-fuel combustion, and 4) chemical looping combustion. In the post-combustion approach, CO₂ is separated from the flue gases after burning the fuel, typically using an absorption process that relies on amines such as monoethanolamine (MEA). Other approaches exist such as adsorption or membrane separation [68], however these remain under development, as absorption is the only technology that has been implemented on industrial scale [69]. One of the main drawbacks of post-combustion carbon capture is the large parasitic economic and energy loads, arising from the low levels of CO₂ in the flue gas, which typically only varies between 4 and 15% [70]. Consequently, very large equipment is needed for handling the huge volume of gas, inducing high capital costs, in addition to a hefty energy penalty from the heating or depressurization processes used to regenerate the expensive sorbent [71]. These costs are therefore often unjustifiable for small-scale implementations.

Pre-combustion carbon capture involves partially oxidizing the fuel, biomass in this case, then treating the resulting syngas typically by reacting it with steam in a catalytic water-gas shift reactor to produce CO₂ and H₂, which are subsequently separated in processes similar to those used for the post-combustion approach. In pre-combustion however, the CO₂ concentration in the product of the WGS reactor is usually between 15-60%, which means that a less energy intensive absorption process is required. Lin et al. [72] studied

the thermodynamic performance of a 719 MW co-generation system producing MeOH and power. The effluent from the MeOH reactor was treated and stripped from CO₂, before burning the leftover gas for power. Li et al. [73] also modelled a 728 MW biofuel-power co-generation system in which the H₂ from the pre-combustion carbon capture process was used for the synthesis of SNG. Despite the lower energy demands and equipment size, the total capital costs of the catalytic WGS reactor and absorption system remain significantly high, even for large-scale implementation. Consequently, two of the very few pre-combustion carbon capture facilities worldwide have recently come to a halt [71, 74].

Carbon capture can also be implemented via oxy-fuel combustion, where oxygen is used instead of air for burning the fuel, generating a N₂-free high-purity CO₂ exhaust. Obviously, the main bottleneck in this approach is the provision of pure O₂. Cryogenic air separation units (ASUs) have been implemented on a large scale, however, the associated operating and capital costs are often unreasonable for small-scale systems. A techno-economic study conducted by López et al. [75] showed that ASU are not a favorable solution for 15 MW oxy-fuel combustion systems, as they represented around 25% of the total plant cost. In the numerous studies reviewed by Yadav and Mondal [76], ASUs were also seen to induce 6 to 10% energy penalty on oxy-fuel combustion power systems, the sizes of which varied between 460 and 800 MW. A promising alternative for decentralized applications could be reversible solid oxide cells, whose additional H₂ and electricity production features could potentially justify the initial costs. Oxy-fuel gasification with SOECs has been studied on several occasions for a N₂-free syngas required for biofuel synthesis, as discussed in the previous sections. However, the required electrical energy is normally assumed to be an input to the system. A self-sustainable solid oxide cell-integrated polygeneration system that runs solely on biomass is therefore still to be designed.

Chemical looping combustion (CLC) is a process involving an oxygen carrier that is continuously circulating between two fluidized bed reactors, one for the fuel and the other is for the air. The carrier is typically a metal (Me_xO_y), which is oxidized when it comes into contact with the air and subsequently reduced in the fuel reactor. Here, the biomass is first gasified, and the released volatiles then react with the Me_xO_y producing CO₂ and H₂O, as shown in figure 2.3. Given that the fuel and air never come into contact with each other in CLC systems, a N₂-free exhaust with a high concentration of CO₂ is generated from the fuel reactor. Abuelgasim et al. [77] reviewed numerous CLC test facilities with capacities ranging from 0.2 kW to 4 MW, operated using gaseous, solid or even liquid fuels. Despite the decent carbon capture efficiency and the low energy penalty, the commercialization of CLC technology remains under development. The degradation of the oxygen carrier is a major concern, inducing extra costs and environmental harm. The use of copper for instance results

in an extraordinarily high conversion efficiency, but the metal oxygen carrier has a notably low lifetime as it readily agglomerates. Nickel on the other hand has a much longer lifetime, but its toxicity has led to a decline in its use. Recent efforts are being directed towards combined oxides, such as calcium and manganese, to selectively exploit the advantages of different materials [78].

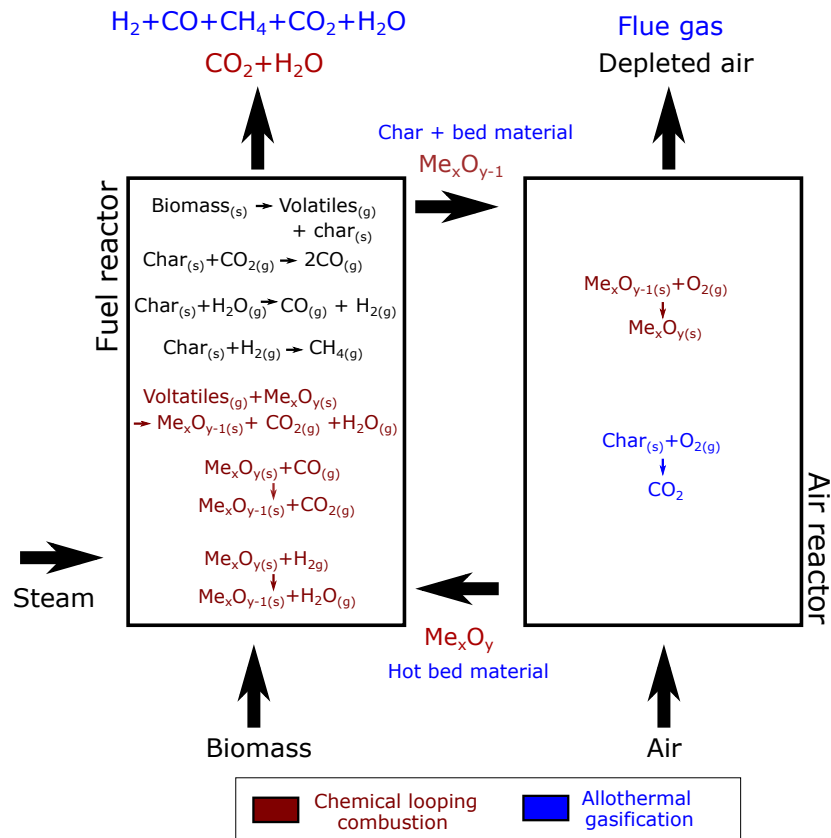


Figure 2.3 The concept of chemical looping combustion and allothermal dual-fluidized bed gasification. Chemical reactions used from [79].

Chemical looping has been also used for gasification (partial oxidization) by The Vienna University of Technology for the production of N_2 -free syngas, in what is known as the dual-fluidized bed (DFB) gasification. The first reactor is a bubbling fluidized bed that is fed with steam for biomass gasification from which char (leftover gasification products) and bed material (ex: silica sand) are transferred via an inclined chute to the second reactor, which is a fast circulating fluidized bed combustor. The combustion gases are separated in a cyclone where the hot bed material is returned via a loop seal to the gasifier, to provide the required heat for the endothermic gasification reactions. The chute and loop seal are fluidized by steam, and this prevents leakage between the two reactors, providing almost N_2 -free syngas even if air is used in the combustor [80], as depicted in figure 2.3. The use of

O_2 nonetheless generates an additional high-purity CO_2 exhaust stream. This idea has been briefly suggested in a review paper by Heidenreich and Foscolo [17], but rarely investigated in DFB systems. In a recent review paper, Hanchate et al. [81] presented a summary of several DFB pilot plants, with capacities ranging from 20 kW to 200 MW. The commercial medium-scale 8-MW DFB gasification plant in Güssing, Austria, that has been successfully operated for around 15 years was also discussed, along with the Gothenburg Biomass Gasification (GoBiGas) natural gas plant in Sweden, which is planned to be restarted by the end of 2023 following its halt in 2018. Current research on DFB gasifiers aim to incorporate catalytic bed material such as dolomites, olivine or nickel-based catalysts, amongst others, for in-situ reduction of contaminants in the produced syngas. More details on tar abatement catalysts are provided in appendix B.

2.2 Diffusive-thermal flame instabilities

Following the discussion of biomass polygeneration systems, we next switch the focus to the physics of diffusive-thermal combustion instabilities that are prone to occur in highly-diluted syngas flames, as motivated in section 1.4. Such intrinsic flame instabilities are also relevant to various practical applications that go beyond syngas burners in biorefineries. For instance, DTIs play a key role in the extinction/re-ignition dynamics of non-premixed flames, and therefore, pollutant formation of locally quenched flames interacting with the walls of compression ignition engines or gas turbines [82]. When it comes to industrial safety, the increased flame surface area following the onset of cellular instabilities could significantly accelerate the propagation rate of unconfined deflagrations, and hence, the severity of accidental explosions [83]. An adequate understanding of the instability mechanism would aid in predicting the severity of the event, and proper mitigation strategies. Regarding numerical modelling, DTIs that scale with the flame thickness are often filtered out by Large Eddy Simulations of turbulent combustion which exhibit desperate scales [84]. A proper description of these small-scale cells could be incorporated into the sub-grid models for improved accuracy without compromising computational efficiency. While turbulent flames are by definition perturbed, over a wide range of length scales, intrinsic cellular instabilities must be properly resolved as they could significantly modify the flame behaviour. This was observed by Yang et al. [85], whereby instead of a $\beta = 0.5$ exponent for the turbulent flame speed-Reynolds number relation, $\tilde{S}_T \sim Re_{T,f}^\beta$, for a cellularly-stable turbulent flame, $\beta = 0.27$ and 0.33 were obtained for the wrinkled and corrugated flamelets combustion regimes, respectively, when intrinsic cellular instabilities formed. Liu et al. [86] also recently observed that the formation of cellular instabilities could turn a laminar freely propagating flame turbulent. This phenomenon is known as self-turbulization, whereby the wrinkled flamefront imposes a turbulent character in the otherwise quiescent neighboring flow field. This evolution in flow regime could be critical in extreme cases of deflagration-to-detonation transition (DDT), leading to supernova explosions.

While DTIs could be observed in both premixed and non-premixed flames, we choose to focus on non-premixed flames as diffusive-thermal effects play a major role in the overall stability of these flames as illustrated next, not to mention the fact that non-premixed combustion constitutes a significant fraction of industrial burners such gas turbines and compression ignition engines. In premixed combustion, the intrinsic hydrodynamic effects that result from thermal expansion have a pronounced parasitic influence on the stability of the flame, as first recognized independently by Landau [87] and Darrius [88]. To illustrate the Darrieus-Landau instability, consider an infinitely thin premixed flame that has been slightly perturbed as

shown in figure 2.4. Thermal expansion renders the normal downstream velocity component greater than the normal upstream one. Given that the tangential velocities are conserved on both sides of the flame front, the flow must therefore diverge and slow down when approaching the convex flame surface, with the opposite scenario occurring at the concave surface. Since the flame speed is essentially constant, the changes in flow velocities due to flame front curvature are not balanced, and this pushes the convex and concave surfaces into the unburned and burned sides, respectively. As a result, such infinitely thin flames are always unstable, regardless of the wavelength of the induced perturbation.

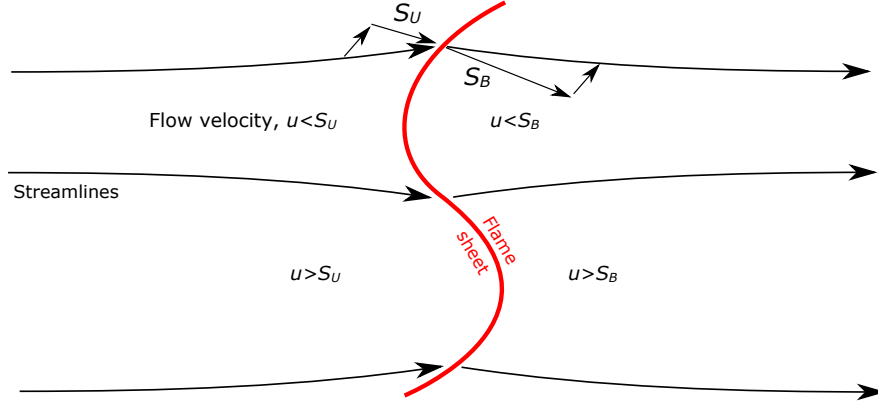


Figure 2.4 Mechanism of the hydrodynamic (Darrieus-Landau) instability. Reproduced with permission from [21].

However, as the thickness of the flame increases, diffusive effects become more pronounced as discussed in section 1.4, where depending on the Lewis number, they either suppress the ubiquitous hydrodynamic instability or enhance it. This can be seen from the following approximation of the growth rate ω of a spatial disturbance with wavelength k applied to a planar premixed flame, which was extracted from [89]:

$$\omega = S_L k \omega_{DL} - S_L l_f [B_1 + Ze(Le - 1)B_2 + PrB_3] k^2 \quad (2.5)$$

with Pr being the Prandtl number, and the three B_i coefficients always positive as they depend only on $\sigma = \rho_u/\rho_b$, the density ratio of the unburnt and burned gases. The Darrieus-Landau instability is represented by the ω_{DL} term, which is a positive and monotonically increasing function in terms of σ , confirming that thermal expansion always tends to exert a destabilizing effect on the flame, no matter the wavelength of the disturbance. This could lead to large cusps in the flame as shown in figure 2.5 a), which is reproduced from the modelling work of Creta et al. [90]. However, the term that multiplies l_f in equation 2.5 also shows that the Darrieus-Landau instability can be stabilized by diffusive-thermal effects for

a sufficiently thick flame, if the Lewis number is sufficiently large. Otherwise, for small Lewis numbers, small-scale corrugations driven by DTIs are superimposed on the Darrieus-Landau instability as shown in figure 2.5 b). The resulting propagation speed of the diffusive-thermal unstable flame is significantly faster than one where only the Darrieus-Landau effects are active (figure 2.5 a), and follow a different scaling law [90]. Therefore, from this discussion, one could see that an interplay between diffusive-thermal and hydrodynamic mechanisms, the individual contribution of which is often non-trivial to separate, dictates the stability of premixed flames.

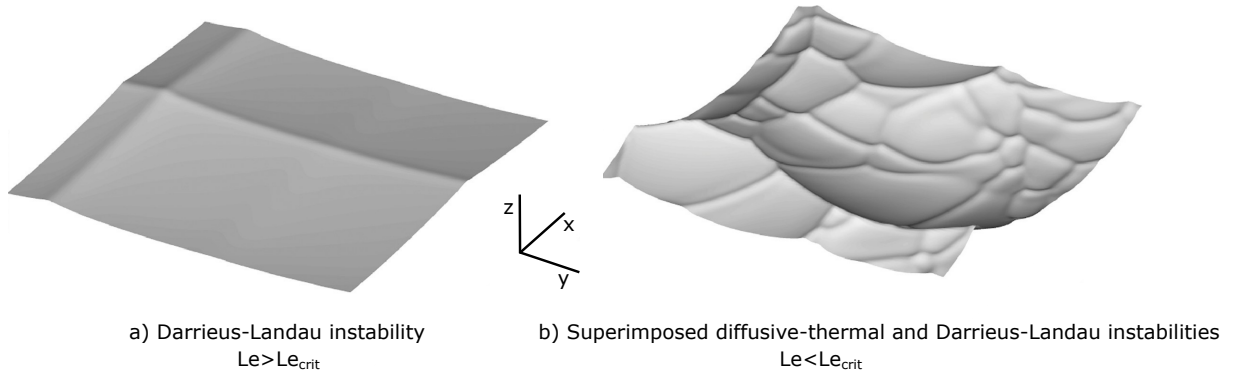


Figure 2.5 Hydrodynamically unstable premixed flame front with a) suppressed and b) superimposed DTIs. Reproduced with permission from [90].

When it comes to non-premixed combustion, the effect of thermal expansion on the flame stability becomes secondary, as assessed by Matalon and Metzener [91] using the large activation-energy asymptotics approach, which is discussed in section 2.2.2. When comparing a constant-density solution to one where thermal expansion was taken into account, a qualitative agreement in terms of the predicted instability type was revealed. The Lewis number maps of the different instability patterns were similar, highlighting the major role played by diffusive-thermal effects in the stability of non-premixed flames. The role of thermal expansion was secondary, and mainly limited to the parameter space describing the onset of instabilities, where a destabilizing effect on the formation of cells was observed, and vice versa for pulsations. Therefore, with this a posteriori justification, we limit our discussion of diffusive-thermal instabilities to non-premixed flames.

As introduced in section 1.3 and figure 1.2 b), it is useful and often justifiable to assume that the reactions occur significantly faster than the mixing processes in diffusion flames, which restricts the reactions to a thin zone that separates the fuel-rich and oxidizer-rich zones. Under the condition of a sufficiently large Damköhler number, which is the ratio of

the characteristic flow time over the chemical reaction time, the reaction zone collapses into a sheet, and information on the reaction mechanism becomes no longer required to determine the flame characteristics. This fast-chemistry regime is also known as the Burke–Schumann limit [92], shown at $D_a \rightarrow \infty$ on figure 2.6. The latter illustrates the typical S-shape behaviour and different burning regimes of diffusion flames as a function of the Damköhler number. As we move away from the intense combustion regime, by increasing the reactants velocities for instance (reduced residence time), finite-rate chemistry becomes relevant as we reach a marginal stability state D_a^* , beyond of which DTIs begin to form. The governing parameters that dictate the characteristics of these instabilities are discussed later. As D_a is further reduced, we reach the turning point $D_{a,ext}$, beyond of which we fall into the lower branch where the flow becomes chemically frozen, and therefore, the flame is extinguished. Physically, this happens when a significant portion of the available chemical energy is not released during the relatively short residence time in the reaction zone, i.e. when the flame exhibits significant reactants leakage. The theoretical solution on the middle branch shows an increase in combustion intensity with decreasing Damköhler number, and therefore represents a physically unrealistic case.

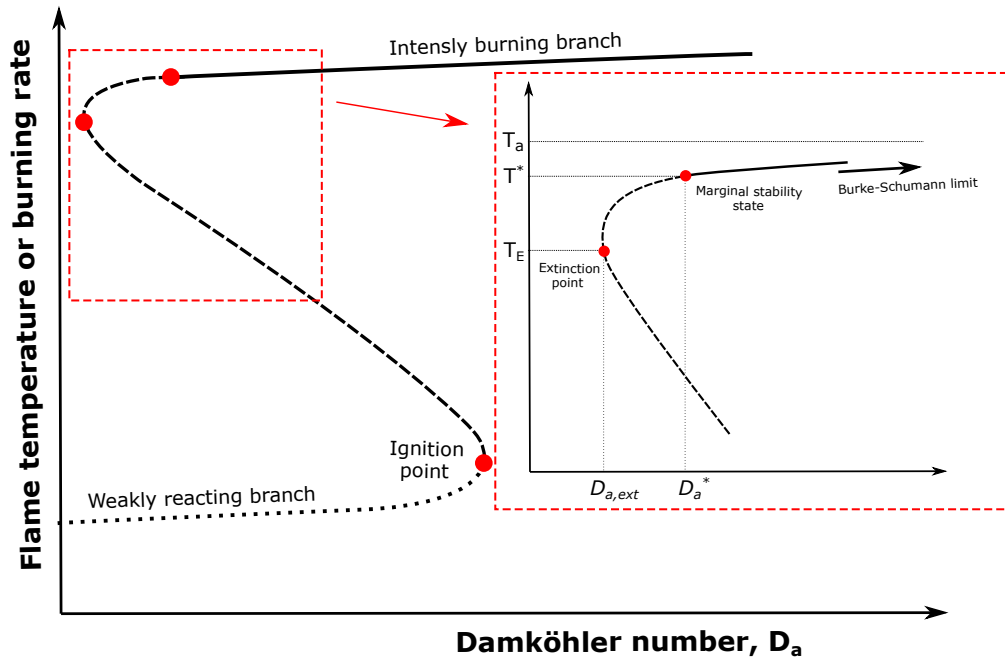


Figure 2.6 Typical S-shape response curve of diffusion flames [21]

Cellular and pulsating flames are the two major types of DTIs that are often discussed in the literature. A mechanistic illustration of the former in diffusion flames is shown in figure 2.7 a), where the hatched regions represent the cells, which are zones of enhanced reaction

rates, local temperature maxima, and consequently, sinks for the reactants. As illustrated by the dashed lines, the reactants supply is non-uniform to the local temperature maxima, from which heat must be conducted away at a relatively low rate for the spatial perturbations to be sustainable. Therefore, analogous to DTIs in premixed flames, one of the main requirement for cellular instabilities is a low thermal over molecular diffusivity ratio, i.e. small Lewis numbers. Figure 2.7 b) illustrates the mechanism of pulsating instabilities. We consider a case where a small disturbance is applied to the position of a planar fuel-rich diffusion flame. As the flame moves to the fuel side, the combustion intensity increases, but in the case where the Lewis number is large, the resulting heat transfer rate is much faster than the reactants supply, which drops the flame temperature and pushes the flame towards the oxidizer side. Here, the combustion intensity becomes lower and the flame becomes fuel starved, which pushes it back to the fuel side as the pulsation cycle repeats.

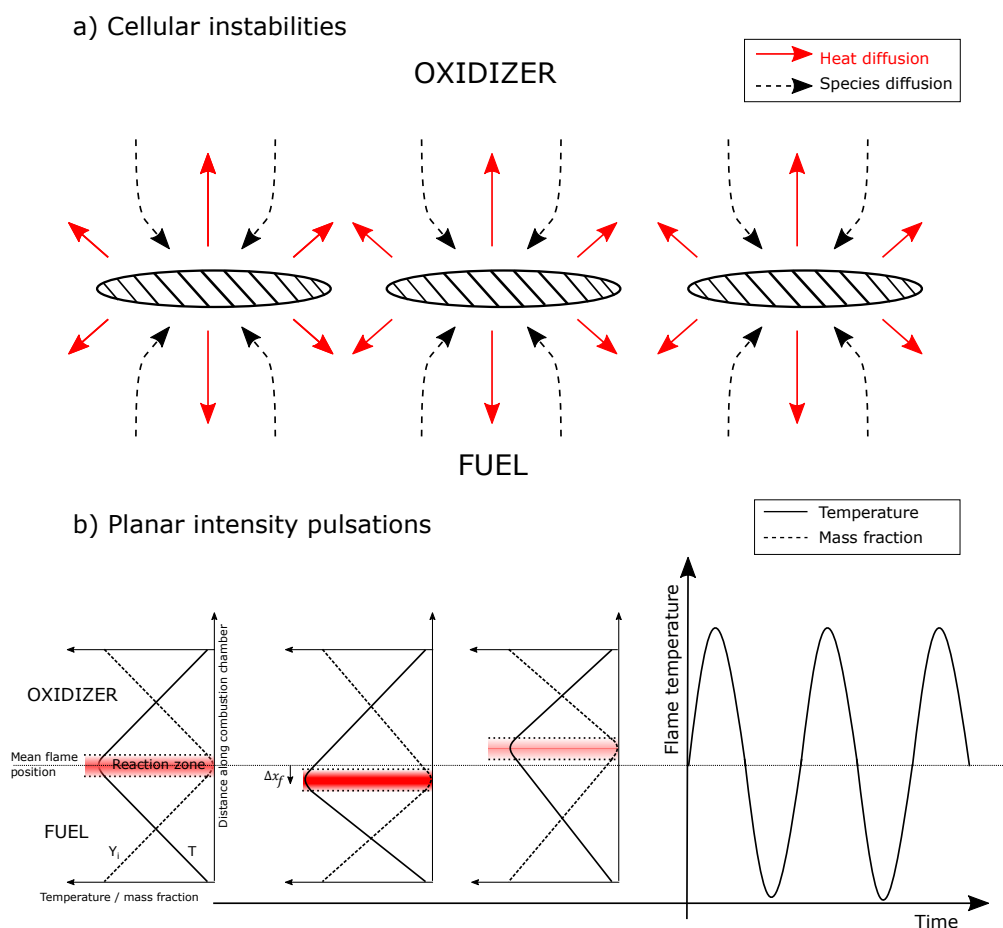


Figure 2.7 Mechanistic illustration of a) cellular and b) pulsating instabilities in diffusion flames.

2.2.1 Experimental studies

The first experimental report on cellular instabilities in diffusion flames dates back to the 1950s, when Garside and Jackson [93] published photographs of polyhedral cellular H_2 jet flames that were diluted with CO_2 or N_2 . High flow rates, corresponding to low Damköhler numbers, were necessary for the onset of these instabilities. Dongworth and Melvin [94] then studied weakly burning H_2 -air flames in a Wolfhard-Parker burner that is shown in figure 2.8 a). This burner contains three adjacent slots (oxidizer-fuel-oxidizer), with a large length to width aspect ratio which renders the flame essentially two-dimensional. N_2 was used as a diluent, and as its molar concentration was gradually increased to 88.5%, the planar base of the flame turned cellular. Seeding the flow revealed cross-stream H_2 leakage to the oxidizer side when cellular instabilities formed. To provide further insight, Chen et al. [95] considered various hydrocarbon fuels and inert gasses using the Wolfhard-Parker burner. This yielded a wide range of Lewis numbers, between 0.21 and 1.83 for the fuel, and between 0.36 and 1.64 for the oxidizer. The authors observed that their cellular flames always had a Lewis number of the more completely consumed reactant below unity. This criterion happened to be also consistent with previously published experimental observations. The cells were observed only at the base of overventilated flames, since D_a is the smallest there relative to the tip of the flame. On the contrary, when underventilating the flame by reducing the flow velocity, D_a became small at the tip as well, which rendered the flame cellular almost throughout.

Lo Jacono et al. [96] studied cellular $\text{H}_2 - \text{O}_2$ jet diffusion flames that were highly diluted with CO_2 . A parameter space covering the extinction and stability limits was provided in terms of the fuel and oxidizer concentrations. Different modes of cellular instabilities were observed, all of which exhibited a fuel Lewis number sufficiently below unity. The number of cells varied between one and six, and some of them were also rotating along the flame axis in a mixed cellular-oscillatory mode. In agreement with previous experimental studies, cellular instabilities were favored at higher oxygen concentrations, which highlighted the important role of the mixture strength in the onset of these instabilities. In a later study, Lo Jacono et al. [97] used both the jet and Wolfhard-Parker non-premixed burners to describe the influence of the underlying hydrodynamics on cellular instabilities. Hydrodynamic length scales such as the jet shear layer thickness and jet width were considered, while neglecting the smaller length scales on the order of the flame thickness. As a result, an expression scaling the cell size with the jet vorticity thickness and mixture strength was proposed, which given the assumptions, only holds for conditions not too close to extinction. Otherwise, the flame thickness must be incorporated in the analysis, most probably through the Damköhler number.

Ishizuka and Tsuji's [98] also observed cellular instabilities in the form of stripped flames

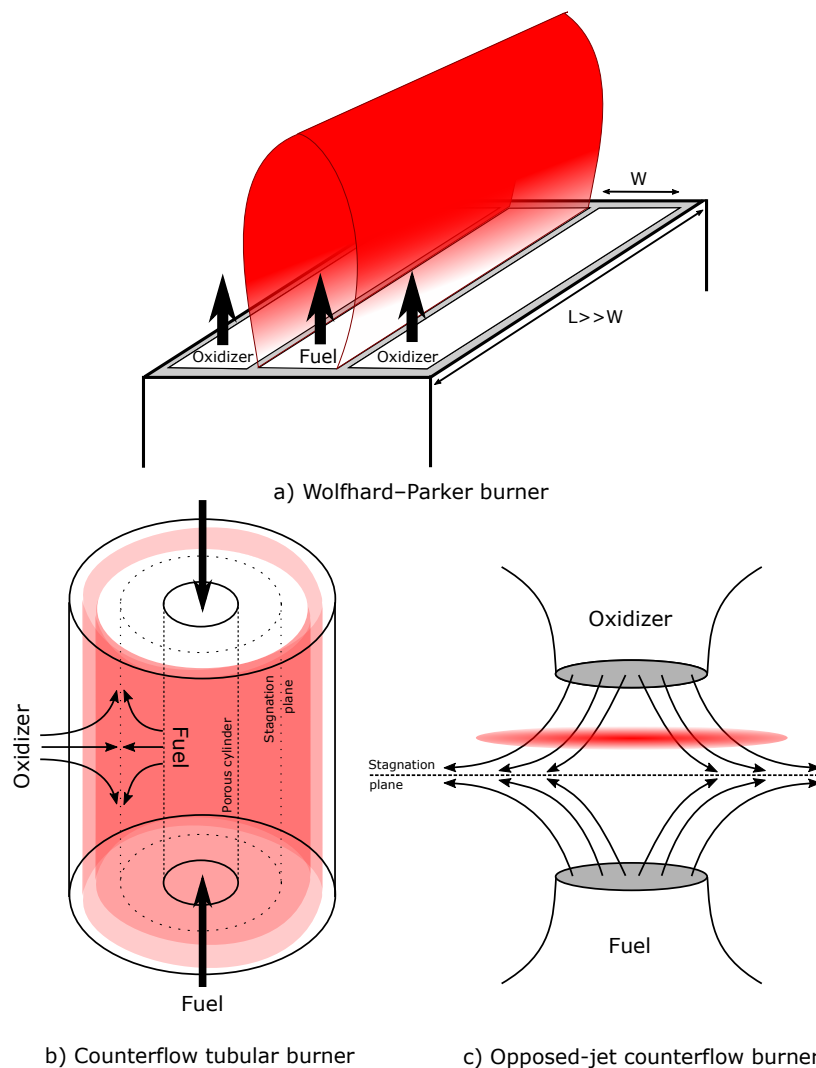


Figure 2.8 Schematic representation of the a) Wolfhard-Parker, b) counterflow tubular, and c) opposed-jet counterflow burners.

or elongated cells in highly-diluted $\text{H}_2 - \text{N}_2/\text{Ar}$ mixtures in a counterflow tubular burner. Similar cellular instabilities in counterflow slot-jet $\text{H}_2 - \text{N}_2$ diffusion flames were also reported by Kaiser et al. [99]. In tubular configurations, a diffusion flame is established in the forward stagnation region of a porous cylinder from which the fuel is ejected into a surrounding oxidizer stream, as shown in figure 2.8 b). These burners are ideal for studying stretch and curvature effects, since these flame parameters can be varied independently, and are also uniform across the flame front [100]. Hu et al. [101] showed that for sufficiently low Lewis numbers, a concave (negative) flame curvature reduces the combustion intensity, rendering the flames more susceptible to extinction. The opposite argument applies for convex flame curvatures. A parameter space mapping the onset of cellular instabilities and extinction

limits was given, in terms of the stretch rate and flame curvature. The fragmentation of stable $\text{H}_2 - \text{N}_2$ flames was discussed in a more detailed study by Shopoff et al. [102]. A 2-cell stripped flame formed as the stability limit was crossed, with the number of cells seen to increase with stretch rate. In the process, the subdivision of the elongated cells took place in their locally concave midsections, where the combustion intensity was the weakest. Due to its convex curvature, combustion was the strongest at the edges of the stripped flame, which eventually turned fully convex (circular cells) at sufficient high stretch rates.

Chan and Tien [103] were among the first to experimentally discuss oscillating flames, by considering various liquid and solid fuel configurations, such as wick, rod, and tube flames. To limit external flow disturbances, such as the well-known buoyancy-driven flame flicker phenomenon, the combustion process took place in a closed low-pressure chamber that was filled with air. The oxygen concentration inside the chamber decreased with time, before pulsations were observed near the extinction limit. In the wick configuration, that is used for commercial candle for instance, the instabilities led to a constant up and down movement (6-9 Hz) of the bottom part of the flame where the combustion intensity was notably weaker than the stationary tip, as revealed by temperature measurements. Dietrich et al. [104] reported a similar behaviour in their microgravity candle flames, that were produced on board the U.S. Space Shuttle to eliminate buoyancy effects. Pulsations were observed a few seconds before extinction, which were manifested as symmetrical back and forth flame front movement along the candles axis, with a frequency between 0.8 and 1.0 Hz.

Oscillations were also reported in coflow spray diffusion flames by Levy and Bulzan [105], which led to the periodic contraction and expansion of the whole flame volume at a frequency of 1-5 Hz. The fuel droplets generated from an ultrasonic atomizer were supplied in the inner stream, which was surrounded by a coaxial flow of air. Golovanevsky et al. [106] then conducted more systematic experiments using a similar Burke-Schumann type spray burner to pin point the driving mechanism behind these oscillations. As the fuel liquid fraction was reduced by heating the supply line, the pulsation frequency decreased monotonically, reaching zero (non-oscillatory) when all the fuel was supplied as vapor. In addition, stable butane flames that were diluted with N_2 started exhibiting pulsations when they were injected with water droplets. These findings provided evidence that in spray flames, the mass and heat transfer mechanism of droplets play a key role in the pulsating instabilities.

Moving to gaseous fuels, Füri et al. [23] studied pulsating instabilities in methane and propane jet diffusion flames. Similar to the aforementioned wick flames, the observed pulsations were also initiated from the colder anchoring flame edge. This also caused the hotter tip of the flame to oscillate at a similar frequency, but with a 180° phase shift. When the inert was

changed from SF_6 to N_2 , the stable propane flame with a fixed mixture strength started oscillating, as Le_F and Le_o increased from 0.92 to 1.83, and 0.45 and 1.03, respectively. Contrary to the aforementioned studies on cellular instabilities, an increased propensity for pulsating instabilities to form was reported here with higher mixture strengths or fuel-rich conditions.

Despite the large number of experimental investigations on diffusive-thermal instabilities in laminar diffusion flames, from which a lot of insight has been obtained, theoretical models can aid in drawing a more complete picture. Such studies are discussed next.

2.2.2 Theoretical studies

Deriving a theoretical flame stability model using the aforementioned experimental configurations could be a fairly cumbersome task, even using numerical methods. While simulations on unstable jet, opposed-flow, and tubular diffusion flames have been performed [107–112], yielding valuable data on the flame structure and nonlinear behaviour, the underlying hydrodynamics, which involve three-dimensional shear and strain effects remain fairly complicated. Since we seek a profound understanding of intrinsic diffusive-thermal phenomena, the one-dimensional chambered diffusion flame configuration could in theory be retained with minimal compromises. A schematic representation is shown in figure 2.9. The combustion chamber is a straight duct that is uniformly supplied with fuel from the bottom, and the top of which the conditions are "magically" kept constant by a sufficiently fast transverse stream that uniformly supplies the oxidizer species and evacuates the combustion products. The former counter diffuses downwards against the bulk flow to reach the flame. The species transport is one dimensional and the flow is unstrained, and consequently, the absence of complexities from hydrodynamic effects has motivated various researchers to adopt the one-dimensional chambered diffusion flame configuration, to gain fundamental insight into DTIs. Unlike in premixed flames, and as discussed earlier, diffusive-thermal effects are the main source of flame front instabilities in diffusion flames, with thermal expansion having only a secondary influence [91]. With this justification to filter out hydrodynamic disturbances, the majority of theoretical studies on diffusion flames have adopted constant density models for simplicity.

The first attempts to model one-dimensional diffusion flames date back to the 1940-1950s, where the focus was on basic flame parameters such as its shape, temperature, and extinction limits [113–115]. The latter was determined when the governing simplified steady-state equations failed to yield a solution. Then came Kirkby and Schmitz [116] in the 1960s, who using numerical methods, were the first to study the stability of the planar flame solution by monitoring its transient behaviour to infinitely small disturbances. They demonstrated that

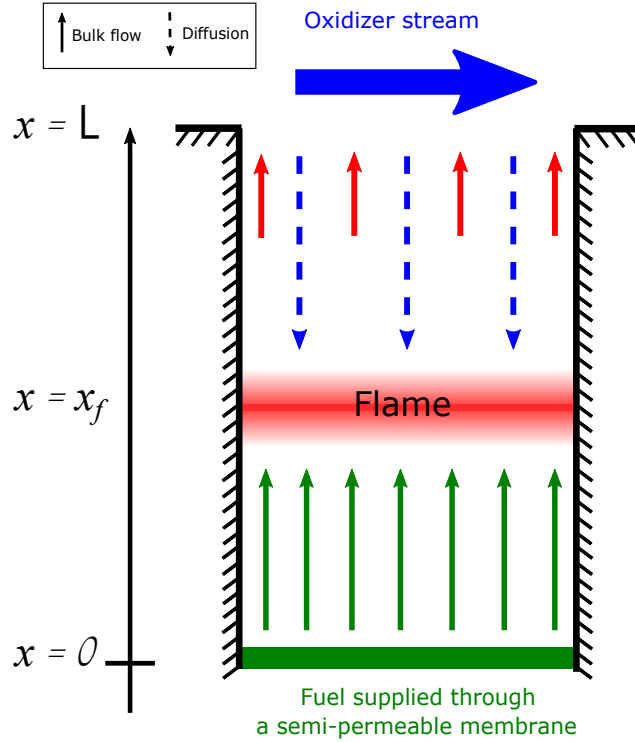


Figure 2.9 Schematic representation of the idealized one-dimensional chambered diffusion flame theoretical construct.

DTIs can lead to extinction and therefore, reduce the operating parameter space predicted by earlier simplified models. The possibility of intensity pulsations to onset at non-unity Lewis numbers was also introduced, however, the laborious numerical approach used allowed only a limited number of parameters to be investigated. Also, a single effective Lewis number was considered, which unlike in premixed flames, can lead to loss in information in diffusion flames where the diffusion of the two reactants can be relevant. The same effective Lewis number can be obtained from different combinations of two reactants, and can therefore result in different instabilities. This was revealed in later studies (discussed below), who demonstrated the importance of considering two Lewis numbers in diffusion flames, one for the fuel and another one for the non-premixed oxidizer.

The introduction of activation energy asymptotic by Liñán's [117,118] work on counterflow diffusion flames in the 1970s was a landmark that inspired the development of more comprehensive theories for diffusion flames, circumventing the need for excessive computational resources and improving the inadequate picture depicted by numerical models. The crux of this approach involves assuming a large Zel'dovich number $Ze \gg 1$, confining all the chemical reactions to a thin zone, which is a sheet when viewed on the much larger diffusion scale $\mathcal{O}(1)$. Jump conditions are used to relate the external flow field on either side of the thin reaction

zone and resolve its structure on the $\mathcal{O}(Ze^{-1})$ scale, using higher order approximations for the fuel and oxidizer leakage across the flame.

Matalon et al. [119] were among the first to apply activation-energy asymptotics on the one-dimensional chambered diffusion flame configuration, albeit the focus was not flame instabilities. The objective was rather to determine analytical relations for the flame response, in terms of the unburnt fuel fraction, over the entire Damköhler number range, including explicit expressions for the ignition and extinction points. It was shown that below a certain D_a , which can result when the fuel is supplied excessively fast, the unburnt fuel fraction becomes unity, which corresponds to an extinguished state.

To study instabilities, Kim et al. [120, 121] then performed linear stability analysis on a one-dimensional flame using the Zel'dovich number as a large perturbation parameter. It was revealed that when the Lewis number is less than unity and very close to the extinction point, cellular instabilities with a size comparable to the reaction zone thickness would develop with a fast time scale that is comparable to the chemical reaction time. These are commonly known as fast-time or high-frequency instabilities, as originally introduced by Buckmaster et al [122]. Despite the valuable insights, only stoichiometric conditions were considered, and the fuel and oxidizer Lewis numbers were assumed equal ($Le_F = Le_o$).

The aforementioned shortcomings were addressed by Cheatham and Matalon [123], who proposed a general asymptotic formulation for diffusion flames (time-dependent and multi-dimensional), which was subsequently used to study the stability of planar diffusion flames. A broad range of conditions were investigated, including non-stoichiometric flames with unequal fuel and oxidizer Lewis numbers. Contrary to what was suggested in [120, 121], this study revealed that DTIs in diffusion flames are not restricted to the high-frequency instability mode, and can occur at Damköhler numbers significantly larger than the initially believed critical value. More precisely, DTIs were predicted for $D_{a,ext} < D_a < D_a^*$, with $D_a^* - D_{a,ext} = \mathcal{O}(1)$. Consequently, cells with sizes comparable to the diffusion length this time were discussed, i.e. between 0.5-2 cm, which was consistent with the majority of cellular flames reported experimentally, unlike the high-frequency instabilities whose relevance is quite limited.

The dependence of the cell size on both Le_o and Le_F as two separate parameters was also clearly highlighted. In addition, the propensity of cellular instabilities to form was shown to increase as the mixture strength decreased, or in another words, under fuel-lean conditions. The focus of this work was cellular instabilities only, which technically meant that only the real values of the two-dimensional disturbance growth rate from the linear stability analysis were considered, with Le_F and Le_o being both assumed less than unity. To address pulsation instabilities, Kukuck and Matalon [124] then considered the opposite case, i.e. where the

imaginary part of the growth rate to a planar disturbance is positive, and where both Le_F and Le_o are greater than unity. Contrary to cellular instabilities, it was shown that the propensity for pulsations to form increases with mixture strength. The pulsation frequencies scaled with the flow time, predicting values between 1-6 Hz, which were consistent with the range reported in experiments. It should be emphasized that this model is based on linear stability analysis, which can identify the critical conditions and physical mechanisms responsible for the onset of oscillations. However, if the time evolution of the pulsations beyond their onset is of interest, nonlinear analysis is required. Such investigations can predict the end fate of the oscillations, which could lead to extinction if an unbounded solution was obtained. For more details, interested readers are kindly referred to Cheatham [125] and Wang et al. [126].

Despite the fact that two unequal Lewis numbers were considered in the two aforementioned models [123, 124], the range was restricted to either above or below unity, depending on whether cellular or pulsation instabilities were being modelled. Experimental observations [23] on the other hand, suggested that contrary to inferences that could be made at that time from premixed flames, pulsations could form when either the fuel or oxidizer Lewis numbers is below unity, under the condition that the other Lewis number is sufficiently large, and vice versa for cellular instabilities. This ultimately led Metzener and Matalon [127] to propose one of the most comprehensive diffusion flame stability models that is known to date, which is based on the general asymptotic diffusion flame theory of [123]. The Lewis numbers of both reactants were varied from small below unity values to sufficiently larger than unity, and both the real and imaginary parts of the two-dimensional disturbance growth rate were considered, which account for potential mixed cellular-oscillatory instabilities.

Consequently, an instability map in terms of Le_o and Le_F was provided as replicated in figure 2.10, where generally speaking, stationary cells were formed at small Lewis numbers, while oscillations were predicted at larger Le 's. Travelling waves or oscillatory cells were observed at intermediate Lewis numbers. In addition, it was confirmed that it is sufficient for either Lewis numbers to be less than unity for cells to onset in diffusion flames, assuming the other Lewis number is sufficiently large, and vice versa for oscillations. Strictly speaking it was shown that the available enthalpy (h_f) and the local mixture strength (γ) at the flame sheet, with $\gamma < 0$ representing lean combustion, were the two most relevant parameters in ultimately predicting the instability type. Stationary cells form when the available enthalpy is excessive ($h_f > 0$) and when $\gamma < 0$, and transitions into the high-frequency mode as $\gamma = 0$ is approached. Planar intensity pulsations on the other hand onset when the available enthalpy is deficient ($h_f < 0$). Here again, the flame pulsates under the fast-time mode at $\gamma \approx 0$, and transitions into moderate frequencies at $\gamma > 0$.

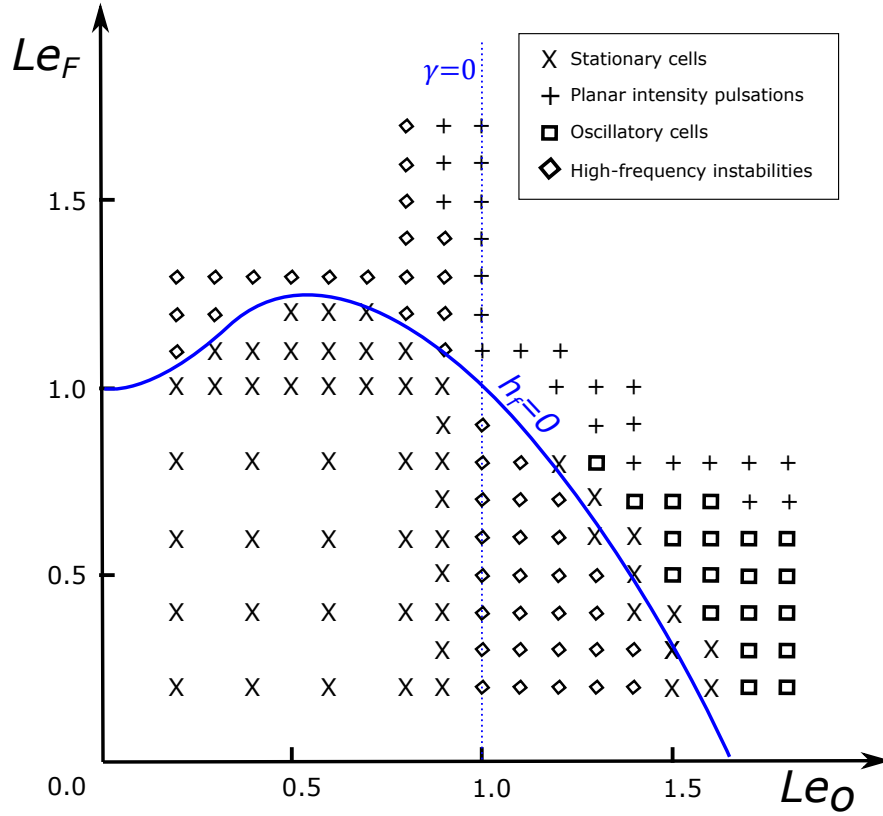


Figure 2.10 Map illustrating the various types of instabilities in terms of the fuel and oxidizer Lewis numbers. Data extracted from Metzener and Matalon [127] at $\phi = 1.0$ and $\Delta T = 0$.

Despite qualitatively agreeing with different experimental observations, the absence of a burner at that time that can produce unstrained diffusion flames meant that Matalon et al. [123, 124, 127] stability model was lacking quantitative experimental validation. Out of the different research burners discussed in section 2.2.1, the counterflow configurations come closest to the idealized one-dimensional diffusion flame. For instance, planar flames can be generated in opposed-jet counterflow burners (figure 2.8 c), which have been extensively used to study different combustion aspects such as flame chemistry and extinction. However, the inevitable radial flow renders the flame subject to significant amount of stretch. In an attempt to minimize these radial flow effects, Han et al. [128] adopted a large radius of curvature (522 cm) porous sphere to inject the fuel into a slow buoyancy-driven oxidant flow. This is another type of counterflow diffusion flame configuration, and is commonly known as the "Tsuji" burner. The strain rate was estimated to be 1.4 s^{-1} , and flame instabilities such as stripes and periodic holes were observed. However, given the limitations imposed by gravity on the alignment of the fluxes and gravity vectors, the parasitic influence of hydrodynamics persisted, which ultimately hampered the quantitative comparison with analytical models.

Therefore, all the experimental studies at that time were limited to burners that provided non-uniform oxidizer boundary conditions. Strictly speaking, a burner design that is identical to the convectional one-dimensional chambered configuration of figure 2.9 is impossible to realize in practice, and this is mainly attributed to the nature of the oxidizer stream, whose large transverse flow rate would inevitably induce perturbations, particularly near the edges of the combustion chamber. Consequently, an alternative design of top part of the idealized burner was needed, as discussed next.

2.2.3 Unstrained diffusion flame burner

To overcome the aforementioned issues, researchers from École polytechnique fédérale de Lausanne (EPFL) [129] supplied the oxidizer species axially using many thin capillaries, between which the combustion products were allowed to escape. As shown in figure 2.11 a), this meant that the oxidizer species had to initially mix with the combustion products flowing upwards in a three-dimensional flow field which was called the injection layer (figure 2.11 b), below which the oxidizer starts counter-diffusing towards the flame. This design also meant that gravity no longer imposes limits on the alignment of the fluxes and gravity vectors, meaning that one-dimensional species transport could in theory be achieved.

The key to accomplish uniform oxidizer concentration below the injection layer, and therefore mimic the idealized diffusion flame configuration, boils down to adequately reducing the needles spacing and flow rate, such that the flow non-uniformity in the injection layer occurs at small scales compared to the phenomena being studied. The authors used $25 \times 25 = 625$ stainless steel capillaries with: 1 mm O.D. and 0.8 mm I.D. arranged on a Cartesian grid with a 1.78 mm center-to-center spacing. The side of the combustion chamber square cross-section had a length of 46 mm. The fuel was introduced from the bottom of the combustion with an upward bulk velocity through a porous plate. Consequently, an ultra-low strain rate of $1s^{-1}$ was obtained, however subtle inaccuracies in the mark I burner design rendered the flames slightly asymmetrical and curved as shown in figure 2.12 a). This often led to rapidly moving unstationary cells when the instabilities were triggered as shown in figure 2.12 b). Temperature measurements in the exhaust stream revealed significant inhomogeneity, which explains the asymmetric flame behaviour. This resulted from attaching all the hot components of the facility to one side of the burner support column. Regarding the flame curvature effects, it was initially believed that they are mainly caused by heat loss to the combustion chamber windows. However, after using a secondary burner to heat the combustion chamber walls from the outside at the flame height, the persistence of flame curvature limited the source of the problem to the exhaust system.

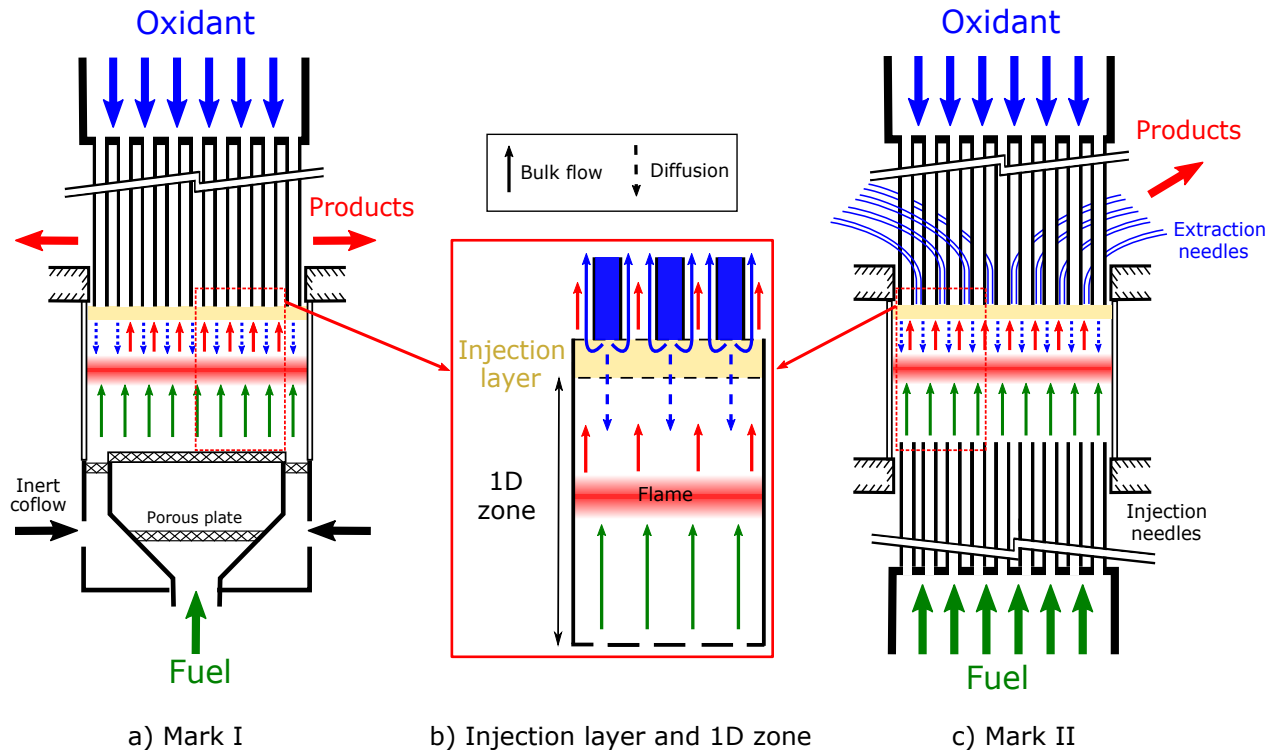


Figure 2.11 Schematic representations of a) the mark I version of the one-dimensional unstrained diffusion flame burner, b) injection layer, and c) mark II burner design with the extraction needles.

Consequently, the limitations of the promising mark I design were addressed by Robert and Monkewitz [130], who introduced a more advanced mark II version of the 1D burner. As shown in figure 2.11 c), an additional set of needles that are interlaced within those of the oxidizer was used to enhance the evacuation uniformity of the combustion products. $31 \times 31 = 961$ hypodermic needles with: 1 mm O.D. and 0.8 mm I.D. were used for injecting the oxidizer, while $32 \times 32 = 1024$ stainless steel tubes with 1.2 mm I.D. were used for the products. The spacing on the Cartesian grid of the needles array was 2.5 mm, and the side of the combustion chamber was 77.5 mm. The length of the latter could be varied between 20 and 80 mm. The needles array was heated for temperature homogeneity in an adequately insulated plenum. To account for velocity reduction effects near the combustion chamber walls, the peripheral evacuation tubes inner diameter was reduced to 1.0 mm. Also, the chimney walls were made from Macor ceramic to minimize conduction heat losses, contrary to the uninsulated brass used in the mark I burner, which resulted in colder less viscous and therefore, faster flow near the walls of the combustion chamber. In addition, to minimize heat loss effects to the colder windows, a quartz cylinder that spanned the entire length of the combustion chamber was used to divide the flame into two: An inner part where

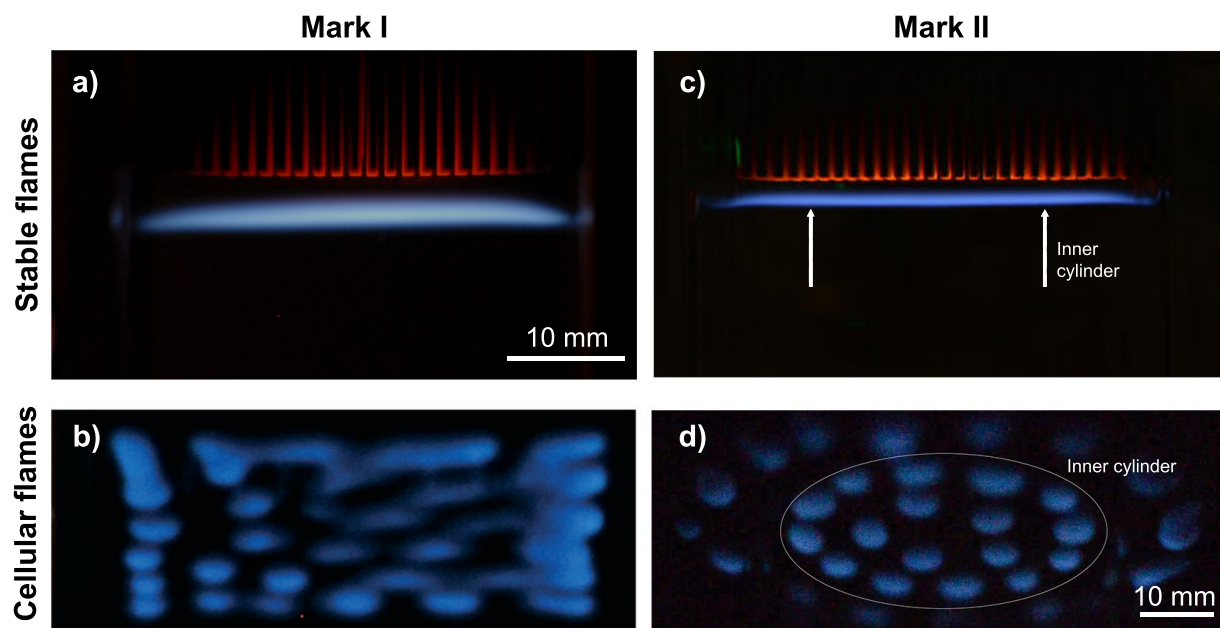


Figure 2.12 Stable and cellular flames generated in the mark I and II versions of the unstrained diffusion flame burner.

the measurements were taken, and an outer shielding flame to provide adequate heating. Finally, to guarantee a symmetrical division of any heat loss effects, the attachments used were symmetrically placed along the four corners of the burner.

Significant improvement was immediately observed when looking at the flatness of the flame, as shown in figure 2.12 c). Furthermore, the total flame stretch was evaluated to be as low as $0.05s^{-1}$. Laser Doppler Anemometry was used to calculate the flow strain component of the total flame stretch, while direct chemiluminescence was used to determine the contribution from any curvature effects. Besides the homogeneous velocity profiles obtained from LDA measurements, it was confirmed that the aforementioned injection layer thickness was 2.5 mm, which was similar to the needles spacing as initially expected. To assess the spatial homogeneity of the species concentration below the injection layer, a thoroughly calibrated mass spectrometer was used. The measured species concentrations were fairly uniform as the sampling probe was swept across the combustion chamber cross-section, with a maximum of 10% variation.

The incorporation of the mass spectrometer also meant that the boundary conditions at the top of the one-dimensional combustion zone, and therefore the initial mixture strength, can be finally accurately determined. This is because a significant fraction of the supplied oxidizer, which could reach $2/3$, is directly evacuated with the hot combustion products, and

only a limited amount, which cannot be known solely from the supplied oxidizer properties, reach the one-dimensional zone. This was another major improvement from previous investigations using the mark I burner, where the initial mixture strength was erroneously estimated from the oxidizer stream, which hindered the comparison with analytical solutions. Having overcome this issue, figure 2.13 compares the experimentally measured flame structure in the mark II burner to that predicted by the idealized one-dimensional diffusion flame analytical solution, where strong agreement is revealed. Based on these findings, and after being long thought to be a formidable challenge, a good experimental approximation of unstrained diffusion flames was finally realized, which paved way for quantitative comparison with flame stability models.

In a subsequent publication, Robert and Monkewitz [131] exploited the mark II 1D burner to study diffusive-thermal instabilities that onset in unstrained diffusion H_2 flames. Starting from stable conditions near the Burke–Schumann limit where the combustion is significantly faster than the residence time, the Damköhler number was gradually reduced beyond the marginal stability state and down to the extinction limit. The Damköhler number was controlled through the flame temperature, which was changed via the amount of CO_2 dilution. As the combustion intensity of H_2 was reduced, a hole first forms in the flame sheet, which then multiplies at lower Damköhler numbers forming a partly cellular flame, where the cells are not completely detached. This eventually transitions into a fully cellular flame at sufficiently low Damköhler numbers. It worth mentioning that the cells were reported to be stationary as shown in figure 2.12 d), and devoid of the fast motion observed in the mark I burner. This provides complementary evidence for the highly unstrained nature of the flow field.

To evaluate the thermophysical flame properties, such as the thermal/molecular diffusivity, heat conductivity, and density, a one-dimensional diffusion flame model was implemented in Cantera. The aforementioned properties were needed for the evaluation of fundamental parameters such as the reactants Lewis numbers, which are needed for the reliable comparison with stability models. The numerical model was initiated with boundary conditions, such as the fuel/oxidizer side temperatures and concentrations, measured from the experiments. Unsurprisingly, the resulting species and temperature profiles were in very good agreement with the experiments. The $H_2 - CO_2$ flames had $Le_{H_2} \approx 0.25$ and $Le_{O_2} \approx 0.85$, which according to the theoretical stability map similar to that of figure 2.10, are conditions favoring cellular instabilities, as was indeed observed in reality. In addition, the sizes of the cells were measured, and in agreement with theoretical predictions, they scaled approximately linearly with the diffusion length $l_D = D_{th}/U$.

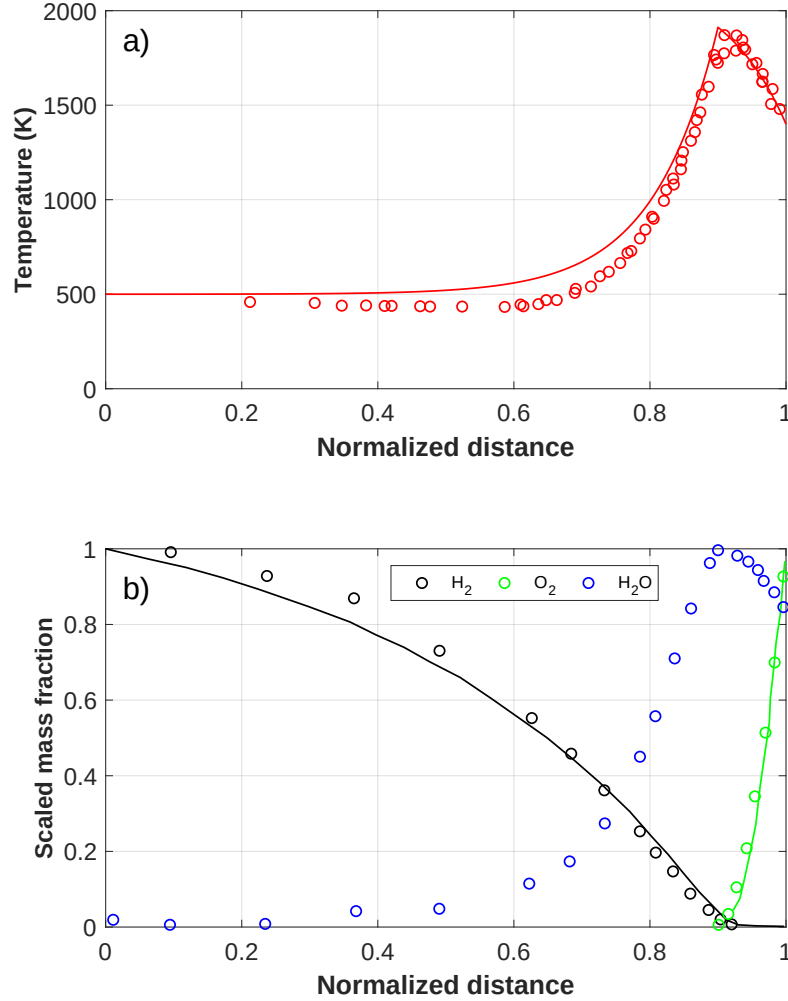


Figure 2.13 Comparison between experimental measurements ($\circ$) of H₂ flames ($X_F = 0.35$, $U \approx 20$ mm/s) in the mark II burner and the analytical one-dimensional diffusion flame solution (—). a) Spatial variation in temperature at $\phi = 0.5$ and b) reactants concentration at $\phi = 1.0$. Data extracted from [130].

To observe pulsating instabilities in the H₂ flames, the Lewis numbers had to be increased. Although replacing CO₂ with He, which is a significantly more mobile species, increased Le_o to 1.25, the absence of CH* chemiluminescence in the resulting pulsating flames rendered them extremely dim and difficult to capture with the available measurement tools. To remedy this issue, the H₂ fuel was replaced by CH₄, which yielded $Le_{CH_4} \approx 1.25$ when diluting with He, and therefore, planar intensity pulsations as theoretically expected. Significant reactants leakage across the oscillating flame sheet was measured using the mass spectrometer, a behaviour that was also predicted by theoretical models as discussed earlier.

The frequency of the pulsations was also determined using a fast Fourier transform routine, and when multiplied with the thermal diffusion time, the resulting product scaled with the Damköler number.

