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Title: Petroleum Oil Using a Developed Demetallization Agent

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affiliée à l'Université de Montréal

**Microwaves-assisted demetallization and desulfurization of heavy petroleum
oil using a developed demetallization agent**

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Département de génie chimique

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

Mai 2019

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Cette thèse intitulée :

Microwaves-assisted demetallization and desulfurization of heavy petroleum oil using a developed demetallization agent

présentée par **Mai Abdelnaby ATTIA**

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

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DEDICATION

To the souls of my beloved parents whom their hopes were behind what I have achieved.

To my beloved family without whom I could not reach anything.

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Thanks are to God for everything I have in my life.

I would like to sincerely thank my supervisor, Professor Jamal Chaouki for his guidance, encouragement, understanding, and friendship during my Ph.D. For everything you have done for me, Professor Jamal Chaouki, I thank you.

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Mai Attia

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RÉSUMÉ

Les scientifiques du XXI^e siècle ont mis au point de nouveaux procédés pour la transformation de l'énergie et ceux-ci ouvrent la voie à un avenir plus durable. Cependant, l'aspiration à atteindre les objectifs de l'Accord de Paris est malheureusement encore très éloignée. De nouvelles technologies permettant une production élevée d'énergie et une réduction des émissions de carbone sont nécessaires pour atteindre cet objectif. Outre l'innovation dans les technologies pour la production d'énergie renouvelable, l'innovation dans les secteurs d'utilisation finale est aujourd'hui l'un des besoins les plus pressants. Les résultats d'une telle feuille de route comprennent l'intégration rapide de l'électrification des secteurs d'utilisation finale et l'intégration d'une part élevée d'énergie renouvelable dans les systèmes existants. L'industrie chimique et pétrochimique dépend du pétrole pour plus de 50% de leur consommation totale en énergie. L'utilisation d'électricité propre ainsi que des techniques de chauffage non conventionnelles ont ouvert la voie à une révolution dans les industries ces dernières années. Les techniques de chauffage les plus courantes qui ont été mises en œuvre comprennent le chauffage par induction, le chauffage au plasma, par ultrasons et par micro-ondes.

Ce travail a mis l'emphase sur les applications de ces techniques et plus particulièrement sur le chauffage par micro-ondes pour la démétallisation et la désulfuration du pétrole. Les raisons en sont que les métaux et le soufre dans le pétrole posent des défis majeurs aux restrictions imposées à la production de mazout. Les métaux de transition, plus particulièrement le vanadium et le nickel ainsi que les composés soufrés sont encore présents dans l'huile sous forme de complexes stables. Ces complexes sont solubles et ont un impact négatif sur les machines lors du processus du raffinage et sur d'autres aspects du procédé.

Ce travail a permis d'extraire sélectivement le vanadium et le nickel grâce à cinq nouvelles méthodologies inventées. En outre, il élimine les composés de thiophène qui sont aussi présents avec les métaux en utilisant deux processus d'extraction différents dans les mêmes conditions de réaction. Le processus développé sur la base des méthodologies inventées est écologique et rentable, car aucune opération supplémentaire telle qu'un processus d'émulsification n'est requis et aucun solvant n'est consommé pendant la réaction. L'extraction des métaux et du soufre contenu dans le pétrole a été réalisée à l'aide d'un nouvel agent chimique. Les micro-ondes ont pu fournir

l'énergie nécessaire à la séparation des contaminants présent dans le pétrole. Les conditions optimales de réaction ont été déterminées et appliquées. Les résultats obtenus ont été comparés à ceux du chauffage conventionnel. Cinq huiles différentes provenant de différentes régions du monde ont été traitées pour valider le concept des méthodologies inventées. Les résultats obtenus montrent une différence significative entre l'efficacité d'élimination d'éléments sélectionnés. Plus de 95% de la teneur totale en vanadium présent dans le pétrole brut iranienne a été éliminée en utilisation la conversion d'énergie en micro-ondes, contre 33% pour le transfert de chaleur superficiel. Le rendement obtenu pour l'élimination du soufre par chauffage conventionnel a été de 20% pour le pétrole iranien et de 60% pour le pétrole de Bassora. Toutefois, l'élimination du soufre présent dans le pétrole a été de 99% lorsque le processus d'extraction a été effectué en présence de micro-ondes.

L'interaction entre les micro-ondes et les métaux crée des points chauds locaux au niveau des liaisons métalliques, ce qui entraîne par conséquent un affaiblissement de la liaison entre les métaux et les quatre atomes d'azote dans le noyau de la porphyrine. Ceci, à son tour, améliore la décomposition facile et rapide des liaisons métalliques et la libération des métaux du noyau du cycle de la métalporphyrine. En outre, la forte interaction des autres métaux sous forme de sels polaires dans le pétrole stimule l'élimination de ces métaux du pétrole brut. Cela signifie que le chauffage par micro-ondes améliore l'élimination sélective des métaux du réseau des huiles et maintient le squelette principal de l'huile sans dégradation supplémentaire. En conséquence, le rendement de l'huile traitée n'est pas affecté par rapport aux autres technologies de démétallisation. Les résultats scientifiques de ce travail ont été documentés dans cinq demandes de brevet et six publications scientifiques.