2.3 Syngas diffusion flames

Despite our profound understanding of DTIs in single-species fuel flames, through theoretical and experimental work, the nature of DTIs in multi-fuel mixtures, such as syngas, remains unknown. Instabilities in syngas mixtures have been discussed in premixed flames, such as the McKenna burners [132, 133], Bunsen burners [134, 135], and spherically expanding flames [136, 137], however under a significant influence of aerodynamic effects. Consequently, the instabilities reported are often a combination of hydrodynamic, diffusive-thermal, and in some cases buoyancy effects, with scarce reference to any potential DTI pulsations from CH_4 , CO , or any other large Lewis number species. When it comes to laminar syngas diffusion flames, the literature mainly focuses on flammability limits and emissions. These studies mostly rely on opposed-jet counterflow and coflow jet burners, both of which inevitably induce significant flame stretch. Nonetheless, the main findings of some of these studies are discussed next to provide insight on the consequences of diluting syngas with CO_2 , H_2O and N_2 and the effect of flame stretch, which is ubiquitous to practical burners.

2.3.1 Opposed-jet flames

Opposed-jet non-premixed configurations (figure 2.8 c) allow for the independent variation of the flame dilution and stretch, which are two important parameters for extinction behavior and flammability. Syngas studies using such burners are discussed here, followed by coflow configurations in the next section.

Flame stretch has a substantial effect on the extinction mechanism, especially for nonequid-diffusive mixtures. When subjected to low stretch, flame extinction is prone to occur via quenching where combustion suffers from low temperatures and possibly excessive radiative losses. In their study on CO_2 -diluted syngas flames, Park et al. [138] demonstrated the key role radiation could play at low stretch by relying on numerical simulations. At low strain rates, the difference in the maximum flame temperature between a model that takes radiation into account and one that does not was large. This discrepancy grew as the CO content in syngas was increased since the CO and CO_2 formed are important radiation sources. This was not the case at high strain rates, since blowoff, which is caused by incomplete chemical reactions due to insufficient residence time, is the main reason behind the extinction

of highly-stretched opposed-jet flames. This observation was also supported by Aggarwal et al. [139], who when reducing the oxygen concentration in the oxidizer stream, reported a drop in the flame temperature and OH concentration, with the scalar dissipation rate, a parameter quantifying how much the flame is strained, staying constant.

Insight on the mechanism of CO_2 , H_2O , and N_2 dilution-induced syngas extinction was provided by Shih and Hsu [140] using numerical simulations. The authors dissected the inert, diffusive-thermal, chemical, and radiation effects of dilution on flame extinction, by utilizing five slightly-modified artificial species in their model. The inert effect of dilution always resulted lower flame temperatures, as the concentrations of the reactants dropped despite maintaining the same thermal and transport properties as syngas. Conversely, the diffusive-thermal effects of dilution increased the flame temperature via the preferential diffusion of H_2 , despite the higher heat capacities of the inert species. Contrary to CO_2 and N_2 , the isolated chemical effects of H_2O dilution contributed to boosting main exothermic reactions, by enhancing chemical reaction rates of OH and HO_2 -producing radicals. When it comes to heat loss by radiation, the deterioration in flammability from H_2O addition was the greatest, followed by CO_2 , and N_2 . While some flammability limits were provided to represent the ensemble of the aforementioned four effects, this investigation was performed only for a single strain rate, 10 s^{-1} .

Consequently, in a later study [141], the same group provided syngas flammability limits for a wide range of stretch rates, ranging from the quenching to the blowoff limits. The maximum flammable dilution quantity was the greatest for N_2 for all stretch rates, however, a crossover was observed between CO_2 and H_2O . When operating below 10 s^{-1} , H_2O -diluted syngas was less flammable than CO_2 -diluted mixtures, and vice versa near the blowoff limit. Although on their own, CO_2 species are more radiative than H_2O , the enhanced chemical effect when adding the latter to syngas significantly enhances the production of CO_2 among other radiative species via intermediate reactions. This caused the radiation effects of H_2O dilution to be significantly larger than that of CO_2 , and along with the enhanced chemical effects, this explains the reduced flammability limits of H_2O -diluted syngas near the quenching limit. At high stretch rates, the radiative effects were negligible, particularly when compared to the diffusive-thermal effects, which were mainly responsible for the lower flammability of CO_2 -diluted flames near the blowoff limit. Despite the wide range of stretch rates considered, CH_4 -free syngas with a constant H_2/CO ratio of unity was only studied.

The flame structure and extinction behavior of diluted SOFC anodic syngas, leftover after partially reacting, were simulated by Aggarwal et al. [139]. By volume, the syngas mixture contained $X_{\text{H}_2} = 12.2\%$, $X_{\text{CO}} = 5.5\%$, $X_{\text{H}_2\text{O}} = 58.4\%$, and $X_{\text{CO}_2} = 24.0\%$. The spatial

variation of the species in the flame revealed that the H_2 and CO oxidation zones were separated. Hydrogen, being more reactive, supplied hydroxyl (OH) radicals to CO to form CO_2 on the oxidizer side. Additional insight on the flame structure was provided by Park et al. [138] who investigated the influence of dilution and syngas composition. It was observed that with no CO_2 dilution, the H_2 and CO reactions zones were separated. On the other hand, when 30% CO_2 was added, the H_2 and CO species were consumed in the same region. This also caused the overlap region between the CO and O_2 to increase, which meant that the CO oxidation route became more dominant. It was also observed that at a high H_2/CO ratio, H_2O -leading reaction routes became dominant. But on the contrary, when the CO content was increased, the $\text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2$ route dominated, while H_2O -leading ones diminished.

The benefits of increasing the oxygen concentration in the oxidizer stream of syngas flames were highlighted through the simulations of Safer et al. [142]. As the concentration of O_2 was changed from 21% to 30%, the maximum flame temperature increased by 10% and 18% for $\text{H}_2/\text{CO} = 0.25$ and 4.0 respectively. This also led to the increase in the blowoff limits, and consequently the flammability range. The CO_2 concentration was increased as well by 27% and 34% for $\text{H}_2/\text{CO} = 0.25$ and 4.0 respectively. This is one of the reasons why oxyfuel combustion can facilitate carbon capture and storage. Despite having less N_2 in the oxidizing stream, O_2 enrichment resulted in an increase in NO concentrations since the Zeldovich mechanism was proven to be the dominant route for its formation. It was suggested that to minimize NO production for high H_2/CO ratios, burners should operate at high strain ($> 100 \text{ s}^{-1}$) rates, and vice versa for low H_2/CO ratios ($< 5 \text{ s}^{-1}$).

2.3.2 Coflow flames

Conclusions drawn from studies on coflow flames have direct implications on many commercial combustion systems as this configuration approaches many common non-premixed systems (ex: gas turbines), and allows for multidimensional flame analysis. Contrary to the aforementioned studies on opposed-jet flames, some of the main studies found in the literature involve experimental work.

Xu et al. published several interesting works relying on OH^* -chemiluminescence to study different aspects of coflow syngas diffusion flames [143–145]. In a recent article, the authors investigated the flame attachment mechanism under a wide range of syngas composition (5%-95% to 95%-5% $\text{H}_2 - \text{CO}$) [143]. OH dense regions coincided with zones of maximum heat release and temperature as expected. Inside the fuel tube, H_2 oxidation never took place, but syngas pyrolysis was observed with the backwards-diffusion of HCO and HO_2 radicals.

The diffusion of H_2 and CO from the inner fuel to the outer oxidizer stream was responsible for the flame attachment, which was enhanced by increasing the H_2 content in syngas. The high reactivity of the former caused the attachment point of the flame to take place further upstream compared to syngas mixtures with lower H_2 content.

In another study, the same group studied the effect of the oxidizer stream dilution on the flame shape and pollutant emissions [144]. It was observed that H_2O and CO_2 dilution had opposite effects on the flame shape, with the addition of the former reducing the flame height and radius. A temperature drop was measured when the N_2 content in the oxidizer stream was replaced by either H_2O or CO_2 , which consequently also reduced pollutant emissions. The same authors [145] conducted another experimental study on the coupling between H_2 concentration in syngas and H_2O and N_2 diluents. The concentration of OH radicals was used to monitor the combustion intensity, where it was interestingly noted that for a H_2O -diluted oxidizing stream, the maximum OH concentration and flame temperature decreased with increasing H_2 concentration in syngas. The opposite behaviour in terms of OH concentration was observed when N_2 -diluted oxidizer was used. To provide further insight on this counter intuitive observation, the authors used numerical simulations that revealed OH concentration trends that agreed well with the experimental ones. Similar to the previously discussed work by Shih and Hsu [140], the different dilution effects were isolated, where it was shown that H_2O had low and high chemical and thermal effects, respectively, which caused a weakened formation of OH via $H + H_2O \rightleftharpoons OH + H_2$.

Other studies found in the literature on coflow syngas diffusion flames relied purely on numerical calculations. Xi et al. [146] simulated the effect of syngas dilution and composition on NO emission. Similarly to the previously discussed studies, the thermal route dominated the production of NO molecules, which was evident from the drop in the OH radical concentration, a key indicator of heat release. Piemsinlapakunchon and Paul [147] also relied on computer simulations to study the effect of syngas composition on heat generation and pollutant emissions, where it was shown that enhancing the CO content in syngas would boost the flame heat flux. When the H_2/CO ratio was decreased from 3 to 1/3, the average heat flux jumped by 142%. The addition of CH_4 to syngas also yields larger heat fluxes, but to a much larger extent. With only 20% CH_4 enrichment, the average heat flux increased by 42%.

CHAPTER 3 RESEARCH OBJECTIVES

3.1 Critical assessment of the literature

3.1.1 Modelling of polygeneration systems

From the literature review of section 2.1, one could see that the co-generation of biofuel/heat and power has been investigated on several occasions, even in some cases with carbon capture and storage. Several other studies discuss the tri-generation of electricity, heating, and SNG/MeOH. However, the thermodynamic feasibility of converting biomass to electricity, biofuel, heat, and a CO₂-rich stream, simultaneously, remains to be investigated. These four products are in high demand in agricultural greenhouses, a venue usually surrounded by abundant residual biomass.

In addition, the majority of the thermodynamic studies in the literature investigate large-scale systems with biomass capacities exceeding 100 MW. Despite their robustness and efficiency, expensive single-purpose components and severe operating conditions are often used, which are economically unjustifiable for small-scale implementations that only harness a few MWs of biomass energy. For instance, most of the MeOH-producing systems studied use reactors operating between 60 and 100 bar, which could impose serious risk for public safety in decentralized implementations such as agricultural greenhouses. These systems also often recycle a significant fraction of the product stream back into the MeOH reactor, to enhance its yield, which significantly increases the equipment size and cost.

The incorporation of versatile and flexible components in decentralized polygeneration systems has the potential to significantly enhance the economic viability of the process. For instance, a reversible high temperature fuel cell such as SOFC can replace cryogenic air separation units for O₂ production, CO₂ absorption systems and catalytic WGS reactors for H₂ supply, along with gas turbines for electricity production. As mentioned in section 2.1, the feasibility of coupling SOFCs with biomass gasifiers to generate electricity from syngas has been experimentally proven on several occasions recently. In addition, thermodynamic simulations have been conducted to investigate the enhanced biofuel output resulting from H₂-enrichment and oxy-fuel gasification with the help of SOECs. However, to the author's knowledge, there are no studies that simultaneously exploit all the aforementioned features of reversible fuel cells in a polygeneration biomass gasification system.

3.1.2 Diffusive-thermal instabilities

Diffusive-thermal instabilities have been observed in several premixed and non-premixed burners, as discussed in section 2.2. To eliminate the parasitic hydrodynamic effects, which play a secondary role in the stability of diffusion flames, theoretical studies adopt the one-dimensional chambered diffusion flame configuration, from which fundamental understanding of the complex underlying mechanism has been obtained. These findings were also experimentally validated upon the realization of a quasi-unstrained diffusion flame burner. However, these efforts have only been placed to study single-species fuels. The instabilities in mixtures of distinctive combustible species such as syngas remain unknown. The simultaneous presence of H_2 with a notably high molecular diffusivity, and CO/CH_4 with much lower mobility requires further research to predict the characteristics of the resulting instabilities.

Syngas combustion is expected to play a major role in the energy landscape of decentralized polygeneration systems. As presented in section 2.3, research on the flammability of syngas diffusion flames rely on burners that induce significant flame stretch such as the opposed-jet or coflow configurations, hampering fundamental analysis on DTIs. This is mainly because non-premixed burners producing unstrained flames are challenging to implement, with two scarce versions designed by École polytechnique fédérale de Lausanne (EPFL). These have nonetheless never been used to study DTIs in multi-fuel mixtures. In addition, even the most advanced version of the one-dimensional diffusion flame burner cannot accommodate gaseous fuels with a high water vapor content, such as biomass-derived syngas. Consequently, a new mark III burner design that can accommodate humid fuels is needed.

3.2 Specific objectives

Based on the aforementioned research needs, the objectives for this thesis were specified as follows:

1. Evaluate the thermodynamic performance of systems producing biofuel (natural gas or methanol), electricity, heat, and a CO_2 -rich stream with biomass as the sole input.
2. Develop an unstrained diffusion flame burner that can be operated with fuels containing high vapor content.
3. Experimentally characterize diffusive-thermal instabilities in unstrained H_2 - CO - CH_4 - CO_2 - H_2O diffusion flames.

3.3 Articles outline

The results of this research are discussed in the next four chapters, each presented in a format of a journal article, as summarized next:

Article 1: Thermodynamic analysis of novel methanol polygeneration systems for greenhouses. This work presents two new MeOH polygeneration system designs. Each one considers a different gasification technology, where a simple downdraft gasifier is compared to a more efficient yet more complicated dual-fluidized bed approach. In both cases, the H_2 , O_2 , and electricity generation capabilities of reversible solid oxide cells are exploited, and parametric analysis is conducted to highlight the flexibility of the systems. The paper has been published in *Biomass Conversion and Biorefinery* [148].

Article 2: Thermodynamic analysis of small-scale polygeneration systems producing natural gas, electricity, heat, and carbon dioxide from biomass. In this article, two SNG polygeneration systems have been modelled, with new designs that differ from article 1 as the conversion process and efficiency of SNG is different than that of MeOH. The electricity storage potential of the polygeneration system is also explored, which is promoted by the utilization of RSOCs. The work is currently under review in *Energy* [149].

Article 3: Experimental characterization of diffusive-thermal instabilities in CO_2 -diluted H_2 - CH_4 -CO unstrained diffusion flames. This paper investigates diffusive-thermal instabilities in dry syngas flames using the mark II version of the 1D burner. Flame stability limits are provided for a broad range of fuel blends, and the instability patterns are mapped in terms of the fuel composition and mixture strength. High-speed imaging is used to characterize the size of the cells, along with the frequency and amplitude of pulsations. This paper has been published in *Combustion and Flame* [150], and part of the work has been presented in the 13th United States National Combustion Meeting [151].

Article 4: Diffusive-thermal instabilities in unstrained H_2O -diluted syngas diffusion flames. The mark III version of the unstrained diffusion flame burner is presented in this article, where the characteristics of the flames generated are compared with theoretical predictions. This is followed by a discussion on the diffusive-thermal instabilities that form in syngas mixtures with very high water content. The effect of H_2O dilution on the instability type, size, and frequency is detailed. This article is currently under review in *Combustion and Flame* [152], and part of it has been presented during the Canadian Section of the Combustion Institute Spring Technical Meeting 2023 [153].

CHAPTER 4 ARTICLE 1: THERMODYNAMIC ANALYSIS OF NOVEL METHANOL POLYGENERATION SYSTEMS FOR GREENHOUSES

Published online in *Biomass Conversion and Biorefinery* on 2 July 2021 [148]

By

Elie Antar, and Etienne Robert

Abstract

This work presents the modeling and thermodynamic analysis of two novel small-scale poly-generation systems that are capable of simultaneously converting residual biomass to methanol (MeOH), electricity, heat and a CO₂-rich stream for agricultural greenhouses. The first system is based on a downdraft gasifier, while the second relies on a dual fluidized bed (DFB) gasifier. Both configurations leverage the H₂, O₂, and electricity generation capabilities of reversible solid oxide cells (RSOCs). The Aspen Plus process simulator is used to model the thermodynamic performance of the proposed polygeneration systems, which operate at total efficiencies ranging from 83.9 to 85.0%. From a biofuel and electrical efficiency perspective, the system based on a DFB gasifier is superior, providing the added benefit of enabling carbon capture and storage, as a N₂-free stream with a molar purity exceeding 90% CO₂ is generated, which could be readily liquefied or sequestered.

4.1 Introduction

The agricultural sector is currently heavily reliant on costly and unecological products derived from fossil fuels for its energy-intensive activities, and contributes approximately 10% of the total greenhouse gas (GHG) emissions in Canada [154]. According to the Report on Energy Supply and Demand [155], agricultural activities consume around 6.7% of the total refined petroleum products used in the country. Farmers mainly depend on diesel fuel and gasoline for transportation and powering machinery. Moreover, in temperate climates such as Canada, heating typically represents 70-85% of the total energy expenses of greenhouses [20], with fuel oil and natural gas highly relied on. Canadian agricultural facilities also use 1.9% of the total electricity consumed in the country [24] for artificial lighting and powering electrical machinery. High-purity carbon dioxide is another resource highly demanded in greenhouses since its concentration in ambient air is too low for optimum crop growth, particularly during the day time when it is around 150 ppm [66]. A CO₂-rich stream is often injected into the greenhouse atmospheres to attain the optimal CO₂ concentration range of 700-1000 ppm,

which has shown to enhance crop yield by 20 to 60% [67].

Residual lignocellulosic biomass, a potentially carbon neutral and renewable energy resource [156], is abundant in agricultural areas. Its use in greenhouses is currently mostly limited to biomass boilers, which in addition to their emission indicators being on par with hard coal [157], are typically only able to provide part of the required heat, with the peak thermal load along with the locally required transportation fuel, electricity, and CO₂ being covered by fossil-based products, as mentioned earlier. The reliance of farmers on these resources can be greatly minimized, and their energy sustainability can be considerably enhanced if gasification-based polygeneration systems are deployed in agricultural settings to harness the potential of the local energy resources.

Polygeneration systems are suitable for decentralized applications such as greenhouses as they can offer high overall thermodynamic efficiencies [158], which can remain essentially unaffected by the choice of operating pressures. This is a considerable advantage since for the synthesis of common storable biofuels such as methanol or dimethyl ether, the high operating pressure range of 50 – 80 bar needed for maximum yield [11, 59] would impose serious safety consideration when implemented in a greenhouse. A safer operating pressure range of 20 – 30 bar causes a significant drop in biofuel yield, but this is compensated in polygeneration systems by: 1) using the unconverted syngas output of the biofuel reactors for the generation of electricity needed by the greenhouse, and 2) directly using the generated heat from the exothermic biofuel reactors and the residual off-gas burners to meet the large heat demands of the greenhouse. This, and the fact that biomass transportation costs are minimized since the plants are installed next to the renewable biomass resources [159] have the potential to outweigh the additional equipment costs associated with polygeneration plants when compared with traditional heating approaches, making this an attractive option for greenhouse applications.

Studies in the literature of biomass gasification-based systems, which are largely based on steady state thermodynamic modelling, target a broad range of potential applications, nonetheless, the specific needs of greenhouses remain largely unaddressed. For instance, single output electricity/biofuel plants are heavily investigated, where using a downdraft gasifier coupled with a 2.5 kW internal combustion engine (ICE), Chaves et al. [160] reported a 16.5% biomass-to-electricity efficiency. Sara et al. [161] analyzed a 100 kW dual fluidized bed (DFB) gasifier-based system for H₂ production, and reported an efficiency ranging between 46-50%. The co-generation of heat and power from biomass is also commonly discussed. Sadegh-Vaziri and Bähler [162] modelled a biomass system consisting of a fluidized bed gasifier and a solid oxide fuel cell (SOFC) that powered a gas turbine by feeding it with the unreacted syngas,

and reported a total efficiency of 56% (electrical and thermal efficiencies of 20.4% and 35.6%, respectively). The tri-generation concept of electricity, biofuel, and heat has also been studied, but to a significantly lower extent. Clausen et al. [60] showed that tri-generation can yield very high overall efficiencies reaching 87-88%, by thermodynamically modelling two systems that produced either methanol (MeOH) or dimethyl ether (DME) as a biofuel. However, no studies were found on polygeneration systems designed to produce simultaneously the four products demanded for greenhouses and the surrounding agricultural activities.

The goal of this paper is to present and thermodynamically analyze two novel polygeneration systems capable of converting residual biomass to MeOH, electricity, heat and a CO₂-rich stream for greenhouses. The proposed systems mainly differ in the gasification stage, where a downdraft gasifier is used in the first system, while a DFB gasification approach is adopted in the second. The paper first discusses the system components chosen and their layouts, followed by the modelling approach implemented using the Aspen Plus process simulator. The energy flow diagrams and parametric analysis are then presented in the results section, followed by a comparison of the energetic performances of both systems.

4.2 Methodology

4.2.1 General design choices

Feedstock

Wood chips is the selected biomass feedstock for this study since it is widely available in agricultural settings and is commonly used in biomass conversion systems studies [163,164]. Its characteristics is shown in 4.1.

Biofuel

MeOH is the liquid biofuel considered useful for greenhouses in this work as it can be readily stored, transported [56], and can completely substitute gasoline in ICEs with minor modifications [58]. In fact, compared to gasoline, MeOH has a higher octane number (107 vs 98), a wider flammability range, and burns cleaner [57]. One of the most important parameters for MeOH synthesis from biomass-derived syngas, besides the operating reactor pressure, is the H₂/CO ratio which is usually kept at 2 [165]. It has been shown that enriching the H₂ content in syngas has the potential of increasing the amount of produced MeOH by up to 150% [166]. A solid oxide electrolysis cell (SOEC) running on internally generated electricity and steam is selected for H₂ syngas enrichment upstream the MeOH reactor in both of the

proposed systems.

Carbon dioxide

The choice of incorporating a SOEC is also motivated by the pure O_2 stream that is generated during the electrolysis process. This stream can play a key role in producing the high-purity CO_2 stream for the greenhouse atmosphere. After the oxy-gasification stage, and following the conversion of the resulting N_2 -free syngas to biofuel and electricity, the leftover stream is mainly diluted with CO_2 and H_2O [139], and can be burned at low temperatures without generating NO_x , yielding an exhaust suitable for greenhouse CO_2 enrichment. SOECs also contribute to higher overall system efficiencies compared to conventional air separation units (ASUs), as was demonstrated by Zhang et al. [53] who reported a total system efficiency increase from 47.9% to 59.1% after replacing an ASU with a SOEC in a biomass to MeOH plant. Butera et al. [62] also reached similar conclusions after integrating a SOEC into a system that converts biomass and electricity into MeOH.

Electricity

Another attractive feature of SOECs exploited in this study is their ability to operate in reverse mode, as SOFCs, generating electricity for greenhouses efficiently from syngas with very low pollutants emissions [52]. Several experimental studies have been published recently reporting successful operation of 800-850°C SOFC units fed with syngas from biomass gasifiers [46,48,49]. The added energy value of using SOFCs instead of conventional heat engines

Table 4.1 Characteristics of wood chips

Ultimate analysis (wt\% dry basis)	Wood chips
C	50.6
H	6.5
N	0.2
O	42
S	0
Proximate analysis (wt\% dry basis)	
Moisture	45
FC	19.2
VM	80.1
Ash	0.7
LHV (MJ/kg wet basis)	12.1
HHV (MJ/kg wet basis)	14.0

was highlighted by other investigations. A 7.3 percentage points increase in system efficiency was obtained by Minutillo et al. [44] after replacing a micro gas turbine (MGT) with a SOFC in a small-scale combined heat and power (CHP) system based on biomass gasification.

4.2.2 Downdraft gasifier-based system

The first system considered relies on a 1 bar downdraft gasifier, a simple gasification approach suitable for small-scale applications (10 kW to 1 MW) [167]. Figure 4.1 shows a schematic representation of the system layout. The biomass is dried by the excess heat of the system to a moisture level of 25% prior to gasification, to lower the CH₄ content in the syngas produced. The gasifier oxidizing agent is pure O₂, which is generated without excess by the SOEC to maintain an equivalence ratio $ER = 0.2$. This yields N₂-free syngas which is cleaned using hot gas techniques, as they are highly recommended for such small-scale facilities since only limited waste handling is required [17]. Particulate matter (PM) is cleared using a cyclone, and tar is reformed in a steam fluidized nickel bed operating at 780°C, with a steam to carbon ratio of 3. Nickel-based catalysts are used for tar decomposition primarily due to their high conversion efficiencies (>99% at 780°C [168]), along with their ability to enhance the H₂ and CO content of syngas and reform methane [169]. The tar-free syngas is then injected into a 400°C ZnO guard bed for acid gas adsorption [162].

To lower the compressor work, the cleaned syngas is cooled to 40°C and water is separated using a flash condenser. The syngas is then enriched with H₂ from the SOEC before compressing it to 30 bar for MeOH synthesis. This operation is usually conducted at pressures between 60 to 80 bar [59], but as a compromise between MeOH conversion efficiency and the complications associated with higher operating pressures, a lower pressure of 30 bar is selected in this study. In the MeOH synthesis subsystem (Fig. 4.1), the syngas is cooled to 225°C and injected into an isothermal reactor with Cu/ZnO catalyst [59]. The mixture exiting the MeOH reactor is cooled to 40°C and sent to a flash separator. The liquid mixture is crude MeOH, and the exiting gas stream (unreacted syngas) is sent to a SOFC operating at 850°C and 1 bar. The SOFC generates a net output of electricity (Fig. 4.1, dashed line) after powering the SOEC and the syngas compressor. The high temperature of the SOFC is maintained by heating the inlet anodic and cathodic streams using the high-temperature exhaust streams. At this stage of the process, the leftover syngas is highly diluted in CO₂ and H₂O, and is sent to a burner to exploit the remaining energy for generating steam for the nickel fluidized bed. After combustion, the exhaust gas is expected to be clean enough to be injected into a facility that requires CO₂ enrichment, such as a greenhouse. Further details on the operating conditions of each unit in the system can be found in section 4.2.4.

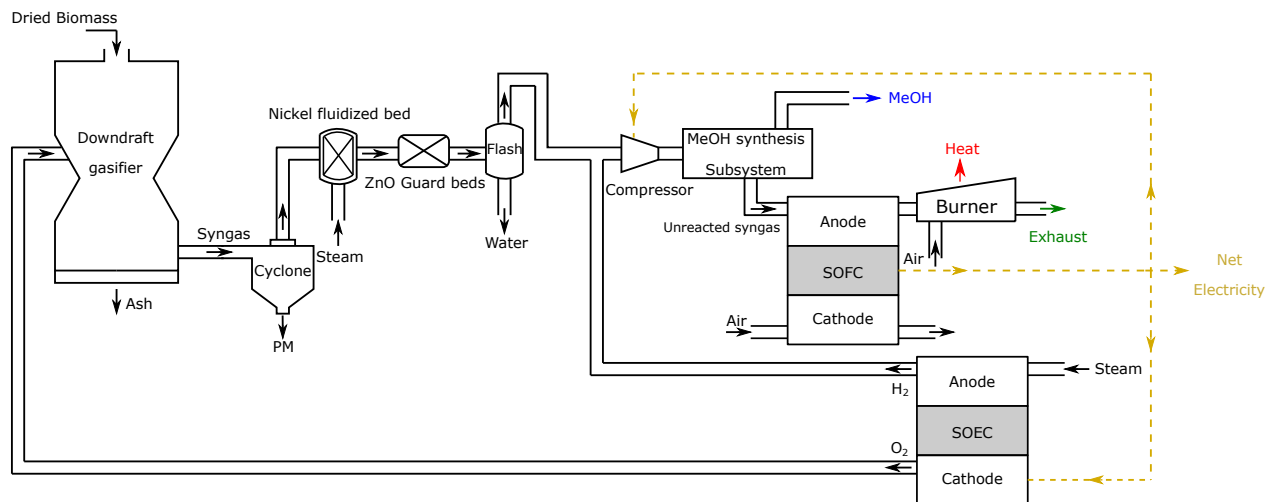
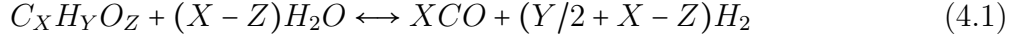


Figure 4.1 Simplified schematic representation of the downdraft gasifier-based system

4.2.3 Dual fluidized bed gasifier-based system

A DFB gasifier operating at 1 bar and 850°C is used in the second proposed system, shown in figure 4.2. The gasification agent is steam generated using the heat from the residual gas burner. This gasification approach was developed by the Vienna University of Technology, and is sometimes referred to as fast internally circulating fluidized bed (FICFB). The dried biomass (moisture = 25%) is gasified in a bubbling fluidized bed, which operates at a steam to biomass ratio $S/B = 1.5$, to ensure low CH_4 content in the syngas. The residual char and bed material are transferred via an inclined chute to a fast circulating fluidized bed, where pure O_2 at 450°C from the SOEC is used for oxy-fuel combustion. The combustion gases are separated in a cyclone where the hot bed material is returned to the gasifier, via a loop seal, to provide the required heat for the endothermic gasification reactions. The chute and loop seals are fluidized by steam, preventing gas leakage from the combustion zone and providing N_2 -free syngas from the gasification chamber even if air is used as an oxidizing agent [81]. The reason motivating the use of pure O_2 as an oxidizing agent in the proposed system is the resulting CO_2 -rich exhaust that has a molar purity greater than 90%, suitable for sequestration/liquefaction. This idea has been briefly introduced in the review paper of Heidenreich and Foscolo [17], but is scarcely investigated in DFB gasifier-based systems in the literature despite its potential to render the biomass conversion process carbon negative. The syngas generated from the DFB gasifier has a large heating value and H_2 content (high cold gas efficiency), suitable for subsequent fuel synthesis [170]. The remainder of the system for syngas cleaning and conversion is similar to the description in section 4.2.1. Here again, just enough O_2 is generated by the SOEC to combust the char in order to sustain gasification

g/Nm³ [81] for the downdraft and DFB gasifiers, respectively. For both gasifiers, 5.5% of the input biomass HHV is considered to be lost as heat in the gasification process.



Then, the exiting stream is injected into an adiabatic RGIBBS reactor where equilibrium is attained through methane steam reforming and water-gas shift (WGS) reactions:



The SEP blocks are used to simulate the guard beds operating at 400°C, with full acid gas removal, and a temperature drop across the bed assumed at 100°C. The FLASH₂ block is used for the adiabatic flash separators, and the COMPR block is used for the adiabatic compressors. The compressors discharge pressure is specified at 30 bar, with an isentropic efficiency of 80%.

An RGIBBS block operating at 225°C and 30 bar is used to replicate chemical reactions 4.3 and 4.4 that occur in catalytic methanol reactor [53]:



Chemical equilibrium calculations with temperature approach are often used in system studies to model reactors with finite residence time, 15°C is used here for both reactions [60]. For the exothermic MeOH reactions, which are favored at low temperatures, equilibrium is evaluated at temperatures slightly higher than the reactor temperature to account for non-equilibrium effects.

Figure 4.3 shows the Aspen Plus flowsheet used to model the SOFC. The anode's "AN-HEAT" and cathode's "CAT-HEAT" are two heat streams required to increase the temperature of the injected syngas and air flowing in the SOFC to 850°C obtained from the hot exhaust gas. The SEP block "CAT" is used to separate O₂ from air and supply it as "O₂-AN" to the anode, as in practice only the O₂ content in air is conducted across the electrolyte. The required flowrate of air is determined by the fraction of the supplied fuel that reacts to produce power in the unit, also known as the utilization factor, which is set at $U_f = 0.7$ [51]. The anode is modelled by an RGIBBS reactor "ANODE" operating at 1 bar. The reactions taken into

account are the WGS reaction (Eq. 4.3) and that for H₂ oxidation [51]:



Reactions involving CH₄ and CH₃OH are not considered as their concentrations in the syngas stream entering the SOFC are minute (CH₃OH < 0.7% and CH₄ < 0.05%), and also since their reforming reactions require considerably higher pressures (approximately 20 bar for CH₄) [163]. The operating voltage (V_{op}) of the SOFC is calculated from the average Nernst voltage (V_N) assuming a constant area specific resistance (ASR) [163, 176, 177] of 0.2 Ωcm^2 as per the following equations:

$$V_{op} = V_N - iASR \quad (4.6)$$

$$i = I/A = n_{H_2,r}(nF)/A \quad (4.7)$$

$$V_N = V^\circ - \frac{\Delta\hat{s}}{nF}(T - T_o) - \frac{RT}{nF} \ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} \quad (4.8)$$

$$V^\circ = -\frac{\Delta\hat{g}_{rxn}^\circ}{nF} \quad (4.9)$$

where $n_{H_2,r}$ is the number of H₂ moles undergoing electrochemical reactions at the anode. The active cell area (A) is chosen such that $i = 1 \text{ A/cm}^2$. The average molar composition of the reactants and products are used for calculating the activity of species in the products or reactants streams $a_{products}^{v_i}$ and $a_{reactants}^{v_i}$. A user-defined script with the aforementioned equations is compiled in a CALCULATOR block, which then instructs the FSPLIT block “Q-SPLIT” to divide the total enthalpy change “Q-RAW” from the “ANODE” block into an electrical stream “ELE” (equal to the calculated electrical power) and a heat stream “HEAT” (equal to the difference between the enthalpy change and electrical power).

The RSTOIC block is used to model the SOEC [51], with an operating temperature of 850°C and pressure of 1 bar. The inverse of reaction 4.5 is used for H₂O electrolysis with a fractional conversion equal to the $U_f = 0.7$. The amount of H₂O fed into the SOEC is determined by the amount of O₂ required by the gasifier. Equations 4.6 to 4.9 are used to calculate the operating voltage and current of the SOEC. The ASR and active cell area were equal to the values chosen for the SOFC since the system could in theory be operated using a single

based on the overall economic returns, where a trade-off between recovering all the generated sensible heat and reducing the overall system cost/complexity may be made. As a result, the thermal and consequently overall efficiencies presented next can be thought of as the real-life upper bounds of the proposed polygeneration systems. η_{ele} , η_{th} and $\eta_{biofuel}$ are expected to have positive values, which implies that the system does not rely on external energy sources other than biomass.

4.3.1 Downdraft gasifier-based system

Sankey diagram and overall efficiencies

The Sankey diagram of the downdraft biomass gasifier-based system is shown in figure 4.4. The operating mode described in section 4.2.2 ensures that the system electricity generation is maximized. As can be seen, the main energy losses occur in the drying and gasification stages, where a total of 10.7% of the input biomass energy is lost. The cold gas efficiency (η_{CG}) of the downdraft gasifier based on the lower heating value of the biomass (LHV) is 75%. Steam at 780°C is generated from the leftover syngas burner and is added to the nickel fluidized bed reactor for tar abatement. The cleaned syngas is then enriched with H₂ from the SOEC for enhancing the MeOH yield, which is $\eta_{MeOH} = 10.3\%$ with a H₂+CO conversion of 15.1%, a reasonable value considering the relatively low operating pressure.

The unreacted syngas and air that are fed to the SOFC are heated to 850°C by the hot exhaust stream, which is thus cooled to 76°C. The electricity yield of the SOFC is 32.3% of the system's input biomass energy, with 13.7% and 9.3% being fed to the SOEC and the syngas compressor, respectively, yielding a net electrical efficiency $\eta_{ele} = 9.2\%$. The SOFC also converts 17.1% of the input biomass energy as sensible heat, with the remaining energy (34.5%) being exploited in the unreacted syngas burner (adiabatic flame temperature of 1070°C). Accounting for all useful thermal energy generated (ex: MeOH reactor, syngas cooling, syngas burner, etc.) and consumed (SOEC, steam generator, etc.), the system yields a net thermal efficiency $\eta_{th} = 65.1\%$, resulting in a total system efficiency $\eta_{tot} = 84.6\%$. Regarding the possibility of CO₂ greenhouse atmosphere enrichment, the burner's exhaust gas contains 0.89 kg of CO₂ per kg of input biomass.

Parametric analysis

The influence of the hydrogen recycling fraction, active cell surface areas, ER and MeOH reactor pressure on the performance of the downdraft gasifier-based system has been investigated and is presented here. The H₂ produced by the SOEC can either be recycled to the

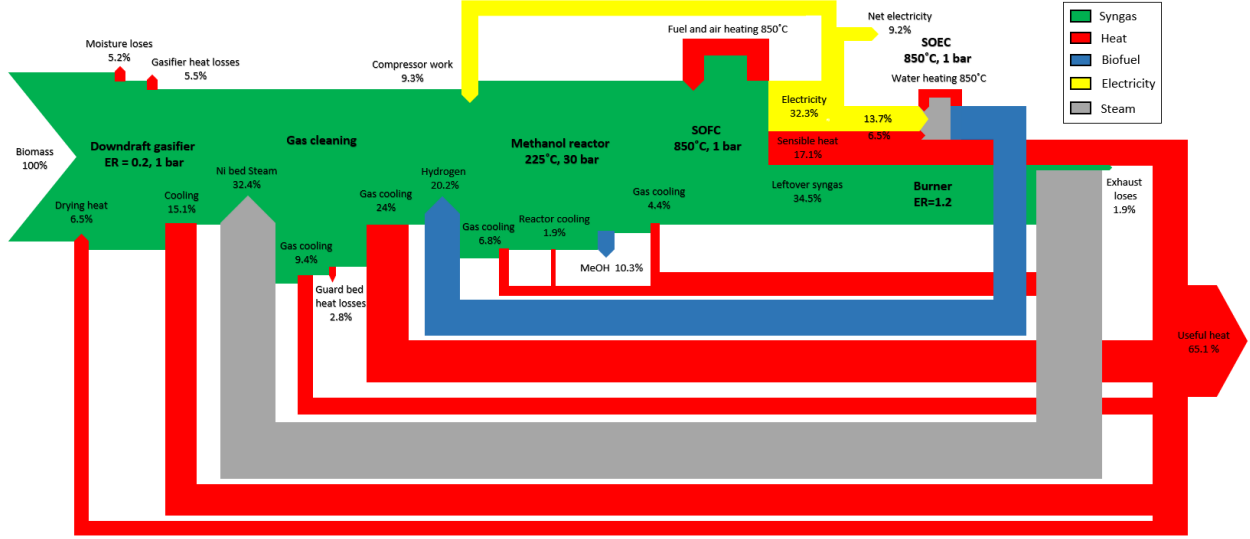


Figure 4.4 Sankey diagram of the downdraft gasifier-based system

MeOH reactor to increase its conversion efficiency, or kept as a separated stream to yield a net output ($\eta_{H_2} > 0$). Figure 4.5 (a) shows the variation of the system efficiencies as a function of the H_2 recycling fraction, defined as the ratio of the mass flowrate recycled into the MeOH reactor to the total H_2 generated from the SOEC. With no H_2 recycling ($\eta_{H_2} = 20.3\%$), the efficiency of MeOH synthesis is only $\eta_{MeOH} = 8.7\%$ at the 30 bar reference pressure considered here. This is because the H_2/CO ratio provided by the downdraft gasifier is approximately equal to 1, a low value for MeOH synthesis [59]. As H_2 starts to be injected upstream of the MeOH reactor, η_{H_2} drops to zero, while η_{MeOH} reaches 10.3%. The electrical and thermal outputs are increased as well, with η_{tot} remaining approximately constant. This shows that the system is effectively converting the chemical energy of gaseous H_2 (produced in the SOEC) into chemical energy in liquid MeOH, electricity and heat. The corresponding conversion fractions are 9%, 18% and 73%, respectively.

The lines with markers on Figure 4.5 (a) show the system behavior when the active surface areas of the SOFC and SOEC are doubled. This means that the current densities are reduced by half compared to the plain lines. This in turn improves the electrical efficiencies of both the SOFC and SOEC, and consequently, that of the system. Specifically, η_{ele} increases by 4.2 percentage points ($\eta_{ele} = 13.4\%$ at full H_2 recycling), with η_{th} dropping by an equivalent amount. Hence, the loss of operating voltage and the generation of heat in the SOFC and SOEC units are reduced as expected at lower current densities.

The effect of varying the equivalence ratio ER, defined as the ratio of actual O_2 flow rate to that required for the stoichiometric combustion of the biomass, is shown in Figure 4.5

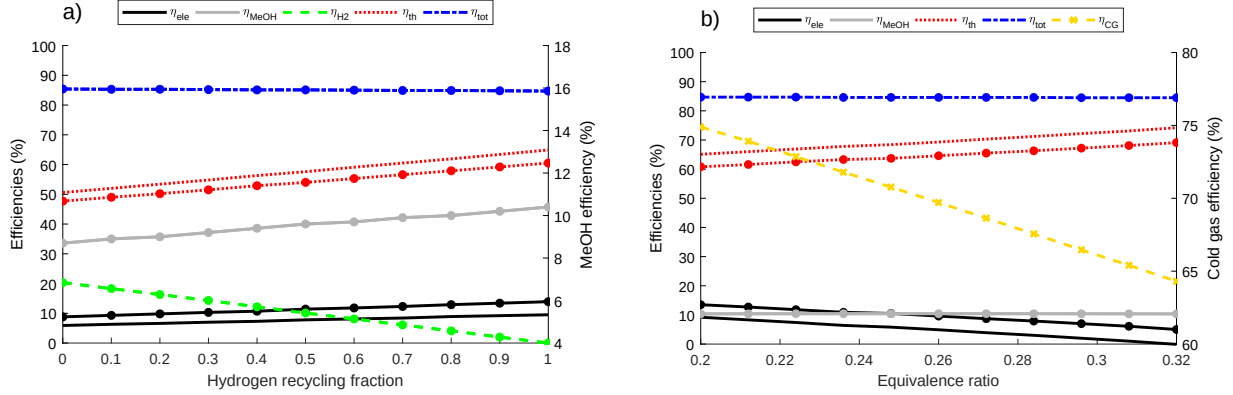


Figure 4.5 Variation of the downdraft gasifier-based system efficiencies with a) H_2 recycling fraction at $ER = 0.2$ and b) ER at full H_2 recycling. The SOFC and SOEC current densities of the lines with markers are half that of the plain ones (double of the active surface areas).

(b). A minimum ER of 0.2 is considered, since lower values would result in lower gasification temperatures, and consequently higher tar concentrations in the syngas. Higher equivalence ratios are attractive for heat generation, and may be deployed when the heat demand by the greenhouse is large. The thermal efficiency is 74.2% at $ER = 0.32$, which is the maximum ER value that can be attained by the system without needing external electricity supply. This is because the electrical efficiency drops at higher ER s as more electricity must be consumed by the SOEC to produce more O_2 for the gasifier. The $MeOH$ yield attains its peak value at $ER = 0.26$, and begins to slowly drop with further increase in ER since the gasifier syngas energy content becomes lower, particularly the H_2 concentration. This is reflected in the gasifier cold gas efficiency, which drops from $\eta_{CG} = 75\%$ at $ER = 0.2$ to $\eta_{CG} = 64\%$ at $ER = 0.32$. Here again, the effect of doubling the active surface area of SOFC and SOEC is shown by the lines with markers. It can be seen that doing so increases the electrical efficiency η_{ele} by 4.5 percentage points.

The effect of changing the operating pressure of the $MeOH$ reactor is important and shown in figure 4.6. These results reveal that the ER range where a net amount of electricity is generated ($\eta_{ele} > 0$) is reduced with higher operating pressures. At 70 bar, electricity must be injected into the system regardless of the value of the ER because of the increased energy demand for syngas compression. $MeOH$ yield is considerably enhanced with high reactor pressures. At 70 bar, $\eta_{MeOH} = 28\%$, which is 2.7 times the $MeOH$ efficiency at 30 bar. This also reduces the thermal energy output as less syngas exits the $MeOH$ reactor unreacted, which leads to less syngas being burned. The low operating pressure chosen for

the baseline cases considered here lowers η_{MeOH} , but greatly simplifies the system design and safety considerations. Also, this is compensated by the fact that other forms of useful energy are produced by the polygeneration system, where it can be seen that the high total efficiency of $\eta_{tot} = 84.6\%$ remains essentially unaffected by the operating pressure.

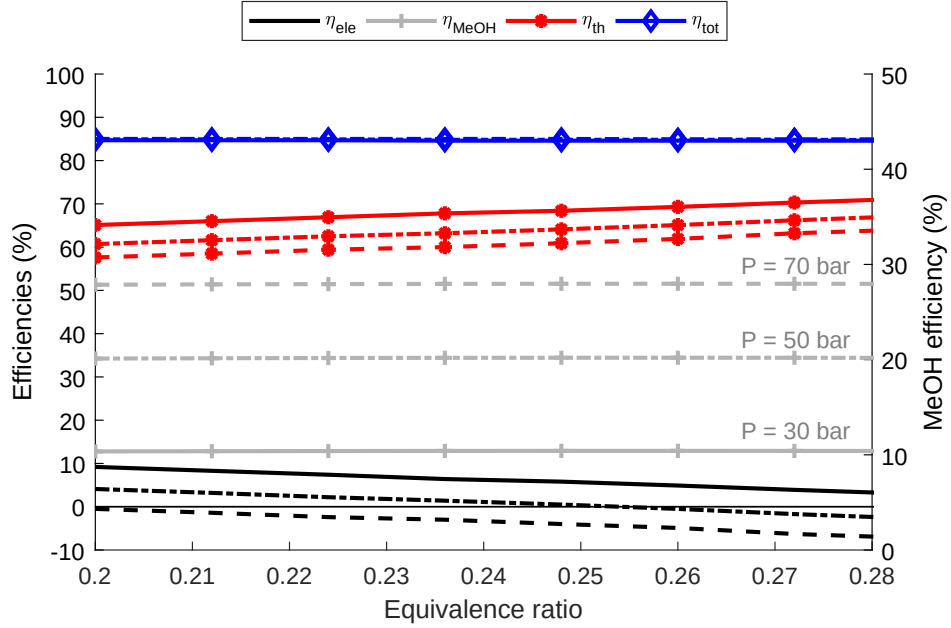


Figure 4.6 Efficiency of the downdraft gasifier-based system with ER at different MeOH reactor pressures (— 30, — — 50, and - - - 70 bar).

4.3.2 Dual fluidized bed gasifier-based system

In the second system considered, the downdraft gasifier is replaced by a steam DFB gasifier. The O_2 from the SOEC is this time injected into the gasifier's combustion chamber.

Sankey diagram and overall efficiencies

The Sankey diagram in figure 4.7 shows the energy flow in the DFB gasifier-based system, with the operating mode described in section 4.3.2 aimed at maximizing electrical yield. 11.3% of the input biomass energy is lost as water vapor in the dryer, as heat in the gasifier, and as hot exhaust gases from the gasifier's combustion chamber. Steam at 450°C is produced by the leftover syngas burner and injected into the gasification chamber. It should be noted that the drying stage is mandatory despite adding steam into the gasifier. This is because for a given steam to biomass ratio, the total water content (steam + biomass moisture)

must be considered against the mass of the dry biomass, the amount of fluidizing steam thus decreases with increasing biomass moisture. Hence, with a 45% moist feedstock, a drying stage is mandatory to ensure adequate fluidization. The resulting cold gas efficiency based on the LHV for the DFB is 87%. After the syngas cleaning stages, the H_2 content is increased using the SOEC output, with the resulting stream compressed to 30 bar and fed into the MeOH reactor, yielding $\eta_{MeOH} = 12.2\%$ with a H_2+CO conversion of 16.6%.

The unreacted syngas from the MeOH synthesis stage is then heated by the hot exhaust stream exiting the SOFC at 850°C , and fed into the unit for electricity generation. The SOFC generates a total electric yield equivalent to 33.9%, out of which an amount equivalent to 8.9% of the input biomass energy is fed into the SOEC, and 8.7% into the syngas compressor, resulting in a net system electricity efficiency of $\eta_{ele} = 16.4\%$. The remaining energy exiting the SOFC is in the form of sensible heat (18.7%) and chemical energy in leftover syngas (34.0%), which is burned for heat with an adiabatic flame temperature of 1420°C . Accounting for all the useful thermal energy generated (ex: MeOH reactor, syngas cooling, leftover syngas burning, etc.) and consumed (biomass drying, SOEC, steam generator, etc.), the system results in a thermal efficiency of $\eta_{th} = 56.3\%$. This leads to an overall efficiency for this DFB gasifier-based system of $\eta_{tot} = 84.9\%$.

This system has two gas streams that could be used for greenhouse atmosphere CO_2 enrichment. The first is the exhaust of the gasifier's combustion chamber, and the second is the exhaust of the syngas burner. The former produces 0.13 kg of CO_2 per kg of input biomass with a molar CO_2 purity that exceeds 90%. The absence of N_2 allows for convenient CO_2 liquefaction or sequestration. Hence this approach has the potential to render the biomass conversion process carbon negative. The air-blown syngas burner produces an exhaust stream with 0.79 kg of CO_2 per kg of input biomass at 29% molar purity.

Parametric analysis

The performance of the DFB gasifier-based system is shown in figure 4.8 as a function of the ratio of the actual over the baseline recycled H_2 flow from the SOEC. The baseline case represents a H_2 recycling fraction (as defined in section 4.3.1) of one, where all the H_2 made available by the SOEC is recycled in the syngas when producing exactly the amount of O_2 required for the gasifier. Two zones are distinguished by shading, with their interface representing the baseline case. In the unshaded zone, the H_2 recycling fraction is changed between zero and one. Without H_2 recycling, the MeOH and electrical efficiencies drop to $\eta_{MeOH} = 11.1\%$ and $\eta_{ele} = 13.1\%$. These values increase approximately linearly to $\eta_{MeOH} = 12.2\%$ and $\eta_{ele} = 16.4\%$ at full recycling, with the fractional conversion of H_2 energy into

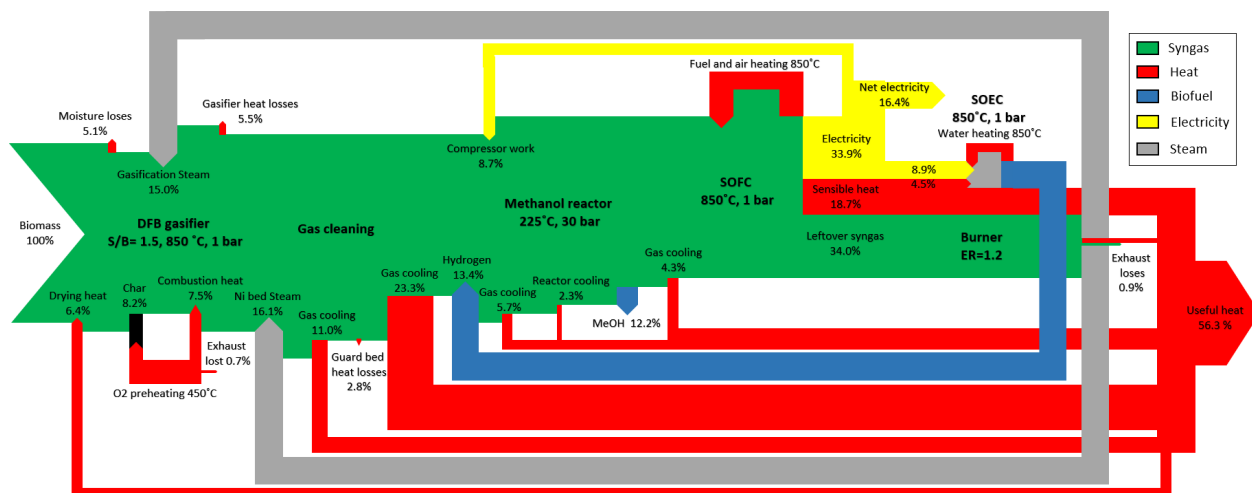


Figure 4.7 Sankey diagram of the DFB gasifier-based system

MeOH and electricity being 9.0% and 24.6%, respectively. The remaining 66.4% goes to heat.

Since at full H_2 recycling the electrical yield η_{ele} is relatively high, more electricity can be sent to the SOEC to produce more H_2 in order to boost MeOH synthesis. The system performance under these conditions is shown in the shaded zone of figure 4.8. MeOH conversion efficiency η_{MeOH} increases from 12.2% to 14.1% when all the electricity is used to generate H_2 . This results in a 3.5% increase in the mass flow rate into the reactor. If the active areas of the SOFC and SOEC units are doubled from the reference case (SOFC current density $i = 1$ A/cm²), the MeOH conversion efficiency η_{MeOH} can reach 15%, with a 5.7% increase in the mass flow rate into the MeOH reactor relative to the baseline case (lines with markers in figure 4.8). In the shaded zone, the system converts 12% of the electrical energy to chemical energy in MeOH, and the remainder to thermal energy. A steam to biomass ratio $S/B = 1.5$ is maintained throughout, implying that an excess pure O_2 stream is generated by the system in the shaded zone which can be useful for other purposes. It should be noted that the amount of O_2 fed into the gasifier's combustor is linked to the S/B ratio. This is because at higher S/B ratios, more char is required to be burned in the combustor to sustain the gasification temperature, and hence, more O_2 is needed. Figure 4.8 also reveals that MeOH synthesis is always increased with more H_2 enrichment. To determine the optimal operating point, the change in the size of the MeOH reactor, as well as the expenses and benefits of using or storing H_2 must be taken into account. This example reveals the usefulness of these parametric studies to investigate the flexibility of the system to respond to different demands. The maximum amount of electricity generated by the second system ($\eta_{ele} = 16.4\%$) is sig-

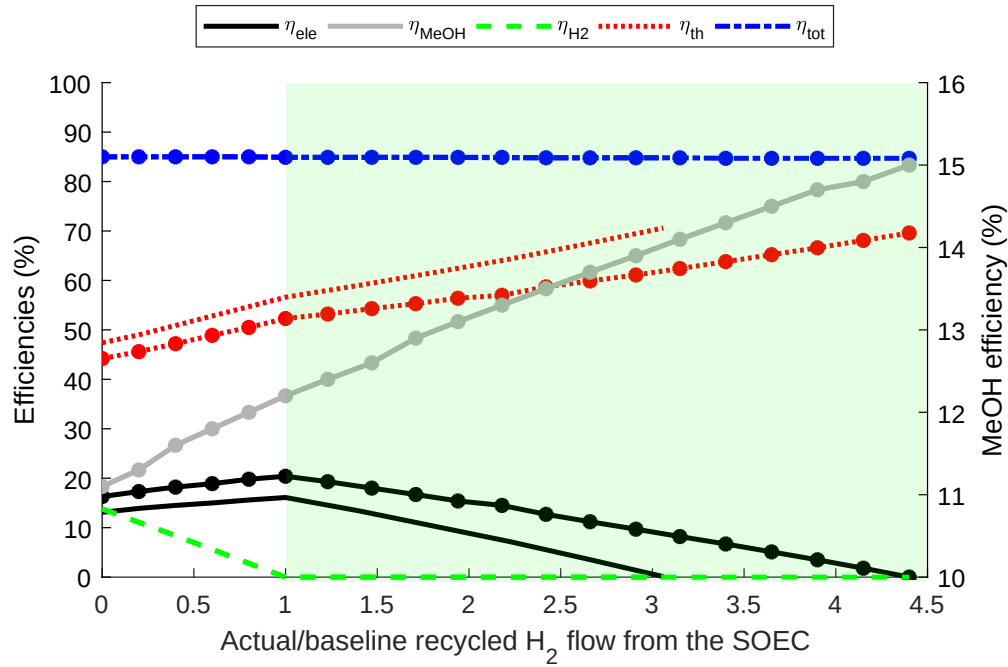


Figure 4.8 Variation of the DFB gasifier-based system performance as a function of the ratio of the actual over the baseline recycled H₂ flow from the SOEC. The SOFC and SOEC current densities of the lines with markers are half that of the plain ones (double the active surface areas).

nificantly greater than that of the first system ($\eta_{ele} = 9.2\%$). Hence, a greater fraction of the unreacted syngas may be sent directly to the burner instead of the SOFC if heat is the most desirable output for the greenhouse. The performance of the second system with different amounts of unreacted syngas being sent to the SOFC is shown in figure 4.9. When the amount of syngas sent to the SOFC is sufficient for it to only power the SOEC and compressor ($\eta_{ele} = 0\%$), the system thermal efficiency attains a peak value of $\eta_{th} = 71.7\%$.

The effect of changing the MeOH reactor pressure is shown in figure 4.10. For the default case of 30 bar, $\eta_{MeOH} = 12.2\%$. With increasing pressure, more MeOH is synthesized from syngas, and η_{MeOH} increases to 30.9% at 70 bar. At this pressure, $\eta_{ele} = 6.3\%$. This excess electricity can be sent to the SOEC to generate more H₂ to further increase the MeOH synthesis. Doing so results in a maximum $\eta_{MeOH} = 32.4\%$ (lines with markers). Similar to the first polygeneration system, it can be seen that the total efficiency of this system remains high at $\eta_{tot} = 84.9\%$ and unaffected by the operating pressure.

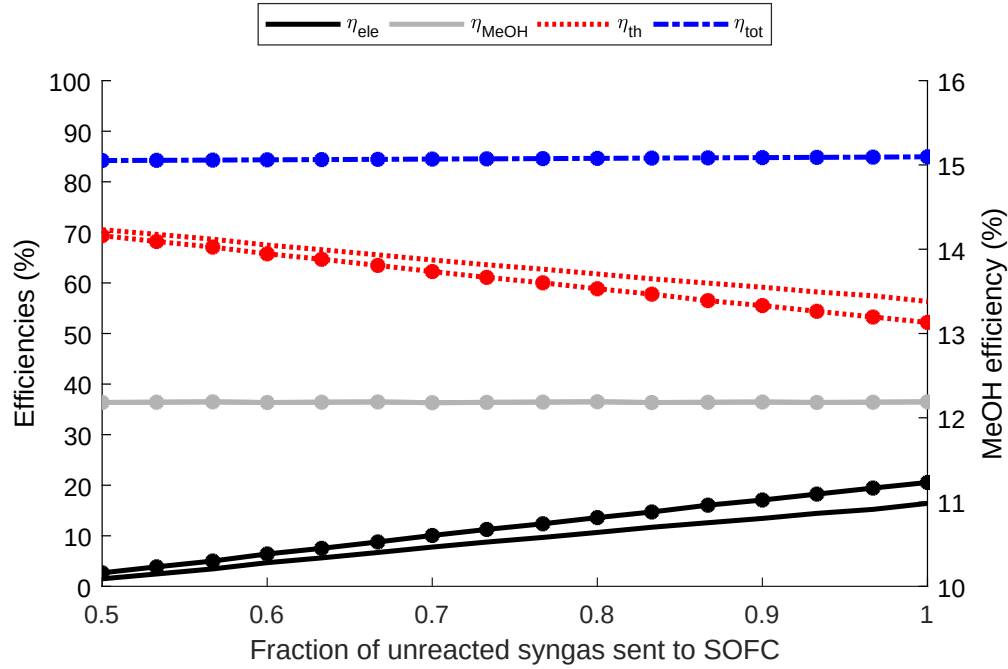


Figure 4.9 Variation of the DFB gasifier-based system performance as a function of the unreacted syngas sent to the SOFC. The SOFC and SOEC current densities of the lines with markers are half that of the plain ones (double the active surface areas).

4.4 System comparison and discussion

To compare the performances of both systems, four cases are considered, each aiming to maximize a different form of energy, as can be seen in tables 4.2 and 4.3, with the results summarized in figure 4.11. In the following, $H_{2,rec}$ denotes the H_2 recycling fraction defined earlier (abscissa of Figure 4.5 (a)). The parameter SOFC split represents the fraction of unreacted syngas sent to the SOFC in the DFB gasifier-based system (abscissa of figure 4.9) with the rest sent directly to the burner. Finally, $H_{2,actual}/H_{2,baseline}$ is the ratio defined earlier of the actual over the baseline recycled H_2 flow from the SOEC (abscissa of figure 4.8).

Case 1 for both systems represents the baseline configuration discussed in sections 4.2.2 and 4.3.2, and aims to maximize electricity generation. Under those conditions, the maximum η_{ele} of the second system is approximately seven percentage points greater than that of the first. The main reason for this difference is that the downdraft gasifier requires a considerably greater amount of O_2 (approximately 1.5 times) compared to the DFB gasifier. This means that more electricity is consumed by the SOEC, thereby lowering the net electrical yield of the first system. Case 2 aims at maximizing the MeOH yield. Due to the higher H_2

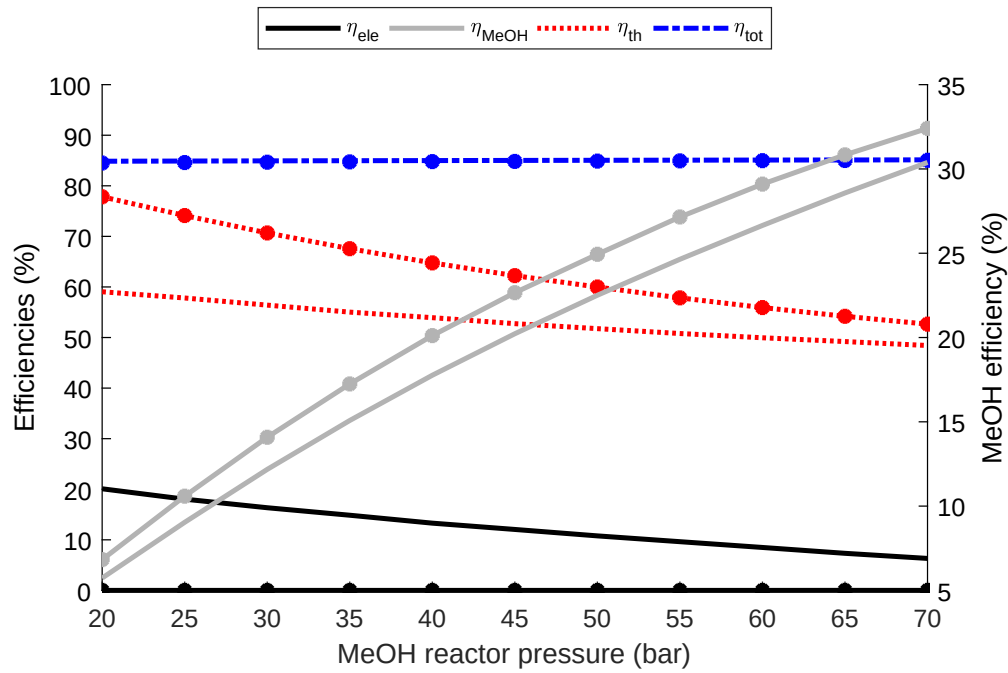


Figure 4.10 Effect of changing the MeOH reactor pressure. The lines with markers represent full depletion of electricity to maximize H_2 enrichment.

content in the syngas generated using the DFB gasifier relative to the downdraft gasifier, the maximum η_{MeOH} for the second system is three percentage points greater. The yield is ultimately limited in both systems by the operating pressure of the MeOH reactor (30 bar) as discussed previously. Similarly in case 3, where the H_2 yield is maximized, the second system is more than five percentage points more efficient than the first. For the final case, the maximum thermal efficiency of the downdraft gasifier-based system is slightly greater than the DFB-based configuration since in the latter, more syngas is converted to MeOH, and less of it is sent to the downstream exothermic components.

Table 4.2 Different operating conditions of the downdraft gasifier-based system with a MeOH reactor pressure of 30 bar.

Case #	Objective	ER	$H_{2,rec}$	η_{ele}	η_{MeOH}	η_{H_2}	η_{th}	η_{tot}
1	Maximizing electricity	0.2	100%	9.2%	10.3%	0%	65.1%	84.6%
2	Maximizing MeOH	0.26	100%	0%	11.0%	0%	73.6%	84.6%
3	Maximizing H_2	0.26	0%	0%	8.2%	26.3%	50.9%	85.4%
4	Maximizing heat	0.32	100%	0%	10.3%	0%	74.2%	84.5%

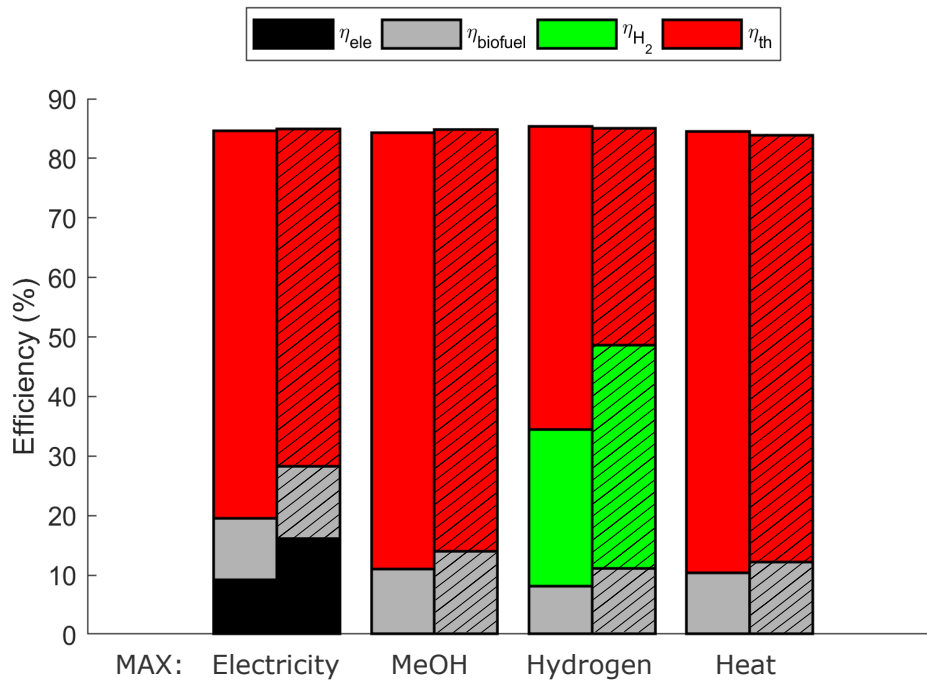


Figure 4.11 Performances of the downdraft gasifier-based system (plain) and the DFB gasifier-based system (hatched) under different conditions (tables 4.2 and 4.3).

4.5 Conclusion

In this paper, thermodynamic models are presented for two novel gasification-based systems capable of producing from wood chips the four main products required by greenhouses. The main difference between the two systems is in the gasification step, where the first system relies on a downdraft gasifier, while the second one uses a DFB gasifier to generate syngas. The remainder of the conversion process is similar, with the cleaned syngas supplied to a MeOH reactor at 30 bar. The unreacted syngas from the MeOH reactor is then injected into a SOFC which powers a SOEC and the syngas compressor, while generating a net output of electricity. The SOEC is used to produce O_2 for the gasifier, and H_2 for syngas enrichment. The remaining depleted syngas is burned to extract its remaining energy as heat. Steady state thermodynamic simulations show that electricity, MeOH, heat, and CO_2 can be simultaneously generated by the polygeneration systems at high overall efficiencies above 83.9% despite operating the MeOH reactors at relative low pressures. The systems are aimed at small-scale decentralized implementation, where low-pressure catalytic biofuel reactors are preferred for safety reasons. This choice is clearly the limiting factor for the maximum MeOH conversion efficiency, which is higher for the DFB gasifier-based system at 14.1% relative to

Table 4.3 Different operating conditions of the DFB gasifier-based system with a MeOH reactor pressure of 30 bar.

Case #	Objective	SOFC split	$H_{2,act}/H_{2,base}$	η_{ele}	η_{MeOH}	η_{H_2}	η_{th}	η_{tot}
1	Maximizing electricity	100%	1	16.1%	12.2%	0%	56.6%	84.9%
2	Maximizing MeOH	100%	2.8	0%	14.1%	0%	70.8%	84.9%
3	Maximizing H_2	100%	0	0%	11.1%	31.9%	42.0%	85.0%
4	Maximizing heat	43%	1	0%	12.2%	0%	71.7%	83.9%

the downdraft gasifier-based configuration at 11.0%. Increasing the pressure from 30 to 70 bar yields almost three times more MeOH in both systems.

Comparing the other energetic yields of the two systems through parametric analyses further highlights the thermodynamic superiority of the DFB gasifier-based configuration. This approach yields higher maximum electrical and hydrogen efficiencies of 16.1% and 31.9%, respectively, greater than those of the downdraft gasifier-based system at 9.2% and 26.3%, respectively. In addition, the system relying on a DFB gasifier provides 0.13 kg of CO_2 per kg of biomass input in a N_2 -free stream with a molar CO_2 purity exceeding 90%. This can be readily liquefied or sequestered meaning that the process could effectively behave as a carbon capture and storage medium.

After revealing the thermodynamic feasibility of the proposed systems in this paper, future techno-economic studies will involve transient systems simulations to properly integrate and optimize the systems in agricultural settings. Temporal consumption data of heat, electricity, fuel, and CO_2 of a typical greenhouse will be used, and proper energy storage mediums will be incorporated in the systems to ensure that the greenhouse demands are always met. The number and sizes of the heat exchangers in the systems will be optimized based on the overall economic returns, where a trade-off must be made between recuperating all the available sensible heat, and reducing the overall systems complexity. Also, the sensitivity of the systems efficiencies with different types of agricultural biomass feedstock will be investigated. Finally, the technical challenges associated with DFB gasifiers [81] will be addressed to ultimately decide which configuration, between the two proposed systems, to adopt in an agricultural greenhouse.

Acknowledgements

The authors are grateful for the funders of this work: the Trottier Energy Institute (Trottier scholarship and project grant) and the Natural Sciences and Engineering Research Council of Canada (NSERC), [PGSD3 - 546588 - 2020].

CHAPTER 5 ARTICLE 2: THERMODYNAMIC ANALYSIS OF SMALL-SCALE POLYGENERATION SYSTEMS PRODUCING NATURAL GAS, ELECTRICITY, HEAT, AND CARBON DIOXIDE FROM BIOMASS

Submitted to *Energy* on 28 June 2023 [149]

By

Elie Antar, and Etienne Robert

Abstract

Agricultural greenhouses are still heavily dependent on fossil fuel-based products despite the abundant residual biomass at their disposal. This paper presents two novel decentralized systems that can convert biomass simultaneously into synthetic natural gas (SNG), electricity, useful heat, and a CO₂-rich stream. To do so, the electricity and H₂/O₂ production features of reversible solid oxide cells (RSOCs) are exploited. A steam dual fluidized bed (DFB) gasifier is used in the first proposed system, while the second one adopts a simpler oxygen/steam-blown downdraft gasification approach. Thermodynamic simulations using Aspen Plus software reveal that the total polygeneration process efficiency could reach 86.6%, with a CO₂ generation capacity exceeding 275 g per kilogram of biomass input. If not used inside the greenhouse atmosphere to enhance crop growth, this high-purity CO₂ stream could be sequestered/liquefied to render the process carbon negative. The flexibility of the polygeneration systems is investigated through parametric analysis, where maximum SNG efficiencies that are on par with large-scale plants are obtained. The possibility of storing surplus electricity from intermittent sources as chemical energy in SNG is also highlighted.

5.1 Introduction

Lignocellulose is the most abundant type of biomass on earth [178]. It can be found in large quantities throughout agricultural areas under the form of wood chips, corn stover, wheat straw, etc. Today, the use of these residual biomasses in the agricultural sector, essentially woody feedstocks, is mostly limited to biomass boilers often to supply heat-intensive needs such as warming greenhouses [20]. These low-efficiency furnaces, compared to natural gas or propane alternatives, usually only satisfy part of the greenhouses heating loads. The outstanding thermal energy requirements, as well as other energy-intensive agricultural practices are still supplied from fossil fuels [155]. Decentralized biomass gasification systems could potentially bridge this gap, while diminishing the expenses and carbon footprint of agricultural

greenhouses. This is because versatile biofuels can be generated by gasification-based systems, which are generally considered the most cost-effective, practical, and efficient approach for converting lignocellulosic biomass [179].

Synthetic natural gas (SNG) is an example of such biofuels, which could be used instead of gasoline and diesel for transportation or power generation in greenhouses [34]. Frequently operated at pressures lower than 10 bar [35], SNG reactors feeding on biomass-derived syngas can be considered safe to adopt in greenhouses, unlike other reactors such as methanol (MeOH) or dimethyl ether (DME) biofuels, which optimally operate at 50-80 bar [11, 59]. Also, syngas conversion fraction to SNG is significantly higher than for other biofuels, often exceeding 90% [180]. This reduces the number and complexity of the crude SNG purifying equipment that must be incorporated in the system. Biomass conversion to SNG has been frequently studied in the literature using flowsheet simulations, where net biofuel efficiencies on the order of 70% (based on the LHV) have been attained [31, 32, 170, 181], albeit scarcely in the context of greenhouse applications. Despite this, single-product systems producing only SNG from biomass usually struggle to compete economically with conventional natural gas [37]. This is especially the case for small-scale applications that use much less than 20 MW biomass thermal power [36].

However, promising economic prospects have been reported for these systems where other useful energy forms besides SNG are co-generated, and most importantly, properly harnessed. For instance, relative to a standalone SNG system, Arteaga-Pérez et al. [182] attained a 12.7% reduction in SNG production cost simply by adopting an integrated plant topology where the heat that is co-generated in abundance during the exothermic SNG process is recovered. Unlike large-scale systems that are centralized, this approach could be readily adopted in small-scale SNG systems decentralized in greenhouses since they require large amounts of heating for most of the year, especially in northern climates. The requirement for heat recovery to improve the economics of small-scale SNG systems was also emphasized in other works [41, 54], where authors also discussed how profitability can be increased by adopting multi-product systems when possible. The polygeneration concept is highly compatible with the energy landscape of agricultural greenhouses, since electricity and high-purity carbon dioxide are also needed, in addition to fuel and heating. Carbon dioxide is usually purchased and injected into the greenhouse atmospheres since its concentration in ambient air is suboptimal for crop growth, being particularly low during day time around 150 ppm [66] relative to the optimal 700-1000 ppm concentration [67]. Despite this fact, biomass systems designed to simultaneously generate these four products have been rarely discussed.

In the literature, the polygeneration concept has generally received less attention than single-

product or co-generation (biofuel or electricity and heat) systems, and is usually not discussed in the context of agricultural greenhouses. For instance, Clausen et al. [60] modelled two 5-MW tri-generation systems converting wood chips into either MeOH or DME, electricity, and heat, at a total efficiency between 87 and 88% (based on the LHV). However, biofuel reactors with pressures exceeding 90 bar were used. Heyne et al. [38] integrated an SNG biomass system with a steam power cycle for tri-generation of SNG, electricity, and district heat. Simulations predicted an SNG efficiency of 69.4% (based on the LHV), but the production of high-purity carbon dioxide was not considered. Jana and De [183] proposed a 4-MW polygeneration plant, which converts agricultural waste to electricity, cooling, heating, and ethanol for rural areas. Techno-economic modelling demonstrated how the inherent flexibility of the polygeneration system and its synergy with the local utility needs contributed to rendering the process profitable. However, the biofuel reactor had to be operated at an elevated pressure of 96 bar. These research needs motivated our recent work [148], where two versions of a four-product polygeneration system were designed to meet the aforementioned needs of agricultural greenhouses. Despite the 85% process efficiency, the biofuel yield had to be limited at only 14%, since MeOH was produced at relatively low sub-optimal pressures for safety considerations. This compromise is alleviated in the work presented here by considering biomass conversion to SNG, which requires less severe conditions for optimal yield, and which could be readily handled or traded by greenhouses using existing natural gas distribution infrastructure.

Therefore, the goal of this study is to present and characterize the thermodynamic performance of novel biomass polygeneration systems that are capable of converting biomass to synthetic natural gas, electricity, heat, and carbon dioxide. These products are highly demanded in agricultural greenhouses, and their simultaneous production efficiencies from biomass remain largely unknown. First, the designs of the two proposed systems are presented, essentially differing in the gasification stage, with steam dual fluidized bed and oxygen/steam-blown downdraft gasifiers considered. A description of the flowsheet modelling approach is then given, followed by the results. Here, the energy flow in each system is detailed, and parametric analysis is shown to highlight the features of each system and their flexibility to accommodate changes in energy demand.

5.2 System description

In this section, the layouts of both proposed systems are discussed, and the design choices for each stage in the biomass conversion process are justified. This is followed by the modelling approach used. The selected feedstock for this study is wood chips, which are widely available

in agricultural settings and are a common choice for thermodynamic biomass conversion studies. Their ultimate and proximate analyses are shown in table 4.1.

5.2.1 Drying and gasification

The first system proposed uses a steam dual fluidized bed gasifier (DFB) operating at atmospheric pressure as shown in figure 5.1. The DFB gasifier was developed by Vienna University of Technology, and is sometimes referred to as fast internally circulating fluidized bed (FICFB). It has been implemented in small-scale configurations rated at a few hundred kilowatts and large-scale multi-megawatts plants [81]. The syngas produced has high CH_4 and H_2 content, which renders steam DFB gasifiers a common choice for SNG production [170]. The process is allothermal, whereby the biomass is gasified by steam in a separate bubbling fluidized bed, and the residual char and bed material is transferred via an inclined chute to a fast circulating fluidized bed, where an oxidant is injected for combustion. The resulting gases are cleared from solid particles in a cyclone where the hot bed material is returned, via a loop seal, to the gasification chamber operating at 850°C to provide the required heat for the endothermic process. The chute and loop seal is fluidized by steam, and this prevents gas leakage from the combustion zone, providing almost N_2 -free syngas, which is crucial for methanation reactors, even if air is used as an oxidant in the combustion chamber. The steam required for gasification is generated at 450°C , by using the system's excess heat, at a steam to biomass ratio (mass-based) of $\text{S/B} = 1.5$.

Before being fed to the gasifier, the biomass moisture content is reduced to 10 % in a steam dryer that harnesses part of the heat generated by the other exothermic components of the system. Instead of being vented, the generated steam from the dryer is recycled into the solid oxide electrolysis cell (SOEC), which plays a crucial role in the CO_2 , SNG, and electricity generation stages as discussed latter. This energy-efficiency measure of coupling a steam dryer to a SOEC has been previously discussed and used by Clausen [55] for the conversion of very wet biomass.

The second system proposed in this study adopts a downdraft gasifier as shown in figure 5.2. This is a simpler gasification approach that can be readily implemented in small and medium-scale systems rated between 10 kW to 10 MW [167]. Prior to gasification, the biomass is dried to 10% moisture in a steam dryer configuration similar to that described above. Within the gasifier, the biomass is first further dried, then pyrolyzed, oxidized, and finally reduced. The flow of solid and gaseous products is co-current, leading to higher gas exit temperatures compared to updraft gasifiers, and consequently less tar in the syngas. A steam-oxygen mixture is used as a gasification agent, which yields N_2 -free syngas with elevated H_2 content,

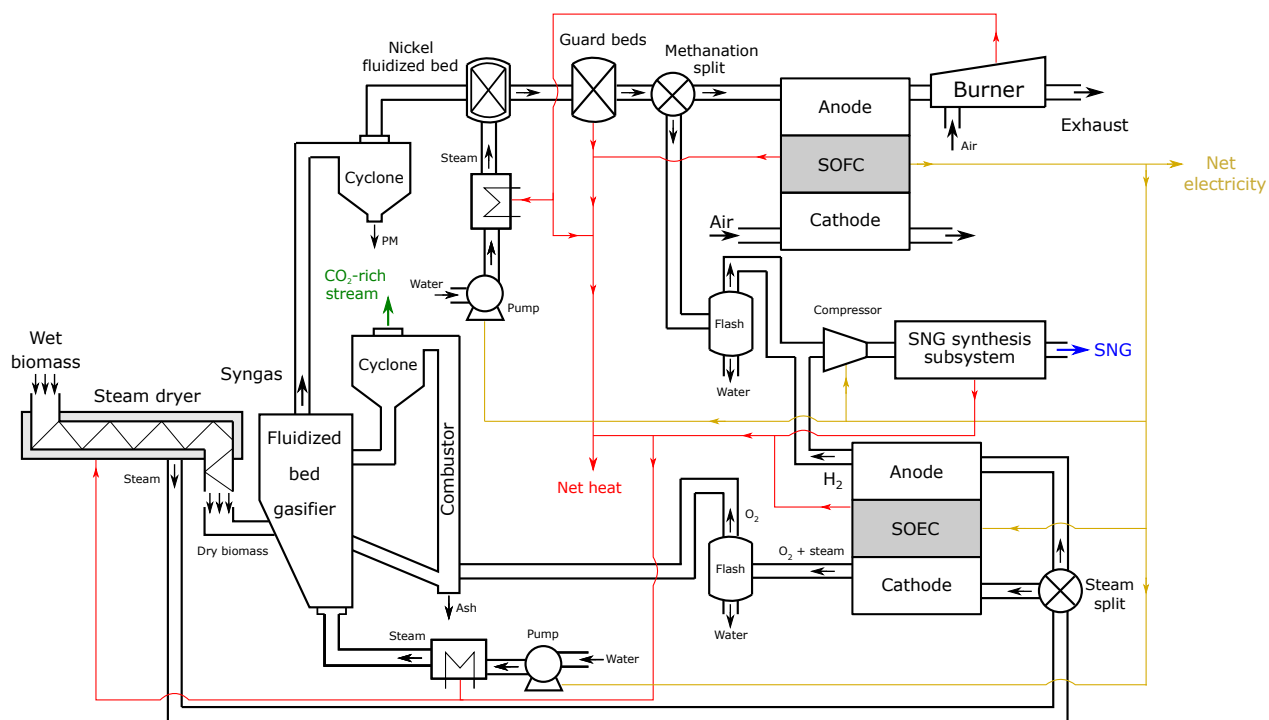


Figure 5.1 Schematic representation of the dual fluidized bed gasifier-based SNG system

as required by the methanation reactor. An SOEC produces this steam-oxygen mixture at an equivalence ratio (ER) of 0.2. The ER is defined as the ratio of the actual over the required O_2 flow rate needed to achieve stoichiometric combustion for a given amount of biomass. A steam to biomass ratio of $S/B = 1.5$ is ensured by generating steam using excess heat from other exothermic components, as the sweeping steam from the SOEC cathode is not enough.

5.2.2 Syngas cleaning

To clear the generated syngas from undesired contaminants that could poison/deactivate catalysts and clog downstream equipment, hot gas cleaning techniques are adopted in both systems following gasification. These are attractive for small-scale applications as only limited waste handling is required, and as less thermal energy is lost since the syngas must not be cooled to low temperatures [17]. As seen from figures 5.1 and 5.2, a cyclone is first used to clear the solid particulate matter (PM) entrained in syngas such as char, ash, soot, dust, etc. Then, a steam fluidized nickel bed operating at 780°C with a steam to carbon ratio S/C of 3 is used for tar abatement. Nickel-based catalysts at this temperature and steam content have been shown to yield very high tar conversion efficiencies ($>99\%$ [168]). The required steam is generated from the combustion of unconverted syngas left over at the end of the biomass conversion process.

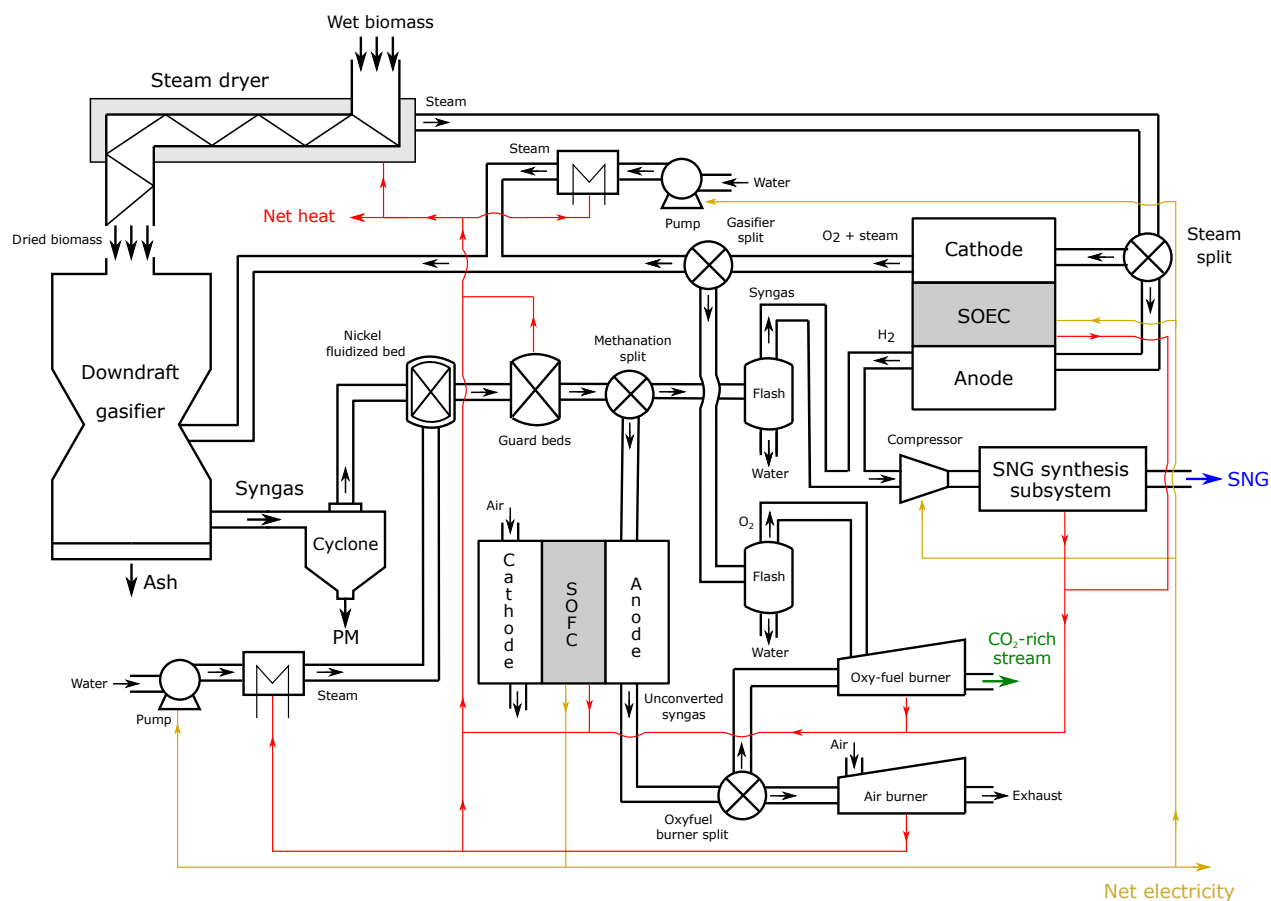


Figure 5.2 Schematic representation of the downdraft gasifier-based SNG system

For the systems to accommodate different agricultural feedstock containing higher sulfur content than wood chips, Sato and Fujimoto [184] proposed doping the nickel-based catalyst with WO_3 to avoid sulfur poisoning. During their 100-hour test, the authors have shown that their $\text{Ni-WO}_3/\text{MgO-CaO}$ catalyst tar conversion fraction remains above 95% even when the H_2S content in syngas is as high as 400 ppm. It should be noted that the H_2S content of syngas is typically on the order of 100 ppm for most biomass feedstock [185]. Following tar conversion, acid gas species such as H_2S and HCl are removed in two in-series ZnO and activated carbon guard beds operating at 400°C [60, 162].

5.2.3 Electricity production

In both systems, the methanation split component shown in figures 5.1 and 5.2 sends part of the cleaned syngas stream for methane synthesis as discussed next, and the other part to an 850°C solid oxide fuel cell (SOFC) for electricity generation. The splitting fraction is variable and offers the flexibility of increasing the fraction of desirable energy forms over others, as

demonstrated in the results section. Part of the electricity generated is used to power the SOEC and other auxiliary components of the system, with the remaining quantity available for powering the greenhouse. Various experimental studies reporting the successful operation of SOFCs with biomass-derived syngas can be found in the literature [46, 48, 49]. A handful of reasons motivate the use of a SOFC in this study, the first being its ability to generate electricity more efficiently and with very low pollutants emissions compared to conventional heat engines [52]. Upon replacing a micro gas turbine with a SOFC, Minutillo et al. [44] realized a 7.3% increase in efficiency for their combined heat and power biomass conversion system. The versatility of SOFCs is also highly compatible with the polygeneration characteristics desired in agricultural greenhouses. It is an exothermic component that co-produces heat at high temperatures, which can be either used internally in the system where needed or supplied to the greenhouse. It is also known for its reversibility, or its ability to operate as an SOEC. When fed with electricity and water, two separate streams of H_2 and O_2 are produced. The former is needed for the methanation stage as shown next, while the latter is crucial for the gasification stage, and as discussed in section 5.2.5, for the production of high-purity CO_2 needed in the greenhouse.

5.2.4 Methantion

Methane is synthesized from syngas according to the CO methanation and water gas shift (WGS) reactions [34]:



The yield is highly dependent on the syngas composition, where a linear combination of reactions 5.1 and 5.2 reveals the optimal feed gas module (M) [186]:

$$M = ([H_2] - [CO_2]) / ([CO] + [CO_2]) = 3 \quad (5.3)$$

with the terms in the square brackets being the molar quantities of the species in the feed stream. As shown in the results section, the syngas module after the gas cleaning stage in both systems is significantly less than three. Nonetheless, the incorporation of SOECs averts suboptimal syngas conversion to CH_4 , whereby the co-generated H_2 is used to enrich the dried syngas stream and render its module optimal at $M = 3$. The conditioned mixture is

then compressed to 10 bar and fed into the “SNG synthesis subsystem” shown in figures 5.1 and 5.2. Here, syngas is cooled and injected into a fixed bed nickel catalytic reactor at 270°C [170]. The exothermic reactor is cooled with water, and the generated steam can be used to heat the greenhouse. Water from the outlet stream of the reactor is condensed in a 40°C flash separator, before purifying the crude SNG stream in a pressure swing adsorption unit (PSA) [32].

5.2.5 Heat and carbon dioxide generation

Following the previous discussion, one could see that several components producing useful heat for greenhouses are already incorporated throughout the biomass conversion process. The final source is found following the electricity generation stage, where the unconverted syngas leftover from the SOFC is burned. Part of the heat is used for generating the steam needed in the tar abatement reactor, and the remaining recoverable quantity is for the greenhouse.

To produce the carbon dioxide required for greenhouse atmosphere enrichment, oxygen from the SOEC is used instead of air in the DFB gasifier combustion chamber, whose sole purpose usually is to produce the heat required for gasification. Heidenreich and Foscolo [17] are one of the few authors to discuss this opportunity with DFB gasifiers, albeit briefly, in their review paper. For the downdraft gasifier-based system, a fraction of the leftover syngas from the SOFC is combusted in an oxyfuel burner as shown in figure 5.2. The required oxygen is generated by the SOEC such that a lean equivalence ratio $ER = 1.2$ is maintained, in addition to the oxygen required for gasification. In both systems, the resulting exhaust stream is of high purity, containing more than 92% CO_2 with the remaining quantity being essentially O_2 . If not used in the greenhouse, these high-purity CO_2 streams could be sequestered or liquefied, potentially rendering the biomass conversion process carbon negative.

5.2.6 Modelling and operating conditions

The Aspen Plus software is used to predict the performance of the biomass conversion systems described above. A steady-state thermodynamics-based modelling approach is implemented, which is a common choice when analyzing the energy feasibility of novel systems and identifying desirable operating conditions. This is because results could be readily generalized, and are independent of the reactors design, unlike kinetic rate models that are also more computationally intensive [31]. The experimentally-validated models of several components used in the proposed systems were previously incorporated, albeit in a different plant layout, in our earlier work. Readers are kindly referred to [148] for the detailed modelling approach and

incorporated user-defined subroutines. Only a summary is given in table 5.1 for convenience. The power outputs of the simulations are made non-dimensional using the thermal power of the biomass input, based on its HHV (500 kW):

$$\eta_{ele} = \frac{P_{net}}{(\dot{m}HHV)_{BM}}; \quad (5.4)$$

$$\eta_{th} = \frac{Q_{net}}{(\dot{m}HHV)_{BM}}; \quad (5.5)$$

$$\eta_{biofuel} = \frac{(\dot{m}HHV)_{biofuel}}{(\dot{m}HHV)_{BM}}; \quad (5.6)$$

$$\eta_{tot} = \eta_{ele} + \eta_{th} + \eta_{biofuel}; \quad (5.7)$$

P_{net} is the net electrical power produced from the SOFC, after powering the auxiliary components, and similarly $\dot{Q}_{net}$ is the neat heat produced after supplying the endothermic processes of the systems. $\dot{m}$ is the mass flow rate of the wet biomass (BM) used or the biofuel produced which could be either SNG or unrecycled H_2 . The goal is to keep the values of the four efficiencies (Eqs. 5.4 - 5.7) positive, and not rely on external energy inputs in addition to biomass.

5.3 Results

5.3.1 Dual fluidized bed gasifier-based SNG system

For a clear demonstration of the energy flow in the dual fluidized bed gasifier-based system, its Sankey diagram is shown in figure 5.3. The energy of each stream is normalized with the thermal energy of the input biomass. 7.5 out of the 9% of the total energy used in the drying stage is recovered as steam. Char with 6% energy content is expended in the combustion chamber of the DFB gasifier, which supplies 5.5% heat to the gasification chamber. Steam with 15% energy content generated from the system's residual heat is injected into the gasifier, leading to a cold gas efficiency of $\eta_{CG} = 88.9\%$. Energy losses at 8.4% are sustained during the gas cleaning stage, after which 25% of the generated syngas is sent for methanation and 75% to the SOFC. This is only a particular case for demonstration, and the effect of varying the methanation split fraction on SNG and other yields is discussed in detail later in this section.

Table 5.1 Summary of the Aspen Plus models used for each component in the systems. Detailed description can be found in Antar and Robert [148].

Components	Model	Operating conditions
Steam dryer	RStoic reactor	$T_{steam} = 200^{\circ}\text{C}$, $P = 1$ bar, $T_{biomass} = 120^{\circ}\text{C}$, 10% moisture level
Steam blower and pumps	Compr pressure changer	$\eta_{isentropic} = 80\%$, $P_{increase} = 0.05$ bar
Dual fluidized bed gasifier	Doherty et al. [173]	$T = 850^{\circ}\text{C}$, $P = 1$ bar, $S/B = 1.5$, $ER_{combustion, chamber} = 1.2$, tar = 9.5 g/Nm^3 , heat loss = 5.5% of biomass HHV
Downdraft gasifier	Han et al. [172]	$T = 775^{\circ}\text{C}$, $P = 1$ bar, $ER = 0.2$, $S/B = 1.5$, tar = 5 g/Nm^3 , heat loss = 5.5% of biomass HHV
Cyclones	SSplit splitters	$T_{loss} = 100^{\circ}\text{C}$, char and ash split fraction = 1
Tar reformer	RStoic + RGibbs reactors [31]	$S/C = 3$, $T = 780^{\circ}\text{C}$, conversion fraction = 1
Guard beds	Sep separator	$T = 400^{\circ}\text{C}$, $T_{loss} = 100^{\circ}\text{C}$, acid gas split fraction = 1
Flash condensers	Flash separator	$T = 40^{\circ}\text{C}$, duty = 0
Compressors	Compr pressure changer	$\eta_{isentropic} = 80\%$, $P_{increase} = 10$ bar
Methanation reactor	RGibbs reactor [187]	$T = 270^{\circ}\text{C}$, $P = 10$ bar, PSA split fraction = 0.98
SOFC	Constant area specific resistance (ASR) [148, 177]	$T = 850^{\circ}\text{C}$, $P = 1$ bar, $U_f = U_o = 0.7$, $ASR = 0.2 \Omega\text{cm}^2$, $i = 0.5 \text{ A/cm}^2$ when the methanation reactor split fraction is zero, with recuperative heat exchangers, $T_{loss} = 100^{\circ}\text{C}$
SOEC	Constant ASR [148, 177]	$T = 850^{\circ}\text{C}$, $P = 1$ bar, $U_o = 0.7$, $ASR = 0.2 \Omega\text{cm}^2$, $V_{opt} = 1.3 > V_{thermoneutral} = 1.29\text{V}$, with recuperative heat exchangers, $T_{loss} = 100^{\circ}\text{C}$
Leftover syngas burners	RGibbs reactor	$ER = 1.2$, $P = 1$ bar, $\eta_{combustion} = 85\%$
Heat exchangers	Heater and HeatX Exchangers	$\Delta T_{min} = 15^{\circ}\text{C}$ (gas-liquid) and 30°C (gas-gas)

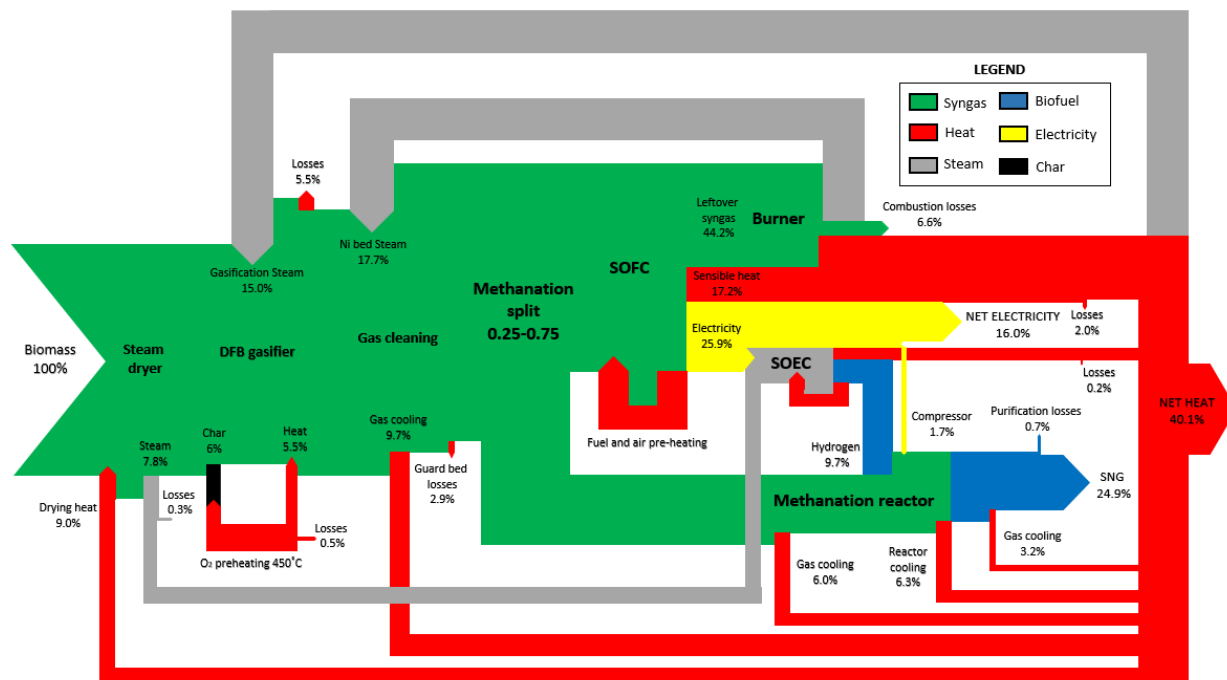


Figure 5.3 Sankey diagram of the dual fluidized bed gasifier-based SNG system. The energy of the streams is normalized with the thermal energy of the biomass input (based on the HHV).

Recuperative heat exchangers are used in the SOFC to heat the input streams from 300 to 850°C, where 25.9% of the total input energy is obtained as electricity. The efficiency of the SOFC based on the first law of thermodynamics is $\eta_{I,SOFC} = 41.8\%$. However, considering the maximum reversible power for the amount of syngas undergoing electrochemical reactions, a decent second law efficiency of $\eta_{II,SOFC} = \eta_{I,SOFC} / \eta_{SOFC, reversible} = 91.3\%$ is revealed. After feeding the SOEC with 8.2% of the total energy as electricity and powering the other auxiliary components, the net electrical efficiency of the system is $\eta_{ele} = 16.0\%$. The SOEC yields 9.7% of the total energy as H₂ at a relatively low efficiency of $\eta_{III,SOEC} = 66\%$, since for it to be exothermic, and hence benefit from much simpler heat management, it has to be operated at or above its thermoneutral voltage of 1.29 V. This is considerably larger than the Nernst or reversible voltage of 0.85 V. The generated H₂ enriches the syngas before being fed into the methanation reactor, which produces SNG at $\eta_{SNG} = 24.9\%$ and an abundance of heat. Summing the total amount of recoverable thermal energy in the system reveals a $\eta_{th} = 40.1\%$, contributing to a total polygeneration process efficiency of $\eta_{tot} = 81.0\%$. On top of this, 96 g of CO₂ is generated for the greenhouse atmosphere per kilogram of 45%-wet biomass input. If desired, this can be considerably increased at the expense of electricity as discussed later.

Figure 5.4 highlights the flexibility of the proposed polygeneration system by showing the

effect of varying the fraction of syngas sent to the methanation reactor (R_{meth}) on the different outputs. This is controlled by the methanation split component shown earlier in figure 5.1. Various H_2 recycling modes are considered as described in table 5.2. For the extreme case of $R_{meth} = 0$, no SNG is produced in all modes, and electricity and heat output are $\eta_{ele} = 25.3\%$ and $\eta_{th} = 43.9\%$, respectively for mode 1. A net quantity of H_2 is also produced at $\eta_{H_2} = 9.5\%$ as none of it can be recycled into the SNG reactor. Nonetheless, this H_2 can be recycled into the SOFC to maximize electricity output to $\eta_{ele} = 28.2\%$ if desired (mode 2). On the other side, the maximum attainable split fraction while simultaneously producing CO_2 is $R_{meth} = 0.7$, yielding $\eta_{SNG} = 53.9\%$. If CO_2 production is sacrificed by turning off the SOEC and using air in the combustion chamber of the gasifier, $R_{meth} = 0.9$ can be achieved, yielding a maximum $\eta_{SNG} = 63.1\%$ (shaded region figure 5.4). Here, no net quantity of electricity is produced, and net heat production drops to $\eta_{th} = 24\%$, since the quantity of leftover syngas from the SOFC sent to the burner decreases. Consequently, this enhances the total system efficiency, which goes from $\eta_{tot} = 78.7\%$ at $R_{meth} = 0$ to $\eta_{tot} = 86.2\%$ at $R_{meth} = 0.9$ as the exhaust losses from the burner are minimized.

The prominent role played by the SOEC in the SNG production process is highlighted by considering mode 0 in figure 5.4. It can be seen that if H_2 enrichment is not adopted at $R_{meth} > 0$, the feed gas of the methanation reactor is always significantly deprived of H_2 , with a module of $M = 1.16$. This clearly limits the SNG yield, which at $R_{meth} = 0.1$ for example is $\eta_{SNG} = 7.1\%$, but which almost doubles to $\eta_{SNG} = 13.7\%$ upon making $M = 3$ as H_2 from the SOEC is used (modes 1 and 2). As the split fraction is increased, the H_2 co-produced by the SOEC as it supplies the combustion chamber of the gasifier with O_2 eventually becomes insufficient to attain $M = 3$. For instance, at $R_{meth} = 0.2$, $M = 2.3$ even when all the produced H_2 is recycled, resulting in only $\eta_{SNG} = 21.3\%$. If more SNG is desired, part of the net electricity produced by the system $\eta_{ele} = 17.8\%$ can be diverted to the SOEC to produce more H_2 and render $M = 3$ (mode 3). Upon doing so, SNG yield increases to $\eta_{SNG} = 26.0\%$, and excess O_2 is produced, which can be used to increase CO_2 production in the oxyfuel burner, as discussed later. As the split fraction is further increased, the entire system's net electricity becomes insufficient to increase the module of the feed gas to $M = 3$. At $R_{meth} = 0.3$, the maximum feed gas module that can be attained is $M = 2.60$, when all the excess electricity from the SOFC is used. The SNG yield at $\eta_{SNG} = 28.5\%$ is still higher than that attained at lower R_{meth} where $M = 3$, but now electricity from an external source, if available, could be injected into the SOEC and get stored as chemical energy in SNG. This concept has been previously investigated on a large scale in the context of flexible energy utilization and storage from intermittent sources such as wind, where bio-SNG is generated from electrolytic H_2 when the prices of electricity are low [54].

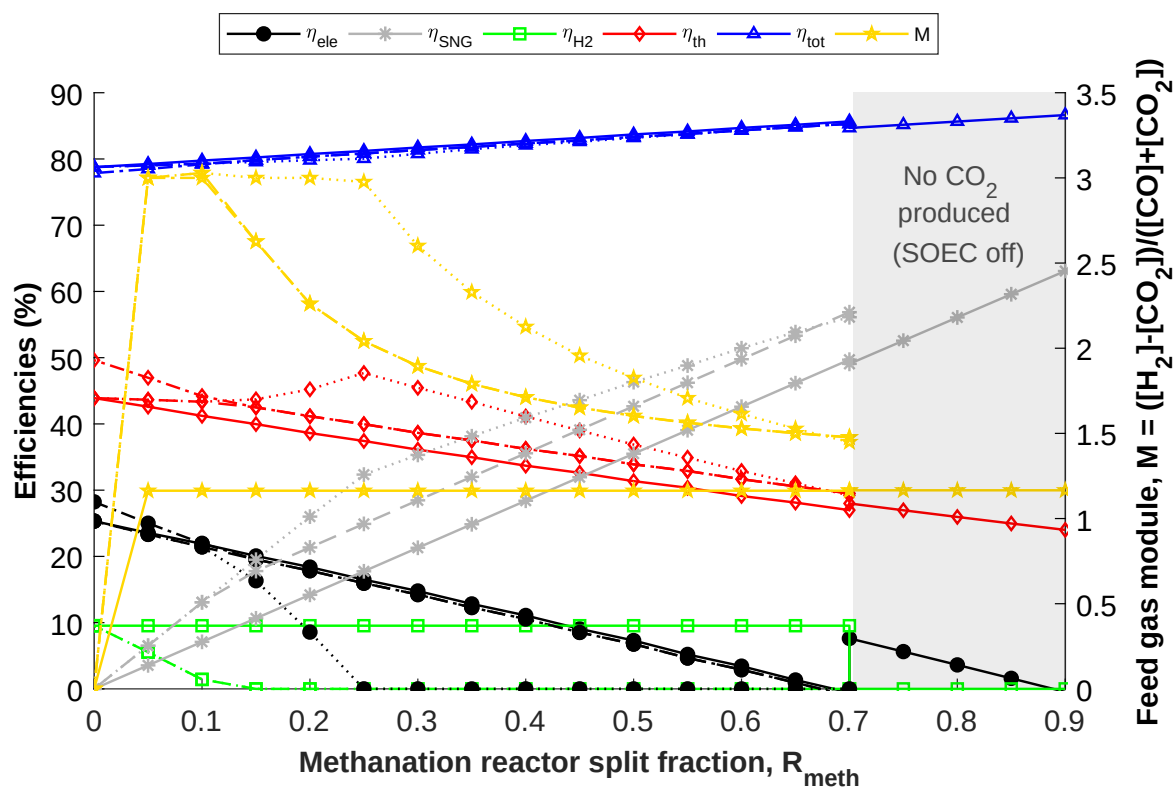


Figure 5.4 Variation in the output of the dual fluidized bed gasifier-based SNG system as a function of the fraction of syngas sent to the methanation reactor. Four hydrogen recycling modes are considered: 0 (—), 1 (---), 2 (— · —), and 3 (·····).

Figure 5.5 presents the resulting changes in efficiencies when electricity is injected into the biomass conversion system at $R_{meth} \geq 0.3$, after using all the power generated from the SOFC (mode 3). Strictly speaking, the conversion fraction of electricity to SNG is dependent on R_{meth} and the amount of electricity to be stored. This is because both of these parameters affect the efficiency of the SOEC, which decreases at smaller R_{meth} and larger electricity input, since the SOEC overpotential is higher. Nonetheless, the implications on SNG yield are negligible at power inputs lower than 10%, and from the slopes of the efficiency lines which are highly linear under these conditions, it is revealed that the system is able to convert roughly 40% of input electricity into SNG, with the remaining 55% to heat, and 5% to unrecoverable losses. Also, for every kilogram of biomass input, injecting an additional 1% electricity into the system contributes to the production of 23 g of CO₂. From a thermodynamics point of view, the maximum amount of electricity that can be stored by the system in SNG for given biomass input is only limited by the syngas module not exceeding $M = 3$. Otherwise, the H₂ conversion fraction to CH₄ and consequently the total efficiency of the process would

Table 5.2 Description of the different H₂ recycling modes adopted in this study

Mode	Description
0	None of the H ₂ co-produced by the SOEC as it feeds the gasifier with O ₂ is recycled into the system.
1	The produced H ₂ is recycled into the methanation reactor to optimize the feed gas module when $R_{meth} > 0$, and any excess is extracted from the system.
2	The excess H ₂ from mode 1 is recycled into the SOFC.
3	All net generated electricity is fed into the SOEC to maximize H ₂ enrichment when needed. Excess O ₂ is produced.

deteriorate. Since the feed gas module decreases with R_{meth} , higher split fractions could in theory offer larger storing capacities. At $R_{meth} = 0.5$ for instance, the maximum amount of electricity that can be stored in SNG is equivalent to 60% of the input biomass energy. This is more than double the maximum energy that can be stored at $R_{meth} = 0.35$. However, injecting this amount of electricity into the SOEC results in a drastic current density (i) increase, 5.8 A/cm² in this case. This is likely to be outside the practical operating range, which requires SOEC-specific kinetic rate attributes to be accurately determined.

The high-purity carbon dioxide generation rate of the system can be increased by burning part of the leftover syngas from the SOFC in an oxyfuel burner, similar to the downdraft gasifier-based configuration. This comes at the expense of the electrical power output since more O₂ must be generated by the SOEC. Figure 5.6 shows the efficiencies as a function of the enhanced CO₂ generation rate at different R_{meth} , when the system is operating under mode 0. The SNG and total efficiencies are not included since they are essentially invariable with the amount of CO₂ produced. The SOEC is mainly responsible for the increased heat generation at higher CO₂ levels, due to its larger overpotential and therefore lower efficiency when more electricity is fed to it. This also explains the parabolic behavior of the system's electrical efficiency curves, where it can be seen that more electricity is consumed per kilogram of CO₂ at higher generation rates for all R_{meth} . For instance, below 0.2 kgCO₂/kg_{Biomass.wet}, electrical output drops on average by 4.6% for every 100g of CO₂ generated per kilogram of wet biomass input. However, between 0.3 and 0.5 kgCO₂/kg_{Biomass}s, a larger amount of electricity at 6.8% is consumed for every 100g of CO₂ produced per kilogram wet biomass input. The maximum high-purity CO₂ generation capacity of the system that can be theoretically attained while only running on biomass occurs at $R_{meth} = 0$. Assuming that the SOEC can accommodate the resulting 3.5 A/cm² current density increase, a maximum of 529 g of CO₂ can be generated per kilogram of wet biomass input. This represents a maximum potential carbon recovery rate of 52 moles per 100 moles of carbon input into the system $n_{C,rec}/n_{C,in}$, as can be seen

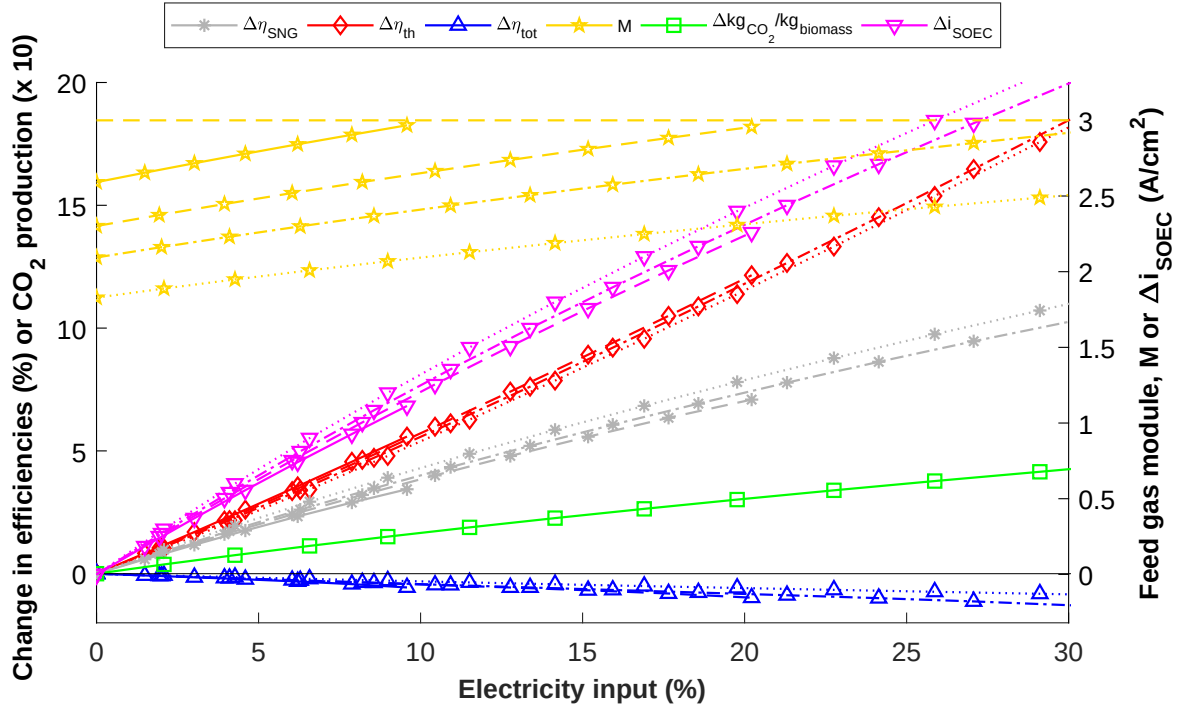


Figure 5.5 Change in output when electricity from an external source is supplied to the system operating under mode 3. $R_{meth} = 0.3$ (—), 0.35 (---), 0.4 (— · —), and 0.5 (·····).

from figure 5.6. At this point, zero net electricity is generated, and H_2 production peaks at $\eta_{H_2} = 25.0\%$.

5.3.2 Downdraft gasifier-based SNG system

The energy flow in the downdraft gasifier-based system is shown in the Sankey diagram of figure 5.7. After the 10%-moisture drying stage, where a significant portion of the generated steam is recovered, the dried biomass is gasified at a cold gas efficiency of $\eta_{CG} = 76.4\%$. This is notably inferior to the efficiency of the DFB gasifier (88.9%), since the quantity of CO_2 that dilutes the generated syngas is 50% larger in the downdraft gasifier. Steam generated from the leftover syngas burner at a total energy of 18.6% is used for tar abatement in the gas cleaning stage, after which a particular methanation split of 0.1 - 0.9 is taken for illustration.

In the SOFC, 29.3% electricity is generated at $\eta_{II,SOFC} = 87.7\%$. However, a large fraction equivalent to 20.9% of the total input energy is directly injected into to the SOEC. This is considerably more than the 8.2% electricity required by the SOEC in the first system,

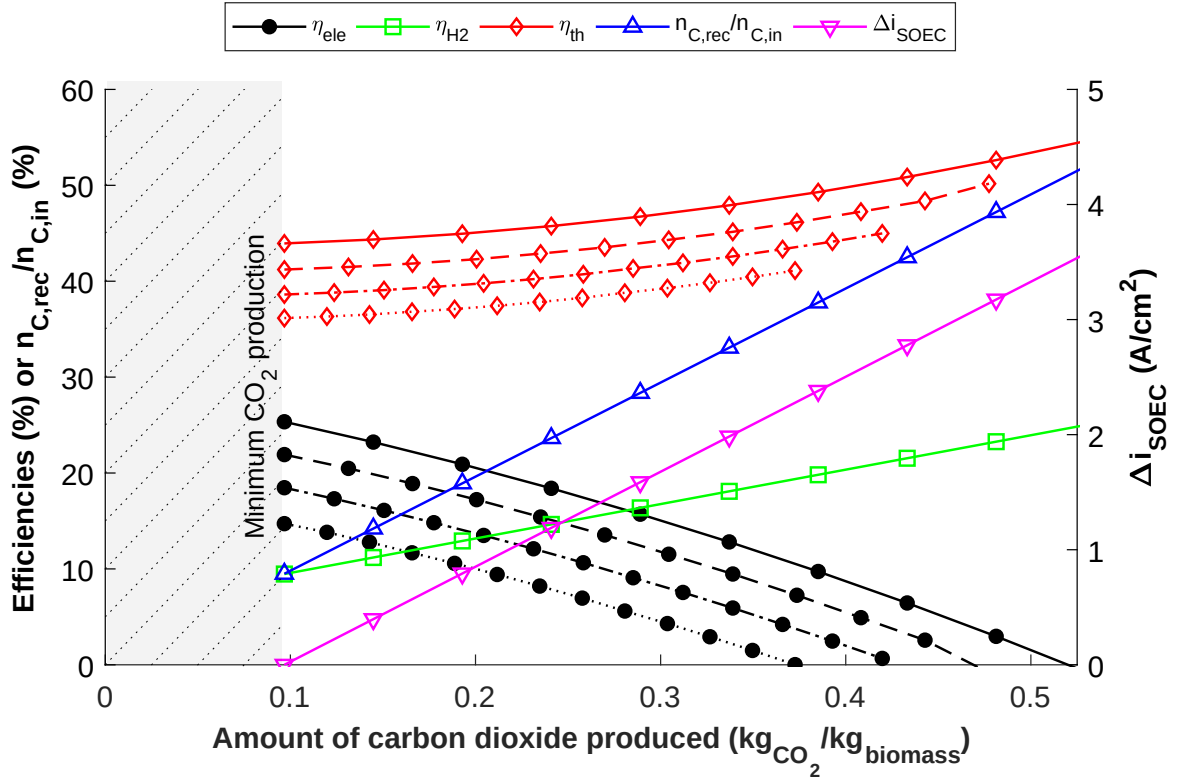


Figure 5.6 Efficiencies at different CO_2 generation rates under $R_{meth} = 0$ (—), 0.1 (---), 0.2 (— · —), and 0.3 (·····). No H_2 is recycled into the system (mode 0).

since the downdraft gasifier requires double the amount of O_2 in the combustion chamber of the DFB gasifier, and since in addition to gasification, an oxyfuel burner must be used here for CO_2 production. After powering the other auxiliary components in the system such as compressors and pumps, a net electrical efficiency of $\eta_{ele} = 7.4\%$ is obtained. Leftover syngas from the SOFC is again split at 0.9-0.1 between the air and oxyfuel burners, which have total combustion losses of 9.1%. For this split fraction, 90 g of CO_2 is generated by the oxyfuel burner per kilogram of wet-biomass input into the system. On the other hand, the SOEC generates 23.2% H_2 , of which, 10.5% is fed to the methanation reactor to render the feed gas module optimal at $M = 3$, and 12.7% is recycled into the SOFC to enhance electricity generation. In the former, 13.7% SNG is synthesized, with the possibility of considerably increasing the yield by varying the methanation split fraction as shown next. Heat is produced by the system at $\eta_{th} = 56.9\%$, leading to a total efficiency of $\eta_{tot} = 78.0\%$, which can also be enhanced by increasing the methanation split fraction.

The effect of varying the methanation reactor split fraction on the output of the downdraft

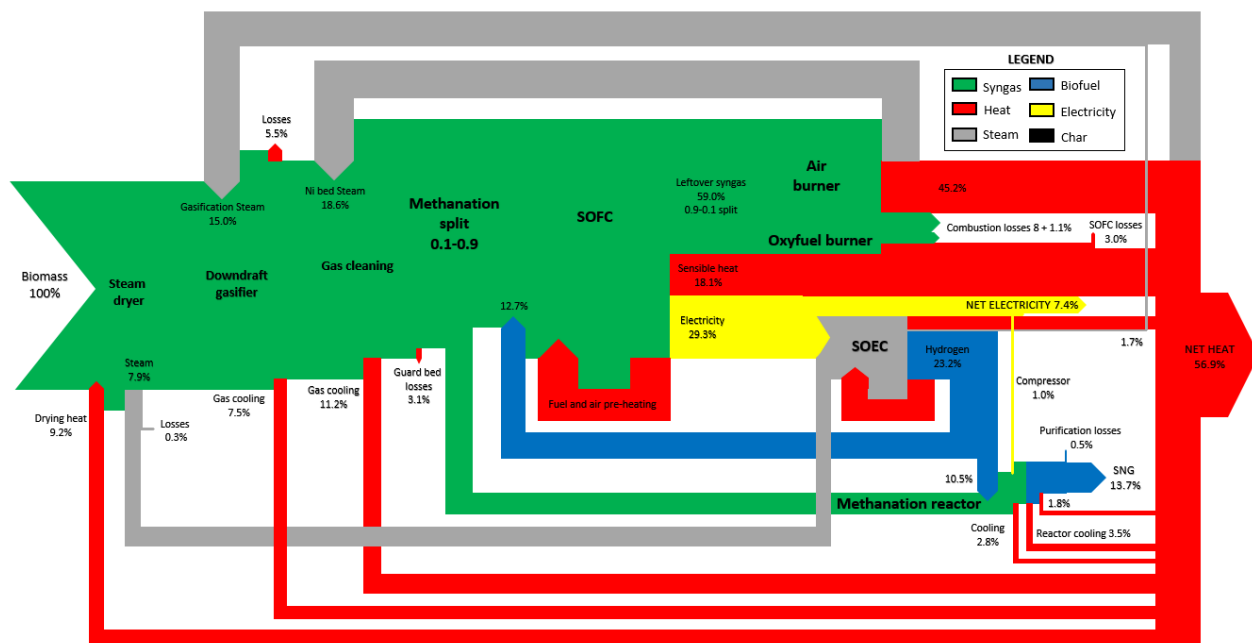


Figure 5.7 Sankey diagram of the downdraft gasifier-based SNG system. The energy of the streams is normalized with the thermal energy of the biomass input.

gasifier-based system is shown in figure 5.8. The trends are similar to the DFB gasifier-based system that was discussed in the previous section (figure 5.4), but the actual efficiencies are clearly different. For instance, the maximum electricity output for the downdraft gasifier-based system is $\eta_{ele} = 16.7\%$ at $R_{meth} = 0$ (mode 2). This is notably smaller than for the DFB gasifier-based system ($\eta_{ele} = 28.3\%$), since more electricity is consumed by the SOEC here, as shown earlier. As a result, this reduces the maximum methanation reactor split fraction that could be attained, which is $R_{meth} = 0.325$ in this case (vs $R_{meth} = 0.65$ for the first system when the SOEC is operational), limiting the maximum SNG yield to $\eta_{SNG} = 33.0\%$ (vs $\eta_{SNG} = 53.9\%$ for the first system). It should be noted that since pure O_2 is crucial for the production of N_2 -free syngas in downdraft gasifiers, not supplying electricity to the SOEC to attain higher R_{meth} is impossible. As shown earlier, this is not the case with the indirect gasification technology used in the first system, where a maximum $R_{meth} = 0.9$ and $\eta_{SNG} = 63.1\%$ can be attained. Therefore, it can be said that adopting a simple downdraft gasification approach comes at a price of lower flexibility in energy output.

As discussed earlier, the fact that the feed gas module is less than $M = 3$ at larger split fractions, even when all the electricity generated by the SOFC is used for H_2 enrichment, means that this system also offers the additional feature of storing electricity in SNG if needed. Figure 5.9 shows the resulting changes in efficiencies when electricity is injected into

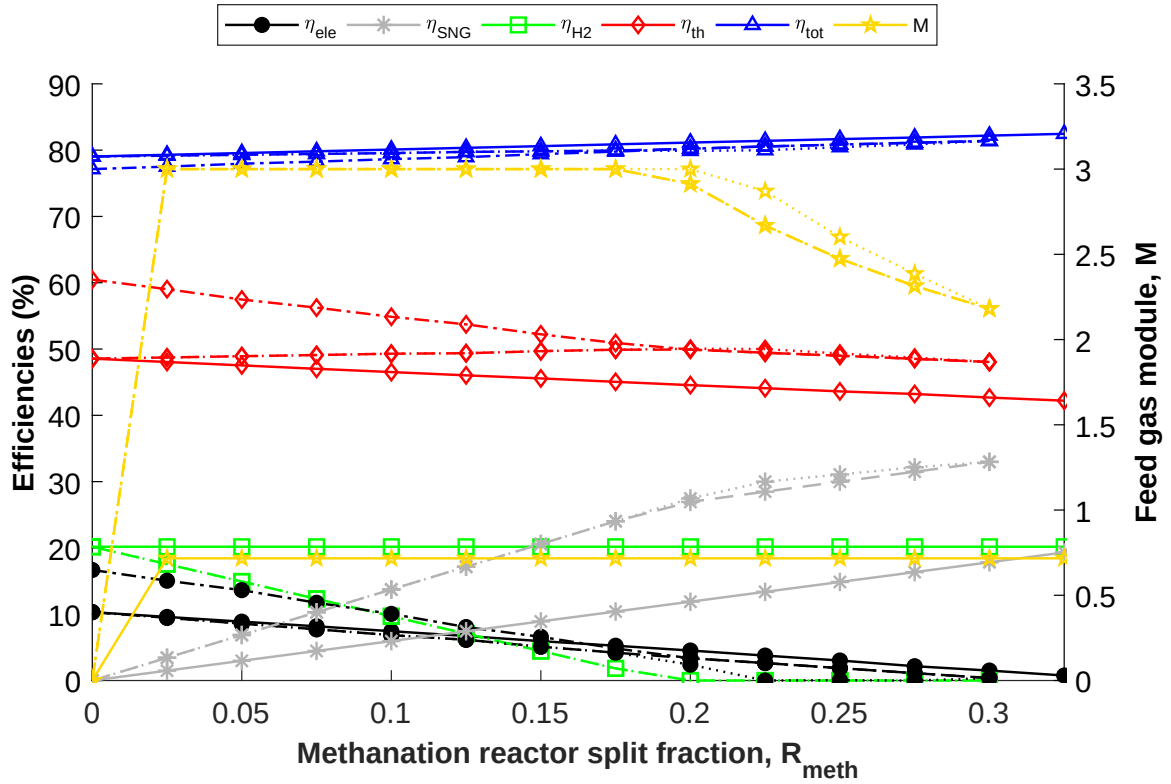


Figure 5.8 Variation in the output of the downdraft gasifier-based SNG system as a function of the fraction of syngas sent to the methanation reactor. No leftover syngas from the SOFC is sent to the oxyfuel burner. Hydrogen recycling modes 0 (—), 1 (---), 2 (— · —), and 3 (·····) are analyzed.

the SOEC of the downdraft gasifier-based system (at $R_{meth} = 0.4$), and compares its storage efficacy to that of the first system (at $R_{meth} = 0.5$). It can be seen that the electricity-to-SNG conversion efficiency of the downdraft gasifier-based system is higher than that of the first system. On average, 54% of the input electricity is converted to SNG, 40% to heat, and the remainder 6% is lost, for a given biomass input. The superior performance is attributed to the SOEC, whose current density is more than 1.5 times less sensitive to the amount of injected electricity when it comes to the downdraft gasifier-based system, leading to a smaller drop in $\eta_{II,SOEC}$ as seen from figure 5.9. This is because the electrode area of the SOEC here is twice as large as that of the first system. Given that the designs of the systems are not focused on electricity storage, which is in fact an additional feature due to the versatility of the proposed configurations, the storage efficiencies can be considered decent. This is in comparison to systems specifically designed for biomass conversion and electricity storage in SNG adopting conventional steam electrolysis which have an efficiency on the order of

70% [39].