ABSTRACT

Even though the current noticeable pace of energy transformation paves the way for a more sustainable future, the aspirational goal to meet the Paris Agreement's Policy is unfortunately still far off. More innovative solutions for high energy and low carbon intensity processes are urgently needed to support accelerated progress toward that goal. Along with the innovation in renewable power generation technologies, innovation in the end-use sectors is nowadays among the most pressing needs. The results of such a roadmap include the prompt embedding of the electrification of end-use sectors and integrating high shares of renewable power into the existing systems.

The chemical and petrochemical industry depends on oils for more than 50% of the total energy consumption. Employing clean electricity with unconventional heating mechanisms has initiated a revolution in the industry during the last few years. The most common heating mechanisms that are being implemented include induction heating, plasma, ultrasound, and microwave heating. This work demonstrates the fundamentals and the application of microwave to upgrade petroleum oils by removing sulfur and metals. The reason behind this election is that metals and sulfur in residual oil are the significant challenges behind restrictions facing fuel oil production. Both metals, particularly vanadium and nickel, and sulfur compounds reside in oil in complex stable forms yet are soluble and have a negative impact on machinery during the refinery processes and other aspects.

This work was successfully accomplished based on five invented processes capable of selectively extracting almost all the minerals, especially vanadium and nickel. Additionally, it excludes the thiophene compounds, which are alongside the metals, with two different extraction mechanisms under the same reaction conditions. The invented processes are green and cost-effective since no supplementary operations, such as emulsification, are required, and no solvents are consumed during the reaction.

The extraction of metals and sulfur from petroleum oil was performed using a novel demetallization-desulfurization agent. A microwave irradiation environment was created to provide the required energy essential for separating the metals and sulfur from the chemical network of the oil. A set of reaction conditions were applied, and the obtained results were

compared against those of conventional heating. Five different oils received from different fields around the world were processed to prove the concept of the invented processes.

The results obtained show a significant difference between the removal efficiencies of selected elements. More than 95% of the vanadium concentration in the raw Iran oil was removed using the energy conversion mechanism of the microwave compared to 33% for the superficial heat transfer mechanism. The removal of sulfur showed a considerable deviation in the removal efficiency using the microwave, 99% compared to 20% and 60%, for Iran and Basra oil, respectively, for the traditional heat.

The interaction between microwave and metals creates local hotspots at the metal bonds, which consequently leads to weakening the bond between the metals and the four nitrogen in the porphyrin ring. This, in turn, enhances the easy and rapid breakdown of the metal bonds and the liberation of metals from the core of the metalloporphyrin ring. Also, the high interaction of the other metals in the form of polar salts exist in the oil boosts the removal of such metals from the crude oil. This means that applying microwave heating enhances the selective removal of metals from the network of the oils and keep the main skeleton of the oil without further degradation. As a result, the yield of the treated oil is not affected compared to the other demetallization technologies.

The scientific outcomes of this work have been documented in Five Patent Applications and Six Peer-Reviewed Journal Publications.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Instantaneous yield of the aliphatic compounds
C	Specific heat
D_p	Penetration depth
E_{rms}	Root mean square of the electrical field
E_a	Activation energy
f	Frequency
H_{rms}	Root mean square of the magnetic field
K	Thermal conductivity
k_0	Pre-exponential factor
L	Transient yield of the condensable gas product
m	Mass
n	Reaction rate
O	Instantaneous yield of the oil product
P	Power
R	The universal gas constant
T	Temperature
t	Time
β	Heating rate
ε^*	Complex permittivity
ε'	Dielectric constant
ε''	Electric loss factor
ε_0	Electric permittivity of free space
ε_{eff}''	Effective dielectric loss factor

μ_0	Magnetic permeability of free space
μ_{eff}	Effective magnetic loss factor
$\tan\delta$	Loss tangent
ω	Angular frequency
α	Attenuation factor
ρ	Density
<i>DM-DSA</i>	Demetallization-desulfurization agent

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CHAPTER 1 INTRODUCTION

The continual decrease in the cost of renewable energy technologies in recent years positions renewable energy generation in direct competition with fossil fuel-based energy. Expanding affordable energy access through renewable resources to different sectors paves the way for a more secure, cost-effective and sustainable future not only for us but the next generations as well. The current trends of renewable energy, which include decentralization and digitalization, significantly promote the growing electrification of industrial end-use sectors. Although the current pace of energy transformation is noticeable, the goal to meet the Paris Agreement's Policy, which aims to limit the global temperature increase with 1.5 °C, is unfortunately still far away. According to IRENA-2018 publications, the prominent efforts that have been made by several countries to revise their policies of national emissions have reduced the projected energy-related carbon emissions of 2015-2050 by 11% compared to the previous estimation. This decline manifests that CO₂ emission of the reference case, which is the scenario that considers the current and planned policies, has dropped from 1380 Gt to 1230 Gt. Although the reduced amount limits the emission rate to 34.8 Gt/y, an increase from 2.6 °C to 3.0 °C in the global temperature is expected by 2050. To maintain global temperature increases at less than 2 °C, as depicted in Figure 1.1, cumulative global emissions must be reduced by 470 Gt over the next 30 years. In other words, the energy-related carbon emission must decrease from 1230 Gt to 760 Gt. This goal can only be achieved by lowering the CO₂ emission rate from 34.8 Gt/y to 9.7 Gt/y by that year, i.e., the generation rate must drop by more than 70%.