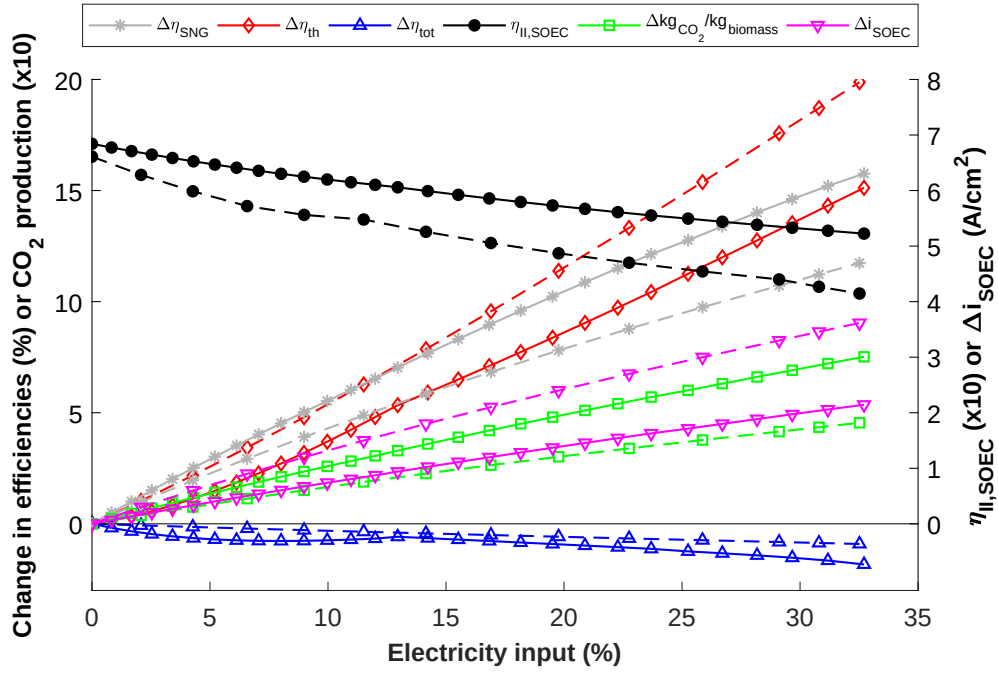


Figure 5.9 Changes in efficiencies when electricity from an external source is injected into the downdraft gasifier-based system (—) and the DFB gasifier-based configuration (---) both operating in mode 3.

In the downdraft gasifier-based system, O_2 must be supplied to the oxyfuel burner for the production of a high-purity CO_2 stream, in addition to the quantity needed for gasification. figure 5.10 presents the variation in efficiencies with the amount of CO_2 produced. The slopes of the trend lines being nearly constant in the range considered, it can be said that electricity production drops only by approximately 3.7% for every 100 g of CO_2 generated per kilogram of biomass input. This is lower than the average electrical power consumed by the DFB gasifier system to produce the same quantity of CO_2 , with its steeper electrical efficiency curve shown in figure 5.10. As discussed earlier, this is attributed to the superior SOEC performance whose current density sensitivity to CO_2 production is conveniently three times smaller. However, the maximum CO_2 quantity that can be generated per kilogram of biomass input in the downdraft gasifier-based system is only 275g at $R_{meth} = 0$ (vs 529 g for the first system). This leads to a maximum carbon recovery rate of 27 moles per 100 moles of carbon input (vs 52 moles for the first system). H_2 production peaks here at $\eta_{H_2} = 28.1\%$.

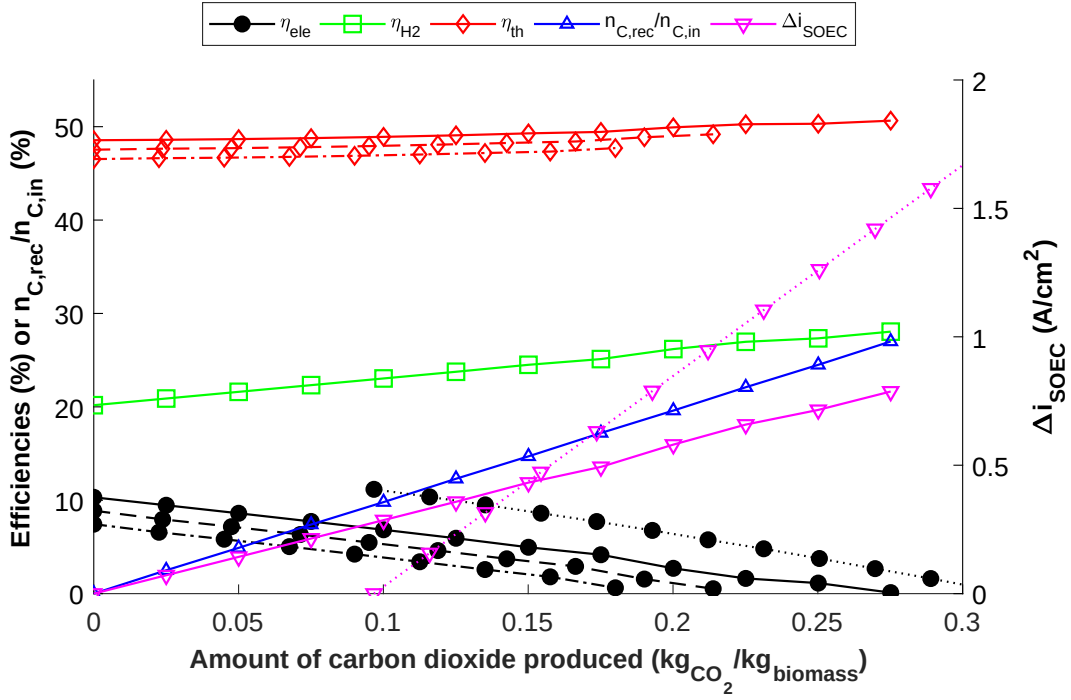


Figure 5.10 Variation in efficiencies as a function of the quantity of CO_2 produced by the downdraft gasifier-based system, when no H_2 enrichment is adopted (mode 0). $R_{meth} = 0$ (—), 0.05 (---), and 0.1 (— · —). Data from the DFB-gasifier system at $R_{meth} = 0.4$ are represented by (·····).

5.3.3 System comparison and discussion

The efficiencies of the two proposed SNG polygeneration systems are summarized in figure 5.11, and compared with two MeOH-based four-product polygeneration plants introduced in previous work and also intended for agricultural greenhouses [148]. Three scenarios are shown, where either electricity, biofuel (SNG or MeOH), or CO_2 are maximized, at the expense of the other products. For the latter case, the operating conditions also always coincide with maximum H_2 yield when none of it is recycled into the systems. The difference in maximum electricity and CO_2 output between the SNG and MeOH systems that use the same gasification technique is mainly due to the operating conditions chosen. For instance, more electricity is produced by the SNG configurations since the SOFC is sized at a lower current density $i = 0.5 \text{ A/cm}^2$ (vs $i = 1.0 \text{ A/cm}^2$ for MeOH systems), while more CO_2 is generated by the MeOH systems since the SOEC was not operated exothermically above the thermoneutral voltage. The 28.2% electrical efficiency that can be attained by the DFB-SNG polygeneration system is similar to that of large-scale biomass combined heat and power

plants [188], and other studies that combine gasification and SOFCs [162,186].

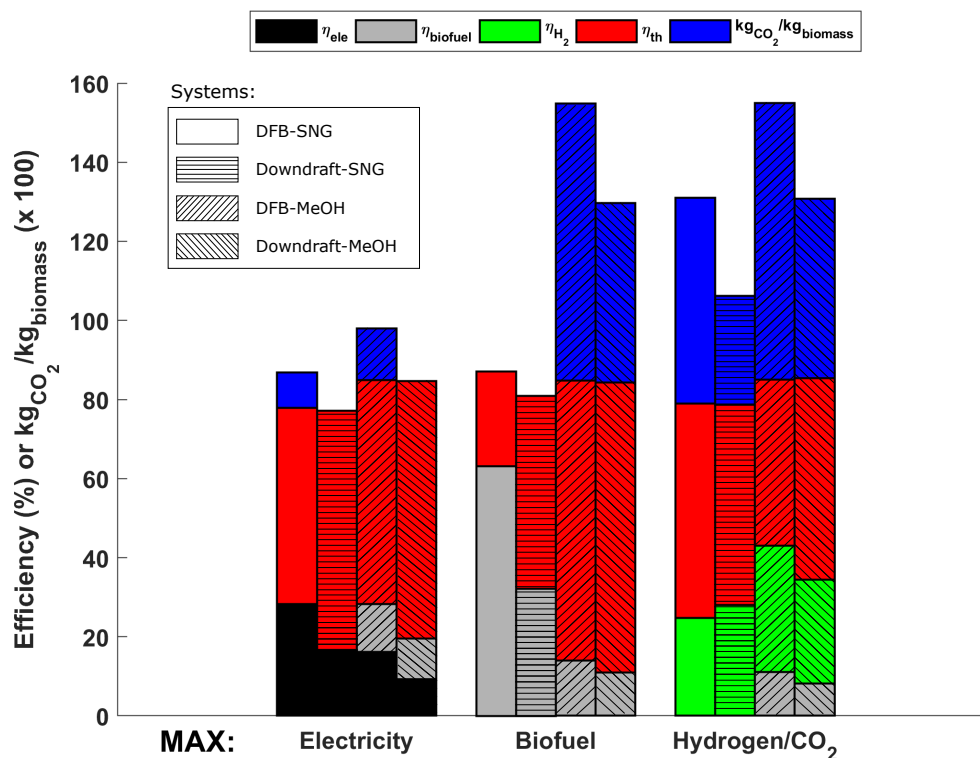


Figure 5.11 Comparison of the proposed SNG systems with MeOH-based polygeneration systems [24]. Three scenarios are considered: maximum electricity, SNG/MeOH, or CO₂.

However, the main advantage of the SNG systems proposed in this paper in the context of safe decentralized operation is clearly the maximum attainable biofuel yield. Due to the milder operating conditions of the chemical reactor and higher syngas conversion fractions, attainable biofuel yields are drastically larger for the SNG systems. For the DFB gasifier-based configurations, maximum $\eta_{biofuel} = 63.1\%$ for SNG, while for MeOH it is only $\eta_{biofuel} = 14.0\%$. The former is comparable with the output of larger single/bi-product SNG systems running on woody biomass [31,32,170,181]. For the systems adopting downdraft gasification in figure 5.11, maximum biofuel yield is 32.2% vs 11.0% for SNG and MeOH, respectively.

For the reasons discussed earlier in the text, the efficiencies of the DFB gasifier-based systems prevail over downdraft gasification in both SNG and MeOH systems. This has the potential to outweigh the added complexity and cost of DFB configurations, in addition to the fact that these gasifiers offer the additional benefit of potentially relying on only one reversible solid oxide cell (RSOC) when proper electricity and gas storage medium is available. The

RSOC can be operated as a SOFC for a fraction of the time for electricity generation, with air from the ambient atmosphere used in the combustion chamber of the gasifier (shaded region, figure 5.4). Part of the generated electricity is stored, and then injected into the RSOC during its reversed SOEC operating mode where the system produces CO_2 . In both of these regimes, heat and SNG are always generated, albeit in variable amounts since H_2 enrichment is only possible in the reverse mode. This subject will be tackled in future works involving transient system simulations, where data acquired from agricultural greenhouses will be used to precisely size the proposed systems, and optimize their economic returns.

5.4 Conclusion

This paper presents the design and modelling of two novel small-scale systems capable of producing synthetic natural gas, electricity, heat, and high-purity carbon dioxide from wood chips for agricultural greenhouses. Two gasification techniques are considered, namely steam dual fluidized bed and steam/oxygen-blown downdraft gasifiers. The versatility of reversible solid oxide cells is exploited in various ways, the first being through the efficient and clean generation of electricity and useful heat from syngas. Part of this electricity is then used to synthesize H_2 via steam electrolysis, enriching the methanation reactor and maximizing its SNG yield. The co-produced O_2 is used in the gasification stage, and for oxyfuel combustion, allowing the production of high-purity CO_2 streams for greenhouse atmosphere enrichment.

The overall process efficiency can reach up to 86.6% and 82.5% for the DFB and downdraft gasifier-based configurations, respectively. The share of SNG, electricity, and heat from the total energy output can be readily varied, reaching values comparable with large-scale product-specific systems for the DFB gasifier-based configuration. In this system, η_{SNG} can be varied between 0 and 63.1%, at the expense of η_{ele} that drops from a maximum of 28.2 to 0%, and η_{th} from 49.6 to 24.0%. While for the system adopting the downdraft gasifier, η_{SNG} can be set between 0 and 32.2%, η_{ele} between 0 and 16.7%, and η_{th} between 42.2 and 60.5%. The reduced complexity and cost of downdraft gasifiers come at a cost of lower flexibility and efficiency, a trade-off that will be further investigated in future techno-economic work. Regarding the production of high-purity carbon dioxide, DFB gasifier based-configurations also offer higher capacities of $529 \text{ gCO}_2/\text{kg}_{\text{Biomass}}$ vs $275 \text{ gCO}_2/\text{kg}_{\text{biomass}}$ for the downdraft gasifier-based system. However, in the latter, the drop in electricity output per unit CO_2 produced and the sensitivity of the SOEC current density are much lower.

The proposed systems also offer the possibility of storing excess electrical energy from intermittent energy sources such as photovoltaic cells or wind power. At higher methanation split fractions, the syngas is always deprived of H_2 for optimal SNG yield. Electricity may

thus be injected into the SOEC to produce more SNG by enhanced H_2 enrichment. This also produces more O_2 for oxyfuel combustion, which increases the high-purity CO_2 generation capacity, and consequently, the potential carbon negativity of the process. The downdraft gasifier-based configuration offers superior electricity-to-SNG conversion efficiency of 54%, vs 40% for the DFB system, due to the SOEC in the former operating at relatively lower overpotentials.

Authors contributions: Elie Antar: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing – Original Draft, Writing - Review & Editing, Visualization, Funding acquisition. Etienne Robert: Conceptualization, Formal analysis, Resources, Writing - Review & Editing, Supervision, Funding acquisition.

Acknowledgements

The authors are grateful for the funders of this work: The Trottier Energy Institute (Trottier scholarship and project grant) and the Natural Sciences and Engineering Research Council of Canada (NSERC) [PGSD3 - 546588 - 2020].

CHAPTER 6 ARTICLE 3: EXPERIMENTAL CHARACTERIZATION OF DIFFUSIVE-THERMAL INSTABILITIES IN CO₂-DILUTED H₂-CH₄-CO UNSTRAINED DIFFUSION FLAMES

Published online in *Combustion and Flame* on 1 February 2023 [150]

By

Elie Antar, Julien Delavande, and Etienne Robert

Abstract

The combustion of multi-fuel mixtures is experimentally studied for the first time in unstrained diffusion flames, where the parasitic hydrodynamic effects present in common research burners are negligible. A broad range of H₂-CO-CH₄ fuels highly diluted in CO₂ is investigated to provide an understanding of the intrinsic diffusive-thermal instabilities (DTIs) that onset in low calorific biomass-derived syngas. For each fuel blend, the burning intensity or the Damköhler number (D_a) is gradually reduced, going through the marginal stability state where DTIs first appear, down to the lean extinction limit. Flame stability limits are provided. From the large difference between the Lewis numbers of the multiple fuel species (Le_i), the cells that onset due to H₂ are seen to interact and compete with the pulsations from CO and CH₄, leading to superimposed cellular-pulsating instabilities. These are thoroughly characterized by measuring the pulsations amplitude, frequency, cell size, number of cells, and fraction of the flame sheet actively burning. An effective fuel Lewis number ($Le_{F,eff}$) calculated from the fuel mixture composition is introduced and used along with the Damköhler number to map the DTIs observed. At lower $Le_{F,eff}$ and D_a , the cellular attributes of the superimposed instabilities dominate, while at larger Lewis numbers and the near marginal stability state, pulsations prevail.

6.1 Introduction

Combustion instabilities are critical phenomena that can damage combustion systems as well as contribute to detrimental effects such as local extinction, pressure fluctuations, and incomplete combustion [189]. Instabilities can arise from the flame interacting with the system/combustion chamber, ex: thermoacoustic instabilities [190], or they can be intrinsic and pertain to the combustion process itself, ex: diffusive-thermal instabilities (DTIs) [191]. The focus of this work is DTIs, which are for instance, relevant in low-emissions lean burners. DTIs can result in cellular [97] or pulsating flame fronts [23]. They are well known to occur

in both premixed and non-premixed configurations. In the latter, since diffusive-thermal effects mainly control the complex extinction and re-ignition processes, hydrodynamic effects can be eliminated from the stability analysis as they play a secondary role [89]. This significant simplification has stimulated the development of numerous stability models based on the unstrained one-dimensional diffusion flame theoretical construct [116], where fundamental insight into DTIs in single-fuel mixtures has been gained, as discussed below. We experimentally replicate this idealized configuration here to investigate DTIs in multi-fuel mixtures.

As shown in figure 2.9 the combustion chamber of the idealized one-dimensional chambered diffusion flame is a straight duct that is supplied at the bottom with fuel at a constant velocity via a semi-permeable membrane, and is exposed to constant conditions at the top. These are assumed to be maintained by a sufficiently fast stream flowing across the top boundary, uniformly removing the combustion products and supplying the counter-diffusing oxidizer. An analytical solution for the steady case can be readily derived since only one coordinate is required to describe the structure of the planar flames. This has been previously discussed in detail elsewhere [192].

The steady solutions constitute the basic state of stability models that introduce perturbations in planar flames and monitor their response over time [119, 121, 122]. These models predict stability when operating far from extinction, and the possibility of DTIs depending on different physical parameters when the lean extinction limit is approached. The theoretical work by Metzener and Matalon [127] is one of the most exhaustive studies to date, where a broad range of parameters was investigated for single-fuel mixtures, such as distinct non-unity Lewis numbers for the fuel (Le_F) along with the oxidizer (Le_o), mixture strength, and flow conditions. It was shown that when DTIs develop in diffusion flames, the reaction sheet exhibits excess or deficiency in available enthalpy ($h_f \neq 0$). This is driven by differential and preferential diffusion of mass or heat (non-unity and unequal Lewis numbers) occurring at Damköhler numbers (D_a) smaller than that of the marginal stability state (D_a^*). The Damköhler number is the ratio of the characteristic diffusion time over chemical reaction time. At $D_a < D_a^*$, cells generally form at Lewis numbers sufficiently below unity, and pulsations onset at high Lewis numbers.

An experimental realization of essentially unstrained one-dimensional diffusion flames was introduced by Robert and Monkewitz [130]. The same burner is used in the present work, in which hydrodynamic effects are avoided by evenly supplying the counter-diffusing reactant and removing the combustion products along the same axis, as discussed in detail in section 6.2.1. Flow field measurements [130] revealed that the stable flames generated by this

burner are subject to minimal residual stretch on the order of 0.05s^{-1} , and that their temperature along with species concentration profiles are in close agreement with the idealized analytical solution. The maximum temperature agrees within 50°C with the adiabatic flame temperature (T_a), demonstrating minimal heat loss effects, especially when operating near the extinction limit where DTIs are observed. Consequently, this burner has been used [131] to validate the DTIs scaling laws predicted by stability theories in single-fuel flames for the first time uncoupled from hydrodynamic effects. The important role played by the Lewis numbers in controlling the instability type was confirmed, as $\text{H}_2\text{-CO}_2$ flames with $Le_{\text{H}_2} = 0.25$ produced cellular flames, while $\text{CH}_4\text{-CO}_2$ mixtures with $Le_{\text{CH}_4} = 0.82$ yielded planar intensity pulsations. Nonetheless, the nature of DTIs formed in multi-fuel mixtures of these distinct combustible gases remains unknown.

The case of $\text{H}_2\text{-CH}_4\text{-CO}$ fuel mixtures diluted in CO_2 is treated in this paper. These mixtures are representative of dry biomass-derived syngas [12], where the combined presence of H_2 , with high diffusivity, and CO/CH_4 with much lower mobility implies that the instability patterns and scaling laws are difficult to predict. The importance of efficiently burning these highly-diluted mixtures on the overall energy balance of biorefineries is significant, particularly for small-scale decentralized implementations [148], well suited to the distributed nature of biomass resources. Previous studies on the stability of syngas flames are largely based on premixed configurations, such as spherically expanding flames [136, 137], flat flame McKenna burners [132, 133], and Bunsen flames [134, 135]. Aspects such as flammability limits, flame structure, and flame speed have been treated. However, the instabilities observed in the burners used were significantly driven by hydrodynamic effects, and were mainly cellular with no reference to any simultaneous flame front oscillations that may onset from CH_4 or CO species.

The goal of this paper is to experimentally investigate the stability of unstrained syngas diffusion flames, where fundamental insight into intrinsic diffusive-thermal phenomena can be obtained in conditions with negligible hydrodynamic and buoyancy disturbances. Starting from the Burke–Schumann limit, where the Damköhler number is very large, extinction is approached for each fuel mixture by decreasing D_a to the marginal stability state, until DTIs are observed, and then to extinction. The parameter space of mixture composition is mapped, with the type of DTIs reported along with their characteristics, such as cell size, pulsating amplitude, and frequency. A generalized DTIs map for syngas mixtures is derived at the end, in terms of a fuel mixture effective Lewis number and the Damköhler number.

6.2 Methodology

6.2.1 Experimental facility

Figure 6.1 shows the experimental configuration of the one-dimensional unstrained diffusion flame burner [193] used in this study. The cross section of the combustion chamber is 77.5×77.5 mm with a geometric length of $L_{geom} = 40$ mm. For a uniform reactants supply, the burner features two arrays of 31×31 hypodermic needles with OD: 1.0 mm and ID: 0.8 mm, placed on a 2.5 mm Cartesian grid at both ends of the combustion chamber. To ensure that temperature, velocity, and species gradients are sufficiently reduced and flame flatness is maximized, a 1 mm thick quartz cylinder with a 45 mm outer diameter is wedged between both needles array in the combustion chamber, as shown in inset c) of figure 6.1, with the measurements performed in the inner flame.

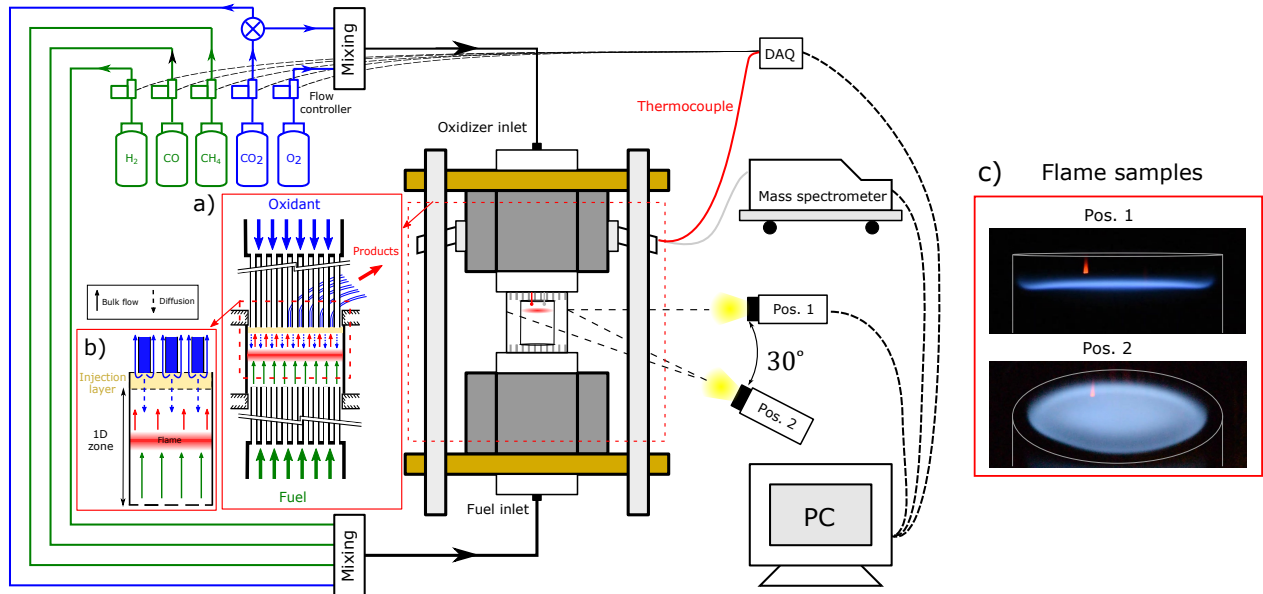


Figure 6.1 Schematic representation of the experimental facility used to create one-dimensional unstrained diffusion flames. Cross-sectional views of the burner showing a) the injection and exhaust needles, and b) the injection layer and the dimensional combustion zone. c) Flame images captured from positions 1 and 2.

The desired H₂, CH₄, CO, and CO₂ fuel mixture composition is introduced into the burner through the bottom needle array using Hastings model HFC-202 flow controllers. The bulk flow rate is kept fixed at 7 SLPM, resulting in an upward fuel velocity of $U = 19.42$ mm/s at the bottom of the burner, where gas is approximately at standard conditions of temperature and pressure. To denote the fuel mixtures, the relative molar fraction of H₂ to CO ($X_{H_2,CO}$), the relative amount of CH₄ to the two other combustible species (X_{CH_4}), and the

total fuel concentration (X_F) are used. The oxidizer stream, comprised of 100% O_2 , is supplied uniformly through the top needles array at flow rates between 3.5 and 10 SLPM, and reaches the reaction zone only through one-dimensional counter-diffusion against the flow of combustion products, as shown schematically in figure 6.1 b). The products are evacuated through another array of 32×32 curved stainless steel tubes (OD:1.4 mm and ID:1.2 mm) that are interlaced in the oxidizer injection array (figure 6.1 a), and the outlet of which is exposed to atmospheric pressure, which is marginally lower than the pressure inside the combustion chamber. Heaters and thermocouples are fitted within the two reactants injection and exhaust plenums to control the temperature of the combustion zone boundaries and avoid condensation within the exhaust stream.

The nature of the oxidant supply in the burner implies the existence of a thin layer just below the top needles, as shown in inset b) of figure 6.1. Here, PIV measurements [130] have shown that the flow is locally three-dimensional and that a portion of the supplied oxidizing species is directly evacuated upwards with the combustion products. Below this so-called injection layer, which has a thickness (Δ) that was conservatively measured to be below 3.0 mm using laser Doppler anemometry (LDA) [193], species concentration becomes highly uniform across the combustion chamber and their transport becomes one-dimensional, mimicking the idealized chambered diffusion flame configuration, with lateral variations in mixture strength below 10% across the flame width, as confirmed by mass spectrometer measurements [130, 193]. Therefore, the effective length of the one-dimensional unstrained combustion zone is $L = L_{geom} - \Delta = 40 - 3 = 37$ mm.

6.2.2 Diagnostics

Due to the aforementioned injection layer, the species concentrations at the top of the one-dimensional combustion zone cannot be directly determined from the mixture properties of the injected oxidant stream. A thoroughly calibrated mass spectrometer [194] is used, where gas samples are collected 3.0 mm below the injection needles, and analyzed in real-time to obtain the concentration of the major species O_2 , CO_2 , and H_2O , with a relative accuracy of 5%. These measurements are used to evaluate the mixture strength (ϕ), which is defined as the ratio of the fuel to oxygen mass fractions at the boundaries of the one-dimensional combustion zone, normalized by their stoichiometric proportions [195].

The thermophysical properties of the reactants and flames produced are evaluated by applying the experimentally measured boundary conditions in a one-dimensional chambered diffusion flame model implemented in Matlab using the Cantera software package [196]. The Lewis numbers are evaluated at the flame location using the multicomponent transport

properties model described in Kee et al. [197]. Excellent agreement between flame structures obtained using this numerical approach and experiments on stable planar diffusion flames has been previously reported [130]. In addition, agreement in terms of flame position can be seen from Figure 3, which presents the simulated syngas flame structure along with the spatial variation of the sampled light intensity from the experiments. Distance is made non-dimensional using the length of the one-dimensional combustion region, $L = 37$ mm. The fuel species mass fractions (Y_F) are normalized with their concentration at the fuel inlet ($Y_{F,0}$), and finally the oxygen mass fraction (Y_O) is scaled with its concentration at the top of the domain and mixture strength ($Y_{O,L}\phi$).

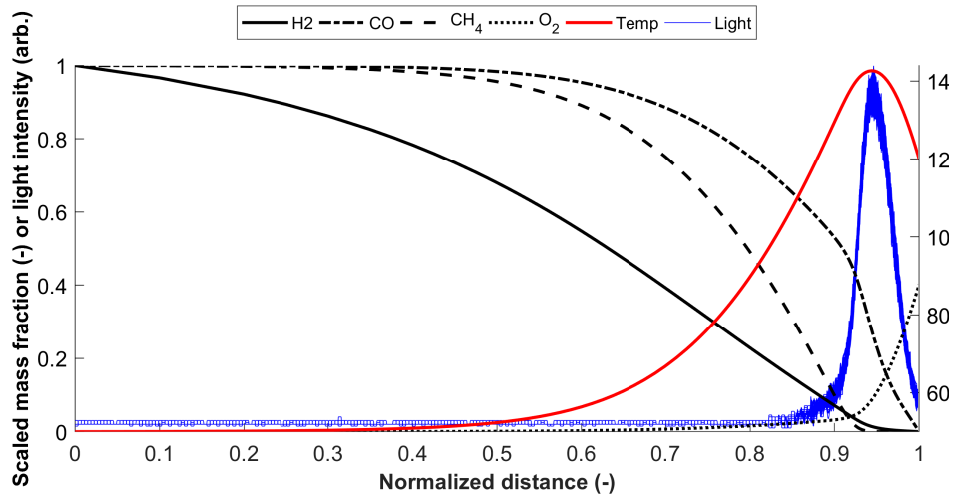


Figure 6.2 Flame structure from the idealized one-dimensional diffusion flame model, and experimentally measured light intensity signal for a mixture with $X_{H_2,CO} = 75\%$, $X_{CH_4} = 15\%$, $X_F = 30\%$, and $\phi = 2.5$.

The flame location in the burner is determined by analysing images acquired using a digital still camera (Nikon D750) placed perpendicularly to the burner axis, shown as position 1 in figure 6.1. To minimize imprecisions from acquired noise, a sampling window that spans 50% of the flat flame width is taken, in which the average location of the maximum light intensity from each pixel column is determined. This optically measured flame position with a spatial resolution of 0.047 mm/pixel or 0.12% discretization uncertainty was previously verified [130] to coincide with the maximum temperature, as also shown in Figure 3, and minimum reactants concentration. The maximum emitted light intensity is also used as a proxy for the flame chemical reaction rate. Its temporal variation is sampled at a rate of 30 Hz, and the Fourier transform is computed to determine the frequency and amplitude of the pulsations.

When spatial inhomogeneity in excessively cellular flames prevents the reliable determination of the emitted light intensity, the variation in flame position (x_f) is used to characterize the intensity of pulsations. As an example, comparisons between the flame position and maximum light intensity signal obtained as the pulsating instability develops are shown in figure 6.3, for two planar flames with CH_4 -CO fuel fractions of 75-25% and 45-55%. It can be seen that the frequencies of both the position and light intensity signals are equal, and that their amplitude of oscillations is proportional to each other. The slight phase delay that is observed as the flame position trails the intensity variation, confirms that the pulsating DTI is intrinsically a variation in the reaction rate, with the flame position then adapting to the change in energy release. These observations are particularly evident with CH_4 -CO 45-55%, as the pulsations intensity grows, but they were reflected in all measurements taken.

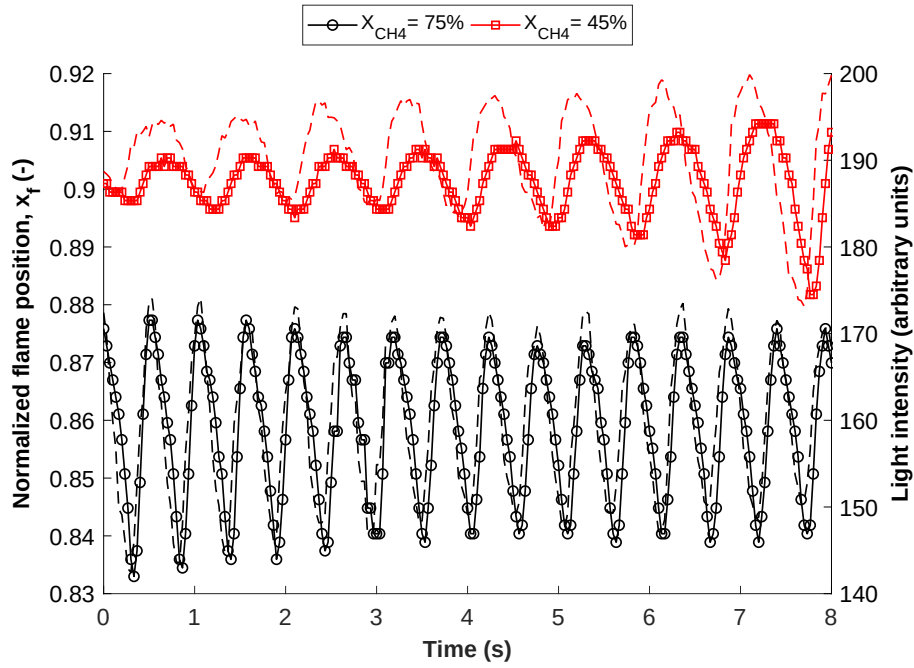


Figure 6.3 Temporal variation of flame position (—), and maximum light intensity emitted (---) for two pulsating CH_4 -CO flames with $X_{\text{CH}_4} = 75\%$, $X_F = 17.5\%$, $\phi = 0.90$, and $X_{\text{CH}_4} = 45\%$, $X_F = 16.5\%$, $\phi = 0.84$.

To capture cellular instabilities, another camera is used to view the flame from below, with a 30° upward angle (position 2, figure 6.1). An image analysis code implemented in Matlab is used to compute the fraction of the cylinder cross-section where the flame burns, as well as the number and distance between the cells that form on the periphery of the combustion zone. For the latter, the light intensity signal along a circle that is centered in the middle

of the flame and that passes through each of the outermost cells is extracted, as shown in figure 6.4. The mean arc length between each peak is computed and represents the reported cell size in this study.

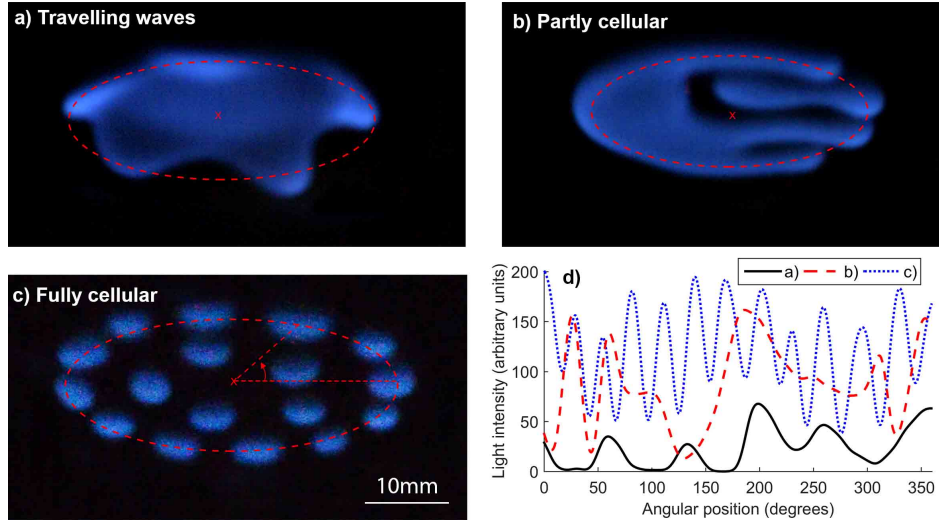


Figure 6.4 a) Flame with travelling waves at $X_{H_2,CO} = 75\%$, $X_F = 22\%$, and $\phi = 0.49$, b) partly cellular flame at $X_{H_2,CO} = 75\%$, $X_F = 19\%$, $\phi = 0.63$, and c) fully cellular flame at $X_{H_2,CO} = 100\%$, $X_F = 17\%$, and $\phi = 0.75$, with X_{CH_4} always 0%. d) Gaussian-filtered light intensity along circles that pass through the centers of the outermost cells for each of the three cellular flames shown, used to calculate cell size.

6.2.3 Parameters of interest

Theoretically, the onset and characteristics of DTIs in one-dimensional unstrained diffusion flames are dependent on the following five parameters [127]: ΔT , D_a , ϕ , Le_F and Le_o . In this section, the methods used to control these parameters in our experimental configuration are discussed. The first parameter, ΔT , is the temperature difference between the top (T_L) and bottom boundaries of the one-dimensional combustion zone. Its influence on the general behaviour of DTIs is relatively minor, and it is kept approximately constant in our burner at $\Delta T = 700^\circ\text{C}$ using the plenum heaters.

The second parameter, D_a , can be varied through the flame temperature, which we adjust using the fuel CO_2 dilution. The computation of D_a from the experiments is discussed latter in section 6.3.1. It should be noted that in theoretical studies, D_a is controlled through the residence time by changing the bulk velocity, while keeping other parameters constant. However, in the experimental configuration used, the range of achievable bulk velocities does not cause significant changes in D_a , and the strong coupling between the bulk velocity and

the flow in the injection layer, which alters the top boundary conditions, further complicates this approach.

The third parameter, the mixture strength, is measured using the mass spectrometer described in the previous section. For a given fuel concentration, the mixture strength can be varied by adjusting the flow rate or O_2 concentration of the supplied oxidizer stream into the burner. However, the operational ϕ range over which the one-dimensional nature of the flame is preserved can be limited by the appearance of convective instabilities. As ϕ largely controls the flame position, leaner flames position themselves lower in the burner. Consequently, the hot gas layer associated with the flame heat release is lowered in the relatively cooler surrounding fluid, and the temperature stratification becomes unstable leading to Rayleigh–Bernard convection cells [198]. These undesirable buoyancy-driven effects are easy to detect and avoid, since they lead to very large-amplitude cells or ridges that always grow unsustainably with time, and cause the flame to collapse on the bottom needles array of the burner. Consequently, the onset of Rayleigh–Bernard convection cells are averted by studying only sufficiently high flames with $x_f \geq 0.8$.

The forth parameter affecting DTIs is the fuel Lewis number Le_F , which is species-specific for the commonly considered case of single-fuel mixtures. However, in the current study involving multi-fuel mixtures, the simultaneous presence of more than one combustible species naturally motivates the adoption of a fuel mixture effective Lewis number $Le_{F,eff}$:

$$Le_{F,eff} = X_{H_2}Le_{H_2} + X_{CO}Le_{CO} + X_{CH_4}Le_{CH_4} \quad (6.1)$$

with X_i being the molar fraction of species i relative to the other the combustible species in the supplied fuel stream. The Lewis numbers of each reactant in Eq. 7.1 are computed using the one-dimensional chambered diffusion flame model supplied with the experimentally-measured boundary conditions as discussed in section 6.2.2. These Lewis numbers are largely determined by the nature of the most abundant species, which is always CO_2 for the low caloric value syngas mixtures considered here [148]. Therefore, these and the Lewis number of the oxidizer (fifth parameter affecting DTIs) do not vary significantly upon changing the fuel composition. As shown in section 6.3.1, Le_{H_2} only varies from 0.23-0.28, Le_{CH_4} from 0.81-0.96, and Le_{CO} from 0.89-1.07, and finally Le_o from 0.88-1.06 with an average value of 0.97 for all the flame discussed in this paper. The fuel composition is nevertheless reflected in $Le_{F,eff}$, through the X_i terms (Eq. 7.1), whereby a broad fuel composition range such that $Le_{H_2} \leq Le_{F,eff} < Le_{CO}$ is investigated.

For every $Le_{F,eff}$, we transition from a strongly burning stable flame operating near the

Burke-Schumann limit ($D_a \rightarrow \infty$) towards the marginal stability state where the first instabilities are observed. This is accomplished by reducing the fuel concentration at the lower ϕ limit of the burner such that no buoyancy-driven instabilities arise. To maximize the mapped instabilities beyond the marginal stability state, ϕ is gradually varied by changing the oxidizer flow rate within its operation range for every decrement in X_f , until dilution-induced extinction is attained. Only weakly-burning lean flames are investigated, which are relevant to low-emissions syngas combustion. Weakly-burning rich flames are not considered since such conditions cannot be achieved in the experimental configuration used, as the required large ϕ values would push the flame outside the one-dimensional combustion domain and into the injection layer ($x_f > 1$).

6.3 Results

6.3.1 H₂-CO₂ mixtures

The instability type caused by each of the three fuel species (H₂/CO/CH₄) is first individually studied by considering simple fuel mixtures. Starting with H₂-CO₂ mixtures, with $Le_{F,eff} = Le_{H_2}$ being approximately 0.25, the flame stability limits are presented in figure 6.5. DTIs are observed within the shaded zone, while the hatched region represents conditions that could not be tested in our burner as the instabilities are not sustainable, or since buoyancy-driven instabilities appear at low mixture strengths. The latter can be readily identified from the dramatically large and three-dimensional convective cells, which are an order of magnitude larger than the stationary cells from DTIs. This behaviour of buoyancy-driven instabilities was confirmed using a broad range of fuel mixtures, including single-fuel CH₄, where unlike cells from DTIs, buoyancy-driven convection cells of invariable size was always observed, when the flame was sufficiently low. A comparison between Rayleigh–Bernard convection cells, and diffusive-thermal cells is shown in appendix C.1 and C.2. In the former, the inner quartz cylinder is removed from the combustion chamber to better illustrate the instability size.

Travelling waves are the first DTI pattern observed at $X_F = 23.5\%$, as represented by pentagram symbols with filled circular centers in figure 6.5. They consist of five large amplitude waves/cells rotating around the flame center at frequencies between 3.45 and 3.6 revolutions per second (figure 6.4 a). Rotating cells were previously reported on several occasions in H₂ diffusion flames, such as the experimental work by: Lo Jacono et al. [96] using an axisymmetric jet burner, and Hu et al. [101] along with Shopoff et al. [199] using opposed-flow tubular burners. As can be seen from figure 6.5, travelling waves are the only instabilities

observed down to $X_F = 21.5\%$. Beyond this point, rotation stops, holes in the center of the flame start to appear for the first time, and the flame turns partly cellular (figure 6.4 b) as indicated by the circular symbols with open stars in figure 6.5. At $X_F = 18\%$ full cellularity (figure 6.4 c) is finally attained, whereby 17 stationary and completely detached cells form.

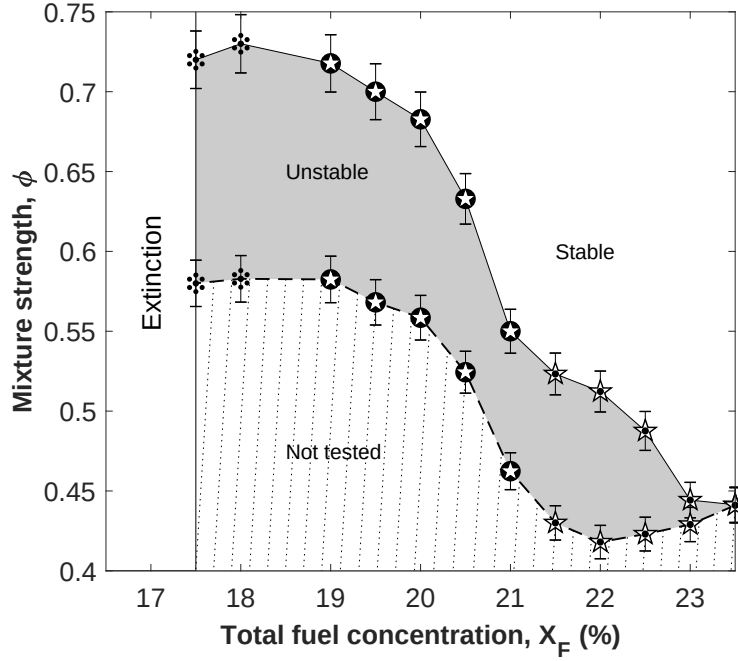


Figure 6.5 Flame stability limits in terms of the fuel concentration and mixture strength for H_2 - CO_2 mixtures. The instability type is represented by symbols. (★): Travelling waves, (⊙): partly cellular, and (⊛): fully cellular. The error bars indicate the uncertainty from the mass spectrometer measurements.

The increase in cellularity at lower X_F , or in other words, lower D_a , is consistent with previous theoretical predictions on the stability of unstrained diffusion flames [123], as shown in the stability map of figure 6.6. At higher D_a , H_2 flames are located outside the stationary cells zone, whereby mixed instability modes such as travelling waves or oscillatory cells are predicted [127]. By reducing D_a , the Lewis number range that leads to stationary cells increases, and eventually includes the H_2 flames observed in our burner. To further illustrate this, the Damköhler numbers of the unstable flames are estimated as per the following definition [123]:

$$D_a = (\lambda / \rho c_p U^2) (R^\circ T_a / E)^3 (\nu_x c_p \bar{W} / q R^\circ W_f) \beta Y_{f,o} p_o \exp(-E / RT_a) \quad (6.2)$$

Owing to the lack of suitable empirical data, the values of the activation energy E and the

Arrhenius pre-exponential factor β are assumed constant for a given fuel. They are selected such that Damköhler number at the marginal stability state for a given $Le_{F,eff}$ is equal to unity [131]. This means that the D_a calculated in this paper is a relative one, for a given fuel composition. This yields an approximation of the top branch of the typical S-shaped response curve of diffusion flames shown in figure 6.7, where the observed transition from travelling waves to full cellularity at lower D_a is highlighted for unstable H_2 flames.

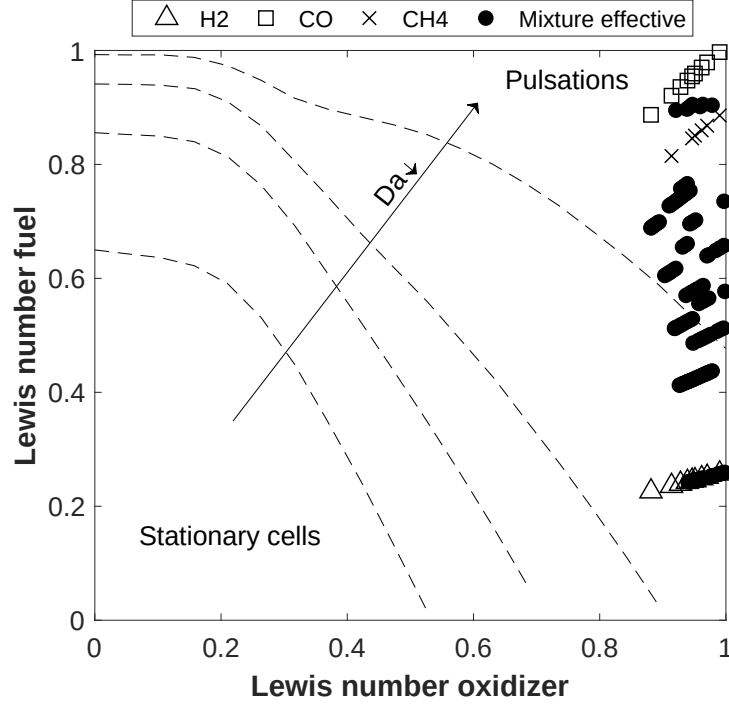


Figure 6.6 Stability map showing the Lewis numbers of the three fuel species and oxygen, as well as the effective Lewis number of the fuel mixture for the different flames studied in this paper. The instability zones are extracted from the theoretical findings of Cheatham and Matalon at $\phi = 1/3$ [123].

Linear stability analysis [123] has shown that the cell size (λ_c) for unstable single-fuel flames should scale as:

$$\lambda_c \sim (2\pi/\sigma^*)l_D \quad (6.3)$$

with σ^* being the non-dimensional preferred wavenumber at the instability onset and $l_D = D_{th}/U$ the diffusion length. σ^* is a function of U , ϕ , D_a , Le_o , and Le_F , and it can be determined numerically using the dispersion relation from stability analysis [127]. However, for the observed cellular H_2 flames, the value of σ^* seems to not vary significantly, as the

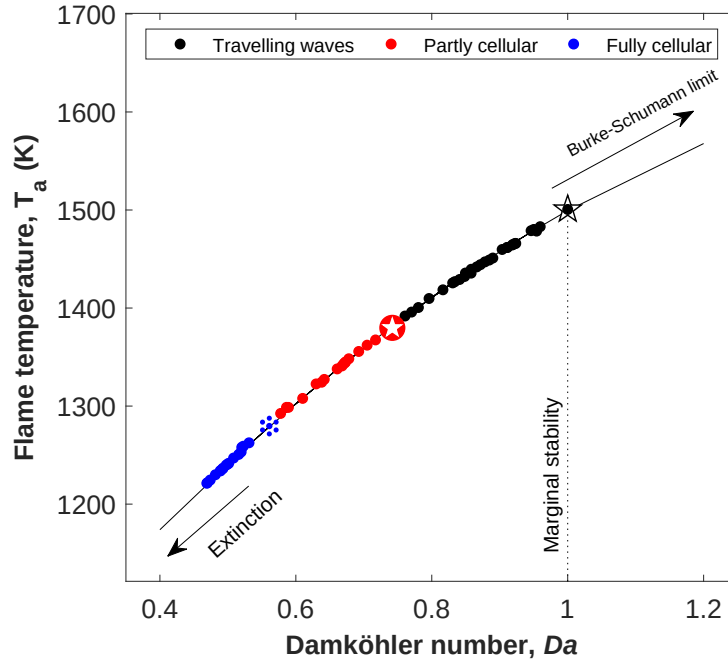


Figure 6.7 Top branch of the S-shaped response curve for the $\text{H}_2\text{-CO}_2$ flames. The shapes of unstable flames are indicated by symbols similar to those of figure 6.5.

measured λ_c values from the experiments scale almost linearly with l_D as shown in figure 6.8. This was also reported in an earlier study using H_2 flames diluted with CO_2 in addition to helium [131].

6.3.2 $\text{CH}_4\text{-CO-CO}_2$ mixtures

Considering first $\text{CH}_4\text{-CO}_2$ mixtures without CO , and with $Le_{F,eff} = Le_{\text{CH}_4}$ approximately equal to 0.87, only planar intensity pulsations are observed in unstable flames. This is consistent with the theoretical instability map of figure 6.6 and other investigations using CH_4 as a fuel [131]. Given that the average Lewis number of CO is 0.98 (figure 6.6), one would expect a similar behavior for CO -rich fuel mixtures. This is confirmed over the broad range of $\text{CO-CH}_4\text{-CO}_2$ mixtures tested, as listed in table 6.1, where the pulsation frequency and amplitude are reported. It should be noted that single-fuel CO-CO_2 mixtures are not investigated since these flames are not sustainable without the small addition of another hydrogen-containing species [141]. Linear stability analysis [124] shows that the pulsation frequency should scale as $f \sim (U^2/2\pi D_{th})\omega_I^*$, where ω_I^* is the oscillation frequency of the most unstable disturbance at marginal stability. An attempt to scale f with $U^2/2\pi D_{th}$ yielded scattered data for the flames presented, meaning that the value of ω_I^* significantly

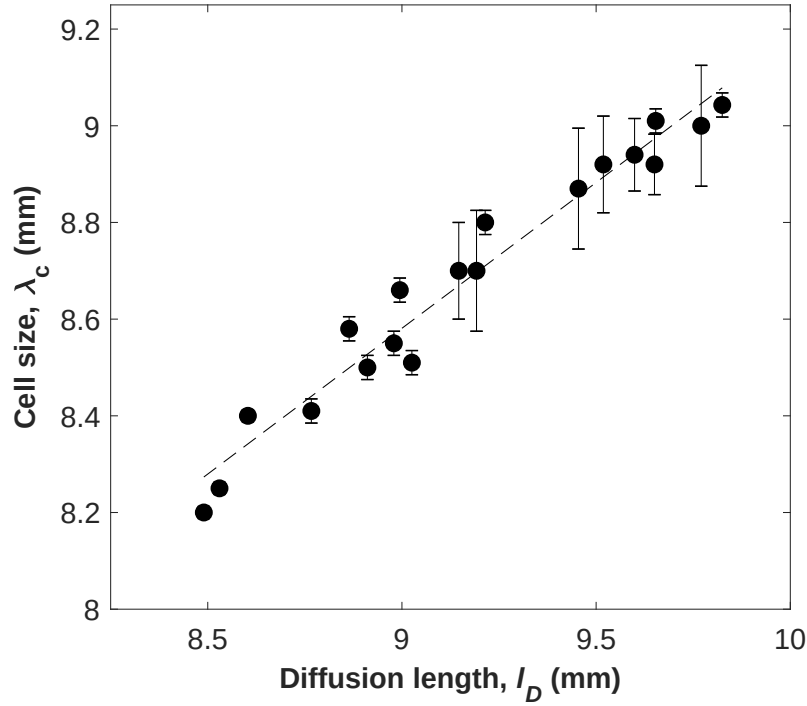


Figure 6.8 Measured cell size as a function of diffusion length for fully cellular $\text{H}_2\text{-CO}_2$ flames

varies. Little has been discussed in theoretical work on the dependence of ω_f^* on the flame parameters such as D_a , ϕ , Le_F , and Le_o . However, as also reported in [131], we observe that for the $\text{CH}_4\text{-CO-CO}_2$ flames, the non-dimensional frequency scales linearly with D_a as shown in figure 6.9. Unlike cellular instabilities, pulsations are extremely sensitive to perturbations in operating conditions, whereby their amplitude unsustainably increases and rapidly extinguishes the flame upon a very small decrease in fuel concentration or minute reduction in mixture strength.

6.3.3 $\text{H}_2\text{-CO-CO}_2$ mixtures

The addition of 25% pulsation-prone CO to H_2 , which typically yields cellular instabilities, is considered. These mixtures yield $Le_{F,eff}$ that is on average approximately 0.42, with their flame stability limits shown in figure 6.10. DTIs form within the shaded zone, and extinction is attained below and to the left-hand side of it. Only the instability type is shown, with its characteristics fully tabulated in appendix C.1. In the vicinity of the marginal stability state ($D_a = 1$ by assumption), when $X_F = 23.5\%$, and down to $X_F = 22.5\%$, only travelling waves are observed in $X_{\text{H}_2,\text{CO}} = 75\%$ flames. The number of waves is always four, exhibiting

Table 6.1 Parameters of the observed pulsating CH₄-CO-CO₂ flames

Fuel	X_F (%)	ϕ	Le_o	$Le_{F,eff}$	Amp. (%)	Freq. (Hz)
100-0% CH₄-CO	13	1.03	1.02	0.91	41	1.26
	12	1.09	1.01	0.91	32	1.18
75-25% CH₄-CO	16	0.94	1.00	0.93	44	1.40
	15.5	0.94	1.00	0.92	20	1.39
	15	0.95	0.99	0.92	28	1.19
60-40% CH₄-CO	16	0.88	0.97	0.91	38	1.19
	15	0.89	0.96	0.91	37	1.05
45-55% CH₄-CO	17	0.81	0.95	0.91	33	1.05
	16.5	0.84	0.94	0.90	42	1.03
	16	0.88	0.94	0.90	34	0.95
	19	0.77	0.92	0.90	29	0.99
30-70% CH₄-CO	18.5	0.83	0.92	0.92	30	0.90
	18	0.83	0.92	0.92	27	0.90

only rotational motion at frequencies varying between 3.1 and 3.4 Hz. Based on our earlier discussion with H₂-CO₂ flames, this is clearly caused by the H₂ in the mixture becoming unstable.

When D_a is reduced to 0.83 at $X_F = 22\%$, the consequences of adding CO to the fuel become visible as additional instabilities appear. Here, when the flame is perturbed, by for example slightly decreasing ϕ from 0.50 to 0.46 (0.25 SLPM increase in the oxidizer stream), flames with travelling waves start experiencing spatially-homogenous perturbations in their chemical reaction rate that are superimposed at 0.95 Hz, a frequency similar to that of the CO-rich fuels discussed in section 6.3.2. These grow after a few seconds into intense pulsations with a steady amplitude of approximately 57%, fragmenting and “prematurely” turning the flame fully cellular, as shown in figure 6.11 and supplemental video #1¹.

After having taken over the travelling wave instabilities, the intensity pulsations of the now cellular flame result in axial oscillations spanning 28% of the combustion domain length. Such strong pulsations could never be sustained in any of the H₂-free flames, which suggest that CO may be extinct at the lowest intensity point of the instability cycle (figure 6.11, position b). The H₂ appears to maintain the combustion process here, as the sizes of the four cells at this position scale linearly with the flame diffusion length, just as for the cells forming in single-fuel H₂ flames discussed in section 6.3.1. This is shown in figure 6.12, where the cell sizes measured at the trough of the pulsation wave are presented for various multi-fuel

¹The supplemental video can be accessed via the online version of the article: <https://www.sciencedirect.com/science/article/pii/S0010218023000214?via%3Dihub>

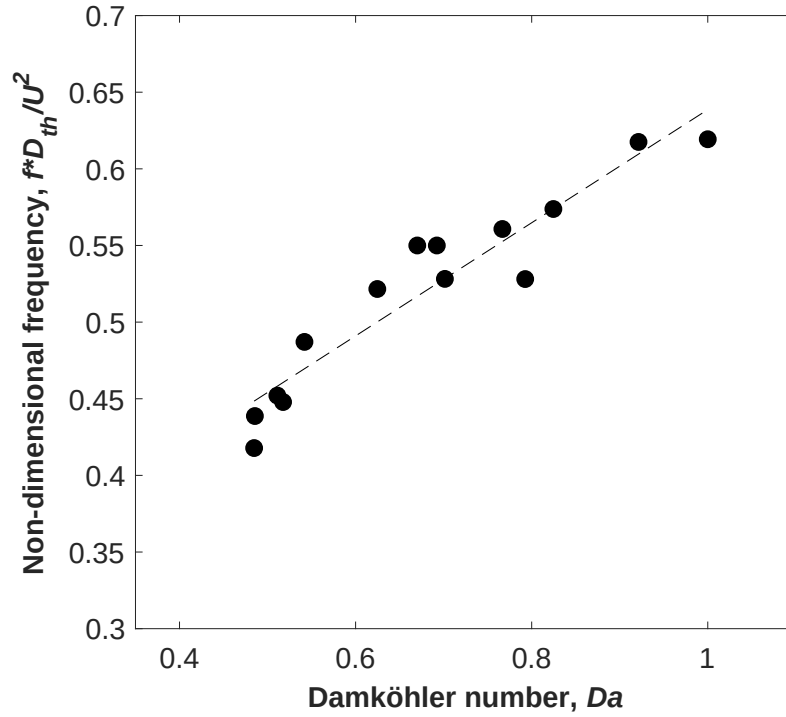


Figure 6.9 Non-dimensional pulsations frequency as a function of Damköhler number for unstable CH_4 -CO mixtures.

flames. When the burning intensity of CO begins to increase, the cell sizes grow in-phase (figure 6.11, position c-e) as the highest intensity point of the cycle is approached. Unlike for CH_4 -CO fuels, the non-dimensional pulsation frequencies of H_2 -containing flames do not scale linearly with the Damköhler number, whereby it is always lower than the linear scaling trend line. This is because the presence of H_2 in the fuel mixture temporarily dampens CO/ CH_4 pulsations after the highest intensity point of the cycle, where the flame lingers around the mean position before the beginning of the next pulsation wave. This can be seen between positions e) and f) in the bottom plot of figure 6.11, where the temporal variation in flame position is shown.

The pulsations intensity required to turn flames with travelling wave instabilities fully cellular decreases with decreasing Da . This is because cellularity is inherently enhanced under these conditions, as was demonstrated earlier using H_2 - CO_2 flames. The variation in the amplitude and frequency of different pulsation-induced cellular flames as a function of the Damköhler number is shown in the unshaded region of figure 6.13. For the 75-25% H_2 -CO case, the pulsations amplitude drops down to 8% at $Da = 0.69$. The periodic variation in the burning area exhibits a similar decrease, varying between 10-93% at $Da = 0.83$, and only between

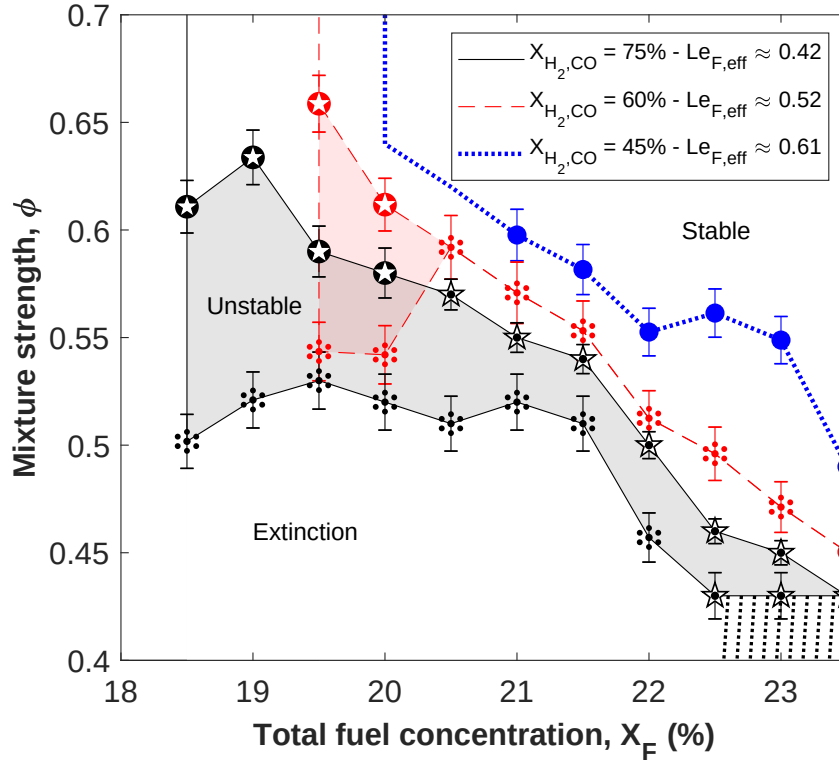


Figure 6.10 Flame stability limits for different $\text{H}_2\text{-CO}$ binary fuels with no CH_4 . The instability type is represented by symbols, and its characteristics are tabulated in appendix C.1. (•): Planar intensity pulsations, (★): travelling waves, (⊗): partly cellular, and (⊕): fully cellular.

43-78% at $D_a = 0.69$ (table C.1). The cell spacing at the lowest intensity point of the cycle is also lowered from 20.1 mm to 14.9 mm as the number of cells increases.

Beyond a sufficiently small Damköhler number, intensity pulsations are no longer required to render flames with high fuel H_2 content fully cellular. This is because H_2 -induced instabilities start manifesting themselves by the formation of stationary cells instead of travelling waves close to the lean extinction limit, as was also demonstrated earlier with $\text{H}_2\text{-CO}_2$ mixtures, and as observed with 75-25% $\text{H}_2\text{-CO}$ flames in figure 6.10 at $X_F = 18.5\%$ and $\phi = 0.61$. Now however, as CO perturbations onset, when ϕ is reduced to 0.5 in the latter case, the superimposed cellular-pulsation instabilities that develop have different characteristics compared to the pulsation-induced cellular flames that are formed at higher D_a . This is reflected by the abrupt trend change in the shaded region of figure 6.13. When D_a is sufficiently low, the chemical reaction rate perturbations triggered by CO are manifested locally within each detached cell, instead of uniformly across a connected flame sheet, resulting in pulsations

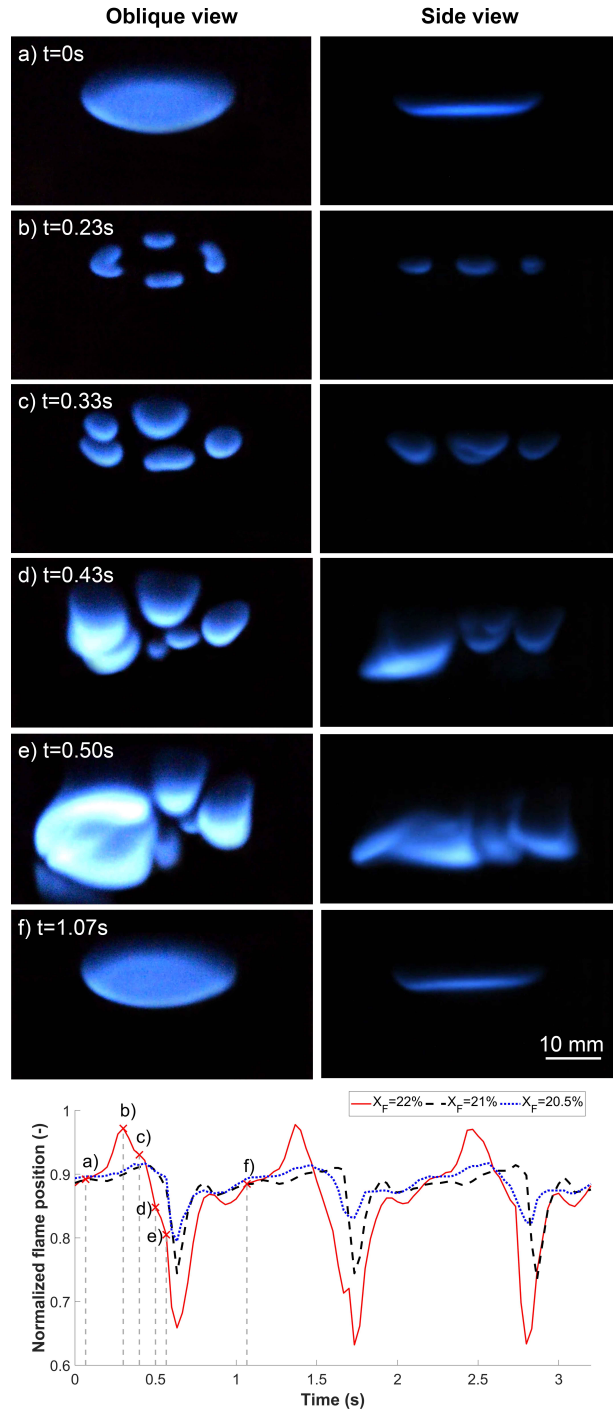


Figure 6.11 (a-f) Oblique and side views showing the instability cycle of a pulsation-induced cellular flame at $X_F = 22\%$, $\phi = 0.46$, $X_{H_2,CO} = 75\%$, and $X_{CH_4} = 0\%$ (Video #1). Below, plot of the time variation in position of three such flames with different total fuel concentrations.

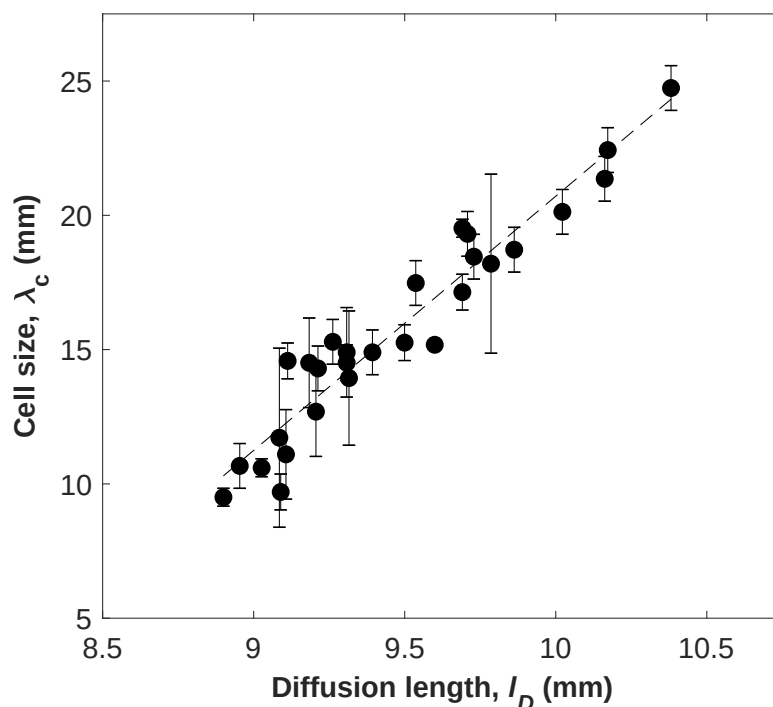


Figure 6.12 Cell size measured at the lowest intensity point of the pulsation cycle for the fully cellular multi-fuel flames. The error bars represent uncertainty from the image analysis technique used and from the simultaneous presence of intensity pulsations.

that are out-of-phase across a fragmented flame. The oscillations are now minimally dampened, with relatively fast frequencies exceeding 3 Hz, and with intensities that always grow unsustainably with time, leading to temporary extinction areas within the flame. The extinct cells are then replenished with ones undergoing earlier stages of the same pulsation cycle. This can be seen from supplemental video #2¹, where these pulsating cells are compared to the other mode with superimposed instabilities, pulsation-induced cells, which was discussed earlier in this section.

It is worth mentioning that the nature and mechanism of these superimposed DTIs in multi-fuel mixtures are different than the DTIs labelled as mixed in single-fuel flames. As discussed in section 6.3.1, the latter often refers to flames with cells rotating or periodically propagating along the flame sheet, and onset when the Lewis number of the only fuel species or oxidizer attains intermediate values. On the contrary, in mixtures such as syngas, the simultaneous presence of fuel species with distinctive Lewis numbers is what leads to super-

¹The supplemental video can be accessed via the online version of the article: <https://www.sciencedirect.com/science/article/pii/S0010218023000214?via%3Dihub>

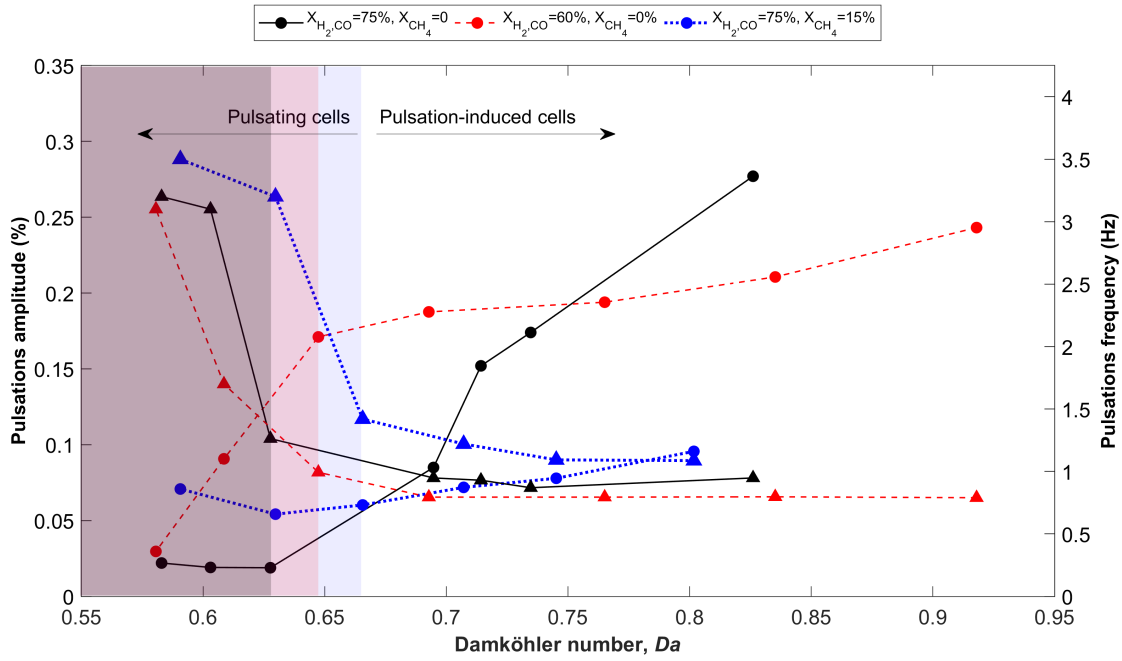


Figure 6.13 Variation in the amplitude (●) and frequency (▲) of the superimposed cellular-pulsations instabilities with Damköhler number. Pulsations amplitude is quantified in terms of the variation in flame position due to excessive cellularity.

imposed instabilities, or cellular flames that experience pulsations in their chemical reaction rates. Unstrained diffusion flames are a convenient choice to demonstrate and study these intricate diffusive-thermal phenomena, which would otherwise be masked or rendered unsustainable by hydrodynamic effects, especially when it comes to intensity pulsations. As a result, studies in the literature addressing the stability of various multi-fuel flames often focus on hydrodynamics-driven cellular instabilities [200–202].

Figure 6.14 tracks the intensities of individual cells, from the moment they are formed and until they are extinguished, at 75-25% H_2 -CO and different Damköhler numbers. It can be seen that the number of cycles that can be sustained by each pulsating cell before extinction decreases with decreasing Da . For $Da = 0.63$, each cell undergoes approximately three pulsation cycles before it extinguishes. However, as Da is lowered to 0.58, the number of pulses before local extinction approaches zero. Given that the actively burning area of the flame also drops, the cells generation rate filling these fastly-extinguishing zones, which is 3.2 Hz, becomes the limiting factor that determines the frequency of the superimposed instabilities near the lean extinction limit.

The carbon monoxide content in the H_2 -CO fuel mixture is now increased to $X_{H_2,CO} = 60\%$,

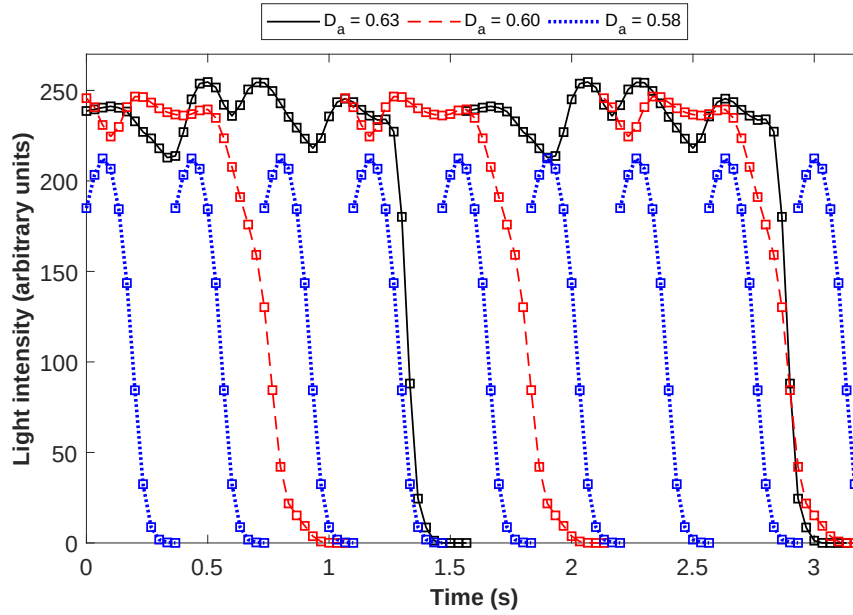


Figure 6.14 Light intensity emitted from pulsating cells at different Damköhler numbers in 75-25% H₂-CO mixtures. Each pulsation cycle represents a different cell before extinction.

yielding a fuel Lewis number of $Le_{F,eff} = 0.52$ on average. From the resulting stability limits shown in figure 6.10, it can be seen that this significantly reduces the operating range where sustainable DTIs form, which in fact shrinks into a line at $X_F \geq 20.5\%$. This is because CO becomes unstable before H₂ in this mixture, as sensitive planar intensity pulsations are observed at the marginal stability state instead of travelling waves. At lower Damköhler numbers, 1-Hz pulsation-induced cells form, since the inherent enhancement in cellularity of H₂ means that lower-amplitude perturbations, 24% in this case, are now required to render the flame fully cellular. Here again, the pulsations amplitudes keep decreasing with Da , reaching 17% at $Da = 0.65$ as shown in figure 6.13. Beyond this point, H₂ cells begin preceding CO pulsations, and the instability zone regains its broadness (figure 6.10). This represents the inherent cellularity tipping point discussed in the previous paragraph, where cellular flames exhibiting fast pulsations at approximately 3 Hz are formed.

As the CO content in the fuel exceeds that of H₂ at $X_{H_2,CO} = 45\%$ with $Le_{F,eff}$ being approximately 0.61, the whole flame stability zone shrinks to a line below and to the left of which the flame is extinct (figure 6.10). Cells are never observed in unstable flames, which exhibit only planar intensity pulsations, indicated by solid circles in figure 6.10. The pulsation frequencies vary between 0.8 and 1.0 Hz (table C.1). The amplitude of pulsations that can be sustained decreases as Da is lowered by decreasing the fuel concentration, going

from 53% at $X_F = 24\%$ to 7% at $X_F = 21\%$. Beyond this point, the pulsations that onset are never steady and their intensities rapidly grow, causing the flame to extinguish within a few seconds.

6.3.4 H₂-CO-CH₄-CO₂ mixtures

The addition of different amounts of CH₄ to $X_{H_2,CO} = 75\%$ mixtures is now considered, with the flame stability limits shown in figure 6.15. For the $X_{CH_4} = 15\%$ case, which yields $Le_{F,eff}$ around 0.50, CH₄/CO-induced instabilities onset before those caused by H₂, as planar intensity pulsations are observed close to the marginal stability state. At lower Damköhler numbers, pulsation-induced cells form, and their amplitudes drop from 10% at $D_a = 0.8$ to 6% at $D_a = 0.67$, below which the inherent cellularity tipping point is crossed as can be seen from figure 6.13.

When the CH₄ in the fuel is increased to $X_{CH_4} = 30\%$ ($Le_{F,eff} \approx 0.6$), cells never form at any D_a . At the marginal stability state, occurring when $X_F = 17\%$, planar intensity pulsations onset with an amplitude and frequency of 22% and 1.0 Hz, respectively. These persist when X_F is decreased to 16.5%, albeit with a lower amplitude of 16%. At even lower D_a , the pulsations that onset are always unsustainable, as the flame is forced during part of the pulsation cycle into the highly oxygenated injection layer in the burner where the flow is three-dimensional.

Comparing the addition of CH₄ to that of CO through figures 6.10 and 6.15, a clear resemblance is observed, highlighting the importance of the effective fuel Lewis number in predicting the type of instabilities formed. In both of these flame stability maps, when $Le_{F,eff}$ is approximately 0.5, the instability zone shrinks after the marginal stability state, as planar intensity pulsations onset followed by pulsation-induced cells. As the lean extinction limit is approached, the instability zone broadens as inherently cellular flames are formed. Similarly, when $Le_{F,eff}$ exceeds 0.6, only planar intensity pulsations are observed in unstable flames, irrespective of whether CO or CH₄ is added.

In fact, if CH₄ completely replaces CO in quantities such that the same $Le_{F,eff}$ is maintained, the same instability types and sequence are always observed. This was confirmed by the flame stability limits produced using a broad range of H₂-CH₄ mixtures. Consequently, a generalized qualitative DTI map is proposed in figure 6.16, in terms of the effective fuel mixture Lewis number and the flame Damköhler number. Using these two fundamental parameters, the various degrees of cellularity and intensity pulsations that can simultaneously form in lean dry syngas flames can be predicted. The map reveals that when $Le_{F,eff}$ is lower than 0.25, unstable flames never exhibit intensity pulsations. Nonetheless, these flames

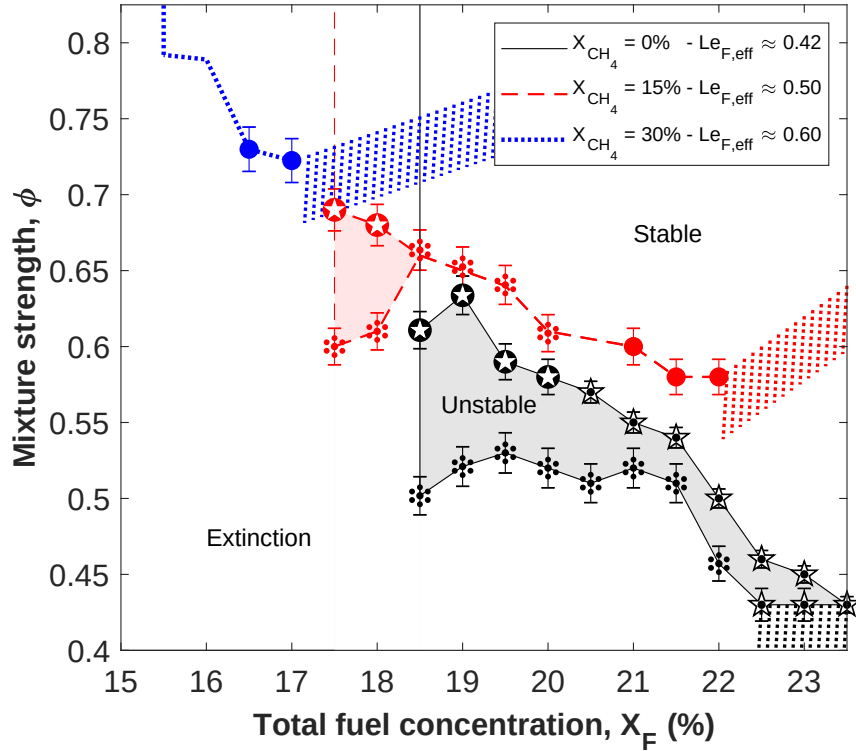


Figure 6.15 Effect of CH_4 addition on the flame stability limits at $X_{\text{H}_2,\text{CO}} = 75\%$. The symbols indicate the type of instability, with its characteristics provided in appendix C.1. (•): Planar intensity pulsations, (★): travelling waves, (⊛): partly cellular, and (⊛): fully cellular. Hatched regions represent conditions that are not tested.

can exhibit various degrees of cellularity going from travelling waves at marginal stability to stationary cells near the extinction limit. For $Le_{F,\text{eff}}$ around 0.4, pulsations can onset simultaneously with cells, and this can lead to pulsation-induced cells at high Da or pulsating cells near the extinction limit, as detailed in section 6.3.3. At $Le_{F,\text{eff}}$ of approximately 0.5, purely cellular flames no longer form, and unstable flames always exhibit pulsations in their chemical reaction rates. Finally, when $Le_{F,\text{eff}}$ exceeds 0.6, flame cellularity is diminished and only planar intensity pulsations onset.

Evidently, owing to the different combustion chemistry of each fuel species, the flammability limits of different fuel mixtures remain unique even if their $Le_{F,\text{eff}}$ is the same. To complete the discussion, the flammability limits for $X_{\text{H}_2,\text{CO}} = \{30\%, 45\%, 60\%, 75\%\}$ and $X_{\text{CH}_4} = \{0\%, 15\%, 30\%\}$ are presented in figure 6.17. Looking at the effect of the H_2/CO ratio, it can be seen that lower fuel concentrations and mixture strengths are required for instabilities to onset at higher H_2 content. Since these conditions result in lower burning in-

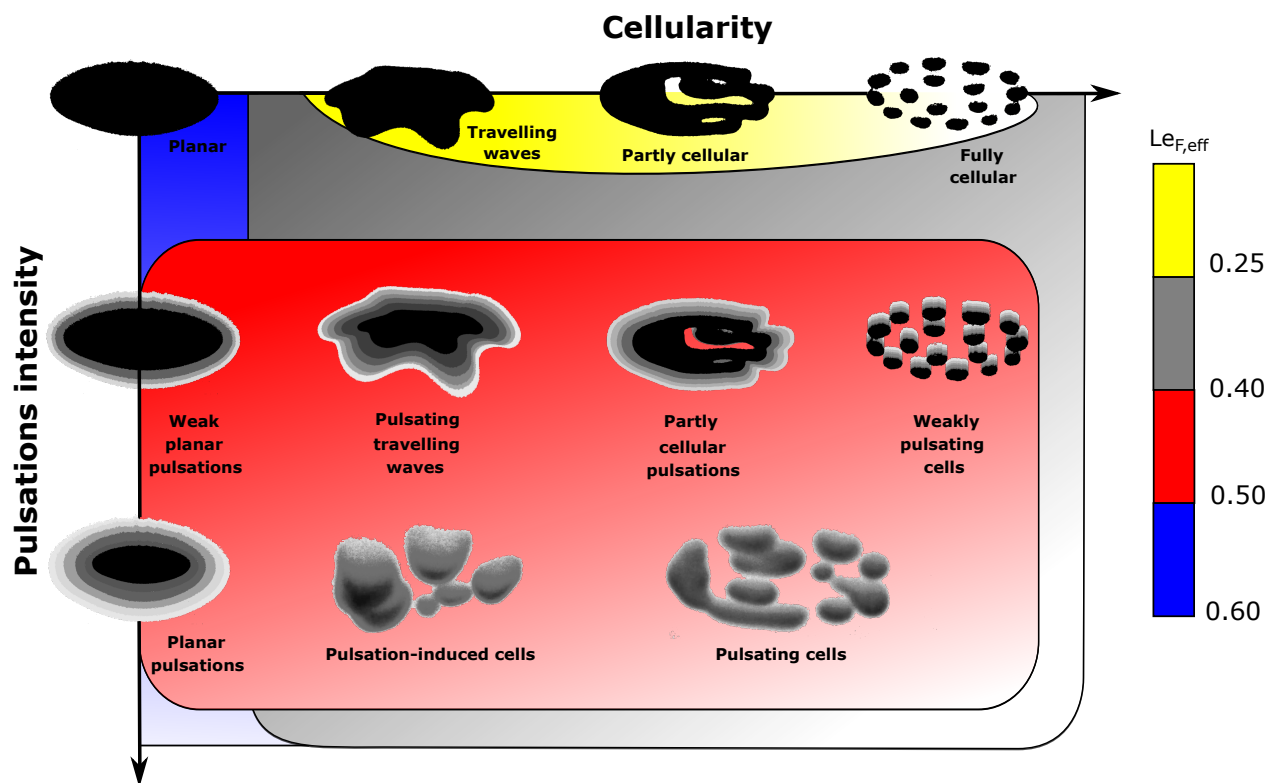


Figure 6.16 Qualitative illustration of the instabilities that onset in unstrained syngas diffusion flames with various fuel mixture Lewis numbers and $Le_o \approx 0.97$. The Damköhler number is represented by the relative shading level, where dark = near marginal stability, and light = near extinction.

tensities, H_2 -rich unstrained syngas flames are deemed more stable than CO -rich blends. For instance, increasing the relative H_2 amount from $X_{H_2,CO} = 30\%$ to 75% results in delaying the onset of DTIs from $X_F = 25\%$ to 23.5% in fuels without CH_4 , and from $X_F = 24\%$ to 20% when $X_{CH_4} = 15\%$ is added. The same conclusion is drawn from the dilution-induced extinction limits, beyond which no flame can be established within the one-dimensional combustion zone at any mixture strength. When the relative amount of H_2 to CO is increased from $X_{H_2,CO} = 30\%$ to 75% at $X_{CH_4} = 0\%$, extinction is delayed from $X_F = 20\%$ to 18.5% , and from $X_F = 18.5\%$ to 17.5% at $X_{CH_4} = 15\%$. This also demonstrates that flammability is substantially enhanced upon the addition of CH_4 to syngas. For example, at $X_{H_2,CO} = 45\%$, extinction is delayed from $X_F = 20\%$ to 18.5% when 15% CH_4 is added to syngas, and down to $X_F = 16\%$ at $X_{CH_4} = 30\%$.

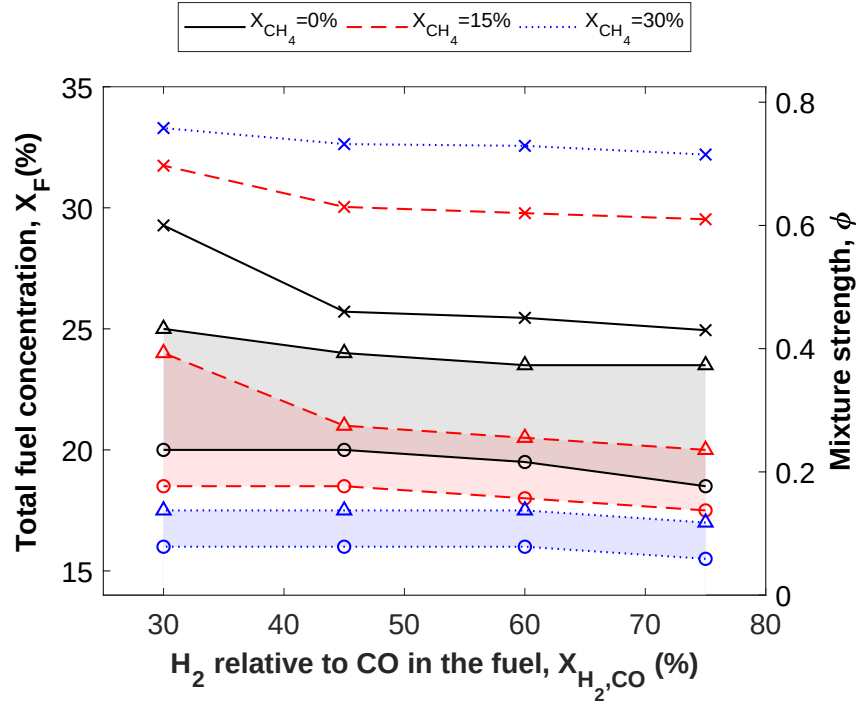


Figure 6.17 Flammability limits for different syngas compositions. The first onset of instabilities is indicated by (Δ), and CO_2 dilution-induced extinction is represented by ($\circ$). Onset of instabilities in terms of mixture strength is also given by ($\times$).

6.4 Conclusion

Unstrained diffusion flames of multi-fuel mixtures are experimentally characterized for the first time in this paper. Understanding of the diffusive-thermal instabilities that onset in lean biomass-derived syngas mixtures is provided, whose efficient combustion plays a crucial role in the overall efficiency of biorefineries. With $Le_o \approx 0.97$ as imposed by the abundant CO_2 species, it is shown that H_2 with $Le_{\text{H}_2} \approx 0.25$ promotes travelling waves in the flame at the marginal stability state, and stationary cellular instabilities at lower Damköhler numbers. On the other hand, CH_4 with $Le_{\text{CH}_4} \approx 0.88$ and CO with $Le_{\text{CO}} \approx 0.98$ both always induce chemical reaction rate pulsations. After determining the flame stability limits for a broad range of $\text{H}_2 + \text{CO} + \text{CH}_4 + \text{CO}_2$ mixtures, the different instability patterns are clearly seen to compete and interact with each other, leading to superimposed DTI modes with various degrees of cellularity and pulsation, depending on an effective mixture-averaged Lewis number of the fuel and on the Damköhler number.

For $\text{H}_2\text{-CO-CH}_4$ fuels with $Le_{F,eff} \geq 0.6$, only planar intensity pulsations with no cellular

instabilities form for all Damköhler numbers beyond the marginal stability state. However, when the fuel mixture contains relatively low amounts of CO/CH₄, such that $0.25 < Le_{F,eff} \leq 0.5$, intense CO/CH₄-induced chemical reaction rate pulsations with an amplitude reaching 57% turn the planar flame front fully cellular. These pulsation-induced cells vary in number between four and eight, as they oscillate in-phase at a CO/CH₄-dominated frequency of approximately 1 Hz. The amplitude of pulsations required to turn H₂-rich fuel blends “prematurely” fully cellular decreases with Damköhler number, and the flame front becomes inherently cellular under sufficiently weakly burning conditions. Now, when the CO/CH₄ perturbations onset, they develop into out-of-phase pulsations across the fragmented flame sheet, with relatively large frequencies that exceed 3 Hz. These superimposed fast pulsations grow unsustainably with time leading to local extinction spots, which are then occupied by other younger pulsating cells. The number of pulses that can be sustained by each cell before extinction and the actively burning area drastically drop as the lean extinction limit is approached, leading to superimposed instabilities with frequencies now dominated by the H₂ cells generation rate, which is approximately 3.2 Hz.

High-speed imaging of the observed superimposed cellular-pulsation instabilities reveals that the cell sizes at the lowest intensity point of the pulsation cycle, where CO/CH₄ burns the weakest, scale linearly with diffusion length. A similar scaling behaviour is observed for the sizes of the cells forming in single-fuel H₂ flames, signalling that CO and CH₄ may be temporarily extinct at the trough of the pulsation cycle, and that the H₂ in the fuel mixture contributes to sustaining these intense pulsations. Extracting the Fourier transforms of the pulsation cycles show that H₂ dampens the CO/CH₄ oscillations, especially when far from the lean extinction limit, as the reduced non-dimensional frequency does not scale with Damköhler number, unlike for CH₄-CO flames.

Acknowledgements

The authors are grateful for the funders of this work: The Trottier Energy Institute (Trottier scholarship and project grant), and the Natural Sciences and Engineering Research Council of Canada (NSERC) through the postgraduate doctoral scholarship (PGSD3 - 546588 – 2020), and discovery grants (RGPIN-03622-2014 and RGPIN-05071-2022).

CHAPTER 7 ARTICLE 4: DIFFUSIVE-THERMAL INSTABILITIES IN UNSTRAINED H₂O-DILUTED SYNGAS DIFFUSION FLAMES

Submitted to *Combustion and Flame* on 29 June 2023 [152]

By

Elie Antar, and Etienne Robert

Abstract

A new version of the unstrained diffusion flame burner that can be operated with gaseous fuels containing high vapor content is introduced. Being a good approximation of the classical chambered diffusion flame solution, the flames generated are essentially devoid from hydrodynamic perturbations present in common research burners. This permits quantitative comparison with theoretical models that are often based on this simple configuration, and paves the way for fundamental experimental studies with vaporized fuels. In this paper, the capabilities of the new burner are exploited to study diffusive-thermal instabilities (DTIs) in H₂O-diluted H₂-CO-CH₄-CO₂ mixtures. H₂O dilution can be significant in biomass-derived syngas mixtures that are not cooled prior to combustion, and that are often burned directly to lower losses as waste heat and pollutant emission in practical combustors. Flammability limits are first presented for a broad range of fuel blends, where the destabilizing effect of H₂O dilution is highlighted. Instability maps in terms of the Damköhler number are then provided to illustrate the different types of superimposed cellular-pulsating instabilities that onset from the simultaneous presence of H₂ with high diffusivity, and CO/CH₄ with much lower mobility. The characteristics of these peculiar instabilities are highly dependent on the H₂O dilution fraction, which increases both the fuel blend and oxidizer Lewis numbers. The degree of cellularity superimposed in the pulsating multi-fuel flame is reduced at higher water content, as the number of observed cells decreases. The opposite effect is observed on the pulsation frequency, which increases at higher water concentrations.

7.1 Introduction

The urgency to reduce greenhouse gas emissions has contributed to a surge in alternative energy carriers research over the past decades, particularly hydrogen-rich fuels such as syngas. Composed mainly of H₂ and CO, syngas can be produced via different thermochemical processes such as gasification or pyrolysis, and from a multitude of renewable and potentially carbon-neutral biomass feedstock such as wood chips or agricultural waste [203]. However,

the diversity in sources often leads to variable proportions of H_2 and CO , along with the inclusion of other hydrocarbons in syngas such as CH_4 , and inert species such as H_2O and CO_2 [164]. This variability in fuel composition can significantly affect the combustion process of syngas, specifically diffusive-thermal instabilities (DTIs) which are the focus of this work.

DTIs are intrinsic combustion phenomena that result from unequal thermal and molecular diffusivities, and that generally lead to cellular or pulsating flames [204]. DTIs have been reported in both premixed and non-premixed configurations using various fuels [89]. However, when it comes to syngas, the majority of the published studies rely on premixed configurations such as flat flame McKenna [132, 133] or Bunsen burners [134, 135], as well as spherically expanding flames [136, 137], in which aerodynamic effects have a significant influence on the flame. The instabilities reported are often a combination of hydrodynamic, buoyancy, and diffusive-thermal effects, and are mainly wrinkled flames, with scarce reference to any potential DTI pulsations from CH_4 , CO , or any other large Lewis number species, which could lead to extinction.

As a result, to uncouple the parasitic hydrodynamic effects from DTIs, we aim to experimentally replicate the idealized one-dimensional chambered diffusion flame configuration. This approach was first introduced by Kirkby and Schmitz [116] as a theoretical construct, and is shown in Figure 7.1. The fuel is assumed to be supplied at a constant velocity via a semi-permeable membrane into the bottom of the straight-duct combustion chamber, which is exposed to constant conditions at the top. The latter are ensured by a sufficiently fast flowing transverse stream that uniformly removes the combustion products and supplies the oxidizing species, which counter-diffuses towards the flame against the upward bulk flow. Therefore, the resulting flame is in theory unstretched, and devoid from hydrodynamic disturbances.

Due to its simplicity, the idealized one-dimensional configuration has been previously used to develop DTIs models, such as the theoretical work of Metzener and Matalon [127]. Their linear stability analysis showed that DTIs arise when preferential diffusion of mass or heat (non-unity and unequal Lewis numbers) lead to excess or deficiency in available enthalpy ($h_f \neq 0$) at the flame sheet with a sufficiently small Damköhler number (Da). The latter is the ratio of the characteristic diffusion time over the chemical reaction time. Unlike premixed flames where a single effective Lewis number is sufficient to predict the characteristics of the DTIs, it was shown that both the fuel and oxidizer Lewis numbers (Le_F and Le_o) must be considered in diffusion flames. Fundamental scaling laws were also obtained for different instability parameters such as cell size or pulsation frequency.

The introduction of an experimental implementation that can mimic the idealized one-

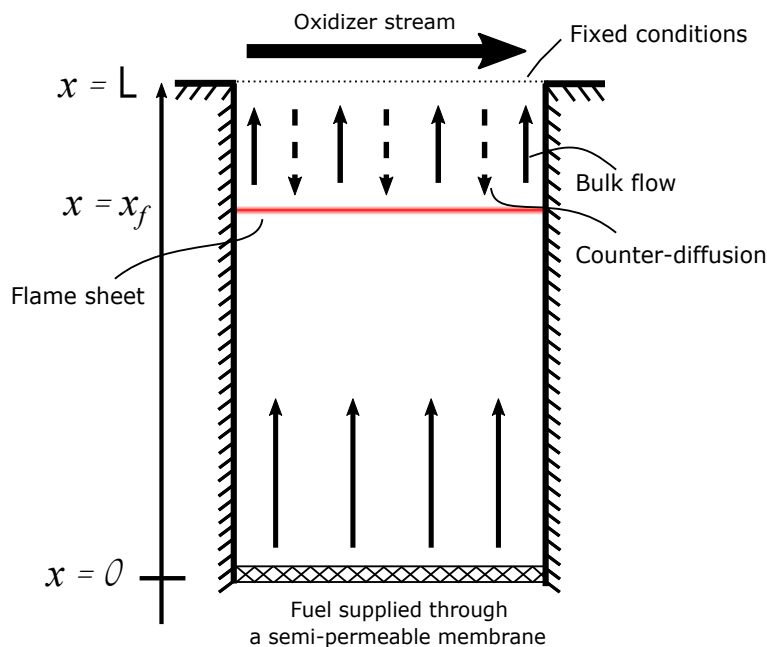


Figure 7.1 The idealized one-dimensional chambered diffusion flame theoretical construct

dimensional diffusion flame by Lo Jacono et al. [195] (mark I unstrained burner), which was subsequently enhanced by Robert and Monkewitz [192] (mark II unstrained burner) has enabled DTI theoretical models to be validated for the first time against experimental data obtained uncoupled from hydrodynamic effects [131]. The flames generated were estimated to have a residual strain rate as low as 0.05s^{-1} . The characteristics of the stationary cells in the small Lewis number $\text{H}_2\text{-CO}_2$ flames, and the pulsating instabilities of the $\text{CH}_4\text{-CO}_2$ flames with a relatively larger Lewis number were in agreement with theoretical predictions.

Much of the work on the stability of unstrained diffusion flames revolved around single-species fuels such as H_2 or CH_4 , until recently when we investigated multi-fuel syngas $\text{H}_2\text{-CH}_4\text{-CO-CO}_2$ mixtures. We showed that the combined presence of H_2 with a high diffusivity, and CO/CH_4 with much lower mobility resulted in superimposed cellular-pulsating flames [150]. These DTIs were characterized by measuring the cell size and pulsation frequency, along with the fraction of actively burning flame sheet. However, only CO_2 was used for dilution, since the mark II version of the unstrained diffusion flame burner was limited to dry gaseous fuels only. The effect of H_2O dilution on the peculiar superimposed diffusive-thermal instabilities remains unknown.

H_2O is a major inert species in biomass-derived syngas in addition to CO_2 , and our recent model of a small-scale biorefinery [148] predicts that its total concentration could reach 70% in some cases before the combustion stage. The heat capacity of H_2O is almost double that

of CO_2 , leading to lower flame temperatures and therefore an increased risk of DTIs. More importantly, diluting with H_2O is expected to have a pronounced effect on the dynamics of the instabilities owing to its distinctive diffusive-thermal properties. Although H_2O can be readily condensed from syngas mixtures in biorefineries, we showed in [148] that a 35 percentage point total efficiency penalty could be incurred by cooling the gas to atmospheric conditions to condense the water. In fact, adopting hot gas handling techniques where thermal energy losses are reduced plays a key role in enhancing the economic viability of biomass conversion systems [41], especially for small-scale decentralized applications that are inherently well suited to the distributed nature of biomass resources. In addition, burning with steam at lower flame temperatures is often favored in different practical combustors to reduce NO_x emission [205], soot formation [206], and radiative heat losses [207].

The goal of this paper is to introduce a new version (mark III) of the unstrained diffusion burner that can be operated with wet gaseous fuels, and utilize this research facility to investigate DTIs in H_2O -diluted H_2 - CO - CH_4 - CO_2 mixtures. In the subsequent sections, the design of the burner is discussed, followed by a characterization of its ability to produce unstrained diffusion flames through comparison with idealized solutions. This is followed by results covering the stability and extinction limits of a broad range of humid syngas mixtures, before characterizing the instabilities that form beyond the marginal stability limit, with a strong emphasis on the effect of H_2O dilution.

7.2 Unstrained diffusion flame burner

7.2.1 Mark III design

Figure 7.2 shows a schematic representation of the mark III version of the one-dimensional unstrained diffusion flame burner. The combustion chamber is a straight quartz glass duct with a 77.5×77.5 mm cross section and a length of 53.8 mm (L_{geom}), and is supplied from the bottom with fuel at a constant bulk velocity and at nearly atmospheric pressure. The oxidizer stream is fed from the top, with the O_2 species counter-diffusing downwards against the combustion products to reach the flame. The flow rates of the gasses are controlled using flow controllers (Hastings, model HFC-202).

Similar to the mark II version of the burner, the conditions at the top of the chamber are kept constant by supplying the oxidizer stream using 31×31 hypodermic needles (ID: 0.8 mm), and allowing the products to evacuate via an interlaced set of 32×32 thin curved stainless steel tubes that are exposed to atmospheric pressure at the outlet. The needles array is placed inside an insulated plenum, which is fitted with heaters and thermocouples

to control the top boundary temperature of the combustion zone and to avoid condensation within the exhaust stream. To shield the central part of the flame where the experiments are conducted from the temperature and species gradients of the colder windows, a 1 mm thick quartz cylinder with a 43.5 mm inner diameter is inserted in the middle of the combustion chamber. This divides the flame into a slightly perturbed outer portion that ensures adequate wall temperatures, and a shielded inner planar flame where the measurements are taken, as shown in Figure 7.2 c).

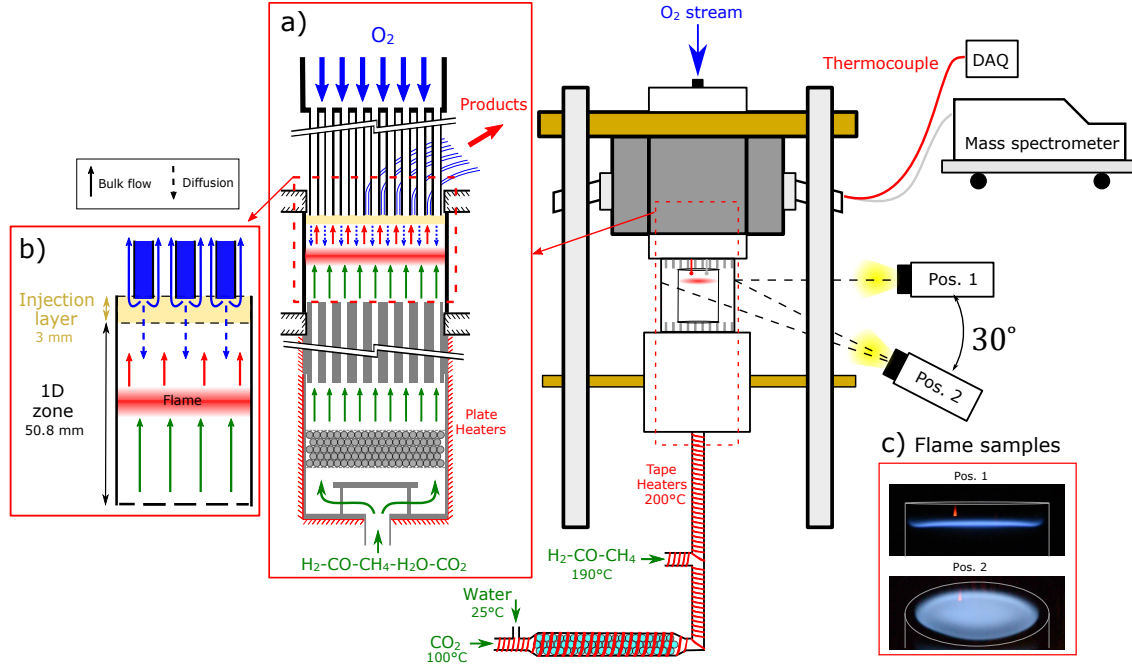


Figure 7.2 Schematic representation of the mark III unstrained diffusion flame burner. Cross-sectional views showing a) the reactants injection and exhaust systems, and b) the injection layer and the one-dimensional dimensional combustion zone. c) Flame samples captured from positions 1 and 2.

Particle Image Velocimetry (PIV) reported in [130] revealed that the nature of the oxidant supply into the combustion chamber creates a thin layer below the top needles array in which the flow is locally three-dimensional, and where a portion of the supplied oxidizing species is directly evacuated upwards with the combustion products. This injection layer is represented schematically in Figure 7.2 b), and was conservatively measured to have a thickness (Δ) below 3.0 mm using laser Doppler anemometry (LDA) [193]. Below the injection layer, species concentration becomes highly uniform across the combustion chamber, with mass spectrometer measurements revealing variations in O₂ concentration just below 10% across the flame width [130, 193]. Therefore, the effective combustion chamber length that mimics the idealized one-dimensional chambered diffusion flame configuration is $L_{geom} - \Delta = 53.8 -$

3 = 50.8 mm.

The main difference between the current and the mark II version [130] of the unstrained diffusion flame burner is the former's ability to operate with fuels having a very high vapor content. As a result, the fuel injection system had to be redesigned. As illustrated in Figure 7.2 a), an aluminum injection chamber (81-mm long) is used, which is uniformly heated by 76-mm long plate heaters from the sides and the bottom. On the top, a 36-mm thick aluminum block is placed and sealed by gaskets, through which an array of 18×18 2-mm diameter holes are made to uniformly supply the fuel into the combustion chamber at 142°C. This block is also uniformly heated from all sides using four PID-controlled plate heaters. The temperature variation across the outlet of the fuel injection block was measured to be less than 2°C, using multispectral-infrared camera (Telops MS-350) as shown in Figure 7.3 a).

To add humidity to the fuel stream, a syringe pump feeds water to a CO₂ carrier stream at 100°C, which is circulated through a 20-cm long tube heated to 200°C and filled with 1-mm glass beads, for uniform evaporation, before being mixed with the remainder of the hot fuel stream of H₂/CO/CH₄ upstream of the injection chamber. Mass spectrometer measurements inside the injection chamber are shown in Figure 7.3 b), using a binary CO₂-H₂O mixture for illustration. The four jumps represent the transient phase when the flowrates and hence, the proportions of the gasses change. After these transient periods lasting on the order of one minute, it can be seen that the water vaporization and mixing processes are steady.

7.2.2 Burner characterization - stable flames

Figure 7.4 shows the structure of a stable H₂ flame generated in the mark III burner, and compares it with the idealized one-dimensional diffusion flame solution at a mixture strength of $\phi = 0.5$. The latter is defined as the ratio of the fuel to oxygen boundary mass fractions, normalized by their stoichiometric proportions. In the literature [195], ϕ is also sometimes referred to as the initial mixture strength, since it is defined at the boundaries of the domain, as stoichiometry is always respected at the flame sheet in diffusion flames. Strong agreement between the produced flame and the idealized solution can be seen in terms of the flame position, and major reactants mass fraction profiles, which are scaled by their respective boundary concentrations. The distance along the combustion chamber is normalized by its length. Similarly, the flame temperature measured using thermocouple probes was shown to agree within 50°C with predictions from the model [130], demonstrating minimal heat loss effects, especially when operating at high dilution levels where DTIs onset.

The species concentrations are measured using a mass spectrometer calibrated for major

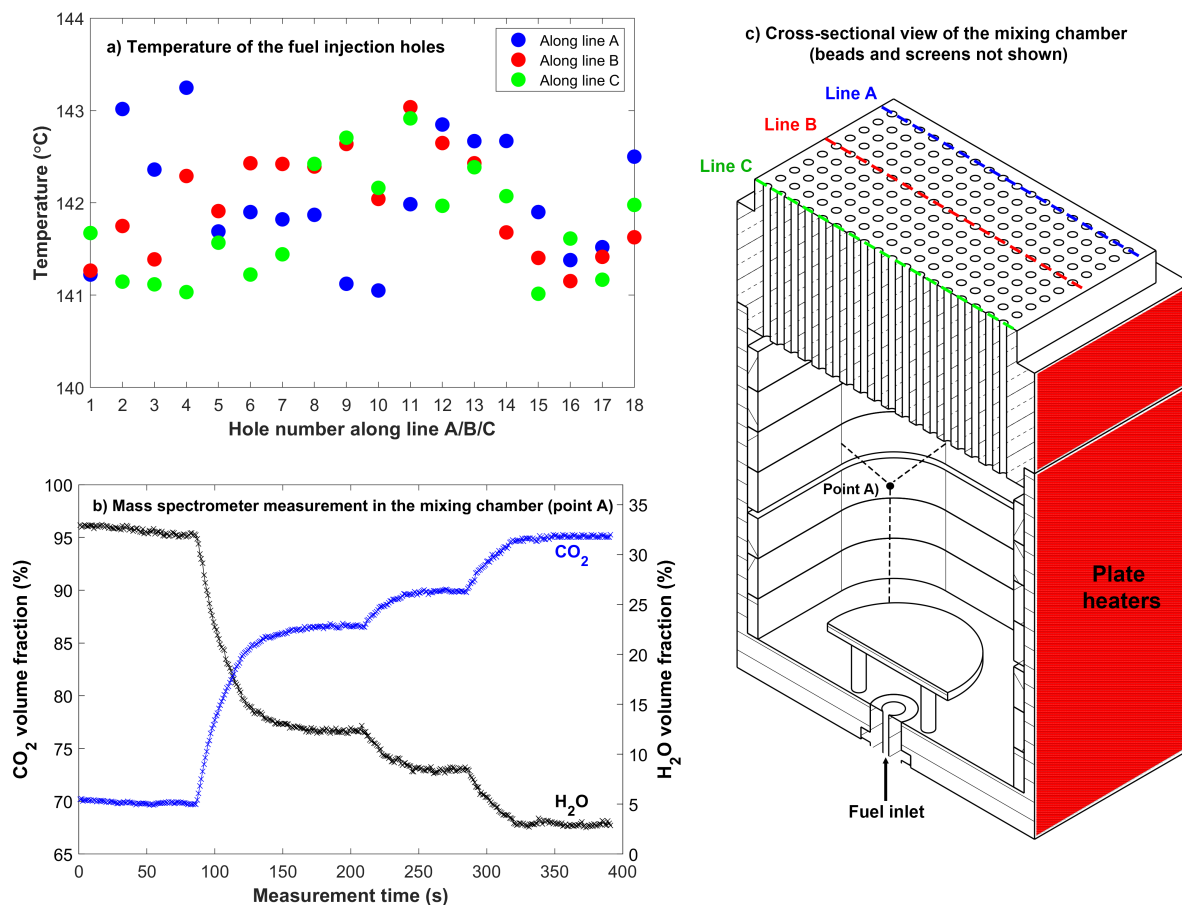


Figure 7.3 a) Temperature of the fuel injection block holes, and b) temporal variation of the gasses volume fraction within the mixing chamber. A cross-sectional view of the latter is shown in c).

species (H_2 , O_2 , CO_2 and H_2O) at a relative accuracy of 5%, which is estimated to increase to 10% in the flame sheet itself due to the relatively higher concentration of radicals [194]. The idealized diffusion flame solution is implemented on Python using Cantera software package [196]. The flame is modelled as a stack (Sim1D) containing from left to right an inlet of the advected flow (Inlet1D), an adiabatic one-dimensional flow field (UnstrainedFlow), and an outlet reservoir with constant boundary conditions (OutletReservoir1D). The low-Mach-number momentum, energy, species and overall continuity equations are solved assuming an ideal gas mixture, and the GRI-3.0 reaction mechanism, while taking into account Soret diffusion effects.

Figure 7.5 provides more evidence for the general agreement between flames generated in our burner and the one-dimensional diffusion flame model. The positions of the maximum

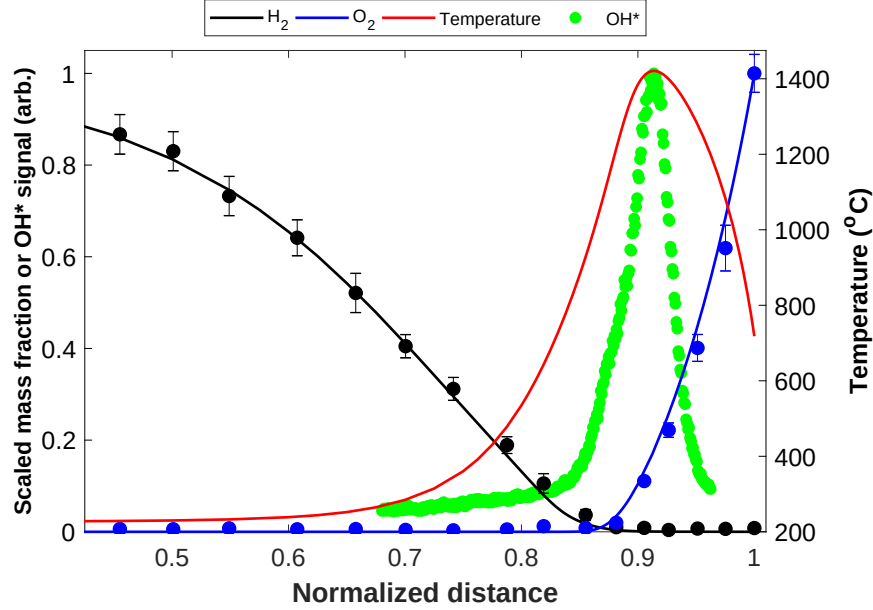


Figure 7.4 Structure of a H₂ flame diluted with 70% CO₂ at $\phi = 0.5$ and $U = 7.6$ mm/s evaluated at the inlet conditions. (o): Experimental data, and (—): one-dimensional diffusion flame model.

natural and OH* chemiluminescence are compared with the location of the maximum temperature from the idealized model for a range of fuel blends, mixture strengths, and inlet bulk velocities. The error bars in the experimental measurements represent the reproducibility of the results through their minimum and maximum values, and the acquired noise that is amplified by the image intensifier. The OH* chemiluminescence measurements are conducted using a 310-nm optical filter (10 nm bandwidth), a UV lens, an image intensifier (UVi model 1850-10), and a high-speed camera (Photron AX-200). The latter is placed perpendicular to the burner axis as shown in Figure 7.2 (Pos. 1). The light signals are normalized by their peak values, and averaged laterally over the flat flame surface, along with temporally over multiple images to reduce noise.

7.2.3 Burner characterization - stability and extinction limits

For a given fuel blend, the total fuel concentration (X_F) of a stable planar flame is gradually reduced in $X_F = 0.25\%$ decrements until the first instability is observed in the flame. Such stability limits are reported in Figure 7.6 a). The mixture strength is kept on average at $\phi = 0.58$, by controlling the flow rate of the oxidizer stream. The fuel concentration at the stability limit is inversely proportional to the inlet bulk velocity, which is selected to be $U = 11$ mm/s

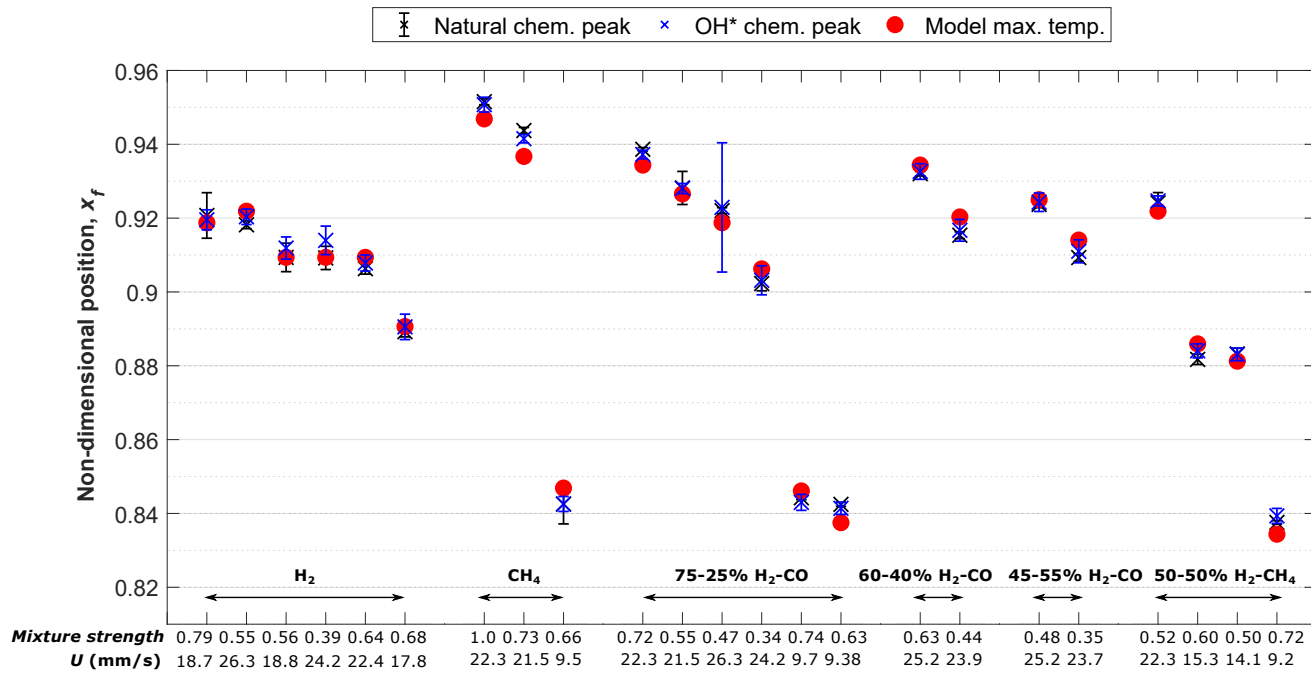


Figure 7.5 Comparison between experimental and modelled flame positions under different conditions.

for the results presented. The fuel species notation first indicates the volume fraction of H₂ relative to CO, followed by the fraction of CH₄ relative to the two other combustible species. For the two inert species, the H₂O molar fraction relative to CO₂ (X_{H_2O}) is indicated. For instance, a 75-25% H₂-CO + 15% CH₄ mixture diluted at $X_F = 30\%$ with $X_{H_2O} = 20\%$ is composed of: 19.1% H₂, 6.4% CO, 4.5% CH₄, 56% CO₂, and 14% H₂O by volume.

The results of Figure 7.6 a) show that replacing CO₂ with H₂O for the same total fuel concentration renders the flame more susceptible to instabilities, for the broad range of fuels considered. For instance, with 75-25% H₂-CO + 15% CH₄, instabilities are first observed at $X_F = 21.0\%$ when the mixture is dry. However, as water replaces 20% of the CO₂ by volume, instabilities onset at $X_F = 23.0\%$, which becomes $X_F = 24.75\%$ at $X_{H_2O} = 40\%$. The reduction in flame stability at higher water fractions can be attributed to chemical effects, whereby the resulting increase in OH radical pool promotes chain terminating reactions such as $OH + HO_2 \rightarrow O_2 + H_2O$ and $OH + H + M \rightarrow H_2O + M$ [141]. The characteristics of the instabilities are discussed in detail in the next sections.

Comparing different fuel blends at a given X_{H_2O} , the measured stability limits show that the flame becomes most prone to instabilities when the CO content in the fuel mixture is

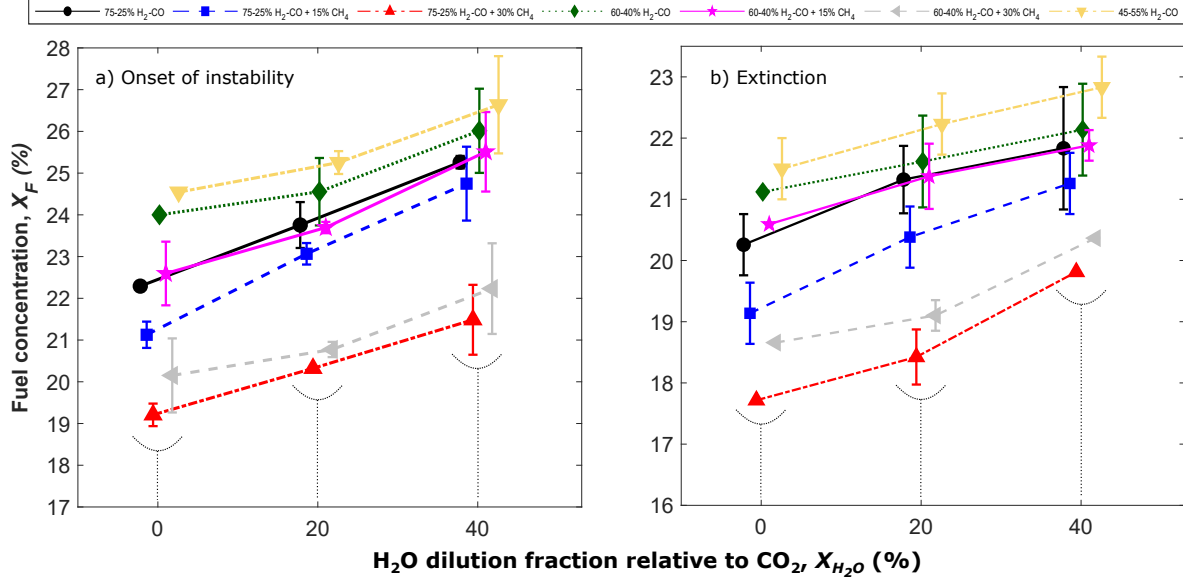


Figure 7.6 Flame a) stability and b) extinction limits as a function of the water dilution fraction for different fuel blends. The inlet bulk velocity is $U = 11$ mm/s. The error bars indicate maximum variation in the measurements, and in a) account for the deviation of the mixture strength from its mean value of $\phi = 0.58$.

increased. For instance, as CO is increased from 75-25% H₂-CO to 60-40% H₂-CO at $X_{H_2O} = 40\%$, the fuel concentration at which instabilities onset increases from $X_F = 25.25\%$ to 26.0% . At 45-55% H₂-CO, instabilities are observed at $X_F = 26.75\%$. In addition, the results show that flame stability is enhanced when the CH₄ content in the fuel is increased. As 15% CH₄ is added to a mixture of 60-40% H₂-CO with $X_{H_2O} = 20\%$, the onset of instability is delayed from $X_F = 24.75\%$ to $X_F = 23.75\%$. When 30% CH₄ is added, the stability limit is further pushed to $X_F = 20.75\%$. Higher flame temperatures are likely to explain these observations, as the volumetric heat release rate of CH₄ is more than triple that of H₂ or CO.

Figure 7.6 b) shows the dilution-induced extinction limits, which are fuel concentrations below which no flame could be maintained. Here, the combustion is excessively weak, whereby the chemical reaction time is very large relative to the residence time. The instabilities that develop are always unsustainable and rapidly extinguish the flame, no matter the boundary oxygen concentration or mixture strength. The extinction limit trends are similar to the stability limits, where it can be seen that higher H₂O volume fractions relative to CO₂ render the flame more prone to extinction, for all fuel blends. This behaviour is also in agreement with low-stretch syngas flammability limits from published numerical simulations [141].

7.3 Diffusive-thermal instabilities

The characteristics of the diffusive-thermal instabilities that are observed beyond the stability limits are presented here. We start by discussing the effect of water dilution on the instability type in subsection 7.3.1, followed by its effect on the characteristic length and time scales in subsection 7.3.2. The results are reported as a function of the mixture strength, fuel and oxidizer Lewis numbers, along with the Damköhler number (D_a). These are the main fundamental parameters predicted by the linear stability theory [127] to dictate the characteristics of the DTIs in unstrained diffusion flames. Given that we are dealing with fuel mixtures, an effective Lewis number ($Le_{F,eff}$) for the fuel mixture is considered:

$$Le_{F,eff} = X_{H_2} Le_{H_2} + X_{CO} Le_{CO} + X_{CH_4} Le_{CH_4} \quad (7.1)$$

where the Lewis number of each fuel species (Le_i) is weighted with its relative concentration in the fuel stream (X_i). The Lewis numbers are calculated at the flame sheet using the one-dimensional chambered diffusion flame numerical model supplied with experimentally-measured boundary conditions. The molecular diffusivity used in the computation of Le_i is a mixture-average one, since the highly-diluted flames studied here are abundant in both CO_2 and H_2O . The mixture strength is calculated from the boundary conditions measured using the mass spectrometer, and the Damköhler number is estimated as per the following equation:

$$D_a = (\lambda/\rho c_p U^2)(R^\circ T_a/E)^3 (\nu_x c_p \bar{W}/q R^\circ W_f) \beta Y_{f,o} p_o \exp(-E/RT_a) \quad (7.2)$$

where the values of the activation energy E and the Arrhenius pre-exponential factor β are assumed constant for a given fuel blend, owing to the lack of suitable empirical data. The values for these two parameters are selected such that Damköhler number at the marginal stability state for a given fuel blend is equal to unity [131, 150]. This means that the D_a calculated in this paper is a relative one, for a given fuel composition.