Although the reference case has decreased by 11%, as aforementioned, the CO₂ emission level increased by 1.4% in 2017. This aspect demonstrates that the stated amount of the reference case does not reflect the current level of energy-related emissions. Based on the present and planned policies, as a result, the world will exhaust its energy-related carbon emissions budget in less than 20 years.

The aspirational goal of the Paris Agreement aims to limit the rise in global temperature to 1.5°C, which means carbon-related emissions should reach “zero” by 2050, but only if negative emission technologies are employed by the second half of the century. Unfortunately, the current and planned policies are not keeping the emission trends on track to meet the goal. Though the

renewable energy sector has made significant achievements during the last few years, to reach the objectives from the current situation progress across the entire power system must increase six-fold. The total share of renewable energy must be increased from 15% of the total primary energy supply (TPES), which was in 2015, to 66% of TPES by 2050. The current reference case, however, would share only 27 % of the TPES, as presented in Figure 1.2. Besides, the TPES is projected to remain flat despite the population and economy growth predicted by 2050. To reach this objective, the rate of energy intensity must be reduced by 2.8 %. On the other hand, TPES in the reference case is predicted to increase by 40% from 2015 levels, i.e., from 500 EJ/y to 700 EJ/y. This increase will create obstacles to improving the energy intensity and keep the improvement in the energy intensity at 1.8%, which is the same as the reference case of 2015, kindly refer to Figure 1.3. To overcome this challenge, it is necessary to increase the rate of improvement of the energy intensity by 1.5x to reach the renewable energy roadmap that maintains the increase in the global temperature at less than 2 °C.

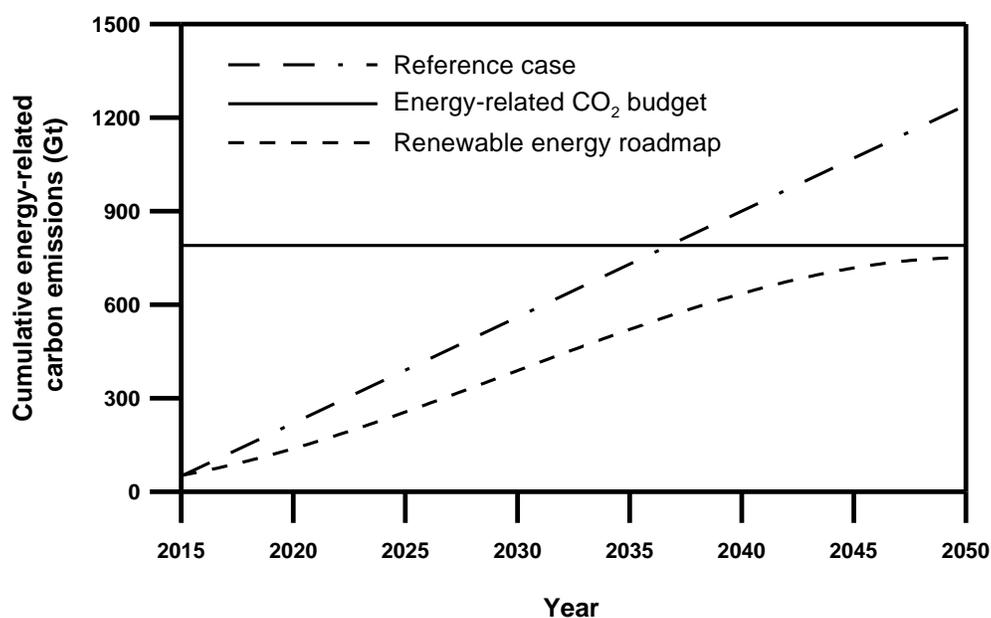


Figure 1.1 Cumulative global energy-related carbon emission (Reproduced from data provided by IRENA-2018 and IEA 2017)