7.3.1 Effect of H_2O dilution on the instability type

For completeness, we first show the instabilities that are promoted by each of the three fuel species individually in Figure 7.7, before discussing multi-fuel mixtures. These maps are generated by gradually reducing the fuel concentration of a strongly burning flame down to the extinction limit, going through the marginal stability state where instabilities are first observed. This is conducted at bulk velocities that vary between $U = 8$ and 24 mm/s

(calculated at the inlet), to maximize the mapped Damköhler number space for each fuel.

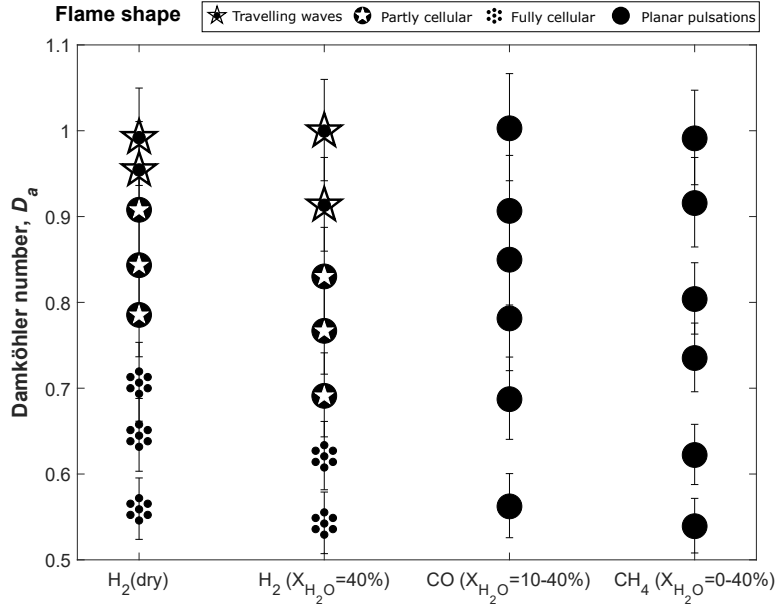


Figure 7.7 Flame instability patterns of single-fuel H_2 , CO and CH_4 mixtures diluted in H_2O and CO_2 . The mixture strength is approximately kept at 0.4 for H_2 ($X_{H_2O} = 0$ and 40%), and varies between 0.5 and 3.0 for the CO and CH_4 flames.

Starting with the H_2 flames at $X_{H_2O} = 0$ and 40%, travelling waves are the first pattern observed at both X_{H_2O} in the vicinity of the marginal stability state ($D_a = 1$, by definition), which manifest as large amplitude cells that vary in number between 4 and 5, corresponding to a cell size between 18.5 and 29.7 mm, and that rotate around the flame sheet at approximately 3 Hz. Details on the optical diagnostics used to measure the instabilities can be found in [150]. This mixed cellular-rotation instability mode is shown in Figure 7.8 a), where the images are taken using a digital still camera (Nikon D5300) with a 30° upward angle (Position 2 in Figure 7.2). At lower Damköhler numbers, the rotation stops and holes appear for the first time in the flame sheet, turning it partly cellular, as shown in Figure 7.8 b). The degree of cellularity keeps increasing as the Damköhler number approaches the lean extinction limit, where fully cellular flames form with detached stationary cells that vary in number and spacing between 12-17 and 8-10 mm, respectively, as shown in Figure 7.8 c).

The behavior of H_2 flames is consistent with the results from the linear stability theory [123], as was also reported in our experiments with the mark II version of the burner [150] using dry H_2 flames. As shown in the Lewis number map of Figure 7.9, at relatively large D_a , Le_{H_2} is located outside the theoretical stationary cells zone and below the planar intensity pulsations zone. Under such conditions, mixed instability modes such as travelling waves

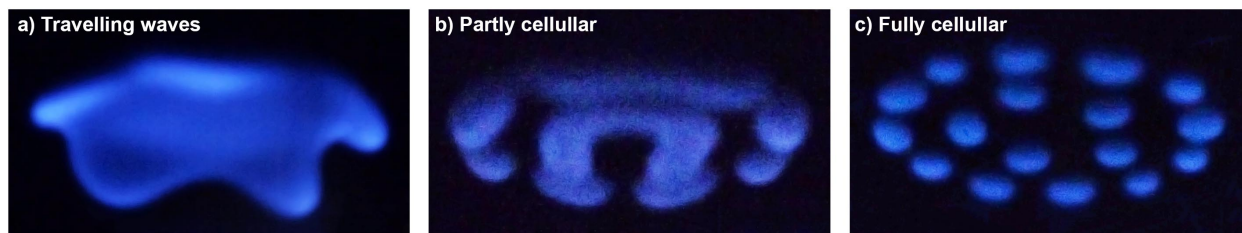


Figure 7.8 a) Travelling waves, b) partly cellular, and c) fully cellular H_2 flames at $\phi \approx 0.4$

are predicted. However, as D_a decreases, the region where stationary cells onset expands, and eventually engulfs the Lewis numbers of our H_2 flames. Such a behaviour is observed for all $X_{\text{H}_2\text{O}}$ tested ($0\% \leq X_{\text{H}_2\text{O}} \leq 40\%$). However, the transition from travelling waves into partial and then full cellularity is delayed to lower Damköhler numbers as the water fraction is increased, as can be seen in Figure 7.7. This is because the Lewis numbers of both H_2 and O_2 increase from 0.22 and 0.88 to 0.27 and 1.0, respectively, as H_2O replaces 40% CO_2 by volume, as shown in Figure 7.9.

Figure 7.7 also presents the instabilities of CO and CH_4 flames at various Damköhler numbers. The mixture strength is varied between $\phi = 0.5$ and 3, and $X_{\text{H}_2\text{O}}$ between 0 and 40%, although for CO , a minimum of $X_{\text{H}_2\text{O}} = 10\%$ is maintained as pure- CO flames were never sustainable, as also reported in [141]. As indicated by the solid circular symbols, only planar intensity pulsations with no cellular instabilities form for these fuels for the wide range of conditions tested. An illustration of the typical periodic variation in flame position resulting from planar intensity pulsations is shown in Figure 7.10 for CO and CH_4 . The observed instabilities is again consistent with previous experimental work [131,150], and with the theoretical stability map of Figure 7.9, where pulsations are predicted for high fuel and oxidizer Lewis numbers. The CO pulsation frequency varies between 0.7-1.2 Hz, and is lower than that of CH_4 at 1.2-2.0 Hz. Besides the nature of the fuel, the pulsation frequency also depends on the operating conditions, particularly the fraction of water dilution, which renders the pulsations faster as explained in subsection 7.3.2.

When it comes to blends of H_2 , CO and CH_4 fuel species, superimposed instability patterns can form [150], whereby CO/CH_4 intensity pulsations onset simultaneously with the cells from H_2 . Next, we discuss the effect of H_2O dilution on these instabilities which can be categorized as: 1) pulsation-induced, or 2) inherently cellular.

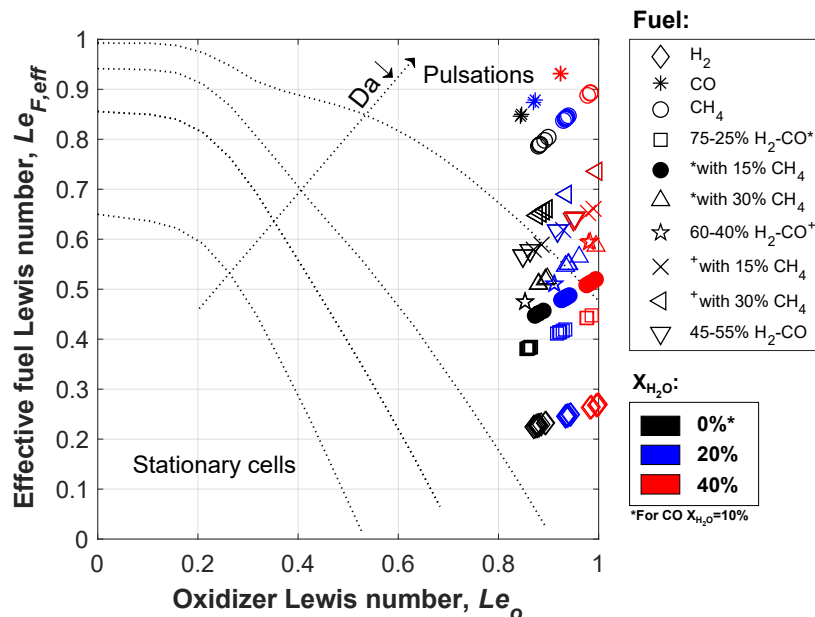


Figure 7.9 Effective fuel blend and oxidizer Lewis numbers for the unstable flames generated in our burner (markers). The instability zones are extracted from the theoretical findings of Cheatham and Matalon at $\phi = 1/3$ [123]. The effect of decreasing the Damköhler number is qualitatively shown by the dotted lines.

Pulsation-induced instabilities

Figure 7.11 shows the instability patterns that occur in 75-25% H_2 -CO flames at different X_{H_2O} . The effect of adding CH_4 or varying the CO content is discussed later. It can be seen that pulsation-induced superimposed instabilities occur at relatively high Damköhler numbers, where the pulsations control the instability frequency and the appearance of cells. As the 75-25% H_2 -CO flame transitions into instability beyond the marginal stability state $Da = 1$ at $X_{H_2O} = 0\%$, spatially-homogenous perturbations in its chemical reaction rate develop at a CO-attributed frequency of 0.8 Hz. Within a few seconds, the intensity of these planar pulsations dramatically grows, leading to the formation of completely detached cells at the lowest intensity point of the cycle, where CO burns the weakest, as shown in Figure 7.12 a) (pos. 2). As the burning intensity of CO starts increasing, the amplitude of the cells grows in-phase (pos. 3), and they eventually merge together as the highest intensity point of pulsation is approached, after which the flame is temporarily no longer cellular (pos. 4), before the repetition of the cycle. This pulsation-induced cellular flame is also shown in supplemental video 1¹.

¹The supplemental videos can be accessed via the online version of the article.

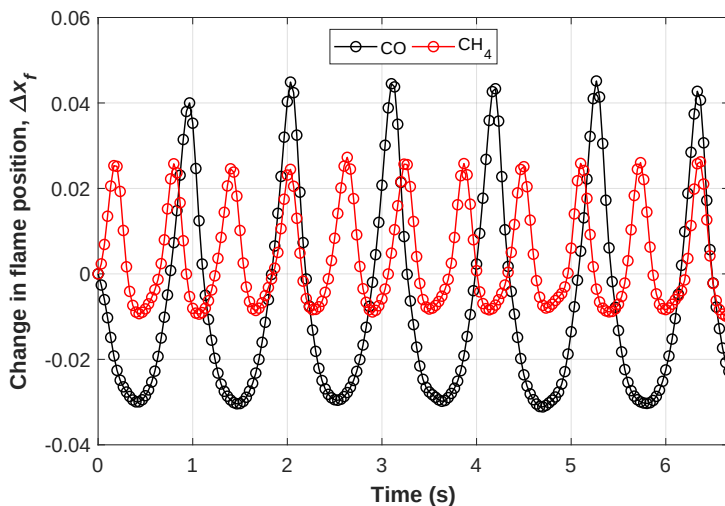


Figure 7.10 Illustration of the typical planar intensity pulsations for CO (0.92 Hz) and CH₄ (1.62 Hz).

When the water fraction in the diluting stream increases from $X_{H_2O} = 0$ to 20%, the cells that are induced by the pulsations at $D_a \approx 1$ are no longer completely detached from each other. Such a partly cellular pulsation-induced flame is shown in Figure 7.12 b). Upon further increasing the water fraction to $X_{H_2O} = 40\%$, no cellular instabilities of any degree are observed in the vicinity of the marginal stability state, as the pulsations become essentially planar as shown in Figure 7.12 c) and supplemental video 2¹. The addition of H₂O as a diluent, replacing part of the CO₂, has therefore suppressed the cellular character of the superimposed instability mode observed at marginal stability for 75-25% H₂-CO.

A similar reduction in the propensity of cellular instabilities forming as H₂O replaces CO₂ can also be noticed at other Damköhler numbers in Figure 7.11. For instance, at $D_a \approx 0.9$, the pulsations result in travelling waves when X_{H_2O} is set to 40%, instead of forming fully cellular flames when $X_{H_2O} \leq 20\%$. The reduction in the degree of pulsation-induced cellularity at higher water fractions is attributed to the increase in the fuel and oxidizer Lewis numbers. As X_{H_2O} increases from 0 to 40% in 75-25% H₂-CO, $Le_{F,eff}$ increases from 0.38 to 0.44, and Le_o from 0.86 to 0.98, as reported in Figure 7.9.

Figure 7.11 also shows that cellularity increases as the Damköhler number decreases when moving further from the marginal stability state, which is consistent with the behaviour of H₂ flames that was discussed earlier. For instance, at $X_{H_2O} = 40\%$, the instabilities in 75-25% H₂-CO flames transition from planar intensity pulsations at the marginal stability state, to

¹The supplemental videos can be accessed via the online version of the article.

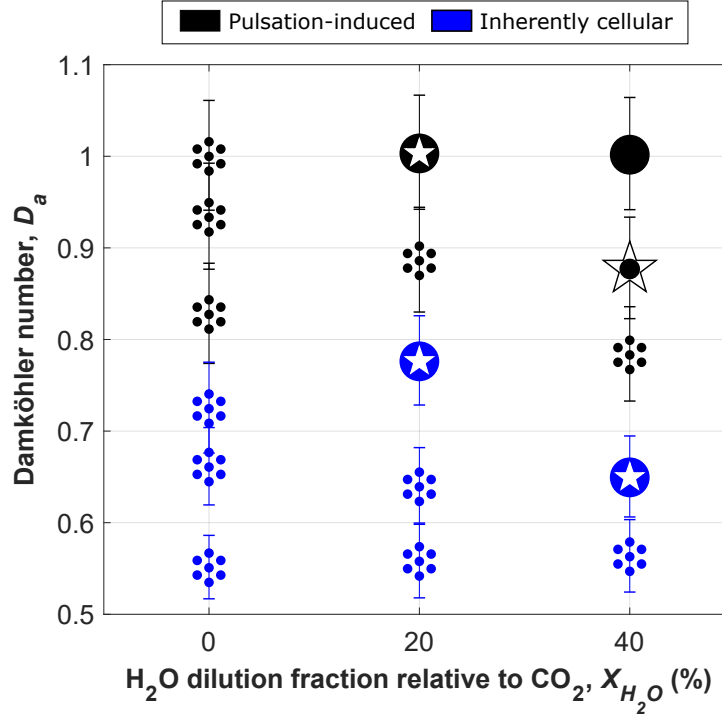


Figure 7.11 Variation in the instability patterns with H₂O fraction relative to CO₂ at different Damköhler numbers for 75-25% H₂-CO. The symbols indicate the shape of the instability: (•): Planar intensity pulsations, (★): travelling waves, (⊙): partly cellular, and (⊕): fully cellular. Mean mixture strength is 0.55 with 0.13 standard deviation.

pulsations-induced travelling waves at $D_a \approx 0.9$, to pulsations-induced fully cellular flames at $D_a \approx 0.8$. Eventually however, as the combustion intensity is rendered sufficiently weak, the flame transitions into the second category of superimposed instabilities: inherently cellular.

Inherently cellular instabilities

At sufficiently small Damköhler numbers, intensity pulsations are no longer required to turn the H₂-rich fuel mixture cellular. Fully cellular stationary flames with no intensity pulsations similar to those of Figure 7.8 c) are observed at $D_a \approx 0.73$ for 75-25% H₂-CO with $X_{H_2O} = 0\%$. However, as the CO chemical reaction rate perturbations grow when D_a is reduced in the now inherently cellular multi-fuel flame, they become superimposed locally within each detached cell, instead of uniformly across a connected flame sheet, resulting in pulsations that are out-of-phase across a fragmented flame. Relative to the previously discussed pulsation-induced cellular flame that forms at larger Damköhler numbers, the oscillations are now minimally dampened, with relatively fast frequencies that exceed 3 Hz, and with intensities that always grow unsustainably with time, leading to temporary extinction areas within the

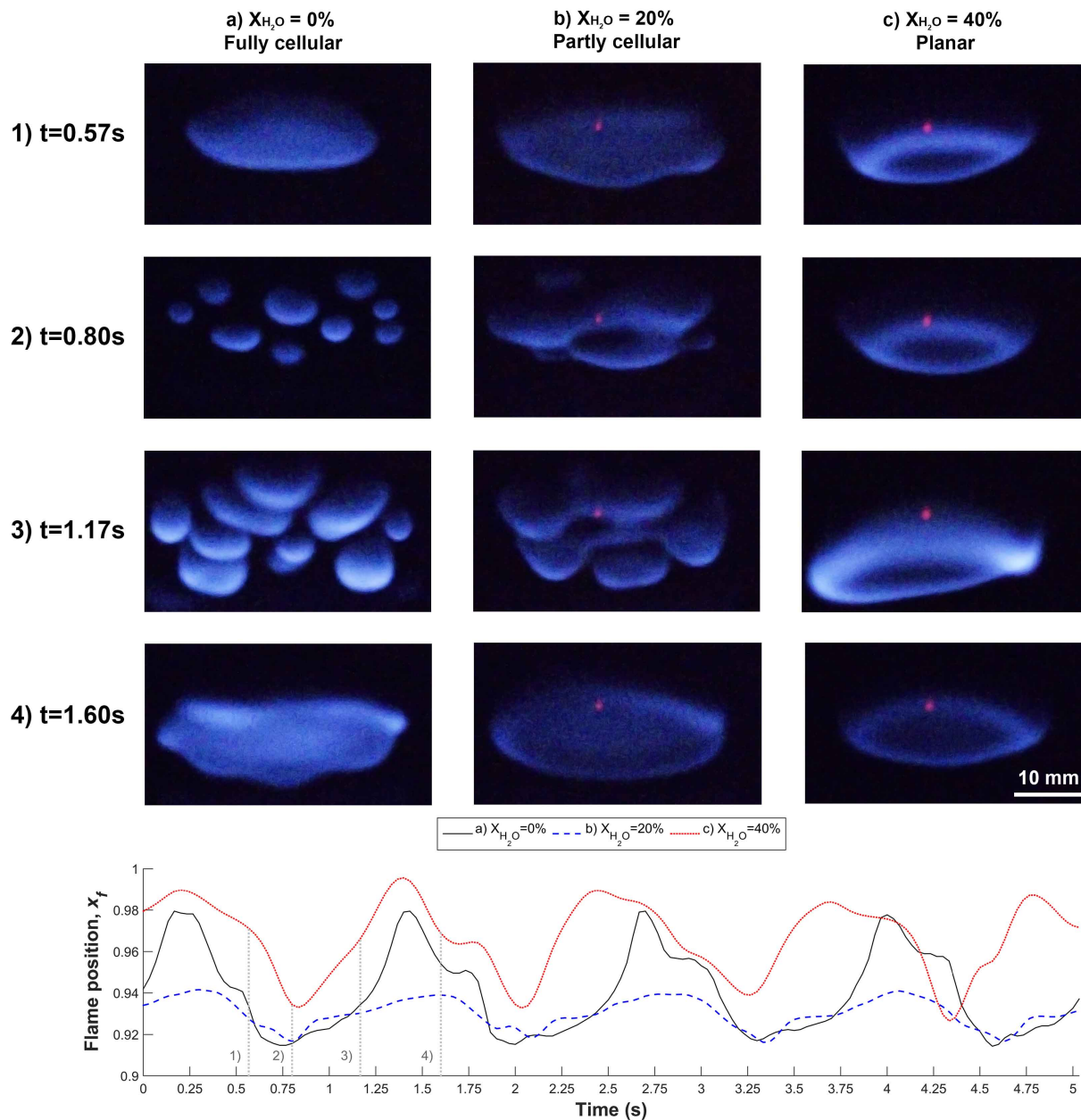


Figure 7.12 Effect of the H_2O dilution fraction on the pulsation-induced instabilities at 75-25% $\text{H}_2\text{-CO}$, $D_a = 1.0$ and $\phi \approx 0.55$ (supplemental video 2).

flame as shown in Figure 7.13. The extinct cells are then replenished with ones undergoing earlier stages of the same pulsation cycle. Such inherently cellular pulsating flames occur near the lean extinction limit, and are compared to pulsation-induced cells in supplemental video 3¹.

¹The supplemental video can be accessed via the online version of the article.

Increasing the fraction of H_2O dilution decreases the Damköhler number range where such inherently cellular instabilities form, as can be seen from Figure 7.11. Lower Damköhler numbers are as a result required to transition from the pulsation-induced mode to the inherently cellular one. For instance, at $X_{\text{H}_2\text{O}} = 20\%$, inherently fully cellular flames first form at $Da \approx 0.63$, instead of $Da \approx 0.73$ when no water is added. At $X_{\text{H}_2\text{O}} = 40\%$, their onset is further pushed towards the lean extinction limit, $Da \approx 0.56$. Figure 7.14 shows the typical chemiluminescence of a single cell at the transitioning point into the inherently cellular instability regime. It can be seen that at $X_{\text{H}_2\text{O}} = 40\%$, the inherently cellular flames are never stationary and always exhibit pulsations, unlike at $X_{\text{H}_2\text{O}} \leq 20\%$ ($Le_{F,eff} \leq 0.4$) where the light signals are relatively stable. Stationary cells are also never observed at $X_{\text{H}_2\text{O}} = 0\%$ when 15% CH_4 is added to 75-25 $\text{H}_2\text{-CO}$, or when CO is increased to 60-40% $\text{H}_2\text{-CO}$. Pulsations always accompany cellular instabilities for these blends. Although their composition is different, these mixtures have $Le_{F,eff} \leq 0.45$ (Figure 7.9), the significance of which is highlighted next.

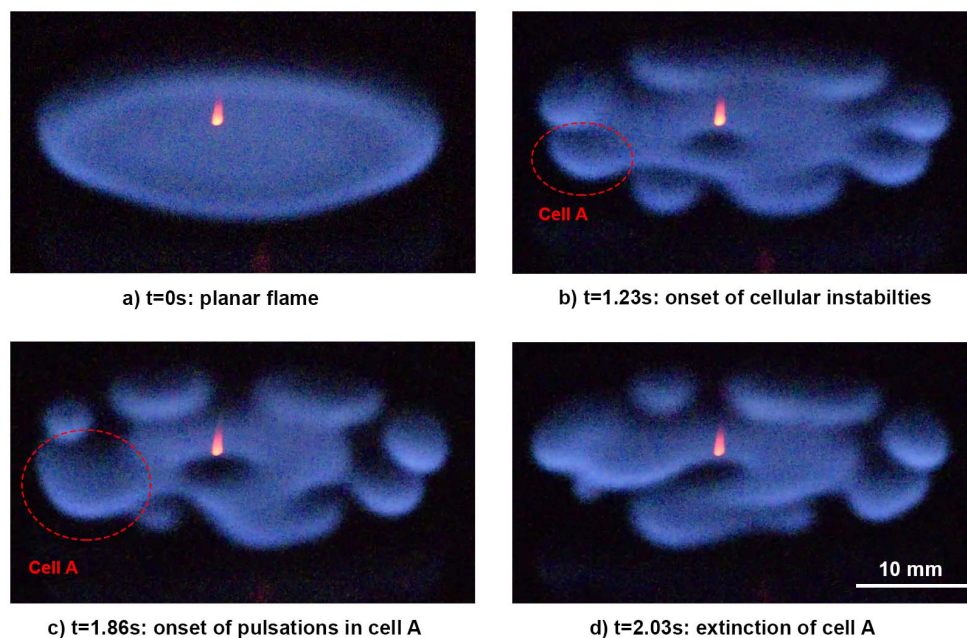


Figure 7.13 Development of inherently cellular pulsating instabilities at 75-25% $\text{H}_2\text{-CO}$, $Da = 0.56$ and $\phi = 0.38$.

Fuel effective Lewis number

Figure 7.15 a) shows the instabilities in 75-25% $\text{H}_2\text{-CO}$ mixtures to which 15% CH_4 is added. Even at $X_{\text{H}_2\text{O}} = 0\%$, planar intensity pulsations form near marginal stability, before the for-

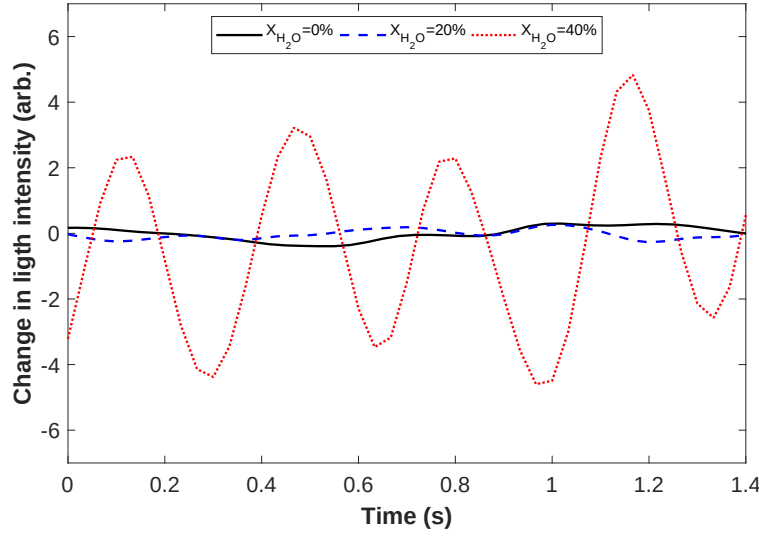


Figure 7.14 Typical variation in the light intensity of a single cell in 75-25% H_2 -CO with a) $X_{H_2O} = 0\%$ ($D_a \approx 0.73$), b) $X_{H_2O} = 20\%$ ($D_a \approx 0.63$), and c) $X_{H_2O} = 40\%$ ($D_a \approx 0.56$), at the transitioning point into inherent cellular instabilities.

mation of pulsation-induced cells, followed by inherently cellular flames at smaller Damköhler numbers. Such patterns are similar to the CH_4 -free case with $X_{H_2O} = 40\%$ (Figure 7.11), which happens to attain a similar $Le_{F,eff} \approx 0.45$.

In Figure 7.15 b), the quantity of CH_4 relative to the other fuel species is increased to 30%. Superimposed instabilities are observed at $X_{H_2O} = 0\%$, and to a lower extent at $X_{H_2O} = 20\%$, where $Le_{F,eff} \approx 0.51$ and 0.55 , respectively. As X_{H_2O} is increased to 40% and $Le_{F,eff}$ becomes approximately equal to 0.6, only planar intensity pulsations form. Similarly, planar instabilities are also observed for CH_4 -free mixtures whose CO content is increased to 60-40% H_2 -CO (Figure 7.15 c) at $X_{H_2O} = 40\%$, where the Lewis number is also $Le_{F,eff} \approx 0.6$. In fact, upon comparing Figure 7.15 b) and c), one can immediately notice the resemblance in the instability patterns for a given water fraction. As shown in Figure 7.9, the two different fuel blends attain the same $Le_{F,eff}$ and Le_o .

As the CO content is increased to 45-55% H_2 -CO, or as 30% CH_4 is added to the 60-40% H_2 -CO mixture, planar intensity pulsations become the only instability observed for all unstable Damköhler numbers, even at $X_{H_2O} = 0\%$. For these blends, $Le_{F,eff} \geq 0.59$. Water dilution nonetheless affects the pulsation frequency of these non-cellular flames, as discussed in the next section.

The aforementioned instability patterns were also reported at the same $Le_{F,eff}$ intervals in our previous experiments with the mark II version of the burner [150]. However, varying

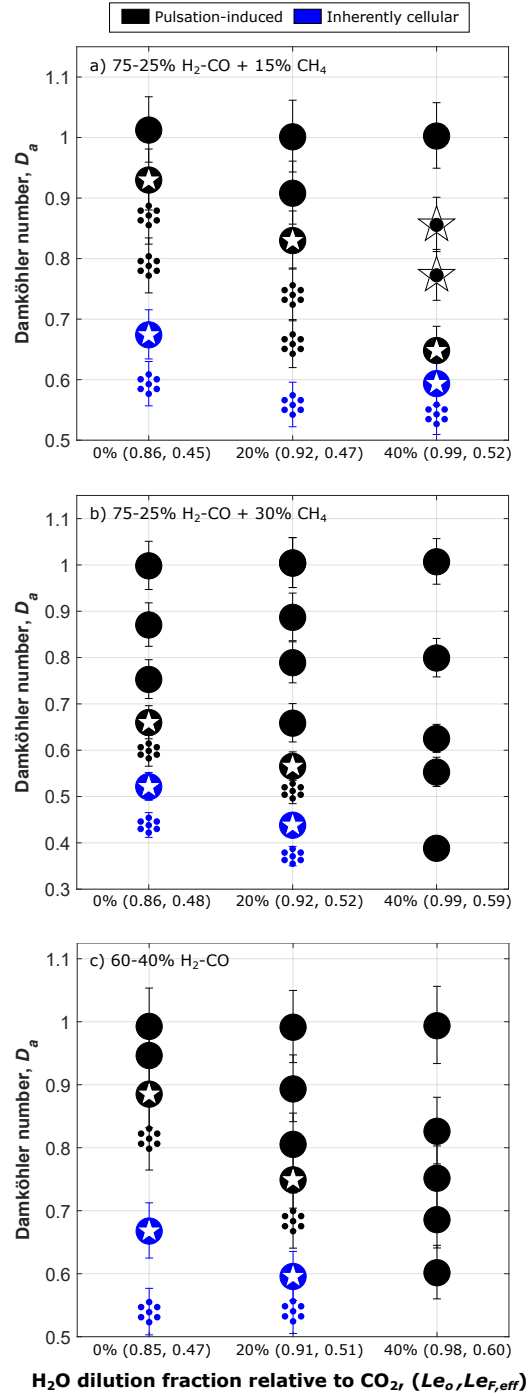


Figure 7.15 Variation of the instability patterns with H₂O fraction relative to CO₂ for a) 60-40% H₂-CO, b) 75-25% H₂-CO + 15 % CH₄, and c) 75-25% H₂-CO + 30 % CH₄. The symbols indicate the type of instability: (•): Planar intensity pulsations, (★): travelling waves, (⊙): partly cellular, and (⊛): fully cellular. Mean mixture strength is 0.61 with 0.17 standard deviation.

the relative amount of combustible species was the only way to control $Le_{F,eff}$, as only CO_2 was used as a diluent. The incorporation of a second diluting species in the current study offers additional means to control $Le_{F,eff}$, and consequently, more evidence on its fundamental significance. Consequently, Figure 7.16 shows a generalized instability map in terms of $Le_{F,eff}$ that is applicable to any mixture of $\text{H}_2\text{-CO-CH}_4$ fuel species diluted at any $\text{H}_2\text{O/CO}_2$ proportions with the mixture strength being approximately $\phi \approx 0.6$ and the oxidizer Lewis number $Le_o \approx 0.95$. The effect of increasing the latter two parameters on the instability patterns is qualitatively shown by the dashed horizontal axis.

7.3.2 Effect of H_2O dilution on the instability size

Number of cells

Figure 7.17 a) presents a box plot of the number of cells (N_{cells}) observed in pulsation-induced cellular flames at different water vapor concentrations relative to CO_2 . The cells are measured at the lowest intensity point of the pulsation cycle, for all the unstable flames that are observed from marginal stability to the lean extinction limit. The data show that

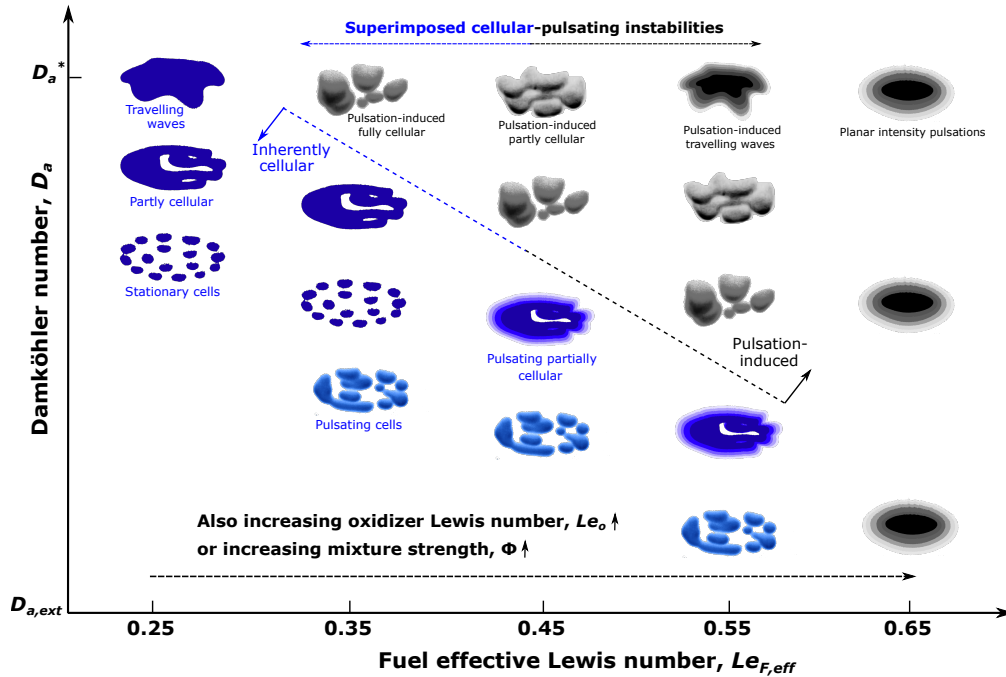


Figure 7.16 Illustration of the sustained instability patterns observed as a function of the effective fuel Lewis number for $\text{H}_2\text{-CO-CH}_4$ mixtures diluted in H_2O and CO_2 at $\phi \approx 0.6$ and $Le_o \approx 0.95$. The effect of increasing Le_o or ϕ is qualitatively shown by the dashed horizontal axis.

the number of cells induced by pulsations decreases as H_2O replaces CO_2 . For the 75-25% H_2 - CO mixture, the median number of cells is 9, which decreases to 6 at $X_{H_2O} = 20\%$, and down to 4 cells at $X_{H_2O} = 40\%$. A similar trend is observed with the other H_2 - CO - CH_4 blends, where it can also be noted that N_{cells} also decreases as the H_2 content is reduced. Similarly, the reduction in N_{cells} with water fraction in inherently cellular pulsating flames is also presented in Figure 7.17 b). Compared to pulsation-induced ones, N_{cells} of inherently cellular flames is generally larger.

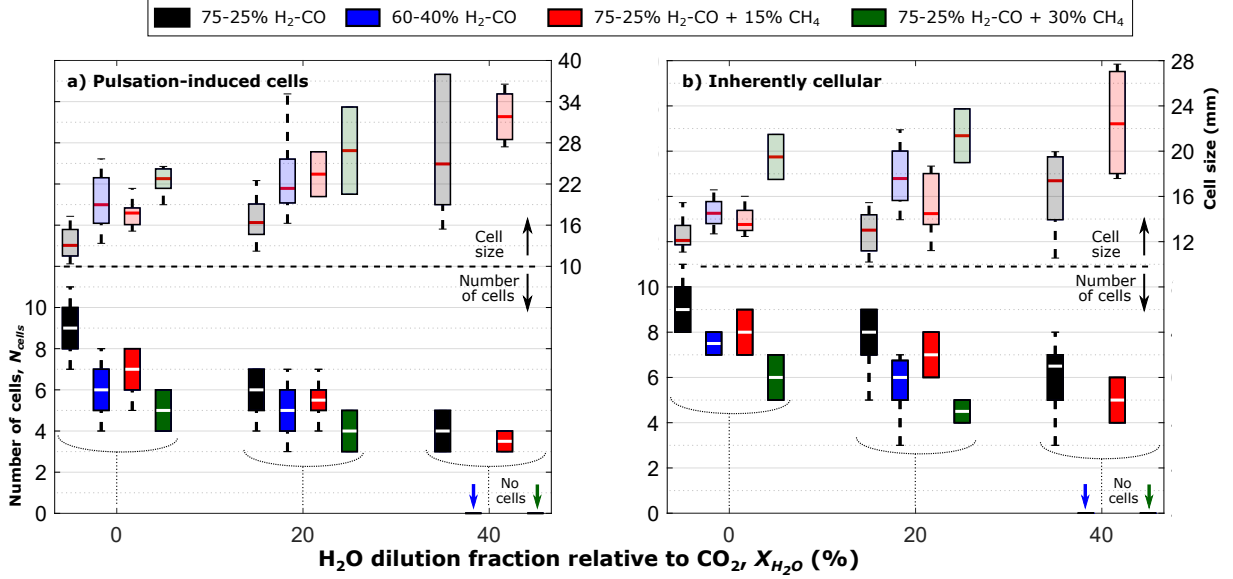


Figure 7.17 Variation in the number and size of cells as a function of the water fraction for a) pulsation-induced cells and b) inherently cellular flames. Box: 25th and 75th percentile, line within the box: median value, and whiskers: minimum and maximum values. Mean mixture strength is 0.59 with 0.18 standard deviation.

In our circular cross-section combustion chamber, the cell spacing (λ_c) is the arc length of a circle that passes through the centroid of each of the outermost cell. Given that it is inversely proportional to the number of cells, λ_c exhibits the opposite behaviour with X_{H_2O} , as also shown in Figure 7.17. Furthermore, in unstrained diffusion flames, the cell size is expected to scale as [123]:

$$\lambda_c \sim 2\pi l_D / \sigma^* \quad (7.3)$$

with $l_D = D_{th}/U$ being the diffusion length, and σ^* the instability wavenumber, which is a fundamental parameter that has been shown to decrease with Le_F in theoretical work σ^* . This is confirmed experimentally after computing the instability wavenumbers of our

inherently cellular flames, as shown in Figure 7.18. The tendency of σ^* to drop with $Le_{F,eff}$ is evident, for all the mixture strengths considered. Given that $Le_{F,eff}$ increases with X_{H_2O} this provides an explanation for the increased cell spacing or reduced number of cells at higher X_{H_2O} .

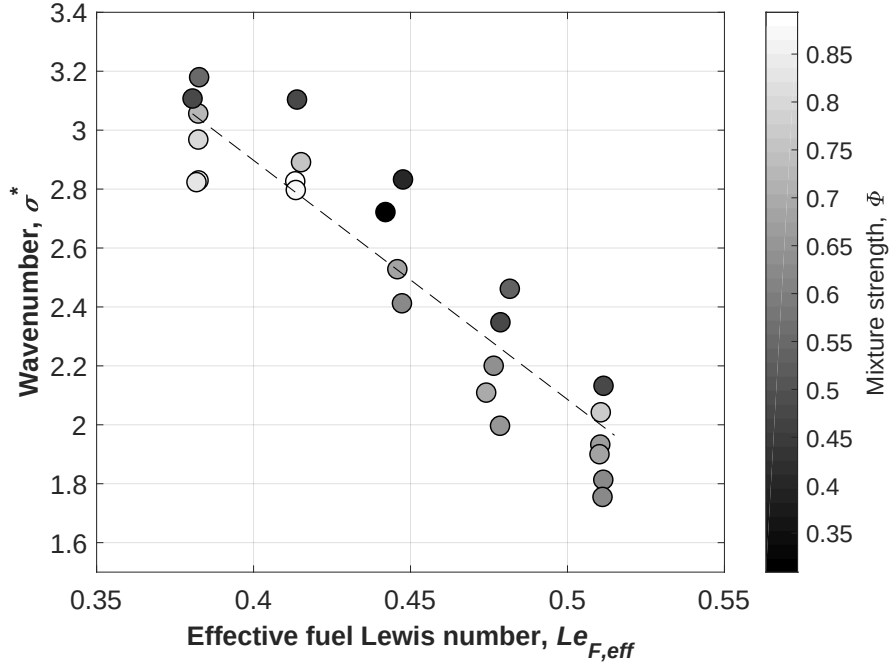


Figure 7.18 Instability wavenumber of inherently cellular flames as a function of the effective fuel Lewis number. The color map shows the mixture strengths of the flames.

Pulsation frequency

Figure 7.19 shows the effect of the water dilution fraction on the frequency (f) of pulsation-induced unstable flames. Both cellular and planar pulsating flames are considered. Unlike the number of cells, the data show that the pulsation frequency increases as H_2O replaces CO_2 . For instance, at 75-25% H_2 - CO with 15% CH_4 , the median frequency increases from 0.91 Hz at $X_{H_2O} = 0\%$, to 1.04 Hz at $X_{H_2O} = 20\%$, and eventually to 1.32 Hz at $X_{H_2O} = 40\%$. This trend is observed for all H_2 - CO - CH_4 fuel blends, across which the frequency is highest for a given X_{H_2O} at the highest CH_4 content. This is consistent with our earlier discussion with single-fuel flames, where CH_4 is shown to pulsate faster than CO .

The non-dimensional frequency is expressed as:

$$\hat{f} = 2\pi f D_{th}/U^2 \quad (7.4)$$

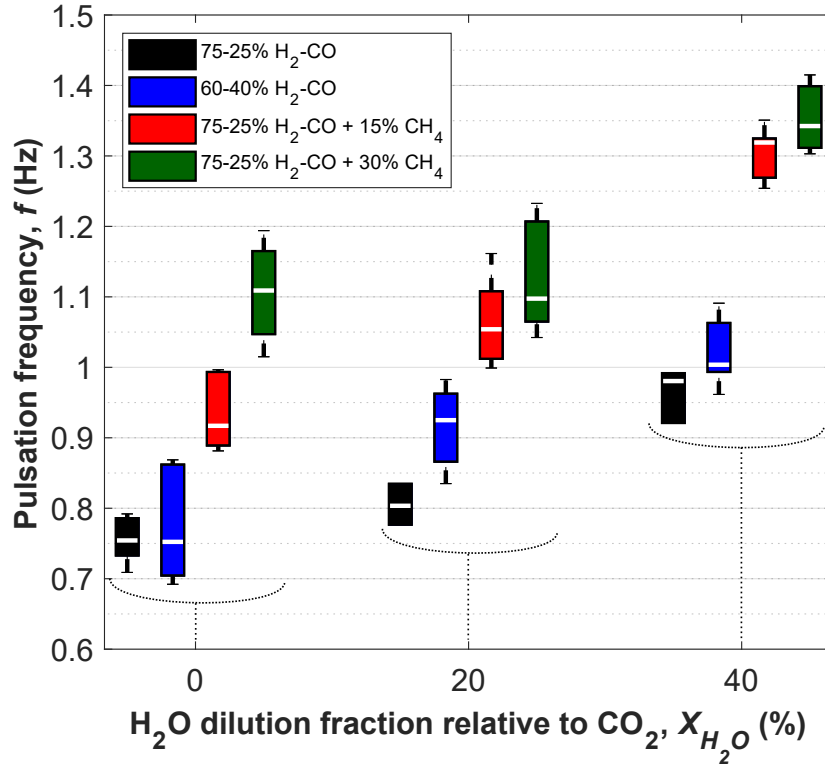


Figure 7.19 Frequency as a function of water fraction in the diluting stream for different pulsation-induced unstable flames. Box: 25th and 75th percentile, line within the box: median value, and whiskers: minimum and maximum values. Mean mixture strength is 0.59 with 0.18 standard deviation.

and theoretical results [127] show that $\hat{f}$ increases with Le_F , and therefore X_{H_2O} , as we confirm in Figure 7.20, where a broad range of mixture strengths is considered. It can be seen that at a given ϕ , the larger the $Le_{F,eff}$, the higher the non-dimensional pulsation frequency. Consistent with theoretical predictions, it can also be seen that the pulsation frequency increases with mixture strength. In fact, the trend appears to be highly linear over a given $Le_{F,eff}$ interval for the conditions tested, as seen from the three fitted lines.

7.4 Conclusion

This paper introduces a new version of the unstrained diffusion flame burner which is used to study the effect of H₂O dilution on diffusive-thermal instabilities in H₂-CO-CH₄ fuels. Obtaining fundamental insight on such complex phenomena is significantly facilitated by the absence of hydrodynamic or buoyancy-driven disturbances, which are parasitic effects omnipresent in common research facilities. The counter-diffusion burner used adopts an

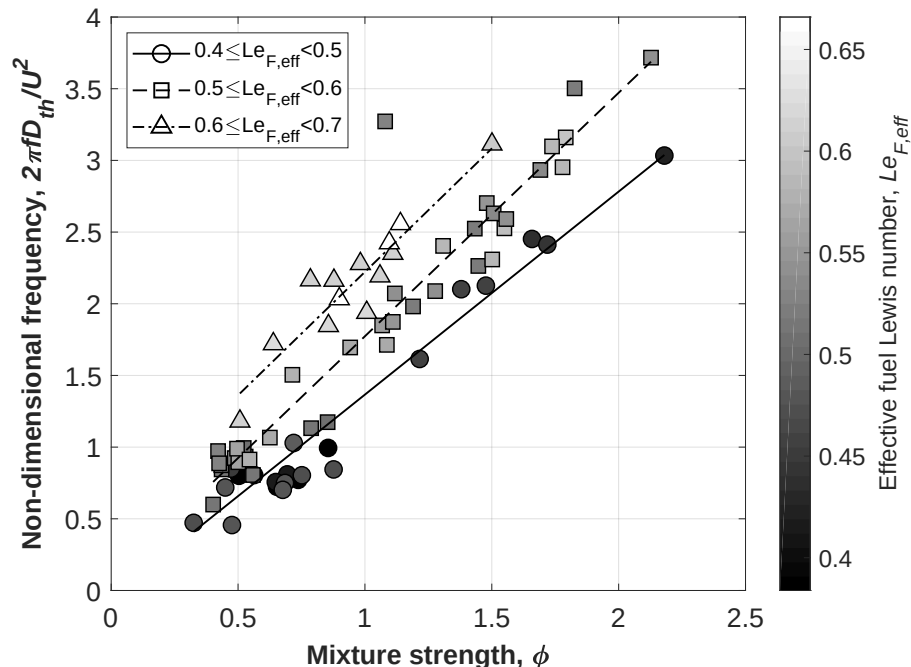


Figure 7.20 Non-dimensional frequency as a function of the mixture strength at different effective fuel Lewis numbers.

evenly heated aluminum perforated injector, to uniformly supply the H_2O -containing fuel mixture into the bottom of the combustion chamber. The one-dimensional nature of the flow in the reaction zone is confirmed by measuring the major species concentration profiles and flame location, which are in excellent agreement with the one-dimensional chambered diffusion flame solution.

Flame stability and extinction limits are provided for a broad range of fuel blends diluted at different H_2O and CO_2 proportions. Burning wet syngas while its still hot has the advantage of enhancing the thermal efficiency of biomass systems as heat losses are reduced. However, results show that as H_2O replaces CO_2 dilution, the low caloric value flame becomes more prone to instabilities and extinction, which must be taken into account in the combustor design.

Beyond marginal stability, the cellular instabilities that onset due to the presence of H_2 are seen to interact and compete with the pulsations from CO and CH_4 , leading to cellular-pulsating flames. These superimposed diffusive-thermal instabilities can be categorized as: 1) pulsations-induced, or 2) inherently cellular. The former onset at relatively large Damköhler numbers, and spatially homogenous pulsations dictate the instability frequency and the in-phase appearance of cells. At sufficiently small Damköhler numbers, the H_2 -containing flame

becomes inherently cellular, and as the pulsations now develop, they rapidly grow out-of-phase in each cell, leading to temporary extinction spots in the disconnected flame sheet. In addition, inherently cellular pulsating flames are minimally damped, and are attribute with a relatively fast frequency which exceeds 3 Hz, compared to the 1-Hz frequency of pulsation-induced instabilities.

Increasing the fraction of H₂O dilution relative to CO₂ is shown to reduce the degree of superimposed cellularity, as the oxidizer and fuel Lewis number increase, rendering the pulsating instabilities planar at sufficiently high water content. The instability types and patterns formed at various fuel compositions are highly dependent on a fuel effective Lewis number, which weighs the three fuel species Lewis numbers by their relative composition in the fuel stream. The fundamental significance of this parameter is confirmed after obtaining the same instability patterns with different fuels whose $Le_{F,eff}$ is rendered equivalent by changing the proportion of H₂O dilution. Consequently, we demonstrate that in syngas mixtures, superimposed cellular-pulsating instabilities form in the vicinity of $0.37 \leq Le_{F,eff} \leq 0.59$. Above this range, planar intensity pulsations devoid of cellular structures onset, and vice versa at low Lewis numbers. The number of cells that form in the unstable flames decreases with water content, and this is attributed to the fundamental instability wavenumber decreasing at higher $Le_{F,eff}$. On the contrary, larger H₂O dilution fractions increase the frequency of pulsations, as the fundamental non-dimensional frequency increases with $Le_{F,eff}$.

The successful realization of a vaporized fuel unstrained diffusion flame burner that is introduced for the first time in this paper paves the way for various interesting research opportunities. Plans are underway to investigate the unstable flame dynamics of liquid biofuels such as methanol, ethanol, and dimethyl ether (DME) in this research facility. Another interesting option would be to study the effect of H₂O dilution on the morphology of soot formation in a one-dimensional flow field which facilitates the comparison with soot models.

Acknowledgements

The authors are grateful for the funders of this work: The Trottier Energy Institute (Trottier scholarship and project grant), the Natural Sciences and Engineering Research Council of Canada (NSERC) through the postgraduate doctoral scholarship (PGSD3 - 546588 – 2020), and discovery grants (RGPIN-03622-2014 and RGPIN-05071-2022), and the Fonds de Recherche du Québec Nature et technologies (FRQNT) through the Doctoral scholarship (B2X).

CHAPTER 8 GENERAL DISCUSSION

8.1 Thermodynamic polygeneration efficiency

In articles 1 and 2 (chapters 4 and 5) of this thesis, the thermodynamic feasibility of the polygeneration of either MeOH or SNG, respectively, along with electricity, heat, and high-purity CO₂ was discussed. For each biofuel, two system designs were proposed that essentially differed in the gasification stage. A simple downdraft gasifier was considered, along with a dual fluidized bed gasifier that produces higher quality syngas, but whose design is more complicated. Experimentally-validated models were used for each component in the systems, and the ASPEN Plus process simulator was used to identify the desirable operating conditions. Hot gas cleaning techniques were adopted for clearing the contaminants from syngas, which reduced the total thermal energy losses from the systems to 15-20%. The cleaned syngas was then enriched with H₂ from a SOEC before being fed into the catalytic biofuel reactors.

The MeOH reactor was operated at a relatively low pressure of 30 bar, compared to the ideal conditions of 60 bar, for safety considerations. Nonetheless, a MeOH production efficiency of 12.2% was obtained. A significant amount of chemical energy was leftover after the MeOH reactor, which exceeded 80% of the initial biomass chemical energy. Recycling part of this gas into the catalytic reactor after separating MeOH should increase the overall yield, however, small-scale systems are known to exhibit diminishing returns as the increased cost associated with a system size that enables such recycling outweighs the enhanced biofuel yield. Consequently, the gaseous product from the MeOH reactor were fed into a SOFC, which produced 33.9% electrical power. Part of this electricity was used to power the compressor, and SOEC, leaving an excess of 16.4%.

The SNG systems on the other hand, had part of the cleaned syngas directly fed to the SOFC as the conversion fraction of the SNG reactor was remarkably high, leaving an insignificant amount of energy leftover. This meant that SNG production came at the expense of electricity generation, whereby the maximum SNG output was 53.9%, while maximum electricity was 28.2%. In addition, the methanation reactor was operated at its ideal pressure of 10 bar, which is conveniently three times lower than that of the MeOH reactor. In both cases, a residual gas burner was used to harness the leftover chemical energy from the SOFCs by generating heat. In addition, both designs were able to provide at least 0.1 kg of CO₂ in a high-purity stream exceeding 90% (molar basis) per kilogram of biomass input. With an overall efficiency that could reach 85%, the thermodynamic feasibility of the polygeneration of MeOH or SNG, along with electricity, heat, and storable CO₂ solely from biomass was

demonstrated.

To put these numbers into perspective, we consider the case where 6350 tons/year of 45 %-moist wood chips are fed to the MeOH-DFB system that is assumed to operate for 8,000 hours/year (average power: 3.1 MW) under a fixed operating mode (case 1, table 4.3). 13,987 MWh of heat would be produced per year, which is equivalent to the annual thermal energy consumed by a typical 20,000 m² tomato greenhouse in Quebec. Out of the 825.5 tons of high-purity CO₂ produced, 380 tons could be used to cover the needs of the greenhouse for enhanced crop growth, with 445.5 tons remaining for sequestration. The latter is equivalent to growing 20,250 trees per year. In addition, a total of 3,743 US barrels of methanol is synthesized, which are sufficient to power five medium-size agricultural tractors operating at an average rate of 30 hp throughout the year. Finally, the surplus 3,977 MWh electricity generated is equivalent to the power consumed by 8,284 light bulbs annually (60W).

8.2 Syngas properties

We leveraged our thermochemical models to predict the relevant leftover syngas compositions and assess the role of the residual gas burner in decentralized polygeneration systems. Figure 8.1 a) presents the properties of the syngas that is burned in the residual gas burner. The data are also given in table 8.1. Twenty representative operating points are taken from the four systems. It can be seen that the chemical energy ($\dot{m}\text{HHV}$)_{syngas} of the leftover syngas contains between 11 to 34% of the initial biomass energy, emphasizing the key role of syngas combustion in these systems. The fuel species are mainly composed of H₂ and CO, with the concentration of CH₄ being less than 1%. In the system designs considered, CH₄ is almost completely reformed in the nickel-based steam fluidized bed reactor that is adopted for tar abatement. Prior to this step, the total CH₄ concentration varied between 6% and 11%, measured relative to the other combustible species. The relative amount of H₂ to CO, which we defined as $X_{H_2,CO}$ in articles 3 and 4, varied between 58 and 81%.

However, and as initially expected, the data of figure 8.1 a) also put into spotlight the significantly high dilution levels in the burned syngas, which promotes diffusive-thermal instabilities. The inert species are essentially composed of H₂O and CO₂, with a total molar fraction varying between 72 and 90%. This meant that the caloric value of the gas to be burned varied between 1.1 and 2.5 MJ/kg only, which is remarkably low when compared to other common fuels such as $LHV_{H_2} = 120$ MJ/kg, $LHV_{CO} = 10.1$ MJ/kg, and $LHV_{CH_4} = 50$ MJ/kg.

The fraction of H₂O relative to CO₂, which we defined as X_{H_2O} in article 4, varied between

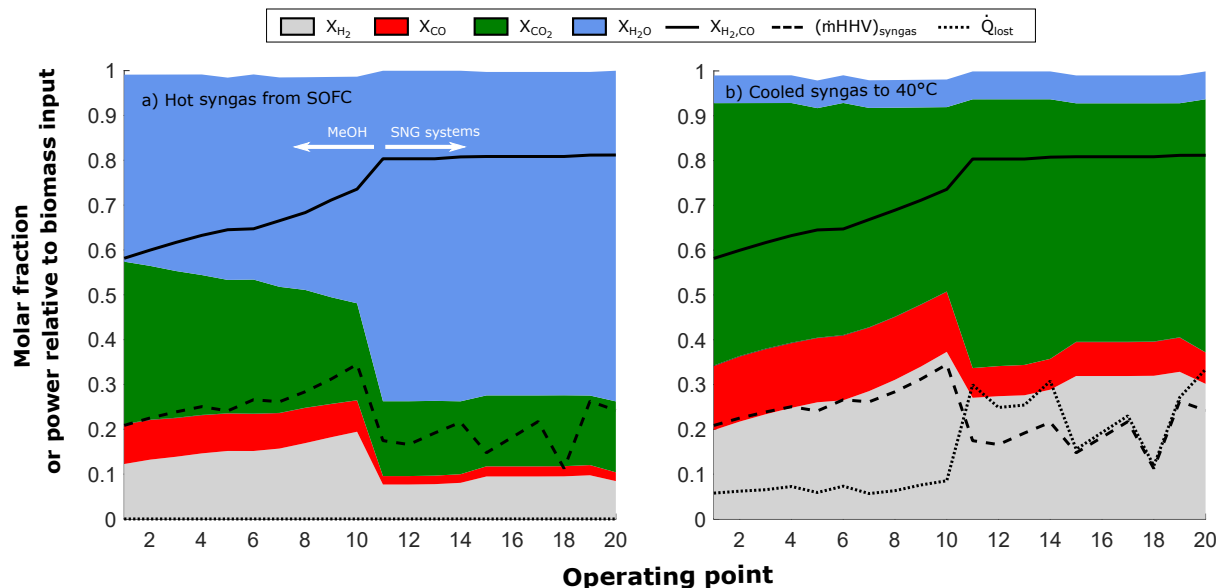


Figure 8.1 The composition of the burned syngas a) as is from the SOFC, and b) after being passed through a 40°C flash separator. Different operating points from the four MeOH and SNG systems are considered.

54 and 82%. One could consider condensing the water from syngas to increase the fuel concentration and hence flame stability, however, this could come at a hefty energy penalty if the released energy is not properly recovered. Figure 8.1 b) presents the properties of the syngas stream after being passed through a flash separator operating at 40°C. A drop in the H_2O concentration can be immediately noticed, causing the dilution levels to decrease to 47 - 66%, and the gas caloric value to increase roughly by three times. However, it can also be seen that the heat released in the condensation process could reach as much as 35% the total biomass energy input. Additional heat exchangers must therefore be incorporated into the system to avoid the deterioration in the process efficiency. In addition, the lower H_2O dilution levels were seen to increase the adiabatic flame temperature by more than 1.5 times, raising concerns over NO_x and soot emission, two interesting subjects for future endeavors.

8.3 Characterization of diffusive-thermal instabilities

In article 3 (chapter 6), the characteristics of the diffusive-thermal instabilities that form in dry-biomass derived syngas were experimentally studied. The mark II version of the unstrained diffusion flame burner was used [130]. We started from a stable flame near the Burke-Schumann limit ($Da \rightarrow \infty$) and gradually increased the dilution level going through the marginal stability state (Da^*) where diffusive-thermal instabilities first onset, and down to

Table 8.1 Properties of the burned syngas as is from the SOFC and (following a 40°C flash separator). Systems notation: I = MeOH-downdraft, II=MeOH-DFB, III=SNG-downdraft, IV=SNG-DFB.

Pt.	Sys.	X_{H_2}	X_{CO}	X_{CO_2}	X_{H_2O}	$X_{H_2,CO}$	X_F	$\dot{m}HHV_{syn}$	$\dot{Q}_{lost}$
1	I	0,12 (0,2)	0,09 (0,14)	0,36 (0,59)	0,42 (0,06)	0,58 (0,58)	0,21 (0,34)	0,21 (0,21)	0 (0,06)
2	I	0,13 (0,22)	0,09 (0,15)	0,34 (0,56)	0,43 (0,06)	0,6 (0,6)	0,22 (0,36)	0,23 (0,23)	0 (0,06)
3	I	0,14 (0,23)	0,09 (0,15)	0,33 (0,55)	0,44 (0,06)	0,62 (0,62)	0,23 (0,38)	0,24 (0,24)	0 (0,07)
4	I	0,15 (0,25)	0,08 (0,14)	0,31 (0,53)	0,45 (0,06)	0,63 (0,63)	0,23 (0,39)	0,25 (0,25)	0 (0,07)
5	I	0,15 (0,26)	0,08 (0,14)	0,3 (0,51)	0,45 (0,06)	0,65 (0,65)	0,24 (0,4)	0,24 (0,24)	0 (0,06)
6	II	0,15 (0,26)	0,08 (0,14)	0,3 (0,52)	0,46 (0,06)	0,65 (0,65)	0,23 (0,41)	0,27 (0,27)	0 (0,07)
7	II	0,16 (0,29)	0,08 (0,14)	0,28 (0,49)	0,47 (0,06)	0,67 (0,67)	0,24 (0,43)	0,26 (0,26)	0 (0,06)
8	II	0,17 (0,31)	0,08 (0,14)	0,26 (0,47)	0,47 (0,06)	0,68 (0,69)	0,25 (0,45)	0,28 (0,28)	0 (0,06)
9	II	0,18 (0,34)	0,07 (0,14)	0,24 (0,44)	0,49 (0,06)	0,71 (0,71)	0,26 (0,48)	0,31 (0,31)	0 (0,08)
10	II	0,19 (0,37)	0,07 (0,13)	0,22 (0,41)	0,51 (0,06)	0,74 (0,74)	0,26 (0,51)	0,34 (0,34)	0 (0,09)
11	III	0,08 (0,27)	0,02 (0,07)	0,17 (0,6)	0,74 (0,06)	0,8 (0,8)	0,1 (0,34)	0,17 (0,17)	0 (0,3)
12	III	0,08 (0,27)	0,02 (0,07)	0,17 (0,6)	0,74 (0,06)	0,8 (0,8)	0,1 (0,34)	0,17 (0,17)	0 (0,25)
13	III	0,08 (0,28)	0,02 (0,07)	0,17 (0,59)	0,74 (0,06)	0,8 (0,8)	0,1 (0,34)	0,19 (0,19)	0 (0,25)
14	III	0,08 (0,29)	0,02 (0,07)	0,16 (0,58)	0,74 (0,06)	0,81 (0,81)	0,1 (0,36)	0,22 (0,22)	0 (0,31)
15	III	0,09 (0,32)	0,02 (0,08)	0,16 (0,53)	0,72 (0,06)	0,81 (0,81)	0,12 (0,4)	0,15 (0,15)	0 (0,16)
16	IV	0,09 (0,32)	0,02 (0,08)	0,16 (0,53)	0,72 (0,06)	0,81 (0,81)	0,12 (0,4)	0,18 (0,18)	0 (0,19)
17	IV	0,09 (0,32)	0,02 (0,08)	0,16 (0,53)	0,72 (0,06)	0,81 (0,81)	0,12 (0,4)	0,22 (0,22)	0 (0,23)
18	IV	0,1 (0,32)	0,02 (0,08)	0,16 (0,53)	0,72 (0,06)	0,81 (0,81)	0,12 (0,4)	0,11 (0,11)	0 (0,12)
19	IV	0,1 (0,33)	0,02 (0,08)	0,16 (0,52)	0,72 (0,06)	0,81 (0,81)	0,12 (0,41)	0,26 (0,26)	0 (0,27)
20	IV	0,08 (0,3)	0,02 (0,07)	0,16 (0,56)	0,74 (0,06)	0,81 (0,81)	0,1 (0,37)	0,24 (0,24)	0 (0,33)

the extinction limit ($D_{a,ext}$). Often favored for lower emissions, the focus was on lean diffusion flames, whereby the boundary O_2 concentration was greater than the stoichiometrically required amount for the given fuel boundary concentration. The physical and thermochemical properties of the unstable flames between $D_a^* \leq D_a \leq D_{a,ext}$ were evaluated. For the former, the cell size, pulsation frequency along with amplitude, and fraction of actively burning flame sheet were measured.

The individual effect of each combustible species was first highlighted by considering single-species fuels. With a small Lewis number ($Le_{H_2} \approx 0.25$), H_2 led to cellular instabilities, with a characteristic cell size that varied between 8.2 and 9.1 mm and that was proportional to the diffusion length of the non-premixed flame. On the other hand, CO with a relatively large Lewis number ($Le_{CO} \approx 0.95$) promoted pulsations in the combustion intensity, which caused the flame sheet to oscillate normal to its surface. The pulsation frequency was approximately 0.8 Hz, and its non-dimensional form was seen to scale with the Damköhler number. CH_4 , which could remain unreformed in syngas, also led to oscillations with a frequency typically around 1.2 Hz.