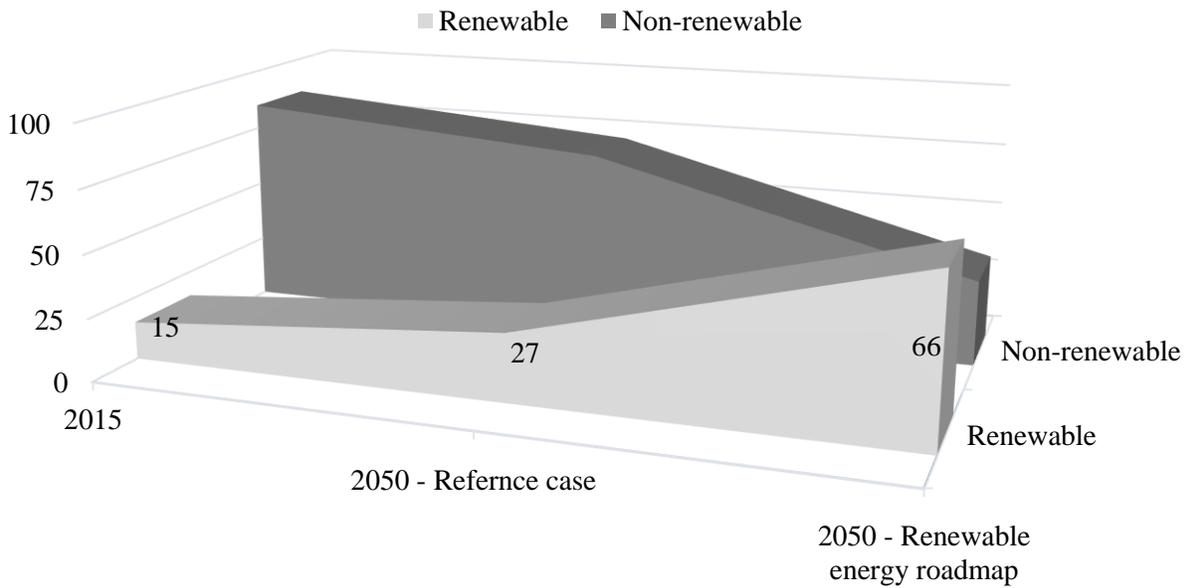


Figure 1.2 Sharing-percentage of renewable energy in the total primary energy supply
(Reproduced from data provided by IRENA 2018 and IEA 2017)

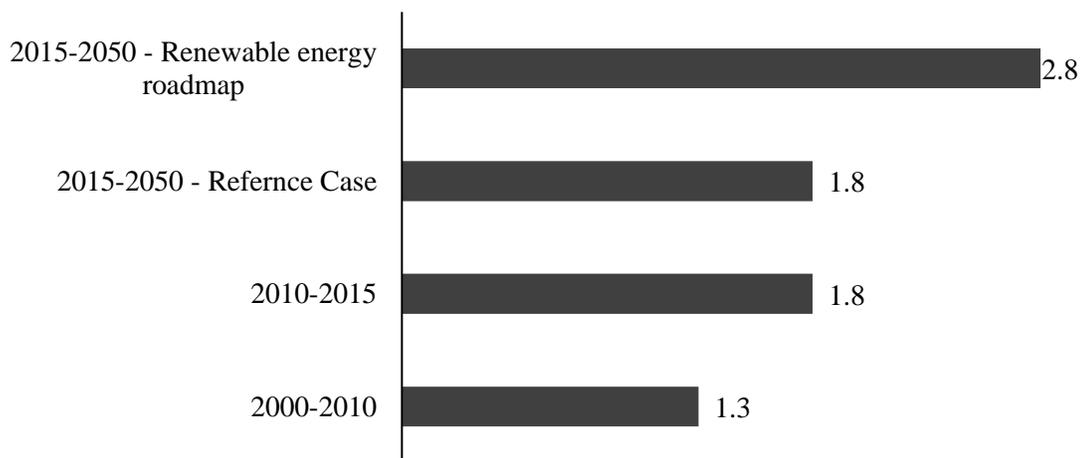


Figure 1.3 Energy intensity improvement percentage (Reproduced from data published by IRENA 2018)

More technological and systemic innovative solutions are still urgently needed for high energy and low carbon intensity processes to support accelerated progress. Continued research and

development on renewable energy in both academia and industry would lead to further approaches for more cost-effective and high-performance systems. Along with the innovation in renewable power generation technologies, innovation in the end-use sectors is presently the most pressing need. This objective can be achieved in two ways: (1) prompt embedding of electrification in end-use sectors; and (2) integration of high shares of variable renewable power into the existing systems.

This strategy provides the optimal pathway to deliver the bulk of the emission cuts needed at the necessary speed. Figure 1.4 presents the world total primary energy demand (unit: million tons of oil equivalent (Mteo)) in 2017 and the expected demand in 2040 in the case of existing energy policies and sustainable development. As is evident, global energy demand grows 30% by 2040, and it is planned to increase electrification transforming traditional ways to meet the demand. Solar power is becoming the cheapest form of new electricity in many countries; consequently, electricity based on solar energy will meet a significant portion of the energy demand.

To sum up, further efforts must be made to embed renewable energy and its conversion mechanisms into the basic energy consumption sectors, e.g., building, transportation, district heat, power, and the industry as well as for improving energy intensification. Beyond this strategy, additional innovation is needed to affordably decarbonize industrial activities, such as iron and steel making, cement production, and chemical and petrochemical production, along with freight and maritime transportation and aviation.

Figure 1.5 demonstrates the percentage of energy and electricity consumption of different industrial sectors. Chemical and petrochemical industries depend on oil for about 50% of the total energy consumption. A considerable amount of such energy is consumed in the upgrading processes – such as removal of hazard contamination from the oil composition. Such contamination is caused by the existence of high levels of metals and sulfur that originally present in the crude oil. Indeed, The presence of both metals and sulfur in crude oil has a jeopardy influence throughout the refinery processes as a result of severe damage to the contact surfaces. Furthermore, it gives rise to numerous environmental problems for both humanity and the atmosphere.

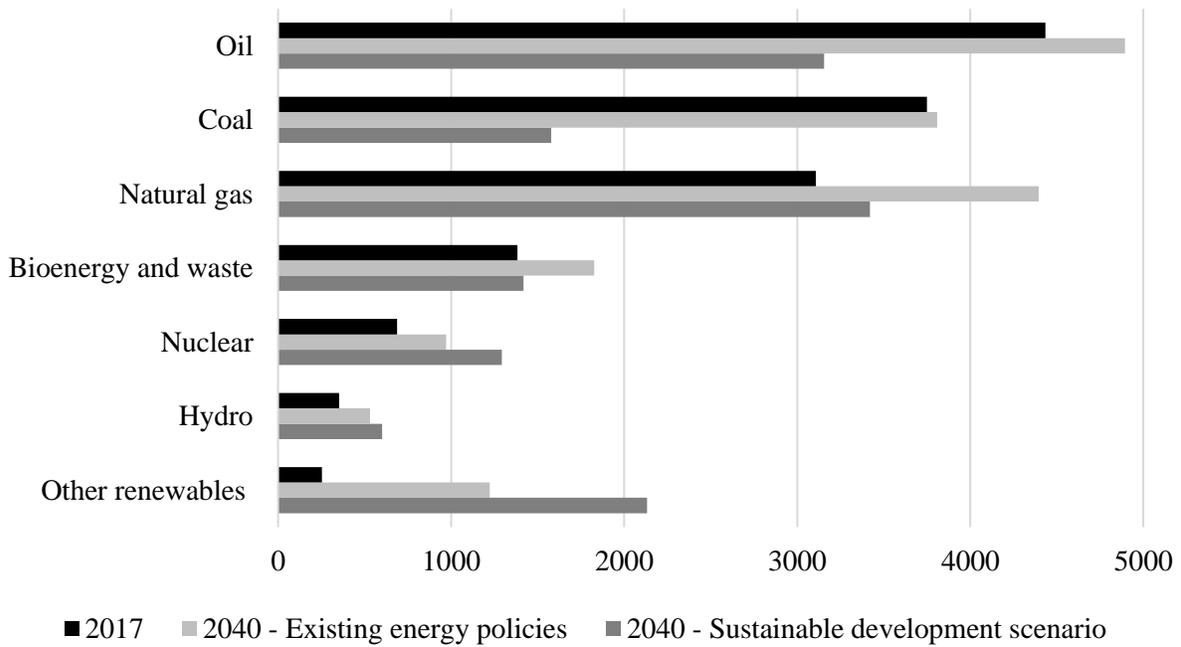


Figure 1.4 World total primary energy demand (Mte) (Reproduced from IEA report 2017)

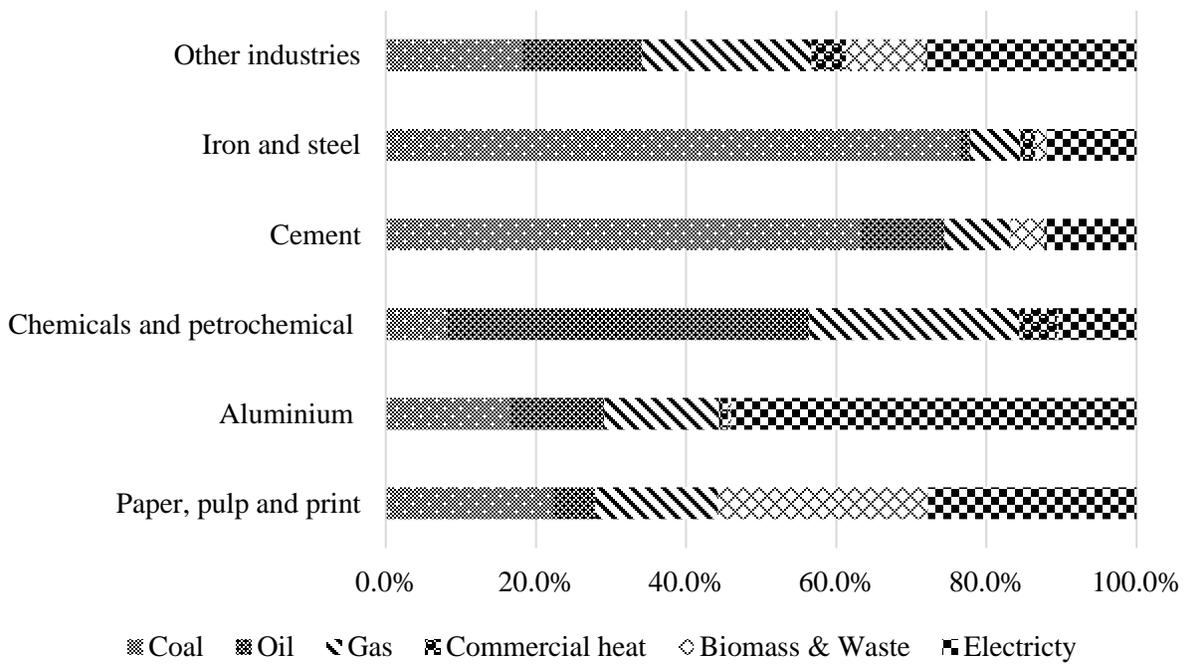


Figure 1.5 Industrial use of energy (reproduced from data published by IEA 2016)