Subsequently, a total of twelve H_2 -CO- CH_4 fuel blends were considered. $X_{H_2,CO}$ was varied between 30 and 75%, in 15% increments, while the relative amount of CH_4 to the other

fuel species was 0, 15, and 30%. Generally speaking, instabilities started forming in fuel mixtures with CO₂ dilution levels beyond 75%, or LHV below 1.78 MJ/kg. This is clearly within the caloric value range of the leftover syngas from the polygeneration systems, which confirms the need for studying the unstable flame behavior. Given that we are dealing with fuel blends, a fuel effective Lewis number ($Le_{F,eff}$) that weighs the Lewis number of each of the three fuel species with their relative concentration was introduced. At $0.4 \leq Le_{F,eff} \leq 0.6$, no matter the relative amounts of H₂-CO-CH₄, peculiar flame dynamics were observed, whereby superimposed cellular-pulsation instabilities formed as a result of mixing fuel species with distinctive diffusive-thermal properties. These superimposed instabilities could be categorized as: 1) Pulsation-induced, or 2) inherently cellular.

Pulsation-induced instabilities occurred in the vicinity of the marginal stability state, where the CO or CH₄ pulsations controlled the appearance of the H₂-attributed cells. The latter formed at the lowest intensity point of the pulsation cycle, when the vigor of the oscillations was sufficiently high. The maximum attainable pulsation intensities in H₂-containing fuel blends were notably higher than that of H₂-free mixtures. In the latter, vigorous oscillations quickly resulted in extinction, unlike in H₂-rich flames that sustained the combustion process in its lowest intensity point via the formation of cells. The size of the latter scaled linearly with the diffusion length, just as with single-fuel H₂ flames, signalling the temporary extinction of CO/CH₄ or their significant leakage. Beyond the lowest intensity pulsation point, the amplitude of the cells grew in-phase at a CO or CH₄ attributed frequency, which was nonetheless slightly dampened by the presence of H₂, as it no longer scaled with D_a . The flame became planar in the vicinity of the highest intensity point, before the repetition of the pulsation cycle.

The propensity of cellular instabilities to form increased as D_a was decreased at high dilution levels or high flow rates, causing the minimum pulsation amplitude required to induce cells to drop. Eventually, as the lean extinction limit is approached, H₂-rich flames became inherently cellular. Now however, the CO/CH₄ oscillations manifested themselves individually in each cell, leading to out-of-phase pulsations across a fragmented flame sheet. The pulsations in the weakly burning flame were minimally dampened with a frequency that exceeded 3 Hz, and with a growing amplitude that extinguished the cells after just a few oscillations. This led to local extinction spots in the flame, which were subsequently occupied by other cells undergoing earlier phases of the instability cycle.

In article 4 (chapter 7), the effect of water on the unstable flame behaviour was discussed. A new mark III design of the unstrained diffusion flame burner was successfully built and operated with syngas mixtures with high water content. It was shown that the characteristics

of the planar flames generated were in strong agreement with the idealized one-dimensional diffusion flame solution. Water dilution had a clear destabilizing effect on the flame, where replacing CO_2 with H_2O for the same sufficiently low total fuel concentration led to the onset of DTIs. Consequently, H_2O dilution also led to lower extinction limits compared to CO_2 , a behaviour which is in agreement with low-stretch flammability limits from published numerical simulations [141]. We also observed that the higher the H_2 content in the fuel relative to CO , the higher the maximum attainable dilution levels. CH_4 was also seen to significantly improve flammability, as the extinction limit was typically delayed by 4% points when 30% CH_4 was added relative to the other combustible species. While extinction was roughly attained between a total dilution level of 77 and 82% at $U = 11$ mm/s (calorific value $\lesssim 1.38$ MJ/kg) in our quasi-unstretched flames, the effect of stretch in practical burners could significantly increase these limits. As discussed in section 2.3, flammability increases when stretching the flame to a certain rate, beyond of which it begins decreasing as the blowoff limit is approached.

Similar to the dry flames, superimposed cellular-pulsating instabilities were observed in humid syngas mixtures, particularly when $0.4 \leq Le_{F,eff} \leq 0.6$. However, the addition of H_2O reduced, and in some instances suppressed, the cellular character of the superimposed instabilities, given that the Lewis numbers of the reactants increased. For instance, instead of forming pulsation-induced cellular flames at the marginal stability state, a 75-25% H_2 - CO flame exhibited partly cellular pulsation-induced instabilities, and eventually planar intensity pulsations with no cells when $X_{\text{H}_2\text{O}}$ was increased from 0 to 20, and 40%, respectively.

In addition, the number of cells decreased when the water dilution fraction was increased. For instance, when the pulsation-induced cellular flames were considered, the median number of cells was seen to drop from 9 to 6, and eventually to 4, when H_2O was increased from 0 to 20, then 40%, respectively for 75-25% H_2 - CO . In terms of fundamental parameters, the instability wave number (σ^*), which is proportional to the number of cells formed in a given combustion chamber volume, decreased with the Lewis number, which itself was increased at higher water concentrations. The pulsation frequency on the other hand exhibited an opposite behavior. For the 75-25% H_2 - CO blend to which 15% CH_4 was added, the median frequency of oscillations increased from 0.91 Hz at $X_{\text{H}_2\text{O}} = 0\%$, to 1.04 Hz at $X_{\text{H}_2\text{O}} = 20\%$, and eventually to 1.32 Hz at $X_{\text{H}_2\text{O}} = 40\%$. Consistent with theoretical predictions, this behaviour is attributed to an increase in the non-dimensional pulsation frequency with the Lewis number.

8.4 General impact

The modelling of new polygeneration processes conducted in this work showed for the first time that it is thermodynamically feasible to simultaneously produce biofuel, electricity, heat, along with a storable CO_2 stream solely from biomass in small-scale decentralized systems. The promising results obtained serve as a stepping stone towards the commercialization of a decentralized biomass conversion technology that could empower farmers and significantly reduce the carbon footprint of the agricultural sector. One of the key components in the proposed systems was the reversible solid oxide cell, which produced electricity in an environmentally-friendly manner, and which electrolyzed steam to H_2 and O_2 when supplied with part of the generated electricity. Our work therefore further motivates the ongoing research that aims to reduce the cost and enhance the robustness of RSOCs, which could replace mature single-purpose components such as air separation units, heat engines, and electrolyzers in many applications. Similarly, adopting hot gas cleaning techniques was key in minimizing the thermal energy losses and complexity of the system, which encourages ongoing research on the development of affordable and robust catalysts, particularly for tar abatement.

We also highlighted the important role of syngas combustion in the overall energy landscape of biorefineries, especially small-scale systems. Due to the significantly high concentration of inert species, diffusive-thermal instabilities were experimentally characterized using an unstrained diffusion flame burner under negligible hydrodynamic disturbances. To the author's knowledge, this represented the first formal investigation of ultra low-stretch multi-fuel flames, which allowed the observation of peculiar flame dynamics. We showed that in mixtures of fuel species with distinct diffusive-thermal properties, superimposed cellular-pulsation instabilities may arise. Systematic experiments were conducted which revealed the underlying instability mechanisms. The published dataset could also serve as a guide and validate future multi-fuel flame stability models. Our data could also be useful for studies of turbulent partially premixed flames which are dominated by diffusion processes, and which could be represented by an ensemble of laminar diffusion flamelets with a one-dimensional inner structure [208]. Finally, the successful realization of an unstrained diffusion flame burner that can be operated with fuels containing high vapor content opens doors for future research with interesting biofuels such as methanol, ethanol, and DME.

CHAPTER 9 CONCLUSION AND RECOMMENDATIONS

9.1 Summary

This thesis addressed two aspects related to decentralized biomass polygeneration systems: 1) Thermodynamic modelling of new system designs, and 2) experimental characterization of the combustion instabilities of syngas. In particular, we consider a process whereby biomass is simultaneously converted to biofuel, electricity, heat, and high-purity CO_2 . These products are highly demanded specifically in agricultural greenhouses, which are surrounded by abundant residual biomass. Given that biomass systems producing the aforementioned four products are rarely discussed, the first objective was to analyze the thermodynamic feasibility of the process. The production of either methanol or synthetic natural gas biofuel among the other three products was considered. Two systems were designed for each biofuel, which essentially differed in the gasification stage. A simple downdraft gasification approach was considered, along with dual-fluidized bed gasification, which conveniently produces syngas with higher H_2 content, but which is more complicated to operate.

The main difference between the MeOH and SNG systems is that in the former, syngas was first passed through the MeOH reactor, and then through an SOFC. However, due to a significantly higher conversion fraction to biofuel, part of the syngas in the SNG systems was fed directly to the fuel cell. Both systems adopted a residual gas burner to harness the leftover syngas chemical energy from the SOFC. Simulations revealed that the total process efficiency could reach 85%. Inherent to polygeneration processes, the system designs allowed the output product mix to be widely varied, and therefore accommodate changes in energy demand. For instance, the SNG-DFB system could produce a maximum of 63.1% of SNG and 24% heat when desired, at the expense of electricity and CO_2 . The same system could also generate a maximum of 28.2% electricity and 49.6% of heat at the expense of the other products.

The chemical energy of the leftover syngas that is fed to the residual gas burner represented as much as 35% of the initial biomass energy. Hence, due to its key role, the combustion characteristics of biomass-derived syngas were then studied. We particularly focused on diffusive-thermal instabilities that are likely to onset in the flame due to the high concentrations of CO_2 and H_2O inert species in the leftover syngas, which reached 90% by volume. Despite the existence of several studies exploring the underlying mechanisms of DTIs in single-fuel species, the behaviour of multi-fuel mixtures such as syngas was unknown. The one-dimensional unstrained diffusion flame burner provides ideal conditions for fundamen-

tal studies on DTIs in the absence of hydrodynamic disturbances. However, even the most advanced version of the burner could not accommodate gaseous fuels with high water content, such as biomass-derived syngas. Consequently, for the second objective of this thesis, a new version of the 1D burner was built and successfully operated with humid fuels. The planar flames produced were in agreement with the idealized one-dimensional diffusion flame solution.

The capabilities of the new burner design were then exploited in the third objective of this work to study the unstable flame behaviour of a broad range of $\text{H}_2\text{-CO-CH}_4$ fuel blends diluted with CO_2 and H_2O . Flame stability and extinction limits were provided, where higher H_2 content relative to CO required higher dilution levels for the onset of instabilities, while replacing CO_2 with H_2O had an opposite destabilizing effect. We introduced a fuel mixture effective Lewis number, which weighs the Lewis number of each combustible species with its relative concentration. Superimposed cellular-pulsating instabilities were observed at $0.4 \leq Le_{F,eff} \leq 0.6$, with Le_o varying between 0.85 and 1.0. The superimposed instabilities were pulsation-induced near the vicinity of the marginal stability state, and transitioned to become inherently cellular near the lean extinction limit.

The cellular character of these superimposed instabilities was reduced as $Le_{F,eff}$ was increased. This happened when the CO and CH_4 content increased relative to H_2 , or when the H_2O replaced CO_2 as inert species. The number of cells dropped at higher $Le_{F,eff}$, while the pulsation frequency increased. The same behaviour was observed when the mixture strength was increased. The degree of cellularity increased as the Damköhler number was reduced, which led the minimum pulsation intensity required to render the flame cellular to drop with Da . The published data from our work represent the first formal investigation of quasi-unstrained diffusion flames of multi-fuel mixtures in the literature.

9.2 Limitations and recommendations for future work

9.2.1 Biomass polygeneration systems

The four polygeneration systems proposed in this work were analyzed only from a thermodynamic point of view. Despite the favorable output, and although multi-purpose components such as RSOCs and DFB gasifiers were adopted, the economic viability of our design choices remains to be rigorously assessed. Ongoing efforts [209,210] in our group are aimed at coupling techno-economic analysis with transient systems simulations, in an optimization process to size the systems based on temporal energy demand profiles of agricultural greenhouses. Daily and seasonal energy storage medium could also be incorporated to reduce the initial

and operating costs.

Such studies would also help decide which of the four system designs, that either differ in the biofuel produced or gasification approach, is the most suitable for agricultural greenhouses. Certain trade-offs with respect to our initial designs could be made, where for instance, the enhanced overall efficiency may not be worth the extra costs of heat exchangers used to recover the excess heat from all the exothermic components of the systems. Moreover, the performances of the proposed systems were only evaluated using wood chips, leaving room for future research to investigate other types of feedstock such as wheat straw and corn stover, among other common agricultural waste.

Following techno-economic optimization, experimental testing of the system components, particularly the catalytic reactors, must be performed to ensure a reliable performance. One of the major issues faced is catalyst deactivation by fouling due to coke deposition. Coke is a major side-product of tar decomposition reactions [211], and its definition is generally broad, encompassing a wide range of polymerized hydrocarbon/carbon molecules with large and variable molecular weights [212]. When its deposition rate is greater than its gasification, which may happen when the tar content in syngas is excessively high, coke can: 1) block the paths of the reactants towards the active sites by adsorbing into the catalyst surface, or by plugging the pores, 2) coke can also completely deactivate the catalyst crystallite by fully encapsulating it, and 3) in extreme cases, coke can also build up in pores and stress the carrier material leading to its fracture and the disintegration of the catalyst.

To reduce their concentration in syngas to safe levels, tar-decomposing catalysts can be used. Nickel is the most used transition metal-based catalyst owing to its high tar conversion, ability to reform methane, and enhancement of the syngas energy content. However, nickel itself is also prone to coking, which if not mitigated, would induce hefty expenses to replace the costly nickel-based catalysts. In the systems proposed, the propensity of coking is reduced by adding steam, such that the steam-to-carbon ratio in syngas is three. This was based on experimental data from the literature where the coking resistance of nickel-based catalysts was tested by subjecting it to synthetic tar. The duration of such experiments is usually a couple of hours only [213,214], and significantly longer tests must be conducted to ensure the reliability of the tar abatement reactor under a wide variety of operating conditions. In addition, other cheaper catalysts such as dolomite, olivine, or biochar could be investigated, and used in hybrid configurations with reactive metal catalysts. Li et al. [215] patented a gasification system relying on less expensive char-supported iron catalysts for tar abatement, with a remarkable anti-coking potential. The char support allowed new active sites to be generated on the iron surface, while the deposited coke got slowly gasified to free other active

sites [216].

9.2.2 Diffusive-thermal instabilities

The physical characteristics of diffusive-thermal instabilities in syngas flames were evaluated using two digital still cameras. One camera was placed perpendicular to the axis of the burner to capture the pulsations, while the other camera was fixed at a 30° upward oblique angle for the cellular instabilities. Given the line-of-sight integrated nature of the resulting images, there was some uncertainty in measuring excessively cellular pulsating flames. The spatially inhomogeneous instabilities led to local out-of-phase extinction and regeneration of cells throughout the flame, which induced variability in the line-of-sight integrated chemiluminescence signal used for measuring the pulsation frequency or cell size. For higher accuracy, OH-planar laser-induced fluorescence (OH-PLIF) can be used, where a laser sheet is tuned to excite the OH molecules which fluoresce during their return to their lower energy states. The OH-specific fluorescence signal is collected by an intensified camera fitted with a bandpass filter, where a spatially resolved 2D image of the flame front is generated from which the cell size and pulsation frequency along with amplitude can be accurately measured.

The laser can also be tuned to excite CH molecules, whose disappearance has been directly correlated with extinction [217]. Consequently, CH-PLIF can be used to assess the combustion efficiency and reactants leakage in flames with superimposed instabilities. These effects could not be assessed in the current work using the mass spectrometer as the pulsation frequency was faster than the sample rate of the instrument. PLIF can also be adopted for measuring emissions, particularly NO_x [218], whose relevance increases if water was condensed from the leftover syngas yielding higher flame temperatures. The formation of soot also becomes a concern, the morphology of which was recently studied in the mark II version of the 1D burner [219], without the added complexities from the strong coupling between fluid mechanics and chemistry present in common research burners. Useful data for soot formation models were generated using $\text{CH}_4 - \text{CO}_2$ flames, which could be complemented in future works by incorporating the effect of H_2O dilution using the mark III 1D burner introduced in this thesis. For illustration, figure 9.1 shows the reduction in soot formation upon replacing 40% CO_2 dilution with H_2O .

The unstrained diffusion flame burner used in this thesis helped understand the underlying mechanisms of the superimposed instabilities in syngas mixtures. Our findings could be complemented by following a similar approach with alternative promising biofuels such as NH_3 that is often blended with H_2 , CH_4 , and DME [220]. Inert species besides CO_2 and H_2O could be used for a wide Lewis number range. For instance, replacing CO_2 with a

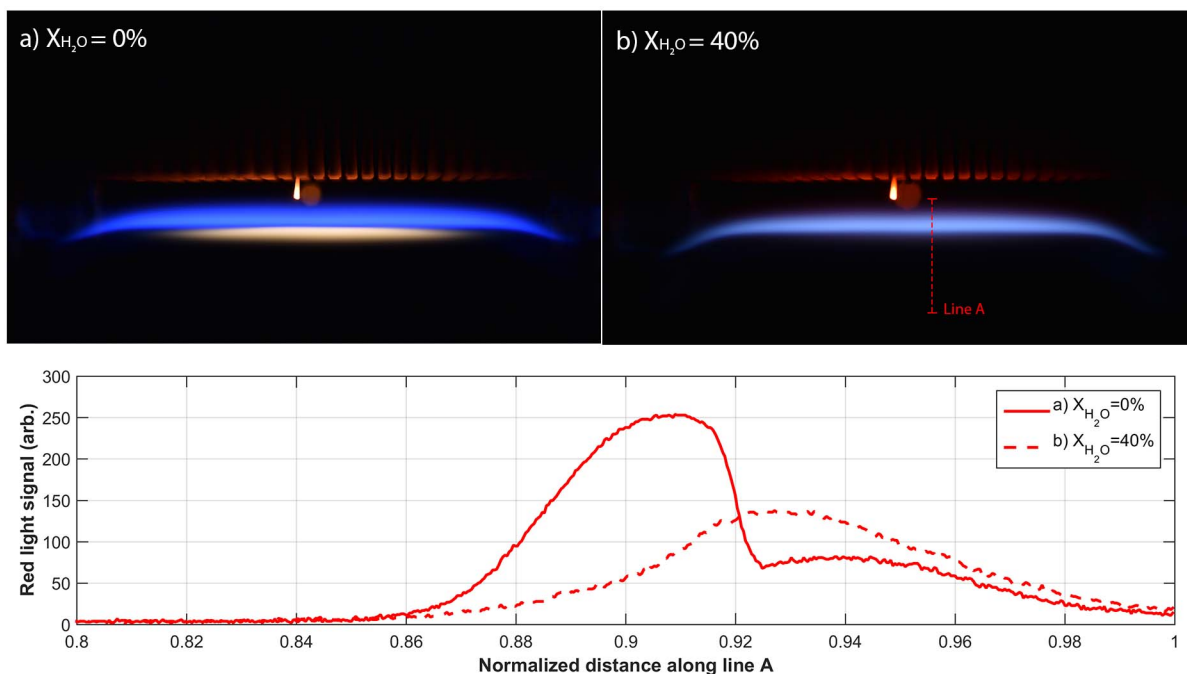


Figure 9.1 Effect of H_2O dilution on soot formation in CH_4 flames with $\phi \approx 2.6$

light inert gas such as helium has been shown to increase the pulsation frequency of CH_4 flames approximately from 1 to 7 Hz [131]. The ability of superimposed cells to form under such short time periods would be an interesting phenomenon to investigate. In addition, the effect of flame stretch on the peculiar superimposed instability modes was not discussed in this work. Future research could also build on our findings by investigating the unstable flame behaviour and extinction limits of stretched syngas flames using counterflow burners where the strain could be systemically varied.

REFERENCES

- [1] H. M. Morgan *et al.*, “A review of catalytic microwave pyrolysis of lignocellulosic biomass for value-added fuel and chemicals,” *Bioresource Technology*, vol. 230, pp. 112–121, 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0960852417300962>
- [2] “Renewable energy explained,” U.S. Energy Information Administration, 2023. [Online]. Available: <https://www.eia.gov/energyexplained/renewable-sources/>
- [3] E. Union, “Directive on the promotion of the use of energy from renewable sources,” 2009. [Online]. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:en0009>
- [4] C.-H. Zhou *et al.*, “Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels,” *Chem. Soc. Rev.*, vol. 40, pp. 5588–5617, 2011. [Online]. Available: <http://dx.doi.org/10.1039/C1CS15124J>
- [5] WSP and Deloitte, “Renewable natural gas production in québec: A key driver in the energy transition assessment of technical and economic potential in québec (2018–2030),” 2018.
- [6] “Overview of canada’s forest industry,” Natural Resources Canada, 2022. [Online]. Available: <https://natural-resources.canada.ca/our-natural-resources/forests/industry-and-trade/overview-canadas-forest-industry/13311>
- [7] “The state of canada’s forests by natural resources canada,” Tech. Rep., 2022. [Online]. Available: <https://natural-resources.canada.ca/our-natural-resources/forests/state-canadas-forests-report/how-much-forest-does-canada-have/17601>
- [8] I. L. Motta *et al.*, “Biomass gasification in fluidized beds: A review of biomass moisture content and operating pressure effects,” *Renewable and Sustainable Energy Reviews*, vol. 94, pp. 998–1023, Oct 2018.
- [9] R. Deshmukh *et al.*, “Thermal gasification or direct combustion? Comparison of advanced cogeneration systems in the sugarcane industry,” *Biomass and Bioenergy*, vol. 55, pp. 163–174, 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0961953413000482>

- [10] Z. Liu *et al.*, “Circulating fluidized bed gasification of biomass for flexible end-use of syngas: a micro and nano scale study for production of bio-methanol,” *Journal of Cleaner Production*, vol. 129, pp. 249–255, Aug 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0959652616303444>
- [11] V. S. Sikarwar *et al.*, “Progress in biofuel production from gasification,” *Progress in Energy and Combustion Science*, vol. 61, pp. 189–248, Jul 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S036012851630106X>
- [12] A. Molino, S. Chianese, and D. Musmarra, “Biomass gasification technology: The state of the art overview,” *Journal of Energy Chemistry*, vol. 25, no. 1, pp. 10–25, Jan 2016.
- [13] I. Wender, “Reactions of synthesis gas,” *Fuel Processing Technology*, vol. 48, no. 3, pp. 189–297, 1996, reactions of synthesis gas. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S037838209601048X>
- [14] T. A. Adams and J. H. Ghouse, “Polygeneration of fuels and chemicals,” *Current Opinion in Chemical Engineering*, vol. 10, pp. 87–93, Nov 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S2211339815000623?via{%}3Dihub>
- [15] S. C. Davis and R. G. Boundy, “Transportation energy data book: Edition 39,” Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), Tech. Rep., 2021.
- [16] S. van Dyken, B. H. Bakken, and H. I. Skjelbred, “Linear mixed-integer models for biomass supply chains with transport, storage and processing,” *Energy*, vol. 35, no. 3, pp. 1338–1350, Mar 2010. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544209005064>
- [17] S. Heidenreich and P. U. Foscolo, “New concepts in biomass gasification,” *Progress in Energy and Combustion Science*, vol. 46, pp. 72–95, Feb 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360128514000495>
- [18] L. R. Clausen, N. Houbak, and B. Elmegaard, “Technoeconomic analysis of a methanol plant based on gasification of biomass and electrolysis of water,” *Energy*, vol. 35, no. 5, pp. 2338–2347, May 2010. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544210000976?via{%}3Dihub>
- [19] “How much electricity does an american home use?” U.S. Energy Information Administration. [Online]. Available: <https://www.eia.gov/tools/faqs/faq.php?id=97&t=3>

- [20] M. S. Ahamed, H. Guo, and K. Tanino, “Energy saving techniques for reducing the heating cost of conventional greenhouses,” *Biosystems Engineering*, vol. 178, pp. 9–33, Feb 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1537511018303957>
- [21] C. K. Law, *Combustion Physics*. Cambridge: Cambridge University Press, 2006.
- [22] G. I. Sivashinsky, J. M. T. Thompson, and P. Gray, “On the intrinsic dynamics of premixed flames,” *Philosophical Transactions of the Royal Society of London. Series A: Physical and Engineering Sciences*, vol. 332, no. 1624, pp. 135–148, Jul 1990. [Online]. Available: <https://royalsocietypublishing.org/doi/abs/10.1098/rsta.1990.0105>
- [23] M. Fűri, P. Papas, and P. A. Monkewitz, “Non-premixed jet flame pulsations near extinction,” *Proceedings of the Combustion Institute*, vol. 28, no. 1, pp. 831–838, Jan 2000.
- [24] “Energy Fact Book 2018-2019,” Natural Resources Canada, Tech. Rep., 2019.
- [25] P. Haro *et al.*, “Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment,” *Applied Energy*, vol. 102, pp. 950–961, Feb 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261912006927>
- [26] J. Meerman *et al.*, “Performance of simulated flexible integrated gasification polygeneration facilities, part b: Economic evaluation.” *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 6083–6102, Oct 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032112004236>
- [27] “Waste2grids.” [Online]. Available: <https://www.waste2grids-project.net/project-2/>
- [28] M. Puig-Arnavat, J. C. Bruno, and A. Coronas, “Review and analysis of biomass gasification models,” pp. 2841–2851, 2010.
- [29] X. Li *et al.*, “Equilibrium modeling of gasification: a free energy minimization approach and its application to a circulating fluidized bed coal gasifier,” *Fuel*, vol. 80, no. 2, pp. 195–207, Jan 2001. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236100000740>
- [30] S. Safarian, R. Unnþórsson, and C. Richter, “A review of biomass gasification modelling,” *Renewable and Sustainable Energy Reviews*, vol. 110, pp. 378–391, Aug 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032119303090>

- [31] T. Gröbl, H. Walter, and M. Haider, “Biomass steam gasification for production of SNG – Process design and sensitivity analysis,” *Applied Energy*, vol. 97, pp. 451–461, Sep 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S030626191200044X>
- [32] A. Tremel, M. Gaderer, and H. Spliethoff, “Small-scale production of synthetic natural gas by allothermal biomass gasification,” *International Journal of Energy Research*, vol. 37, no. 11, pp. 1318–1330, May 2013. [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/er.2933>
- [33] J. R. Centre *et al.*, “Well-to-wheels analysis of future automotive fuels and powertrains in the european context,” Tech. Rep., Apr 2014.
- [34] H. Er-rbib and C. Bouallou, “Modeling and simulation of CO methanation process for renewable electricity storage,” *Energy*, vol. 75, pp. 81–88, Oct 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544214009001>
- [35] S. Rönsch *et al.*, “Review on methanation – from fundamentals to current projects,” *Fuel*, vol. 166, pp. 276–296, Feb 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236115011254>
- [36] S. Wirth and J. Markard, “Context matters: How existing sectors and competing technologies affect the prospects of the Swiss Bio-SNG innovation system,” *Technological Forecasting and Social Change*, vol. 78, no. 4, pp. 635–649, May 2011. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0040162511000047>
- [37] S. Rönsch and M. Kaltschmitt, “Bio-SNG production-concepts and their assessment,” *Biomass Conversion and Biorefinery*, vol. 2, no. 4, pp. 285–296, May 2012. [Online]. Available: <https://link.springer.com/content/pdf/10.1007%7B%7D2Fs13399-012-0048-0.pdf>
- [38] S. Heyne, H. Thunman, and S. Harvey, “Extending existing combined heat and power plants for synthetic natural gas production,” *International Journal of Energy Research*, vol. 36, no. 5, pp. 670–681, Apr 2012.
- [39] M. Gassner and F. Maréchal, “Thermo-economic optimisation of the integration of electrolysis in synthetic natural gas production from wood,” *Energy*, vol. 33, no. 2, pp. 189–198, Feb 2008. [Online]. Available: <https://linkinghub.elsevier.com/retrieve/pii/S0360544207001764>

- [40] M. Gassner and F. Maréchal, “Thermo-economic process model for thermochemical production of synthetic natural gas (sng) from lignocellulosic biomass,” *Biomass and Bioenergy*, vol. 33, no. 11, pp. 1587–1604, 2009. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0961953409001639>
- [41] M. Gassner and F. Maréchal, “Thermo-economic optimisation of the polygeneration of synthetic natural gas (SNG), power and heat from lignocellulosic biomass by gasification and methanation,” *Energy & Environmental Science*, vol. 5, no. 2, pp. 5768–5789, Jan 2012. [Online]. Available: <https://pubs.rsc.org/en/content/articlehtml/2012/ee/c1ee02867g>
<https://pubs.rsc.org/en/content/articlelanding/2012/ee/c1ee02867g>
- [42] M. Minutillo, A. Perna, and E. Jannelli, “SOFC and MCFC system level modeling for hybrid plants performance prediction,” *International Journal of Hydrogen Energy*, vol. 39, no. 36, pp. 21 688–21 699, Dec 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S036031991402641X>
- [43] R. O’hayre *et al.*, *Fuel cell fundamentals*. John Wiley & Sons, 2016.
- [44] M. Minutillo *et al.*, “Coupling of Biomass Gasification and SOFC – Gas Turbine Hybrid System for Small Scale Cogeneration Applications,” *Energy Procedia*, vol. 105, pp. 730–737, May 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610217304241>
- [45] M. Wegener *et al.*, “Biomass-fired combined cooling, heating and power for small scale applications – A review,” *Renewable and Sustainable Energy Reviews*, vol. 96, pp. 392–410, Nov 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032118305525>
- [46] R. Ø. Gadsbøll *et al.*, “Solid oxide fuel cell stack coupled with an oxygen-blown TwoStage gasifier using minimal gas cleaning,” *Renewable Energy*, vol. 139, pp. 1255–1262, Aug 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S096014811930343X>
- [47] P. Fragiaco, O. Corigliano, and G. De Lorenzo, “Design of an SOFC/SOE experimental station: planning of simulation tests,” *Energy Procedia*, vol. 148, pp. 535–542, Aug 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610218304326>
- [48] M. Skrzypkiewicz, M. Wierzbicki, and M. Stpień, “Solid Oxide Fuel Cells coupled with a biomass gasification unit,” *E3S Web of Conferences*, vol. 10, pp. 1–5, 2016.

- [49] A. Baldinelli *et al.*, “Biomass integrated gasifier-fuel cells: Experimental investigation on wood syngas tars impact on NiYSZ-anode Solid Oxide Fuel Cells,” *Energy Conversion and Management*, vol. 128, pp. 361–370, Nov 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S019689041630838X>
- [50] L. Hu, G. Lindbergh, and C. Lagergren, “Performance and durability of the molten carbonate electrolysis cell and the reversible molten carbonate fuel cell,” *The Journal of Physical Chemistry C*, vol. 120, no. 25, pp. 13 427–13 433, Jun 2016. [Online]. Available: <https://doi.org/10.1021/acs.jpcc.6b04417>
- [51] M. Hauck, S. Herrmann, and H. Spliethoff, “Simulation of a reversible SOFC with Aspen Plus,” *International Journal of Hydrogen Energy*, vol. 42, no. 15, pp. 10 329–10 340, Apr 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319917303579>
- [52] C. Bao *et al.*, “Macroscopic modeling of solid oxide fuel cell (SOFC) and model-based control of SOFC and gas turbine hybrid system,” *Progress in Energy and Combustion Science*, vol. 66, pp. 83–140, May 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360128517300394>
- [53] H. Zhang *et al.*, “Solid-oxide electrolyzer coupled biomass-to-methanol systems,” *Energy Procedia*, vol. 158, pp. 4548–4553, Feb 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610219307933>
- [54] H. Æ. Sigurjonsson and L. R. Clausen, “Solution for the future smart energy system: A polygeneration plant based on reversible solid oxide cells and biomass gasification producing either electrofuel or power,” *Applied Energy*, vol. 216, pp. 323–337, Apr 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261918302551>
- [55] L. R. Clausen, “Energy efficient thermochemical conversion of very wet biomass to biofuels by integration of steam drying, steam electrolysis and gasification,” *Energy*, vol. 125, pp. 327–336, Apr 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544217303158>
- [56] G. Bozzano and F. Manenti, “Efficient methanol synthesis: Perspectives, technologies and optimization strategies,” *Progress in Energy and Combustion Science*, vol. 56, pp. 71–105, Sep 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360128515300484>

- [57] N. S. Shamsul *et al.*, “An overview on the production of bio-methanol as potential renewable energy,” *Renewable and Sustainable Energy Reviews*, vol. 33, pp. 578–588, May 2014. [Online]. Available: <http://dx.doi.org/10.1016/j.rser.2014.02.024>
- [58] L. Carvalho *et al.*, “Techno-economic assessment of catalytic gasification of biomass powders for methanol production,” *Bioresource Technology*, vol. 237, pp. 167–177, Aug 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0960852417301268>
- [59] J.-P. Lange, “Methanol synthesis: a short review of technology improvements,” *Catalysis Today*, vol. 64, no. 1-2, pp. 3–8, Jan 2001. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0920586100005034?via%3Dihub>
- [60] L. R. Clausen *et al.*, “Thermodynamic analysis of small-scale dimethyl ether (DME) and methanol plants based on the efficient two-stage gasifier,” *Energy*, vol. 36, no. 10, pp. 5805–5814, Oct 2011. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544211005871>
- [61] L. R. Clausen, “Maximizing biofuel production in a thermochemical biorefinery by adding electrolytic hydrogen and by integrating torrefaction with entrained flow gasification,” *Energy*, vol. 85, pp. 94–104, Jun 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544215003989?via%3Dihub>
- [62] G. Butera *et al.*, “Biomass Conversion to Methanol Integrating Solid Oxide Cells and Two-Stage Gasifier: Effects of Carbon Dioxide Recirculation and Pressurized Operation,” *Chemical Engineering Transactions*, vol. 76, pp. 1177–1182, 2019. [Online]. Available: <https://doi.org/10.3303/CET1976197>
- [63] EPA, “Global Greenhouse Gas Emissions Data,” 2023. [Online]. Available: <https://www.epa.gov/ghgemissions/global-greenhouse-gas-emissions-data>
- [64] H. A. Belhaj, “Chapter 9 - energy transition impact on unconventional reservoirs: Carbon capture and sequestration,” in *Tight Oil Reservoirs*, ser. Unconventional Reservoir Engineering Series, H. A. Belhaj, Ed. Gulf Professional Publishing, 2023, vol. 1, pp. 277–314. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/B9780128202692000044>
- [65] D. Y. Leung, G. Caramanna, and M. M. Maroto-Valer, “An overview of current status of carbon dioxide capture and storage technologies,” *Renewable and Sustainable*

- Energy Reviews*, vol. 39, pp. 426–443, Nov 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032114005450?via=I3Dihub>
- [66] Y. Li *et al.*, “Automatic carbon dioxide enrichment strategies in the greenhouse: A review,” *Biosystems Engineering*, vol. 171, pp. 101–119, Jul 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1537511017308796>
- [67] L.-M. Dion *et al.*, “Biomass Gasification and Syngas Combustion for Greenhouse CO₂ Enrichment,” *BioResources*, vol. 8, no. 2, pp. 1520–1538, 2013.
- [68] C. Chao *et al.*, “Post-combustion carbon capture,” *Renewable and Sustainable Energy Reviews*, vol. 138, p. 110490, Mar 2021. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032120307760>
- [69] K. W. Bandilla, “31 - carbon capture and storage,” in *Future Energy (Third Edition)*, third edition ed., T. M. Letcher, Ed. Elsevier, 2020, pp. 669–692. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/B9780081028865000311>
- [70] J. Godin *et al.*, “Advances in recovery and utilization of carbon dioxide: A brief review,” *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, p. 105644, Aug 2021. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S2213343721006217>
- [71] A. A. Olajire, “Co₂ capture and separation technologies for end-of-pipe applications – a review,” *Energy*, vol. 35, no. 6, pp. 2610–2628, Jun 2010, 7th International Conference on Sustainable Energy Technologies. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544210000848>
- [72] H. Lin *et al.*, “Techno-economic evaluation of coal-based polygeneration systems of synthetic fuel and power with co₂ recovery,” *Energy Conversion and Management*, vol. 52, no. 1, pp. 274–283, Jan 2011. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S019689041000289X>
- [73] S. Li *et al.*, “Exergy analysis and the energy saving mechanism for coal to synthetic/substitute natural gas and power cogeneration system without and with co₂ capture,” *Applied Energy*, vol. 130, pp. 552–561, Oct 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261914002670>
- [74] K. Mattes, “Texas clean energy project: Topical report, phase 1-february 2010-december 2012,” Summit Texas Clean Energy, Llc, Tech. Rep., 2012.

- [75] R. López *et al.*, “Techno-economic analysis of a 15mw corn-rape oxy-combustion power plant,” *Fuel Processing Technology*, vol. 142, pp. 296–304, Feb 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378382015302071>
- [76] S. Yadav and S. Mondal, “A review on the progress and prospects of oxy-fuel carbon capture and sequestration (ccs) technology,” *Fuel*, vol. 308, p. 122057, Jan 2022. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236121019335>
- [77] S. Abuelgasim, W. Wang, and A. Abdalazeez, “A brief review for chemical looping combustion as a promising co2 capture technology: Fundamentals and progress,” *Science of The Total Environment*, vol. 764, p. 142892, Apr 2021. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0048969720364226>
- [78] M. Schmitz and C. J. Linderholm, “Performance of calcium manganate as oxygen carrier in chemical looping combustion of biochar in a 10kw pilot,” *Applied Energy*, vol. 169, pp. 729–737, May 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261916302392>
- [79] T. Song and L. Shen, “Review of reactor for chemical looping combustion of solid fuels,” *International Journal of Greenhouse Gas Control*, vol. 76, pp. 92–110, Sep 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S175058361730837X>
- [80] T. Pröll *et al.*, “Fluidized Bed Steam Gasification of Solid Biomass: Analysis and Optimization of Plant Operation Using Process Simulation,” in *Proceedings of the 18th International Conference on Fluidized Bed Combustion. 18th International Conference on Fluidized Bed Combustion*, 2005. [Online]. Available: <https://asmedigitalcollection.asme.org/FBC/proceedings-abstract/FBC2005/41839/763/310821>
- [81] N. Hanchate *et al.*, “Biomass gasification using dual fluidized bed gasification systems: A review,” *Journal of Cleaner Production*, vol. 280, Jan 2021. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0959652620331930>
- [82] O. Armas, R. García-Contreras, and Ángel Ramos, “Pollutant emissions from engine starting with ethanol and butanol diesel blends,” *Fuel Processing Technology*, vol. 100, pp. 63–72, Aug 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378382012000963>

- [83] C. Regis and L. Bauwens, “Experimental and Analytical Examination of Spherical-Flame Instabilities,” Ph.D. dissertation, McGill University, 2019.
- [84] V. Molkov, D. Makarov, and A. Grigorash, “Cellular structure of explosion flames: Modeling and large-eddy simulation,” *Combustion Science and Technology*, vol. 176, no. 5-6, pp. 851–865, 2004. [Online]. Available: <https://doi.org/10.1080/00102200490428495>
- [85] S. Yang *et al.*, “Role of Darrieus–Landau instability in propagation of expanding turbulent flames,” *Journal of Fluid Mechanics*, vol. 850, pp. 784–802, Sep 2018. [Online]. Available: <https://www.cambridge.org/core/journals/journal-of-fluid-mechanics/article/role-of-darrieuslandau-instability-in-propagation-of-expanding-turbulent-flames/94F86D96A859D63020C2D56F7B030AC5>
- [86] Z. Liu *et al.*, “Self-turbulization in cellularly unstable laminar flames,” *Journal of Fluid Mechanics*, vol. 917, p. A53, 2021. [Online]. Available: <https://www.cambridge.org/core/journals/journal-of-fluid-mechanics/article/selfturbulization-in-cellularly-unstable-laminar-flames/AEEA8C4D709473538AFE4A01DCF7C1C3>
- [87] L. Landau, “On the Theory of Slow Combustion,” in *Dynamics of Curved Fronts*. Elsevier, 1988, pp. 403–411.
- [88] G. Darrieus, “Propagation d’un front de flamme,” Ph.D. dissertation, La Technique Moderne (Paris), 1938.
- [89] M. Matalon, “Intrinsic Flame Instabilities in Premixed and Nonpremixed Combustion,” *Annual Review of Fluid Mechanics*, vol. 39, pp. 163–191, 2007. [Online]. Available: <https://www.annualreviews.org/doi/10.1146/annurev.fluid.38.050304.092153>
- [90] F. Creta *et al.*, “Propagation of premixed flames in the presence of darrieus–landau and thermal diffusive instabilities,” *Combustion and Flame*, vol. 216, pp. 256–270, Jun 2020. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218020300936>
- [91] M. Matalon and P. Metzener, “The effect of thermal expansion on diffusion flame instabilities,” *J. Fluid Mech*, vol. 647, pp. 453–472, 2010. [Online]. Available: <https://doi.org/10.1017/S0022112009993016>

- [92] S. Burke and T. Schumann, "Diffusion flames," *Industrial & Engineering Chemistry*, vol. 20, no. 10, pp. 998–1004, 1928.
- [93] J. E. Garside and B. Jackson, "Polyhedral Diffusion Flames," *Nature* 1951 168:4286, vol. 168, no. 4286, pp. 1085–1085, 1951. [Online]. Available: <https://www.nature.com/articles/1681085a0>
- [94] M. R. Dongworth and A. Melvin, "The Transition to Instability in a Steady Hydrogen-Oxygen Diffusion Flame," *Combustion Science and Technology*, vol. 14, no. 4-6, pp. 177–182, Oct 1976.
- [95] R. H. Chen, G. B. Mitchell, and P. D. Ronney, "Diffusive-thermal instability and flame extinction in nonpremixed combustion," *Symposium (International) on Combustion*, vol. 24, no. 1, pp. 213–221, Jan 1992.
- [96] D. Lo Jacono, P. Papas, and P. A. Monkewitz, "Cell formation in non-premixed, axisymmetric jet flames near extinction," *Combust. Theory Modelling*, vol. 7, pp. 635–644, 2003. [Online]. Available: <https://doi.org/10.1088/1364-7830/7/4/302>
- [97] D. Lo Jacono and P. Monkewitz, "Scaling of cell size in cellular instabilities of nonpremixed jet flames," *Combustion and Flame*, vol. 151, pp. 321–332, Oct 2007. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218007001216>
- [98] S. Ishizuka and H. Tsuji, "An experimental study of effect of inert gases on extinction of laminar diffusion flames," *Symposium (International) on Combustion*, vol. 18, no. 1, pp. 695–703, Jan 1981.
- [99] C. Kaiser, J. B. Liu, and P. D. Ronney, "Diffusive-thermal instability of counterflow flames at low Lewis number," *38th Aerospace Sciences Meeting and Exhibit*, 2000. [Online]. Available: <https://arc.aiaa.org/doi/10.2514/6.2000-576>
- [100] R. W. Pitz, S. Hu, and P. Wang, "Tubular premixed and diffusion flames: Effect of stretch and curvature," *Progress in Energy and Combustion Science*, vol. 42, no. 1, pp. 1–34, Jun 2014.
- [101] S. Hu, R. W. Pitz, and Y. Wang, "Extinction and near-extinction instability of non-premixed tubular flames," *Combustion and Flame*, vol. 156, no. 1, pp. 90–98, 2009. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0010218008002824>

- [102] S. W. Shopoff, P. Wang, and R. W. Pitz, "The effect of stretch on cellular formation in non-premixed opposed-flow tubular flames," *Combustion and Flame*, vol. 158, no. 5, pp. 876–884, May 2011.
- [103] W. Y. Chan and J. S. Tien, "An Experiment on Spontaneous Flame Oscillation Prior to Extinction," *Combustion Science and Technology*, vol. 18, no. 3-4, pp. 139–143, Jun 1978. [Online]. Available: <https://www.tandfonline.com/doi/abs/10.1080/00102207808946845>
- [104] D. L. Dietrich *et al.*, "Candle Flames in Non-Buoyant Atmospheres," *Combustion Science and Technology*, vol. 156, no. 1, pp. 1–24, 2000. [Online]. Available: <https://www.tandfonline.com/doi/abs/10.1080/001022000008947294>
- [105] Y. Levy and D. L. Bulzan, "On the oscillation of combustion of a laminar spray," *Combustion and Flame*, vol. 100, no. 4, pp. 543–549, Mar 1995.
- [106] B. Golovanevsky *et al.*, "On the oscillatory behavior of laminar spray diffusion flames: experiment and theory," *Combustion and Flame*, vol. 117, no. 1-2, pp. 373–383, Apr 1999.
- [107] A. L. Valär *et al.*, "Three-dimensional simulations of cellular non-premixed jet flames," *Combustion and Flame*, vol. 157, no. 4, pp. 653–666, Apr 2010.
- [108] H. S. Bak *et al.*, "A numerical study of the diffusive-thermal instability of opposed nonpremixed tubular flames," *Combustion and Flame*, vol. 162, no. 12, pp. 4612–4621, Dec 2015.
- [109] C. E. Frouzakis *et al.*, "Three-dimensional numerical simulations of cellular jet diffusion flames," *Proceedings of the Combustion Institute*, vol. 30, no. 1, pp. 185–192, Jan 2005.
- [110] S. R. Lee and J. S. Kim, "On the sublimit solution branches of the stripe patterns formed in counterflow diffusion flames by diffusional–thermal instability," *Combustion Theory and Modelling*, vol. 6, no. 2, pp. 263–278, 2007. [Online]. Available: <https://www.tandfonline.com/doi/abs/10.1088/1364-7830/6/2/307>
- [111] E. W. Christiansen, S. D. Tse, and C. K. Law, "A computational study of oscillatory extinction of spherical diffusion flames," *Combustion and Flame*, vol. 134, no. 4, pp. 327–337, Sep 2003.
- [112] C. H. Sohn, S. H. Chung, and J. S. Kim, "Instability-induced extinction of diffusion flames established in the stagnant mixing layer," *Combustion and Flame*, vol. 117, no. 1-2, pp. 404–412, Apr 1999.

- [113] Y. B. Zeldovich, "On the theory of combustion of initially unmixed gases," *J. Tech. Phys, Moscow, 1949*, Translated as Nat. Adv. Comm. Aero., Wash., Tech. Memo., vol. 1296, 1951.
- [114] D. B. Spalding, "A theory of the extinction of diffusion flames," *Fuel*, 1954.
- [115] D. B. Spalding and V. K. Jain, "A theoretical study of the effects of chemical kinetics on a one-dimensional diffusion flame," *Combustion and Flame*, vol. 6, pp. 265–273, Jan 1962.
- [116] L. Kirkbey and R. Schmitz, "An analytical study of the stability of a laminar diffusion flame," *Combustion and Flame*, vol. 10, no. 3, pp. 205–220, 1966. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/0010218066900770>
- [117] A. Liñán, "The asymptotic structure of counterflow diffusion flames for large activation energies," *Acta Astronautica*, vol. 1, pp. 1007–1039, 1974.
- [118] A. Liñán and A. Crespo, "An asymptotic analysis of unsteady diffusion flames for large activation energies," *Combust. Sci. Technol.*, vol. 14, pp. 95–117, 1976.
- [119] M. Matalon, G. Ludford, and J. Buckmaster, "Diffusion flames in a chamber," *Acta Astronautica*, vol. 6, no. 7-8, pp. 943–959, Jul 1979. [Online]. Available: <https://linkinghub.elsevier.com/retrieve/pii/0094576579900808>
- [120] J. S. Kim, "Diffusional-thermal instability of diffusion flames in the premixed-flame regime," *Combustion Science and Technology*, vol. 118, no. 1-3, pp. 27–48, 1996. [Online]. Available: <https://www.tandfonline.com/doi/abs/10.1080/00102209608951970>
- [121] J. Kim, "Linear analysis of diffusional-thermal instability in diffusion flames with lewis numbers close to unity," *Combustion Theory and Modelling*, vol. 1, no. 1, pp. 13–40, 1997. [Online]. Available: <https://doi.org/10.1080/713665228>
- [122] J. Buckmaster, A. Nachman, and S. Taliaferro, "The fast-time instability of diffusion flames," *Physica D: Nonlinear Phenomena*, vol. 9, no. 3, pp. 408–424, 1983.
- [123] S. Cheatham and M. Matalon, "A general asymptotic theory of diffusion flames with application to cellular instability," *Journal of Fluid Mechanics*, vol. 414, pp. 105–144, 2000. [Online]. Available: <https://doi.org/10.1017/S0022112000008752>

- [124] S. Kukuck and &. M. Matalon, "The onset of oscillations in diffusion flames," *Combustion Theory and Modelling*, vol. 5, no. 2, pp. 217–240, 2001. [Online]. Available: <https://www.tandfonline.com/action/journalInformation?journalCode=tctm20>
- [125] S. Cheatham, "On the Structure and Stability of Diffusion Flames," Ph.D. dissertation, Northwestern university, 1997.
- [126] H. Y. Wang, J. K. Bechtold, and C. K. Law, "Nonlinear oscillations in diffusion flames," *Combustion and Flame*, vol. 145, no. 1-2, pp. 376–389, Apr 2006.
- [127] P. Metzener and M. Matalon, "Combustion Theory and Modelling Diffusive-thermal instabilities of diffusion flames: onset of cells and oscillations Diffusive-thermal instabilities of diffusion flames: onset of cells and oscillations," *Combustion Theory and Modelling*, vol. 10, no. 4, pp. 701–725, 2006. [Online]. Available: <https://www.tandfonline.com/action/journalInformation?journalCode=tctm20>
- [128] B. Han *et al.*, "Experimental low-stretch gaseous diffusion flames in buoyancy-induced flowfields," *Proceedings of the Combustion Institute*, vol. 30, no. 1, pp. 527–535, Jan 2005. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0082078404000712>
- [129] D. Lo Jacono, "Experimental study of cellular instabilities in non-premixed flames," Ph.D. dissertation, 2005.
- [130] E. Robert and P. A. Monkewitz, "Experimental realization and characterization of unstretched planar one-dimensional diffusion flames," *Combustion and Flame*, vol. 160, no. 3, pp. 546–556, Mar 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218012003525>
- [131] E. Robert and P. A. Monkewitz, "Thermal-diffusive instabilities in unstretched, planar diffusion flames," *Combustion and Flame*, vol. 159, no. 3, pp. 1228–1238, 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218011003257>
- [132] R. W. Francisco and A. A. M. Oliveira, "Measurement of the adiabatic flame speed and overall activation energy of a methane enriched H₂/CO/CO₂/N₂ low heating value mixture," *International Journal of Hydrogen Energy*, vol. 45, no. 53, pp. 29 533–29 545, Oct 2020. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S036031992032810X>

- [133] W. Jin *et al.*, “Cellular instabilities of non-adiabatic laminar flat methane/hydrogen oxy-fuel flames highly diluted with CO₂,” *Fuel*, vol. 143, pp. 38–46, 2015. [Online]. Available: <http://dx.doi.org/10.1016/j.fuel.2014.11.036>
- [134] J. Natarajan, T. Lieuwen, and J. Seitzman, “Laminar flame speeds of H₂/CO mixtures: Effect of CO₂ dilution, preheat temperature, and pressure,” *Combustion and Flame*, vol. 151, no. 1-2, pp. 104–119, Oct 2007.
- [135] H. A. Yepes and A. A. Amell, “Laminar burning velocity with oxygen-enriched air of syngas produced from biomass gasification,” *International Journal of Hydrogen Energy*, vol. 38, no. 18, pp. 7519–7527, Jun 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319913008264>
- [136] O. Askari *et al.*, “On the flame stability and laminar burning speeds of syngas/O₂/He premixed flame,” *Fuel*, vol. 190, pp. 90–103, Feb 2017. [Online]. Available: <http://dx.doi.org/10.1016/j.fuel.2016.11.042>
- [137] Z. Wang *et al.*, “The Critical Pressure at the Onset of Flame Instability of Syngas/Air/Diluent Outwardly Expanding Flame at Different Initial Temperatures and Pressures,” 2019. [Online]. Available: http://asmedigitalcollection.asme.org/energyresources/article-pdf/141/8/082207/6155655/jert{__}141{__}08{__}082207.pdf
- [138] J. Park *et al.*, “Flame characteristics in H₂/CO synthetic gas diffusion flames diluted with CO₂: Effects of radiative heat loss and mixture composition,” *International Journal of Hydrogen Energy*, vol. 33, no. 23, pp. 7256–7264, Dec 2008. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319908009269>
- [139] S. K. Aggarwal, D. Bongiovanni, and M. Santarelli, “Extinction of laminar diffusion flames burning the anodic syngas fuel from solid oxide fuel cell,” *International Journal of Hydrogen Energy*, vol. 40, no. 22, pp. 7214–7230, Jun 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319915008551>
- [140] H.-Y. Shih and J.-R. Hsu, “Dilution effects analysis of opposed-jet H₂/CO syngas diffusion flames,” *Combustion Theory and Modelling*, vol. 17, no. 3, pp. 543–562, 2013. [Online]. Available: <https://www.tandfonline.com/action/journalInformation?journalCode=tctm20>
- [141] H.-Y. Shih, J.-R. Hsu, and Y.-H. Lin, “Computed flammability limits of opposed-jet H₂/CO syngas diffusion flames,” *International Journal of Hydrogen*

- Energy*, vol. 39, no. 7, pp. 3459–3468, Feb 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S036031991302990X>
- [142] M. Safer *et al.*, “A numerical investigation of structure and emissions of oxygen-enriched syngas flame in counter-flow configuration,” *International Journal of Hydrogen Energy*, vol. 40, no. 6, pp. 2890–2898, Feb 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319914035484>
- [143] H. Xu *et al.*, “Flame attachment and kinetics studies of laminar coflow CO/H₂ diffusion flames burning in O₂/H₂O,” *Combustion and Flame*, vol. 196, pp. 147–159, Oct 2018.
- [144] H. X. et al., “Effects of H₂O and CO₂ diluted oxidizer on the structure and shape of laminar coflow syngas diffusion flames,” *Combustion and Flame*, vol. 177, pp. 67–78, 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218016303649>
- [145] H. Xu, S. Sun, and F. L. et al., “An experimental and computational study of oh formation in laminar coflow syngas diffusion flames,” *Fuel*, vol. 225, pp. 47–53, 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236118305520>
- [146] J. Xi *et al.*, “Effects Effect of CO₂/N₂/CH₄ dilution on NO formation in laminar coflow syngas diffusion flames,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 40, no. 7, pp. 821–829, 2018. [Online]. Available: <https://www.tandfonline.com/action/journalInformation?journalCode=ueso20>
- [147] T. Piemsinlapakunchon and M. C. Paul, “Effects of fuel compositions on the heat generation and emission of syngas/producer gas laminar diffusion flame,” *International Journal of Hydrogen Energy*, vol. 44, no. 33, pp. 18 505–18 516, Jul 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360319919320920>
- [148] E. Antar and E. Robert, “Thermodynamic analysis of novel methanol polygeneration systems for greenhouses,” *Biomass Conversion and Biorefinery*, vol. 13, pp. 8033–8046, 2023.
- [149] E. Antar and E. Robert, “Thermodynamic analysis of small-scale polygeneration systems producing natural gas, electricity, heat, and carbon dioxide from biomass,” *Energy*, 2023, submitted for publication.
- [150] E. Antar, J. Delavande, and E. Robert, “Experimental characterization of diffusive-thermal instabilities in CO₂-diluted H₂CH₄CO unstrained diffusion flames,”

- Combustion and Flame*, vol. 250, p. 112636, 2023. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218023000214>
- [151] E. Antar and E. Robert, “Diffusive-thermal instabilities in unstrained H₂-CH₄-CO diffusion flames diluted with H₂O and CO₂,” in *13th U.S. National Combustion Meeting*, Mar 2023.
- [152] E. Antar and E. Robert, “Diffusive-thermal instabilities in unstrained H₂O-diluted syngas diffusion flames,” *Combustion and Flame*, 2023, submitted for publication.
- [153] E. Antar and Robert, “Unstrained diffusion flames: Characterizing the effect of H₂O dilution on diffusive-thermal instabilities in syngas,” in *Proceedings of Combustion Institute – Canadian Section 2023 Spring Technical Meeting*, May 2023.
- [154] T. Yildirim, T. Bilyea, and D. Buckingham, “Clean Growth in Agriculture,” Tech. Rep. March, 2019.
- [155] Statistics Canada, “Report on Energy Supply and Demand in Canada,” Tech. Rep., 2019.
- [156] V. Dhyani and T. Bhaskar, “A comprehensive review on the pyrolysis of lignocellulosic biomass,” *Renewable Energy*, 2018.
- [157] J. Chau *et al.*, “Techno-economic analysis of wood biomass boilers for the greenhouse industry,” *Applied Energy*, vol. 86, no. 3, pp. 364–371, Mar 2009. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261908001372?via=ihub>
- [158] K. Jana *et al.*, “Polygeneration as a future sustainable energy solution – A comprehensive review,” *Applied Energy*, vol. 202, pp. 88–111, Sep 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0306261917306700>
- [159] M. Villarini *et al.*, “The Case Study of an Innovative Small Scale Biomass Waste Gasification Heat and Power Plant Contextualized in a Farm,” *Energy Procedia*, vol. 82, pp. 335–342, Dec 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610215025503>
- [160] L. I. Chaves *et al.*, “Small-scale power generation analysis: Downdraft gasifier coupled to engine generator set,” *Renewable and Sustainable Energy Reviews*, vol. 58, pp. 491–498, May 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032115014161>

- [161] H. R. Sara *et al.*, “Techno-economic Analysis of Hydrogen Production Using Biomass Gasification -A Small Scale Power Plant Study,” *Energy Procedia*, vol. 101, pp. 806–813, Nov 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S187661021631311X>
- [162] R. Sadegh-Vaziri and M. U. Bähler, “Providing sulfur free syngas to a fuel cell system,” *Energy Procedia*, vol. 159, pp. 448–453, Feb 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610218313365>
- [163] L. R. Clausen, G. Butera, and S. H. Jensen, “High efficiency SNG production from biomass and electricity by integrating gasification with pressurized solid oxide electrolysis cells,” *Energy*, vol. 172, pp. 1117–1131, Apr 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544219302282>
- [164] S. K. Sansaniwal *et al.*, “Recent advances in the development of biomass gasification technology: A comprehensive review,” *Renewable and Sustainable Energy Reviews*, vol. 72, pp. 363–384, 2017.
- [165] G. Butera *et al.*, “Flexible biomass conversion to methanol integrating solid oxide cells and TwoStage gasifier,” *Fuel*, vol. 271, p. 117654, 2020. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0016236120306499>
- [166] L. E. Lücking, “Methanol Production from Syngas Process modelling and design utilising biomass gasification and integrating hydrogen supply,” Master’s thesis, Delft University of Technology, 2017. [Online]. Available: <http://repository.tudelft.nl/>.
- [167] A. Susastriawan, H. Saptoadi, and Purnomo, “Small-scale downdraft gasifiers for biomass gasification: A review,” *Renewable and Sustainable Energy Reviews*, vol. 76, pp. 989–1003, Sep 2017. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032117304471>
- [168] R. Zhang *et al.*, “Catalytic destruction of tar in biomass derived producer gas,” *Energy Conversion and Management*, vol. 45, no. 7-8, pp. 995–1014, May 2004.
- [169] A. Kostyniuk, M. Grilc, and B. Likozar, “Catalytic Cracking of Biomass-Derived Hydrocarbon Tars or Model Compounds To Form Biobased Benzene, Toluene, and Xylene Isomer Mixtures,” 2019. [Online]. Available: <https://pubs.acs.org/sharingguidelines>

- [170] S. Fendt *et al.*, “The potential of small-scale SNG production from biomass gasification,” *Biomass Conv. Bioref.*, vol. 2, pp. 275–283, 2012. [Online]. Available: <https://link.springer.com/content/pdf/10.1007%7D2Fs13399-012-0037-3.pdf>
- [171] P.-C. Kuo, W. Wu, and W.-H. Chen, “Gasification performances of raw and torrefied biomass in a downdraft fixed bed gasifier using thermodynamic analysis,” *Fuel*, vol. 117, pp. 1231–1241, Jan 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236113007242>
- [172] J. Han *et al.*, “Modeling downdraft biomass gasification process by restricting chemical reaction equilibrium with Aspen Plus,” *Energy Conversion and Management*, pp. 641–648, 2017.
- [173] W. Doherty *et al.*, “Aspen Plus Simulation of Biomass Gasification in a Steam Blown Dual Fluidised Bed,” Tech. Rep., 2013.
- [174] T. Damartzis, S. Michailos, and A. Zabaniotou, “Energetic assessment of a combined heat and power integrated biomass gasification–internal combustion engine system by using Aspen Plus,” *Fuel Processing Technology*, vol. 95, pp. 37–44, Mar 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378382011003973>
- [175] L. Yuping *et al.*, “Demonstration of Pilot-scale Bio-dimethyl ether Synthesis Via Oxygen- and steam- enriched Gasification of Wood Chips,” in *Energy Procedia*, vol. 75. Elsevier, Aug 2015, pp. 202–207. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1876610215010711>
- [176] S. Mesfun *et al.*, “Integration of an electrolysis unit for producer gas conditioning in a bio-synthetic natural gas plant,” *Journal of Energy Resources Technology, Transactions of the ASME*, vol. 141, no. 1, pp. 1–12, 2019.
- [177] G. Butera, S. H. Jensen, and L. R. Clausen, “A novel system for large-scale storage of electricity as synthetic natural gas using reversible pressurized solid oxide cells,” *Energy*, vol. 166, pp. 738–754, Jan 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544218320693>
- [178] A. Yousuf, D. Pirozzi, and F. Sannino, *Fundamentals of lignocellulosic biomass*. Academic Press, 2019.
- [179] M. Wang *et al.*, “Theoretical study of the pyrolysis of vanillin as a model of secondary lignin pyrolysis,” *Chemical Physics Letters*, vol. 654, pp. 41–45, Jun 2016.