It has been demonstrated that the concentration of various metals that exist in the heavy crude oil is diversified from a few parts per million to higher than 1000 ppm. Some of the most prominent elements that have been identified into the oil are cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), silver (Ag), sodium (Na), potassium (K), lithium (Li), calcium (Ca), strontium (Sr) and arsenic, etc [1, 2]. Vanadium and nickel are the most prevalent metals in the oil composition; for example, vanadium represents more than two-thirds of the entire metal impurities. Metals, in customary, exist as an oil-soluble form of naphthenic acid or complex organometallic compounds, i.e., the structure of metalloporphyrin ring [3, 4]. Other metals such as calcium, titanium, magnesium, and zinc found in a combination of naphthenic acid as soaps. Indeed, an extensive inspection has been conducted to the porphyrinic form due to the impact of the hazard metals that exist in such chemical form [5]. The removal of metals in the form of metalloporphyrins is a challenge, due to the high stability of the ring and the complete solubility in the oil. Also, the decomposition temperature of porphyrin compounds is usually more than 250 °C. Presence of metals in the heavy crude oil promotes several environmental issues. The most important ones include the emission to the environment as a poisonous gas in the form of SO_x and NO_x. Vanadium oxide reacts with the mucus into the human body, causing the body irritation. Nickel in the form of nickel carbonyl is a carcinogenic matter resulting in numerous types of malignant neoplastic disease. During the refinery processes, metals also play a hazard role in enhancing the corrosion problems to the contacting surfaces. Calcium and magnesium chlorides get hydrolyzed when they subject to temperatures of 170 °C. This leads to producing HCl, which is a highly corrosive agent. Metals have an impediment influence on the efficiency of the catalyst during the refinery process. The main reason behind this aspect is that the fast plugging the pores of the catalyst by minerals, which results in rapid catalyst deactivation. Therefore, it elevates the rate of uptake of the catalyst during the process, which puts up the monetary value of the technique. Also, accumulation of metals on the surface of catalyst exhibits dehydrogenation activity as it boosts the dehydrogenation reactions during the cracking operation. This issue enhances the production of increased amounts of coke and dry gases at the expense of the liquid output. Additionally, if the product is used as a fuel, the metals into the fuel oil will heighten the production of ash. This is because when the oil is exposed to burning, the ash deposits on the engines, causing a significant abrasion of the moving parts [6, 7].

The concentration of sulfur in crude oil depends on many parameters; the most important one is the origin place where it is extracted. In general, the percentage of sulfur concentration in crude oil is ranged from 0.1 wt.% to 15 wt.% [8]. Sulfur exists in such oil in four different forms: Mercaptans, sulfides, disulfides, and thiophenes [9]. The Presence of sulfur in crude oil has an adverse influence during transportation and the upgrading processes of the intermediate and end-products. It has several hazardous impacts on the environment and during the refinery operations.

Regarding the environmental hazards, as far as the sulfur content increases the boiling range raises and the pollution climbs. During the refinery operations, sulfur promotes the catalyst deactivation for its high ability to deposit on the pores of the catalyst. To sum up, the quantity of sulfur in crude oil considerably affects the quality of the oil and, thus, leads to a significant reduction in the price of the end-product.

1.1 Methods of demetallization and desulfurization

During the last few decades, various methods have been developed for refining crude oil through the removal of metals and sulfur. The common techniques applied for such purposes include physical, chemical, and biological methods. The central role of those methods is the conversion of heavy contaminated oil into lighter products that can easily be employed to produce valuable end-products. Most of the methods presented below have been proved and implemented in the lap-scale, and only some of them were successfully performed on the industrial scale. The main reasonbehind this aspect is the several issues that are associated with each technique which obstacle their implementation in the industrial scale.

1.1.1 Physical methods

Distillation

Petroleum heavy oil is a complex matter consisting of a mixture of several hydrocarbons, organometallic compounds, organosulfur compounds, and so forth. Distillation is the first method that has been constructed for crude oil refining since long decades. The process is performed for the separation of various components in the oil into fractions according to their boiling points. The crude oil is primarily heated to an elevated temperature to transfer into the gas phase. Then, the oil

vapor passes into a fractional distillation column at which various components will be recovered based on the variation in the boiling temperatures. Hydrotreating process in a fixed bed reactor is applied after the distillation of the oil by employing a low activity catalyst to extract all the metalloporphyrins. The main advantage of the distillation technique is the separation of adjacent boiling point compounds.

In contrast, the technique suffers from several disadvantages such as the inability for selective removal of metals from the oil. The process is merely adequate to eliminate the metalloporphyrin fractions that include the metals; which declines the oil yield. Additionally, distillation, as a single process, cannot effectively remove metals but it transfers them into heavy fractions.