- [180] P. Haro, F. Johnsson, and H. Thunman, "Improved syngas processing for enhanced Bio-SNG production: A techno-economic assessment," *Energy*, vol. 101, pp. 380–389, Apr 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544216300809>
- [181] B. Rehling *et al.*, "BioSNG-process simulation and comparison with first results from a 1-MW demonstration plant," *Biomass Conv. Bioref.*, vol. 1, pp. 111–119, 2011. [Online]. Available: <https://link.springer.com/content/pdf/10.1007/%7B2Fs13399-011-0013-3.pdf>
- [182] L. E. Arteaga-Pérez *et al.*, "A modelling approach to the techno-economics of Biomass-to-SNG/Methanol systems: Standalone vs Integrated topologies," *Chemical Engineering Journal*, vol. 286, pp. 663–678, Feb 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1385894715015223>
- [183] K. Jana and S. De, "Polygeneration using agricultural waste: Thermodynamic and economic feasibility study," *Renewable Energy*, vol. 74, pp. 648–660, Feb 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0960148114005485>
- [184] K. Sato and K. Fujimoto, "Development of new nickel based catalyst for tar reforming with superior resistance to sulfur poisoning and coking in biomass gasification," *Catalysis Communications*, vol. 8, no. 11, pp. 1697–1701, Nov 2007.
- [185] W. Torres, S. S. Pansare, and J. G. Goodwin, "Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas," <http://dx.doi.org/10.1080/01614940701375134>, vol. 49, no. 4, pp. 407–456, Oct 2007. [Online]. Available: <https://www.tandfonline.com/doi/abs/10.1080/01614940701375134>
- [186] M. Di Salvo and M. Wei, "Synthesis of natural gas from thermochemical and power-to-gas pathways for industrial sector decarbonization in California," *Energy*, vol. 182, pp. 1250–1264, Sep 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544219308527>
- [187] S. Karellas *et al.*, "An evaluation of Substitute natural gas production from different coal gasification processes based on modeling," *Energy*, vol. 45, no. 1, pp. 183–194, Sep 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544212002782>

- [188] J. Islas *et al.*, “Solid Biomass to Heat and Power,” in *The Role of Bioenergy in the Emerging Bioeconomy: Resources, Technologies, Sustainability and Policy*. Academic Press, 2019, ch. 4, pp. 145–177. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/B9780128130568000042>
- [189] L. Jiang *et al.*, “Cellular instabilities of n-butane/air flat flames probing by PLIF-OH and PLIF-CH₂O laser diagnosis,” *Experimental Thermal and Fluid Science*, vol. 118, no. April, 2020.
- [190] T. Poinso, “Prediction and control of combustion instabilities in real engines,” *Proceedings of the Combustion Institute*, vol. 36, no. 1, pp. 1–28, Jan 2017.
- [191] M. Matalon, “Flame dynamics,” *Proceedings of the Combustion Institute*, vol. 32 I, no. 1, pp. 57–82, 2009. [Online]. Available: <http://dx.doi.org/10.1016/j.proci.2008.08.002>
- [192] E. Robert and P. A. Monkewitz, “Experiments in a novel quasi-ID diffusion flame with variable bulk flow,” *Proceedings of the Combustion Institute*, vol. 32 I, no. 1, pp. 987–994, Jan 2009.
- [193] E. Robert, “Experimental Investigation of Unstrained Diffusion Flames and their Instabilities,” Ph.D. dissertation, EPFL, 2008.
- [194] E. Etienne, “Mass spectrometer calibration over wide concentration ranges in multi-component gas mixtures,” *Meas. Sci. Technol*, vol. 21, 2010.
- [195] D. Lo Jacono *et al.*, “An experimental realization of an unstrained, planar diffusion flame,” *Proceedings of the Combustion Institute*, vol. 30, pp. 501–509, Jan 2005. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0082078404000128>
- [196] D. G. Goodwin *et al.*, “Cantera: An Object-oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes,” 2021. [Online]. Available: <https://cantera.org/>
- [197] R. J. Kee, M. E. Coltrin, and P. Glarborg, *Chemically Reacting Flow: Theory and Practice*. John Wiley & Sons, Feb 2003. [Online]. Available: <https://onlinelibrary.wiley.com/doi/book/10.1002/0471461296>
- [198] E. Bodenschatz, W. Pesch, and G. Ahlers, “Recent Developments in Rayleigh-Bénard Convection,” *Annual Review of Fluid Mechanics*, vol. 32, no. 1, pp. 709–778, 2000. [Online]. Available: <https://doi.org/10.1146/annurev.fluid.32.1.709>

- [199] S. W. Shopoff, P. Wang, and R. W. Pitz, “Experimental study of cellular instability and extinction of non-premixed opposed-flow tubular flames,” *Combustion and Flame*, vol. 158, no. 11, pp. 2165–2177, Nov 2011.
- [200] H. Lulic *et al.*, “On polyhedral structures of lean methane/hydrogen Bunsen flames: Combined experimental and numerical analysis,” *Proceedings of the Combustion Institute*, Oct 2022.
- [201] E. C. Okafor, Y. Nagano, and T. Kitagawa, “Experimental and theoretical analysis of cellular instability in lean H₂-CH₄-air flames at elevated pressures,” *International Journal of Hydrogen Energy*, vol. 41, no. 15, pp. 6581–6592, 2016. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0360319915313434>
- [202] T. Piemsinlapakunchon and M. C. Paul, “Effect of syngas fuel compositions on the occurrence of instability of laminar diffusion flame,” *International Journal of Hydrogen Energy*, vol. 46, no. 10, pp. 7573–7588, Feb 2021.
- [203] A. Akhtar, V. Krepl, and T. Ivanova, “A Combined Overview of Combustion, Pyrolysis, and Gasification of Biomass,” *Energy and Fuels*, vol. 32, no. 7, pp. 7294–7318, Jul 2018. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [204] V. Mislavskii *et al.*, “Diffusive-thermal pulsations of burner stabilized methane-air flames,” *Combustion and Flame*, vol. 234, p. 111638, Dec 2021.
- [205] D. Pugh *et al.*, “Influence of steam addition and elevated ambient conditions on NO_x reduction in a staged premixed swirling NH₃/H₂ flame,” *Proceedings of the Combustion Institute*, vol. 37, no. 4, pp. 5401–5409, Jan 2019.
- [206] Y. Wang *et al.*, “A review of the effects of hydrogen, carbon dioxide, and water vapor addition on soot formation in hydrocarbon flames,” *International Journal of Hydrogen Energy*, vol. 46, no. 61, pp. 31 400–31 427, Sep 2021.
- [207] F. Liu, J. L. Consalvi, and A. Fuentes, “Effects of water vapor addition to the air stream on soot formation and flame properties in a laminar coflow ethylene/air diffusion flame,” *Combustion and Flame*, vol. 161, no. 7, pp. 1724–1734, 2014.
- [208] N. Peters, “Laminar diffusion flamelet models in non-premixed turbulent combustion,” *Progress in energy and combustion science*, vol. 10, no. 3, pp. 319–339, 1984.
- [209] D. Rivest, “Techno-economic analysis of a decentralized polygeneration system,” Master’s thesis, Polytechnique Montreal, 2023.

- [210] M. Perron, “Heating of greenhouses from biomass polygeneration systems,” Master’s thesis, Polytechnique Montreal, 2023.
- [211] M. W. Islam, “A review of dolomite catalyst for biomass gasification tar removal,” *Fuel*, vol. 267, p. 117095, May 2020.
- [212] C. H. Bartholomew and R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*. Hoboken, NJ, USA: John Wiley & Sons, Inc., Oct 2005. [Online]. Available: <http://doi.wiley.com/10.1002/9780471730071>
- [213] J. Corella, A. Orío, and J. M. Toledo, “Biomass gasification with air in a fluidized bed: Exhaustive tar elimination with commercial steam reforming catalysts,” *Energy and Fuels*, vol. 13, no. 3, pp. 702–709, 1999. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [214] C. Pfeifer and H. Hofbauer, “Development of catalytic tar decomposition downstream from a dual fluidized bed biomass steam gasifier,” *Powder Technology*, vol. 180, no. 1-2, pp. 9–16, Jan 2008.
- [215] C.-Z. Li *et al.*, “Method of gasifying carbonaceous material and a gasification system,” 2018.
- [216] M. Asadullah, “Biomass gasification gas cleaning for downstream applications: A comparative critical review,” *Renewable and Sustainable Energy Reviews*, vol. 40, pp. 118–132, Dec 2014. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S136403211400584X>
- [217] J. M. Donbar, J. F. Driscoll, and C. D. Carter, “Strain rates measured along the wrinkled flame contour within turbulent non-premixed jet flames,” *Combustion and Flame*, vol. 125, no. 4, pp. 1239–1257, 2001. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0010218001002462>
- [218] K. Keller *et al.*, “Treating nox emission of hydrogen fueled combustion engines by nox storage and reduction catalysts: A transient kinetic study including plif measurements,” *Proceedings of the Combustion Institute*, 2022. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S154074892200058X>
- [219] S. C. Boanta, “Morphological characterization of soot from an idealized diffusion flame and from polymer combustion,” Ph.D. dissertation, Polytechnique Montreal, 2023.

- [220] H. Kobayashi *et al.*, “Science and technology of ammonia combustion,” *Proceedings of the Combustion Institute*, vol. 37, no. 1, pp. 109–133, 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1540748918306345>
- [221] J. Held, “Gasification—Status and technology,” Swedish Gas Technology Centre, Tech. Rep. June, 2012.
- [222] M. L. Valderrama Rios *et al.*, “Reduction of tar generated during biomass gasification: A review,” *Biomass and Bioenergy*, vol. 108, pp. 345–370, Jan 2018. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0961953417304026>
- [223] U. Henriksen *et al.*, “The design, construction and operation of a 75kw two-stage gasifier,” *Energy*, vol. 31, no. 10, pp. 1542–1553, 2006, eCOS 2003. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360544205001246>
- [224] P. Hofmann *et al.*, “High temperature electrolyte supported Ni-GDC/YSZ/LSM SOFC operation on two-stage Viking gasifier product gas,” *Journal of Power Sources*, vol. 173, no. 1, pp. 357–366, Nov 2007. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378775307008919?via={%}3Dihub>
- [225] Y. Zhang, J. Xiao, and L. Shen, “Simulation of Methanol Production from Biomass Gasification in Interconnected Fluidized Beds,” *Industrial & Engineering Chemistry Research*, vol. 48, no. 11, 2009. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [226] J. M. Leimert, P. Treiber, and J. Karl, “The Heatpipe Reformer with optimized combustor design for enhanced cold gas efficiency,” *Fuel Processing Technology*, vol. 141, pp. 68–73, Jan 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378382015001861>
- [227] P. U. Foscolo and K. Gallucci, “Integration of particulate abatement, removal of trace elements and tar reforming in one biomass steam gasification reactor yielding high purity syngas for efficient CHP and power plants.” 16th European Biomass Conference and Exhibition, 2008, pp. 690–698.
- [228] “Chemical Engineering : EU-Project "UNIQUE".”
- [229] A. Gómez-Barea *et al.*, “Improving the performance of fluidized bed biomass/waste gasifiers for distributed electricity: A new three-stage gasification system,” *Applied Thermal Engineering*, vol. 50, no. 2, pp. 1453–1462, Feb 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1359431111007228>

- [230] A. Gómez-Barea, P. Ollero, and B. Leckner, “Optimization of char and tar conversion in fluidized bed biomass gasifiers,” *Fuel*, vol. 103, pp. 42–52, Jan 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236111003735?via%3Dihub>
- [231] P. J. Woolcock and R. C. Brown, “A review of cleaning technologies for biomass-derived syngas,” *Biomass and Bioenergy*, vol. 52, pp. 54–84, May 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0961953413001177>
- [232] N. Abdoulmoumine *et al.*, “A review on biomass gasification syngas cleanup,” *Applied Energy*, vol. 155, pp. 294–307, Oct 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S030626191500728X>
- [233] G. Guan *et al.*, “Catalytic steam reforming of biomass tar: Prospects and challenges,” *Renewable and Sustainable Energy Reviews*, vol. 58, pp. 450–461, May 2016. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032115016998>
- [234] D. Sutton, B. Kelleher, and J. R. Ross, “Review of literature on catalysts for biomass gasification,” *Fuel Processing Technology*, vol. 73, no. 3, pp. 155–173, Nov 2001.
- [235] P. A. Simell, J. K. Leppälahti, and J. B. Bredenberg, “Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials,” *Fuel*, vol. 71, no. 2, pp. 211–218, Feb 1992.
- [236] J. Corella, J. M. Toledo, and R. Padilla, “Olivine or dolomite as in-bed additive in biomass gasification with air in a fluidized bed: Which is better?” *Energy and Fuels*, vol. 18, no. 3, pp. 713–720, May 2004. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [237] D. A. Constantinou, J. L. G. Fierro, and A. M. Efstathiou, “A comparative study of the steam reforming of phenol towards H₂ production over natural calcite, dolomite and olivine materials,” *Applied Catalysis B: Environmental*, vol. 95, no. 3-4, pp. 255–269, Apr 2010.
- [238] J. Ahrenfeldt *et al.*, “Biomass gasification cogeneration – A review of state of the art technology and near future perspectives,” *Applied Thermal Engineering*, vol. 50, no. 2, pp. 1407–1417, Feb 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S135943111100737X>

- [239] C. Pfeifer, R. Rauch, and H. Hofbauer, "In-Bed Catalytic Tar Reduction in a Dual Fluidized Bed Biomass Steam Gasifier," *Industrial and Engineering Chemistry Research*, vol. 43, no. 7, pp. 1634–1640, 2004.
- [240] S. Rapagnà *et al.*, "Fe/olivine catalyst for biomass steam gasification: Preparation, characterization and testing at real process conditions," *Catalysis Today*, vol. 176, no. 1, pp. 163–168, Nov 2011. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0920586111000496>
- [241] Z. Ud Din and Z. A. Zainal, "Biomass integrated gasification-SOFC systems: Technology overview," *Renewable and Sustainable Energy Reviews*, vol. 53, pp. 1356–1376, Jan 2016. [Online]. Available: <http://dx.doi.org/10.1016/j.rser.2015.09.013>
- [242] J. Ren *et al.*, "Biomass thermochemical conversion: A review on tar elimination from biomass catalytic gasification," *Journal of the Energy Institute*, vol. 93, no. 3, pp. 1083–1098, Jun 2020.
- [243] P. Aravind and W. de Jong, "Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells," *Progress in Energy and Combustion Science*, vol. 38, no. 6, pp. 737–764, Dec 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0360128512000214>
- [244] B. Dou *et al.*, "Removal of tar component over cracking catalysts from high temperature fuel gas," *Energy Conversion and Management*, vol. 49, no. 8, pp. 2247–2253, Aug 2008.
- [245] K. Tomishige, M. Asadullah, and K. Kunimori, "Syngas production by biomass gasification using Rh/CeO₂/SiO₂ catalysts and fluidized bed reactor," *Catalysis Today*, vol. 89, no. 4, pp. 389–403, Jun 2004.
- [246] M. Asadullah *et al.*, "Catalyst development for the gasification of biomass in the dual-bed gasifier," *Applied Catalysis A: General*, vol. 255, no. 2, pp. 169–180, Dec 2003.
- [247] T. Miyazawa *et al.*, "Catalytic properties of Rh/CeO₂/SiO₂ for synthesis gas production from biomass by catalytic partial oxidation of tar," *Science and Technology of Advanced Materials*, vol. 6, no. 6, pp. 604–614, Sep 2005.
- [248] S. Anis and Z. Zainal, "Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 5, pp. 2355–2377, Jun 2011. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1364032111000608>

- [249] G. Ravenni *et al.*, “Adsorption and decomposition of tar model compounds over the surface of gasification char and active carbon within the temperature range 250–800 °C,” *Applied Energy*, vol. 241, pp. 139–151, 2019. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0306261919304313>
- [250] Z. Abu El-Rub, E. A. Bramer, and G. Brem, “Experimental comparison of biomass chars with other catalysts for tar reduction,” *Fuel*, vol. 87, no. 10-11, pp. 2243–2252, Aug 2008.
- [251] G. Ravenni *et al.*, “Activity of chars and activated carbons for removal and decomposition of tar model compounds – A review,” *Renewable and Sustainable Energy Reviews*, vol. 94, pp. 1044–1056, 2018. [Online]. Available: <https://doi.org/10.1016/j.rser.2018.07.001>
- [252] Z. Abu El-Rub, E. A. Bramer, and G. Brem, “Review of catalysts for tar elimination in biomass gasification processes,” *Industrial and Engineering Chemistry Research*, vol. 43, no. 22, pp. 6911–6919, Oct 2004. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [253] J. Šulc *et al.*, “Biomass waste gasification – Can be the two stage process suitable for tar reduction and power generation?” *Waste Management*, vol. 32, no. 4, pp. 692–700, Apr 2012. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0956053X11003758>
- [254] E.-I. Koytsoumpa *et al.*, “Modelling and assessment of acid gas removal processes in coal-derived SNG production,” *Applied Thermal Engineering*, vol. 74, pp. 128–135, Jan 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S1359431114001161?via={%}3Dihubhttps://www.sciencedirect.com/science/article/pii/S1359431114001161>
- [255] A. Brunetti *et al.*, “Membrane technologies for CO₂ separation,” *Journal of Membrane Science*, vol. 359, no. 1-2, pp. 115–125, Sep 2010. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0376738809008540>
- [256] K. Panopoulos *et al.*, “High temperature solid oxide fuel cell integrated with novel allothermal biomass gasification: Part I: Modelling and feasibility study,” *Journal of Power Sources*, vol. 159, no. 1, pp. 570–585, Sep 2006. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0378775305016939>

- [257] C. Bang-Møller and M. Rokni, “Thermodynamic performance study of biomass gasification, solid oxide fuel cell and micro gas turbine hybrid systems,” *Energy Conversion and Management*, vol. 51, no. 11, pp. 2330–2339, Nov 2010. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0196890410001603>
- [258] F. Marchelli *et al.*, “Experimental study on H₂S adsorption on gasification char under different operative conditions,” *Biomass and Bioenergy*, vol. 126, pp. 106–116, 2019. [Online]. Available: <http://www.sciencedirect.com/science/article/pii/S0961953419301667>
- [259] M. Stemmler, A. Tamburro, and M. Müller, “Laboratory investigations on chemical hot gas cleaning of inorganic trace elements for the “UNIQUE” process,” *Fuel*, vol. 108, pp. 31–36, Jun 2013. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0016236111003000>
- [260] P. Hasler and T. Nussbaumer, “Gas cleaning for IC engine applications from fixed bed biomass gasification,” *Biomass and Bioenergy*, vol. 16, no. 6, pp. 385–395, Jun 1999. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0961953499000185>
- [261] S. Rapagnà *et al.*, “In situ catalytic ceramic candle filtration for tar reforming and particulate abatement in a fluidized-bed biomass gasifier,” *Energy and Fuels*, vol. 23, no. 7, pp. 3804–3809, 2009.

APPENDIX A BIOMASS GASIFICATION

Among the different types of available gasifiers, fixed and fluidized bed reactors seem to be the most applicable for usage in small decentralized setups. Other gasifier types, such as entrained flow, rotary kiln, or plasma reactors are not discussed here because of their complex operation.

Fixed bed gasification

The two main fixed bed gasifier configurations are the downdraft and updraft gasifiers shown in figure A.1 a) and b). In downdraft gasifiers, biomass is first dried, then pyrolyzed, then oxidized, and finally reduced. The order of the last two stages are exchanged when it comes to updraft gasifiers. In downdraft gasifiers, the solid and gaseous products are co-current as they both move downwards. On the other hand, updraft gasifiers have their solid products moving downwards and gases upwards (counter current). This leads to substantially lower syngas exit temperature, and as a result, higher cold gas efficiency [12]. However, the lower temperature means there will be more tar in the syngas emitted from updraft gasifiers, since less of it will be cracked in the hot zones of the gasifier [221]. With downdraft gasifiers, the tar content in the syngas is much lower. This is one of the main reasons why downdraft gasifiers are usually preferred over updraft reactors for small-scale applications. It should be noted that the flexibility of downdraft gasifiers with moisture content in the feedstock is low compared to updraft gasifiers. Hence, usually a drying pretreatment stage must precede gasification with feedstock containing high moisture content.

Ambient air is often used as a gasification agent, but this results in high N_2 content in syngas, usually between 50-60%. To increase energy density, pure O_2 instead of air can be used, which was also shown to lower the tar content in syngas [222]. Air separation units are traditionally used in large scale systems to separate O_2 from N_2 in the air. But the large investment and operating costs of ASUs make them a poor choice for small scale systems [8]. An alternative approach that has been gaining momentum is steam electrolysis in solid oxide electrolysis cells, which produces O_2 and H_2 when supplied with electricity. The former can be used as a gasification agent, while the latter can be used as a fuel or to enrich H_2 content of syngas. The integration of SOECs in biomass conversion plants is further elaborated in section 2.1.1.

Sometimes pyrolysis and gasification are performed in separate controlled zones, in a process known as multistage gasification. This approach is shown to yield high quality syngas with

a negligible amount of tar [17]. The Viking gasifier developed by the Technical University of Denmark which is shown in figure A.1 c), is a good example of a two-stage gasifier, where the biomass feed rate and pyrolysis time are controlled by a screw feeder [223]. Between the pyrolysis reactor and the downdraft gasifier, partial combustion takes place to destroy the tar and provide energy to sustain the process. A cold gas efficiency of 93% and tar content less than 15 mg/Nm³ have been reported [224]. However, N₂ is still present in the syngas since air is the oxidizing agent. Along with the downdraft gasifier, this innovative gasifier is one of the most common gasifier types found in small-scale systems.

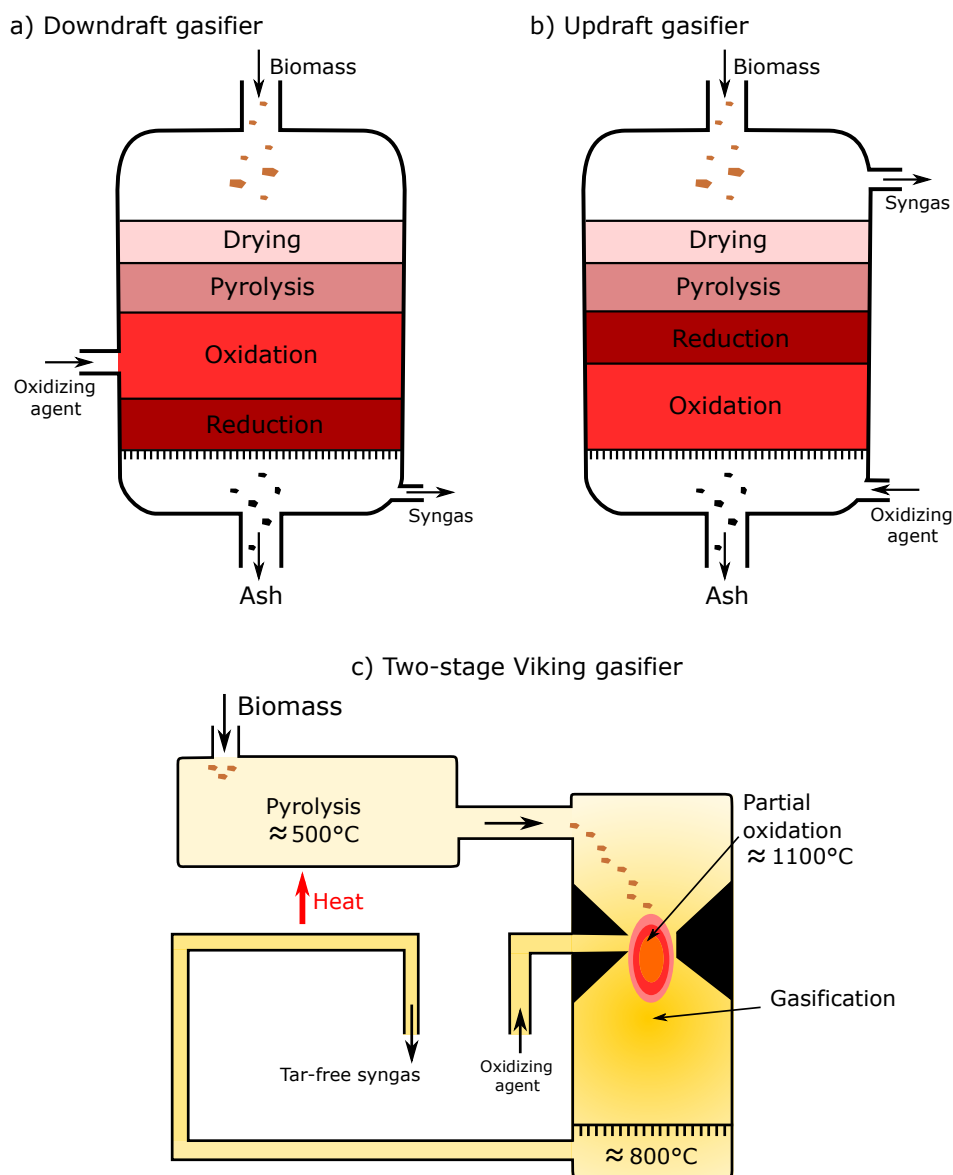


Figure A.1 Schematic representation of the a) downdraft, b) updraft, and c) two-stage Viking gasifiers [221].

Fluidized bed gasification

Fluidized bed gasifiers are known for their excellent solid-gas mixing characteristics, flexibility of entrainment by different gasification agents, high biomass conversion rate, and scalability [10,12]. The ability to fluidize with steam increases the amount of H_2 in the syngas due to the water gas shift reaction. This in turn boosts the carbon conversion rate and consequently biofuel yield, as discussed in section 2.1. Also, fluidized bed reactors allow for using catalytically active bed materials for in-situ tar reforming [17]. Tar is one of the most detrimental contaminants in syngas. Its presence can deactivate catalysts and clog downstream equipment. More on tar and its elimination methods is discussed in section B. On the other hand, a condition on the maximum entrained particle size, usually approximately 10 mm in diameter, is imposed on fluidized bed gasifiers. Also, their operation is more complex compared to fixed bed gasifiers. This renders their investment and operational costs higher.

Conventional fluidized bed gasifiers such as the circulating fluidized bed, or the bubbling fluidized bed are not discussed here. Interested readers are referred to [8,12]. These designs bring limited advantages for the small scale apparatus considered, as they generate syngas with elevated N_2 content (if air is used) and contaminants. The nitrogen content renders the produced syngas energy-light, where it must be cleared using expensive units before injecting syngas into catalytic biofuel reactors [181] to reduce the total flow rate (avoiding oversized equipment), and to avoid catalyst deactivation by NH_3 poisoning.

Dual fluidized bed gasifier

The operating mechanism of dual fluidized bed gasifiers was discussed in section 2.1.3 (figure 2.3). This approach is also sometimes referred to as fast internally circulating fluidized bed gasification (FICFB). The main advantage of DFB gasification is that a N_2 -free syngas is generated as the combustion and gasification chambers are separated [80]. The generated syngas therefore has elevated LHV and H_2/CO ratio, increasing the cold gas efficiency of the gasifier [170]. Hence, the need to use expensive ASUs to provide pure O_2 , and WGS reactors to increase the H_2/CO could be eliminated [225].

DFB gasifiers also have the ability to operate at high pressures, and this was shown to enhance tar cracking [222]. The steam to biomass ratio (S/B), is an important parameter influencing the performance of the gasifier. Increasing the S/B enhances tar reforming and carbon conversion, while lowering the chances of catalyst fouling due to carbon deposition [31]. However, this comes with a penalty as energy is expended in generating the steam. Hence, with competing effects on the system's performance, the value of S/B must be carefully optimized. It should be kept in mind as well that a minimum amount of steam is required

for fluidization. For a given S/B, the amount of fluidizing steam decreases with increasing biomass moisture. Therefore, biomass drying may be required in some instances to ensure adequate fluidization.

Biomass Heatpipe Reformer

The biomass heatpipe reformer (BioHPR) gasifier is another innovative allothermal steam gasifier patented by the Technical University of Munich [226]. In this peculiar setup, only the gasification chamber is pressurized, with char combustion taking place separately at ambient pressure. The combustion heat is transferred to the gasifier using a metal working fluid such as K, or Na. This results in a compact gasifier design that generates high-quality N₂-free syngas with elevated biomass conversion efficiency. Gröbl et al. [31] conducted a thermodynamic analysis for bio-SNG production from biomass using a 1MW BioHPR gasifier. A few gasification parameters were studied, but the most influential was the air preheating temperature, where the cold gas efficiency increased by 10 percentage points with an increase in temperature from 200 to 700°C. Their work also showed that an attractive overall cold gas efficiency of 68% could be attained using the BioHPR gasifier in the process of converting biomass into SNG.

UNIQUE gasifier

In the aforementioned fluidized bed gasifiers, the syngas must be cleaned before being further converted into biofuel. This is because it contains tar, acid gases, and other contaminants in amounts that can poison catalysts. In the UNIQUE gasifier however, the elimination of contaminants takes place in-situ by a patented technology that was investigated in a collaborative R&D European Project [227]. The concept was also exploited for efficient H₂ generation in the UNIfHY project [228].

Catalysts were added to the bed material of the steam fluidized bed, in order to convert some of the tar, and fully adsorb poisoning acid gases. Then, a catalytic filter was integrated in the freeboard to fully separate tar and particulate matter from the syngas [17]. This gasification concept offers several advantages, one of which is the energy efficient gas cleaning approach, which takes place in-bed at hot temperatures. This minimizes the sensible energy losses during syngas cooling and transportation from one equipment to another. The other prominent advantage of the compact design is the saved plant space and number of equipment. Nonetheless, the long term reliability of the technology is still to be proven. The gasification technology was not tested for a long period of time, where catalysts deactivation and filter clogging are prone to occur.

FLETGAS

Similar to Viking fixed bed gasifier, fluidized beds have been used for multistage gasification as well. FLETGAS is a three-stage gasifier with pyrolysis taking place between 700 and 750°C in a first stage fluidized bed reactor [229]. The significant amount tar generated at this stage, is then converted by steam at a high temperature (1200°C) in the second step. In the final stage, gasification of the generated char takes place in a moving bed downdraft gasifier. The architecture of the FLETGAS gasifier permits direct transfer of the pyrolysis char from the first stage to the last through a gas seal solid transport [230]. This provides the unique benefit of having an almost tar-free syngas without the need of in-bed catalysts. However, the generated syngas is N₂-rich, with a low-H₂ composition. As a result, it requires further processing before being injected into biofuel reactors. The operation of the system is relatively complicated as well [17].

APPENDIX B SYNGAS CLEANING

Contaminants such as tar, acid gas, ammonia, particulate matter, and alkali metals are often found in dangerous quantities in the syngas produced by biomass gasifiers. It is necessary to clean the raw syngas since the concentrations of these contaminants usually have detrimental consequences on processes downstream. There are numerous syngas cleaning strategies, with varying equipment size, cleaning efficiency, and energy consumption. Choosing the right syngas treatment technique could be vital for the economic viability of the process [17, 162].

The syngas treatment techniques are generally divided into two categories [231]: 1) hot gas cleaning that occurs above tar condensations points ($T > 300^{\circ}\text{C}$), and 2) cold gas cleaning that takes place below the standard condition water condensation point ($T < 100^{\circ}\text{C}$). Small-scale plants discussed in the literature are usually operated using either or combinations of both gas cleaning methods. Wet and dry cleaning are two subcategories of cold gas cleaning, and are mature approaches with long life times. But these methods lower the overall efficiency of the biomass conversion system due to their low operating temperatures. On the contrary, hot gas cleaning, which are further categorized into thermal and catalytic processes, contributes to higher process efficiency [17], but usually has a shorter lifetime due to the strain imposed on the equipment at elevated temperatures.

Tar

In the context of biomass gasification, all organic compounds in syngas with molecular weight greater than or equal to benzene (C_6H_6) are usually considered as tar [232]. Tar is generated during the biomass pyrolysis/devolatilization stage, and condenses approximately below 300°C to clog equipment. If not reduced to sufficiently low levels, tar can also readily deactivate catalysts. Tar level requirements vary depending on the process for which syngas is intended. Compressors for instance usually require tar concentrations to be less than 500 mg/Nm^3 , while ICEs and fuel cells impose a maximum tar limit of 100 mg/Nm^3 [162, 216]. For catalytic chemical reactors tar levels requirements can be as strict as 0.1 mg/Nm^3 [216].

Tar removal procedures can be classified as either physical or thermochemical [233]. Wet scrubbing is a mature and reliable cold gas cleaning example of the former. Water alone does not suffice as a solvent since the non-polar tar molecules do not dissolve in it. Hence, other solvents, which are usually expensive, are required for effective tar separation. For instance, a rape seed methyl ester (RME) scrubber with a tar cleaning efficiency of 98% is reported to be used in the 8 MW combined heat and power plant in Güssing (Austria) [80].

The RME obtained is then recycled into the combustion bed of the gasifier to avoid liquid disposal [17]. Despite the high tar conversion efficiency and reliability, wet scrubbing occurs at low temperatures relative to gasification and involves several equipment. As a result, its economic and operating costs may not be justified for small-scale systems. This is usually not the case with large-scale systems that heavily rely on this technology [222]. Other physical separation techniques using ceramic filters or cyclones are not efficiency enough on their own for the complete tar removal. A significant amount of the tar remain in the vapor phase following treatment with these methods, which also often suffer from various technical problems such as clogging of filter pores, and handling of toxic tar waste [216].

A convenient alternative option for small-scale setups could be the thermochemical conversion of the condensable tar molecules into lighter non-condensable hydrocarbons. This approach can eliminate the trouble of tar handling, and also contribute to improving the overall process efficiency due to the elevated operating temperatures. The chemical reactions governing the thermal cracking of tar occur at slow rates and usually require elevated temperatures (greater than 1000°C). This is why a catalyst is commonly used for effective tar conversion into useful gaseous products at milder operating conditions [216,233]. The performance of different tar reforming catalysts are discussed next.

Performance of tar-decomposing catalysts

The desirable characteristics of tar-decomposing catalysts are well established [234]: 1) Effective tar removal, 2) methane reforming, 3) provide desirable syngas composition, 4) resistance to fouling by coke deposition, 5) resistance to sintering, 6) regenerability, and 7) strength, and 8) affordability. In this section, the most commonly used natural and synthetic catalysts are assessed based on these criteria, with particular emphasis on their ability to resist fouling by coke deposition.

Natural catalysts

Dolomite, an abundant and cheap mineral found deeply under the ground and which constitutes mainly of Ca, Mg, and CO_3 , is commonly used as a catalyst to decompose syngas tar [222]. The proportions of its three key constituents differ depending on the dolomite source, and this affects its catalytic activity, which generally increases with higher Ca/Mg ratios [235]. Dolomite can undergo calcination, before being deployed for tar removal to increase its cleaning efficiency [233]. A study by Corella et al. [236] showed that calcined dolomite is 1.4 times more effective at tar removal compared to untreated olivine, another natural catalyst. But it is frequently reported in the literature that, contrary to calcinated

olivine, dolomite becomes fragile after calcination [222]. Dolomite also readily suffers from deactivation due to coke deposition, which is why it is usually used in a steam fluidized bed gasifier [222] that has the potential to reduce tar to medium concentrations only of 1000-2000 mg/Nm³ [17]. As a result, natural catalysts are considerably less effective at decomposing tar, especially compared to synthetic metal catalysts [230], and this means that they rarely suffice on their own for close-to-complete tar abatement. When used in a dual fluidized bed gasifier, coking severity reduces as the CaCO₃ catalyst is circulated between the gasifier and the combustor, which leads to the burning of some of the deposited coke [225].

Olivine is another cheap and abundant natural catalyst with Mg, Fe, and SiO₄ constituents [222]. Calcinated olivine has a similar catalytic activity compared to calcinated dolomite [237], and is sometimes favoured for use in fluidized bed gasifiers due to its ability maintain its mechanical strength and resist attrition [17, 233]. Medium tar reduction levels of 1500-4500 mg/Nm³ is usually realized in olivine-bed fluidized bed gasifiers [238]. Hybrid natural-synthetic catalysts are usually used to exploit the advantages of each catalyst, and suppresses their downsides. The impregnation of olivine with nickel results in a catalyst that is resistant to attrition and that is highly active [239]. But this approach usually requires costly measures to be taken to dispose the resulting nickel-loaded ash from the gasifier [17]. Alternatively, the enrichment of the ferrous content in olivine catalysts through impregnation can also be conducted. Apart from the increased tar conversion efficiency, an increase in H₂ and gas yield is also attained. This is mainly due to the WGS reaction that is favoured by olivine. Rapagnà et al. [240] demonstrated the added value of 10 wt% Fe-enriched olivine catalyst to a steam fluidized bed gasifier. The gas and H₂ yields were increased by 40% and 88%, respectively, compared to a natural olivine, and also the tar and methane contents were lowered by 46% and 16% respectively.

Synthetic catalysts: Transition metal-based catalysts

Nickel-based catalysts are one of the mostly used transition metal catalysts for tar decomposition primarily due to their high conversion efficiencies, along with their ability to enhance the H₂ and CO content of syngas, and reform methane [169, 216, 233]. Despite having high activity as well, the other transition metal-based catalysts such as cobalt (Co) are used less often due to their higher costs compared to conventional nickel [169]. Zhang et al. [168] conducted an experimental investigation to study the ability of three nickel-based catalysts with different promoters to destroy tar contained in syngas generated from a seed corn fluidized bed gasifier. Steam-enriched catalytic bed reactors operating between 740-820°C were used. A tar destruction efficiency greater than 99% was reported for all three catalysts, along with an increase in syngas-H₂ content between 6-11%. Similarly, Pfeifer and Hofbauer [214] tested

another three nickel-based catalysts for their tar elimination ability using toluene model tar. A fixed bed quartz catalytic reactor operating between 750-900°C and enriched with steam was used. A 98% tar conversion efficiency was reported from the tests that lasted 12 hours. Corella et al. [213] also reported a high 98% tar elimination efficiency by four nickel-based catalysts from experimental measurements.

Despite their excellent tar conversion efficiency, nickel catalysts are highly susceptible to deactivation by coke deposition as reported in the aforementioned studies and frequently in the literature [168, 214, 241, 242]. One way to mitigate this problem is by increasing the S/C ratio [243], which also increases the energy expenditure of the system due to steam generation. The inclusion of transition metal promoters such as molybdenum (Mo), tungsten (W), and manganese (Mn) with nickel catalysts, has also been used as an alternative approach to sustain high catalytic activity and enhance coke deposition resistance as shown by Dou et al. [244], who reported only minimal coke deposition on the NiMo catalyst that was used to decompose 1-Methylnaphthalene model tar. But the main issue with nickel, and with transition metals as mentioned earlier, is their elevated costs, which explains the large number of studies in the literature investigating coke deposition mitigation strategies with nickel catalysts.

Synthetic catalysts: Nobel metal-based catalysts

Nobel metals catalysts such as platinum (Pt), palladium (Pd), ruthenium (Ru), and rhodium (Rh) have also been used for the effective conversion of tar in biomass gasification syngas. Tomishige et al. [245] compared commonly used nobel metal-based catalysts for tar reduction in syngas from cedar gasification, and concluded that Rh is the most effective catalyst followed by Pt, Pd, and Ru. Asadullah et al. [246] loaded Rh on $\text{CeO}_2/\text{SiO}_2$ to catalytically convert syngas tar from cedar gasification, and to increase the sintering resistance of the catalyst. Appealing results were reported, where the catalyst used was more effective at tar reforming compared to commercial nickel-based ones. Besides the higher conversion efficiency, Miyazawa et al. [247] showed that the $\text{Rh}/\text{CeO}_2/\text{SiO}_2$ is more resistant to coke deposition compared to nickel. In fact, in all of the aforementioned studies, the amount of coke deposited was minimal. However, the main obstacle hurdling the industrial deployment of nobel metal-based catalysts is their cost, since they are even more expensive than nickel [242, 248].

Synthetic catalysts: Carbon-supported catalysts

The use of residual gasification char, also known as biochar, for tar elimination has attracted a

lot of scientific interest due to its continuous production and potential to evade the economic burden of the conventionally used tar-abatement catalysts [248]. The mechanism of tar removal by biochar is highly dependent on the operating conditions, where Ravenni et al. [249] reported that tar is adsorbed at lower temperatures (250-400°C), while it is decomposed at hotter conditions (600-800°C) with a considerably higher cleaning efficiency. The tar removal effectiveness of char compares well with other commercial catalysts as reported by El-Rub et al. [250], who found out that char with 99.6% efficiency, came second after nickel (100%) for maximum naphthalene removal at 900°C, followed by biomass ash (73.7%), FCC (60.3%), dolomite (61%), olivine (55%), and finally silica sand (2%). For maximum conversion phenol at 700°C, nickel (91%) came first followed by dolomite (90%), fluid catalytic cracking (FCC) (87%), char (82%), olivine (42.7%), and lastly sand (34.5%). It has been also shown that biochar has the capacity to decompose toluene with a conversion fraction of 80% at 800°C [251].

Despite all of its appealing features, char is highly prone to deactivation from the deposition of coke. At 800°C, the characterization of char showed that its catalytic deactivation was mainly due to coking [249]. The authors claimed that the addition of H₂O and CO₂, and an elevated temperature can evade this problem by enhancing coke gasification rates. As can be seen, the conclusions drawn from the current literature regarding the potential of biochar for tar abatement are appealing, but are mainly based on the decomposition of model tar. Despite model tar being valuable and handy to use for understanding tar interaction with char, tests with real syngas tar are required, and are scarce. Also, optimum parameters related to the catalyst geometry and operating conditions must be determined through rigorous experimentation, to find the right balance between tar conversion and coke gasification. Ravenni et al. [251] listed the following influential biochar catalyst parameters for investigation in future endeavours: reactor temperature and pressure, syngas composition, residence time, catalyst specific surface area, pore volume, and pore size distribution.

Other synthetic catalysts

To overcome the elevated costs of highly active noble and transition metals-based catalysts, Li et al. [215] patented tar abatement technology relies on less expensive char-supported iron catalysts. The inventors reported tar reduction capacities up to 100 mg/Nm³, with high resistant to catalyst deactivation. Its distinctive anti-coking ability comes from the fact that the char support allows the generation of new active sites on the iron surface, while the deposited coke gets slowly gasified to free other active sites [216]. Alkali metal catalysts such as lithium (Li), sodium (Na), potassium (K), and rubidium (Rb) have also been used to enhance the quality of syngas by decomposing tar through steam reforming. Most of the

times they are added to the gasifier bed, where ash, which is considered another alkali metal catalyst, is formed and contributes to the reduction of tar content [252]. But as frequently reported in the literature, these catalysts readily evaporate, promote particle agglomeration at high temperatures, and are hard to recover [222,233].

Acid gas

Acid gas contained in syngas is usually in the form of H_2S and HCl [231]. CO_2 is considered as another acid gas present in syngas, but its removal is not mandatory. The sulfur content comes from the biomass itself and is usually around 0.1% by weight for woody materials, and 0.3% for carbonaceous feedstock such as coal [216]. The same applies to the chlorine content, however, its concentration in biomass is usually much lower. The operation of syngas-fed ICEs is not affected by the presence of acid gas. However, when it comes to more sophisticated applications such as biofuel synthesis, the concentration of acid gas in syngas exiting the gasifier is always above the maximum allowable limit for catalyst poisoning [216,253]. For instance, fuel cells and catalytic reactors require to have sulfur content below 1 ppm, and chlorine content below 1 ppb [11,17].

To meet these stringent requirements, acid gas can be separated by four main techniques [166]: 1) absorption, 2) adsorption, 3) membrane separation and 4) cryogenic distillation. Absorption, a cold gas cleaning technique, is the most mature technology, and is most often relied on for high gas removal rates on commercial scales [254]. Acid gas absorption can take place physically, or chemically. The second technique, adsorption, is a promising hot gas cleaning technique and an active area of research. Membranes are traditionally investigated for post-combustion CO_2 removal, and are very sensitive to CO_2 concentration and pressure [255]. Although it has been reported that this technology can be used for the removal of H_2S as well, it is still not reliable enough for acid gas removal from syngas at the current time [65]. Cryogenic distillation is another novel acid gas separation technique, which relies on distillation at very low temperatures and high pressures. Owing to the operating conditions, this method is energy-intensive, and has been reported to be feasible only for elevated CO_2 concentrations [65]. For the aforementioned reasons, absorption and adsorption are the only acid gas cleaning techniques discussed next.

Absorption

Acid gas absorption can be categorized as either physical or chemical. The latter requires chemical solvent regeneration through boiling, inducing often unjustifiable energy costs for small-scale systems. The two well-established physical absorption technologies are Recti-

solTM and SelexolTM [187]. The former uses chilled MeOH solvent at around 20 bar, and between -75 and -30°C, while the latter relies on polyethylene glycol (PEG) solvent at around 20 bar, and between 0 and 25°C [166]. Although these methods are attributed with high separation efficiency and equipment lifetime, a heavy energy penalty is induced due to the aforementioned operating conditions [254]. Moreover, the water content in syngas is condensed in the process, and this may require generating and adding steam downstream in order to avoid carbon deposition on the catalysts of fuel reactors [187]. Koytsoumpa et al. [254] compared different absorption techniques for the removal of acid gas in a coal-to-SNG process via gasification. Different physical solvents like RectisolTM and SelexolTM and chemical solvents like K₂CO₃ and MDEA were analyzed. In all cases, the syngas after the absorption process was clean enough to be injected into the methanation reactor. Results showed that RectisolTM, compared to SelexolTM, consumed more power and required lower solvent flow rate. On the other hand, K₂CO₃ solvent consumed more heat and required higher solvent flow rate compared to MDEA. Despite this, the former required less cooling and induced less heat losses to the system. Comparing physical and chemical solvents, the former consumed considerably larger amounts of power. On the other hand, chemical techniques required a significantly greater amount of heating requirements due to their energy-intensive solvent regeneration system.

Adsorption

Adsorption of acid gas using sorbents has the potential to avert the high energy losses and investment costs attributed with the aforementioned absorption techniques. CaCO₃ or CaO sorbents may be used as a first stage acid gas removal. When more cleaning is required, NaHCO₃ can readily eliminate all the HCl from the syngas [187]. It is recommended to remove chlorine content first to avoid possible interactions between HCl and the sorbent used for sulfur content removal [256]. For the latter, ZnO can be used with a maximum allowable operating temperature of 500°C to avoid sorbent sintering. This can be exceeded by utilizing a more thermally stable metal oxide sorbent like MnO, which can operate at 800°C. Sadegh et al. [162] conducted simulations of a biomass gasification system with sulfur and chlorine content adsorption using MnO and Na₂CO₃ sorbents respectively. The cleaned syngas was fed to a hydrogen fuel cell, and the overall process with hot gas cleaning proved to be theoretically more efficient compared to similar cases reported in literature [257]. The reliability of MnO sorbent was tested experimentally, where it was reported that MnO sintering was observed during sorbent regeneration. The authors suggested mixing the sorbent with an inert material to avert thermal sintering, and planned to prove the feasibility of the process in future work. Before justifying the feasibility of a biomass conversion plant with acid gas adsorption,

sorbent regeneration through temperature swing adsorption (TSA) or PSA has to be carefully assessed or otherwise the process of frequently replacing the sorbent would render the system economically inviable. This is the main problem could potentially hurdle the adoption of acid gas adsorption technology.

As mentioned in section B, the valorization of gasification char and its use for contaminant elimination is an active research area. The incorporation of the abundant char has the potential to lower the economic burden of acid-gas sorbent replacement. Due to its large surface area and carbon content, it can be used as a sorbent. Marchellie et al. [258] experimentally studied the capabilities of char to adsorb H_2S . Five different char samples were collected from real gasification plants with either wood chips or wood pellets feedstock. A maximum adsorption capacity of $6.88 \text{ mg}_{\text{H}_2\text{S}} \text{ per g}_{\text{char}}$ was obtained. This was comparable with adsorption capacities of commercial activated carbon. It was shown that the main parameters influencing the adsorption capacity of char are: the specific surface area, metal content, and oxygen content. The obtained results were promising, and highlighted the potential of directly re-using gasification char for H_2S adsorption. However, they are considered preliminary, as a binary $\text{H}_2\text{S} - \text{N}_2$ gas mixture was used instead of syngas.

Other than ex-situ treatment, sorbents can be added to the fluidized bed inventory to adsorb noxious acid gas. Calcined or unclaimed CaCO_3 can adsorb acid gas to medium levels, but not enough for injection into fuel cells or catalytic biofuel reactors [17]. Stemmler et al [259] investigated the addition of different sorbents to the bed inventory of the UNIQUE gasifier for acid gas cleaning. It was shown that Ca or Cu based catalysts were only able to lower H_2S concentration to 100 ppm. However, using a Ba based sorbent, developed by Forschungszentrum Jülich, yielded H_2S and HCl concentrations below 1 ppm and 1 ppb respectively.

Ammonia

The nitrogen content in syngas is mainly present in the form of NH_3 , N_2 , and HCN . NH_3 is usually in concentrations around 1000-5000 ppm [162]. When it comes to ICEs, the threat posed by NH_3 is not on the operation of the device itself, but on the environment. This is because NH_3 can be readily converted to noxious NO_x and consequently violate emission standards [216]. In chemical reactors and fuel cells, NH_3 can also cause catalyst deactivation [216]. Water scrubbers are commonly used to fully separate NH_3 . But as discussed earlier, physical separation techniques add to the complexity of the system, especially if small scale, due to the handling of waste and lower thermodynamic efficiency. The other cleaning options are the catalysts used for the transformation of tar (B), almost all of them are effective in

ammonia cracking [11].

Alkali metals removal

Vaporized K and Na are usually present in syngas in trace amounts, with KCl being the compound with greatest concentrations [17]. These contaminants condense at temperatures below 500°C [256], and can cause fouling on downstream devices. It is recommended to have alkali metal concentrations below 50 ppb and 10 ppb for ICEs and catalytic reactors respectively [216]. Metals can be removed by cool filtering or hot adsorption. It is well agreed that aluminosilicates have the ability to lower alkali content to minute levels, and are quite cheap materials to get and dispose [259].

Particulate matter

PM encompasses micron size ash from alkali matter of the biomass, and unconverted carbon in the form of dust. PM size ranges from 1 to 100 μm , and depending on the choice of the gasifier design, the amount of PM in the syngas will differ [11]. Generally speaking, the amount of PM in syngas emitted from fluidized bed gasifiers is greater than that emitted from fixed bed gasifiers [216]. This is due to the greater gas velocities in the fluidized bed. Allowable limits of PM differ depending on the downstream application. In the simplest of cases, even the direct combustion of syngas requires PM to be lower than 50 mg/Nm³ [11]. PM may block the nozzles of ICEs, while what remains in the exhaust gas may pose environmental concerns. This is why it is recommended to keep syngas PM below 50 mg/Nm³ when injected into an internal combustion engine [260]. When it comes to fuel cell applications, PM has the potential to adversely affect the operation of the anode, and is recommended to be below 0.1 mg/Nm³ [162]. Stringent rules are forced when it comes to biofuel synthesis, where PM must be fully eliminated before injecting syngas into a catalytic reactor [216].

Nowadays, technologies for the removal of PM are mature, and mostly based on inertial separators. Cyclones are typically used right after the gasifier to eliminate most of the particles with diameters greater than 10 μm . After that, different devices may be used to fully eliminate PM with diameter greater 1 μm [11]. Hot PM eliminators include filters or electrostatic separators, where the cleaning efficiency usually drops with elevated temperatures. Cold PM eliminators such as wet scrubbers can be used as well. A cleaning efficiency greater than 90 % is usually reported for wet PM removal with diameters greater than 5 μm [11]. When it comes to in-situ gas cleaning, filters mounted in the freeboard of a fluidized bed gasifier readily clears out all the PM in the generated syngas [261]. When fitted with a catalysts, these filters also convert tar as discussed in section B.

APPENDIX C SUPPLEMENTARY MATERIAL OF ARTICLE 3

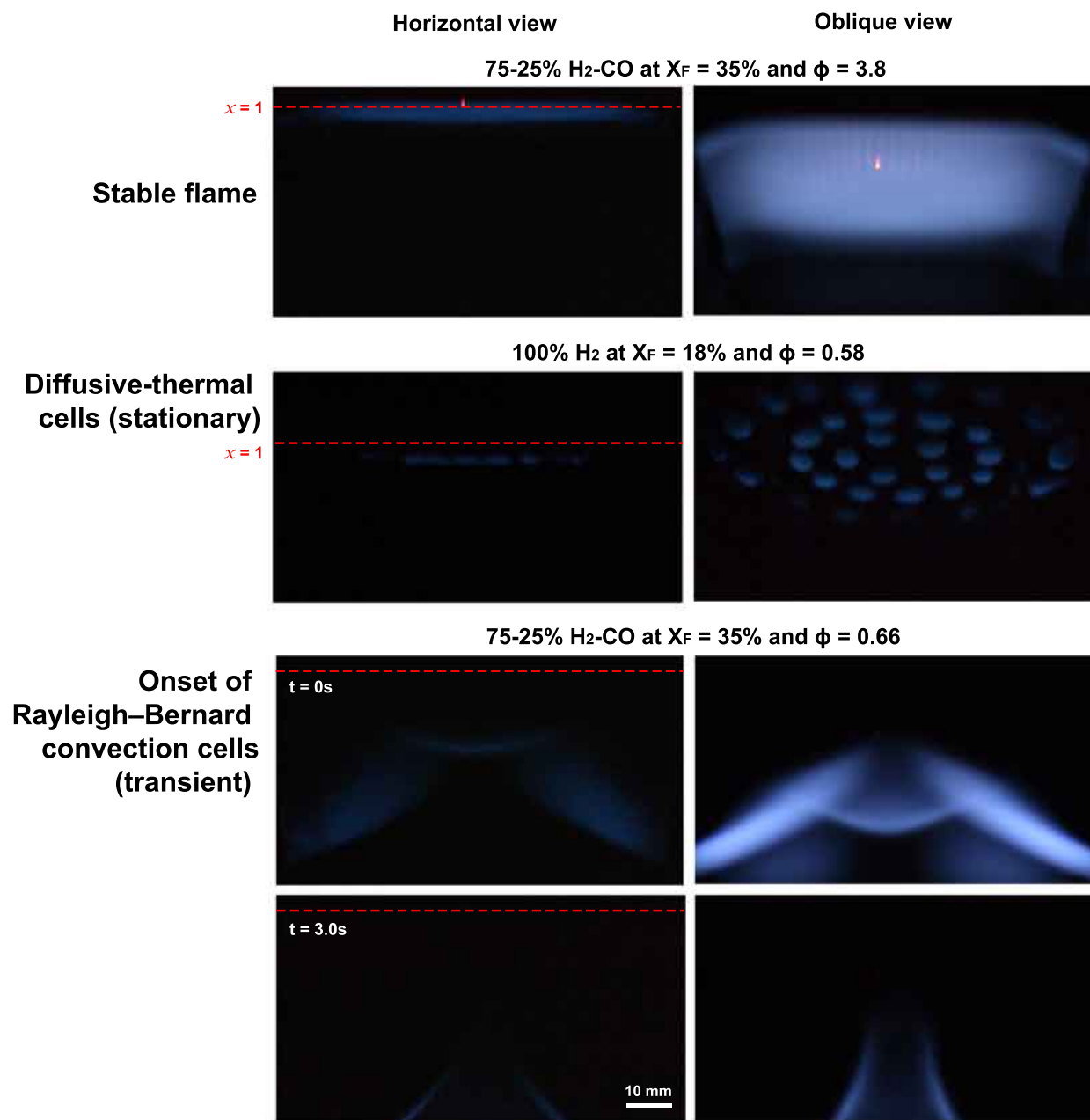


Figure C.1 Comparison between stable flames, diffusive-thermal instabilities, and bouyancy-driven instabilities, with the inner cylinder removed from the combustion chamber.

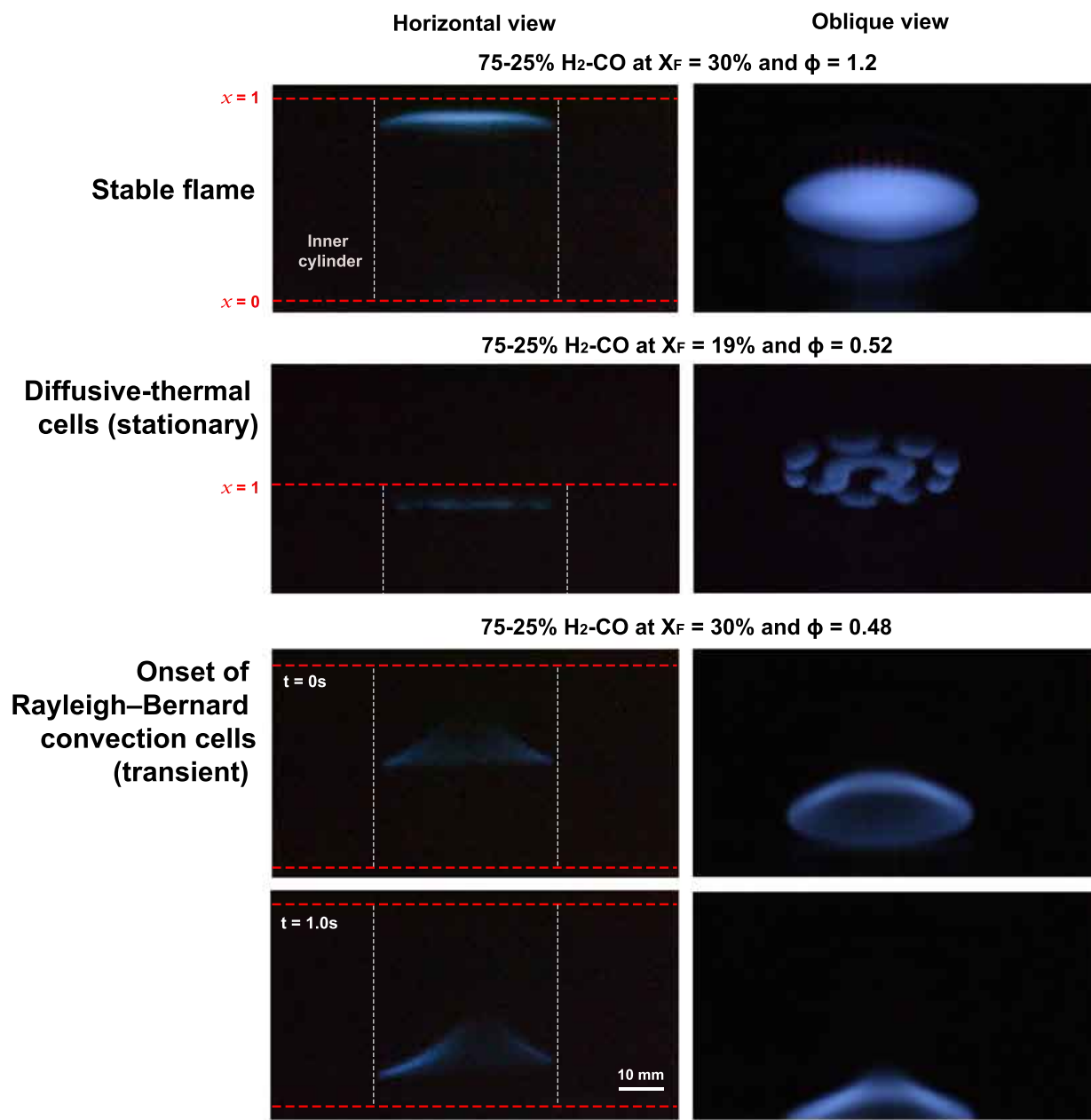


Figure C.2 Comparison between stable flames, diffusive-thermal instabilities, and bouyancy-driven instabilities. The vertical dashed lines represent the inner quartz cylinder.

The supplementary videos (2) can be accessed via this URL.

Table C.1 Characteristics of the TDIs observed in the different H₂-CO-CH₄ mixtures from the stability limits of figures 6.10 and 6.15.

Flame	X_F	ϕ	Le_o	$Le_{F,eff}$	Instability	Pulsations		Burning area (%)	Cells ^d	
					type	Amp (%)	Hz		Size (mm)	#
$X_{H_2,CO} = 75\%, X_{CH_4} = 0\%$ ^a										
1	23.5	0.43	0.98	0.44	Travelling waves	0	3.4	78	25.4	4
2	23	0.45	0.97	0.44	Travelling waves	0	3.3	66	28.4	4
3	23	0.43	0.97	0.44	Travelling waves	0	3.3	71	28.4	4
4	22.5	0.46	0.97	0.43	Travelling waves	0	3.1	71	29.7	4
5	22.5	0.43	0.97	0.43	Travelling waves	0	3.1	71	27.6	4
6	22	0.5	0.96	0.43	Travelling waves	0	2.9	75	18.5	5
7	22	0.46	0.96	0.43	P-IC ^b	28	0.9	10-93	20.1	4
8	21.5	0.54	0.96	0.43	Travelling waves	1	1	67-70	13.5	7
9	21.5	0.51	0.96	0.43	P-IC	20	0.9	24-81	19.3	4
10	21	0.55	0.95	0.43	Travelling waves	0	1	76	17.1	7
11	21	0.52	0.95	0.43	P-IC	15	1	38-79	17.4	5
12	20.5	0.57	0.95	0.42	Travelling waves	1	1	74-75	15.3	7
13	20.5	0.51	0.95	0.42	P-IC	8	0.9	43-78	15.2	5
14	20	0.58	0.95	0.42	Partly cellular	2	1.1	63-75	14.5	4
15	20	0.52	0.95	0.42	Pulsating cells	4	1.2	64-70	14.9	8
16	19.5	0.59	0.94	0.42	Partly cellular	1	1.5	61-70	14.5	4
17	19.5	0.53	0.94	0.42	Pulsating cells	4	1.3	55-60	13.9	9
18	19	0.63	0.94	0.42	Partly cellular	0	-	71	10.6	4
19	19	0.52	0.94	0.42	Pulsating cells	1	3.1	58-59	12.7	7
20	18.5	0.61	0.93	0.41	Partly cellular	0	-	65	9.5	4
21	18.5	0.5	0.93	0.42	Pulsating cells	2	3.2	47-51	11.7	10
$X_{H_2,CO} = 60\%, X_{CH_4} = 0\%$ ^a										
22	23.5	0.45	0.95	0.53	PIP ^c	1	1.1	77-80	-	0

Table C.1 continued from previous page

23	23	0.47	0.94	0.53	P-IC	24	0.8	19-99	21.4	5
24	22	0.51	0.94	0.52	P-IC	21	0.8	23-90	18.5	6
25	21.5	0.55	0.93	0.52	P-IC	19	0.8	26-86	17.5	6
26	21	0.57	0.93	0.52	P-IC	18	1	16-77	14.9	5
27	20.5	0.59	0.93	0.52	P-IC	17	1	19-79	15.3	6
28	20	0.61	0.92	0.51	Partly cellular	1.5	1.1	43-78	14.3	5
29	20	0.54	0.92	0.51	Pulsating cells	9	1.7	27-76	14.5	9
30	19.5	0.66	0.92	0.51	Partly cellular	1	1.2	66-72	12.9	4
31	19.5	0.54	0.92	0.51	Pulsating cells	3	3.1	50-70	11.1	6
$X_{H_2,CO} = 45\%, X_{CH_4} = 0\%$										
32	24	0.46	0.92	0.62	PIP	53	1	48-86	-	0
33	23.5	0.47	0.92	0.62	PIP	22	1	39-88	-	0
34	23	0.55	0.91	0.61	PIP	21	1	44-86	-	0
35	22.5	0.56	0.91	0.61	PIP	21	0.9	38-84	-	0
36	22	0.55	0.91	0.61	PIP	18	1	55-78	-	0
37	21.5	0.58	0.91	0.61	PIP	16	0.9	47-72	-	0
38	21	0.6	0.9	0.61	PIP	7	0.8	50-65	-	0
$X_{H_2,CO} = 75\%, X_{CH_4} = 15\%$										
39	22	0.58	1	0.51	PIP	1	1.3	70-71	-	0
40	21.5	0.58	0.99	0.51	PIP	3	1.2	64-74	-	0
41	21	0.6	0.99	0.51	PIP	2	1.2	65-74	-	0
42	20	0.61	0.98	0.5	P-IC	10 ^a	1.1	30-76	24.7	5
43	19.5	0.64	0.97	0.5	P-IC	8 ^a	1.1	50-64	22.4	5
44	19	0.65	0.97	0.5	P-IC	8 ^a	1	40-72	20.1	6
45	18.5	0.66	0.96	0.49	P-IC	6 ^a	1.2	40-63	18.7	8
46	18	0.69	0.96	0.49	Partly cellular	4 ^a	1.4	66-67	14.7	7
47	18	0.61	0.96	0.49	Pulsating cells	5 ^a	3.2	41-56	19.3	7
48	17.5	0.68	0.95	0.49	Partly cellular	7 ^a	3.3	53-65	13.2	6
49	17.5	0.6	0.95	0.49	Pulsating cells	7 ^a	3.5	48-58	18.8	7

Table C.1 continued from previous page

$X_{H_2,CO} = 75\%, X_{CH_4} = 30\%$										
50	17	0.72	0.97	0.6	PIP	22	1	34-53	-	0
51	16.5	0.73	0.97	0.6	PIP	16	1.1	25-53	-	0

^aPulsations amplitude given in terms of the variation in flame position due to excessive cellularity.

^bP-IC: Pulsation-induced cells.

^cPIP: Planar intensity pulsations.

^dCells characteristics given at the lowest intensity point of the pulsation cycle.