Solvent extraction

A solvent extraction method is an ancient approach that has been applied for the removal of vanadium and nickel metalloporphyrin compounds from the crude oil. The key concept of the process is using various extracting solvents during the elimination process. Each solvent is employed during the process should be able to extract one or more composite that contains the metals from the complex composition of the oil. The solvent extraction method is performed at a temperature range from 27 °C to 93 °C. The solvent regeneration process is done at a temperature of less than 52 °C through exposure to a highly aromatic oil stream [2]. The solubility of the solvents is a significant parameter that affects the solvent extraction process. It depends on some characteristics such as dispersion forces, dipole-coupled forces, and H-bonding forces. Gamma-butyrolactone found to be the most proper solvent for metalloporphyrins extraction with selective removal of vanadium and nickel [10]. Applying a considerable volume of solvents is a significant issue facing this process, as it gives a low oil yield. Additionally, such a technique is only suitable for the oils containing high bitumen content. Also, the process is convenient for removing the metalloporphyrin fraction which impacts negatively on the oil yield.

Filtration

Recently, an innovative technique has been performed in the field of demetallization of petroleum oil by utilizing membrane technology. This novel technology helps in reducing the amount of sulfur, metals, and asphaltene. Indeed, such a method was reported to be used for recovery of

solvents after first extraction, phase separation, or dilution step. The main disadvantage of this approach is the long processing time that consumes too much time.

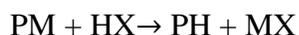
1.1.2 Chemical methods

Thermal cracking

Thermal cracking, it is also called visbreaking, is another technique for refining the crude oil through reducing its kinematic viscosity and concentration of the metals exist in the oil. The process is accomplished by applying a thermal cracking for the large hydrocarbons into a furnace to minimize the viscosity and enhancing the production of light hydrocarbons [11]. The total percentages of Ni, V, and S that the visbreaking method can remove are 12%, 13%, and 5%, respectively. Some improvements have been addressed to this process for raising the percentage of the metal removal, which is achieved by the addition of aqueous ammonium solution to the oil. This modification increases the metal removal to 26%, 20% and 14% for Ni, V, and S, respectively. Indeed, using the ammonium-water solution instead of water only limits the cock deposition from 0.61% to 0.27 % [12]. The main advantage of the process is to help dwindle the residual oil production from the distillation process of crude oil. In contrary, there are several disadvantages in this technique such as high process energy losses, low conversion efficiency, and deposition of cock-forming olefins and asphaltene in the visbreaker, which can undergo a subsequent transformation process forming tar and hardly recyclable residues [13].

Using a chemical agent

Handling the heavy crude oil through a demetallization process using acids is an efficient process that has been applied since many years. The interaction between the acid and the oil containing the metals can be explained by the following replacement reaction.



The main objective of using acids is to remove the sulfur, nitrogen and metal content from the crude oil. The process has been applied for the purification of animal and vegetable oils. Since more than a hundred years the idea was to upgrade petroleum oil using sulfuric acid. Marcusson

and Eickmann in 1908 implemented the earliest work on the precipitation of asphaltenes by employing the low boiling point naphtha. This process followed by fractionation of naphtha soluble material with concentrated sulphuric acid [14]. Indeed, applying the sulphuric acid in the demetallization process faces several challenges, because some of the acids transfer into sulfur dioxide during the treatment process. Accordingly, the formed sulfur dioxide undergoes a further reaction with the unsaturated hydrocarbons and goes in a side reaction forming bi-products. This, in turn, increases the complexity of the oil and decrease the rate of the elimination process[2]. Also, sulfuric acid reacts with the hydrocarbons in the oil, which leads to increasing the acid's quantity that required for the process and declines the amount of oil produced.

1.1.3 Hydrotreatment

The conventional hydrotreatment, it is also called the hydrogenation process (HMD-HSD) is one of the most effective methods for demetallization and desulfurization of crude oil. In such a method, compounds comprising sulfur, nitrogen, oxygen and/or metals are extracted through a hydrogenation process. Around 90% of metals in the feedstock can be withdrawn using a catalyst containing Ni, Co, and Mn [14]. The size of the residual molecules is an essential parameter that controls the process, and in general, it depends on the origin, nature, and the chemical composition of the feedstock. Additionally, the catalyst type, pore size, surface area, and residence time are relevant parameters in HDM process.

Although hydrodemetallization and hydrodesulfurization are ones of the most efficient techniques for metals and sulfur removal, they have several disadvantages. The most important ones include catalyst deactivation in an extremely short time, due to the accumulation of metal oxides on the pore of the catalyst[15]. This aspect, in turn, increases the amount of hydrogen necessary to accomplish the process and lowers the yield production due to the carbon rejection [1]. Moreover, the process has an adverse influence on the equipment during the refinery processes. Also, the extremely high cost of the process due to the elevated pressure which reached up to 100 atm, temperature up to 400 °C, and higher hydrogen concentration are common drawbacks in such method. Hydrodesulfurization process can not extract the high molecular weight sulfur compounds such as 4,6-alkyl substituted dibenzothiophene, due to the steric hindrance adsorption of such

compounds on the surface of the catalyst. This issue significantly impacts negatively on the activity of the catalyst and prevent the transformation of the compound into H₂S.

To sum up, a significant portion of the percentage of energy consumption related to the chemical and petrochemical industry is being replaced by electricity. As a result, chemical processes are now undergoing radical changes to combine technological innovations and the urgent need to tackle climate change. The Struggle between the clean electricity with un-conventional heating mechanisms has revolutionized the industry in the last few decades. The most common heating mechanisms include induction heating, plasma, ultrasound, and microwave heating. This work demonstrates the fundamentals and the application of microwave to upgrade petroleum oils by removing sulfur and metals.

CHAPTER 2 LITERATURE REVIEW

In the scientific publications, several investigations have been documented for metals and sulfur removal from heavy petroleum oil. The main two research groups in this field work on (1) developing a novel technique for the extraction process, and (2) improving the understanding of the removal mechanism. Most of the researchers of those groups have carried out their studies using various model compounds instead of using the complex heavy oil. The reason behind this strategy is to better understand the removal mechanism in an ideal way and avoid the complex composition of the heavy crude oil. The most common model compounds that have been employed in the previous studies are revealed in Table 2.1

Table 2.1 Various model compounds for the demetallization process (reprinted from reference [1])

Model compound	Reference
Nickel protoporphyrin disodium (NiPPDS)	[6]
Vanadyle tetraphenyl porphyrin (VOTPP)	[16-18]
Vanadyl octaethyl porphyrin (VOEP)	[6, 19]
Nickel tetra-(3-methylphenyl) porphyrin (Ni T3MP)	[20]
Nickel tetraphenyl porphyrin (NiTPP)	[21]
Vanadyl oxide octaethyl porphyrin (VOOEP)	[17]
Nickel etio porphyrin (NiEP)	[19, 22]
Nickel octaethyl porphyrin (Ni OEP)	[23]
Vanadyl etio porphyrin (V EP)	[22]
Vanadyl mesotetraphenyl porphyrin (VO MTPP)	[24]

For better implementing the sulfur and metal removal process, determining the exact concentration of such contamination before the removal process is a must. For this reason, several attempts have been built at the expense of determining the amount of metals into the different origins of crude oil. Ali et al. [25] have designated the quantities of various metals that exist in four market quality Arabian crude oil. The authors have detected that the amount of vanadium and nickel were ranging from 2.2 ppm to 57.9 ppm and from 0.55 ppm to 16.7 ppm respectively. They also determined the amount of sulfur located in such oils and affirmed that it was ranging from 1.1 wt.% to 2.8 wt.%. A patent has been implemented for metal extraction by Yamada et al. [26] who have invented a novel technique for metals extraction from the waste oil.

In such a technique, the oil was heated to 177°C - 238 °C, then a reaction between the oil and an organic solvent took place under a reflux condition. After the reaction had completed, The mixture was exposed to centrifugation process, and the residual oil containing 154 ppm of V was heated to 182-216 °C for 1 hour under reflux with hexane. This process gave the oil with 0 ppm V soluble in hexane after the centrifugation. Another method was conducted by Koseoglu, O.R., et al.[27] for the demetallization of the heavy crude oil using solid adsorbent materials such as attapulgite clay, alumina, silica gel, and activated carbon. The feed stream was contacting one or more solid adsorbents inside a mixing vessel for a time adequate to achieve the complete absorption of almost all the metals components present in the crude oil. Then, the mixture was exposed to atmospheric flash distillation followed by a vacuum flash distillation process for assortment the low boiling point fractions that including low concentrations of undesired metals. Both of the two distillation processes were implemented to recover part of the adsorbent that was applied during the adsorption method for the reusing again in the same process

A biological method using a microbial treatment for the demetallization process was enforced by Salehizadeh, H., et al. [17]. *Aspergillus* sp that was isolated from the contaminated soil has the capability of consumption of the vanadium oxide octaethyl porphyrin (VOOEP). Such fungi induce a degradation process for about 55% of VOOEP along seven days under the optimum conditions of temperature 30 °C, PH of 5.5, and initial concentration of 20mg/l. It was noticed during the process the existence of free vanadium with a high concentration in the aqueous phase; this indicates that the fungi helped to liberate the vanadium from the porphyrin moiety. The main drawbacks of this method are the long residence time reaches to several days. Additionally, the method suffers from a lack of selectivity in removing the metals from the oil, but it can exclude all the metalloporphyrin fraction which decline the oil yield [6, 7].

Kutowy, O., et al. [28] have applied a filtration technique for heavy molecular weight residues and inorganic substances removal from the aliphatic hydrocarbon liquids. These liquids exemplified in spent diesel lubrication oil, crude oil or pipeline blend crude oils and heavy oils, and bitumen. The removal process was employed by passing the liquid oil through a membrane with a swelled outer layer containing a microporous, polysulfone compound, an aliphatic liquid hydrocarbon membrane. The viscosity of the liquid hydrocarbon should decrease either by heating or by using

solvents before contacting the membrane. This method was found to be convenient for N, S, Al, Cr, Cu, Ni, V removal from the various types of oils that have mentioned above. Arod et al.

Arod et al. [29] have worked on the demetallization process using the ultrafiltration method of vacuum residue at an elevated temperature about 330 °C. A ceramic membrane was employed in such method with an average diameter of 10 nm, and the system was adjusted at a flow velocity of 5.6 m/s and transmembrane pressure of 500 kPa. The authors have claimed that the process declined the asphaltene content in the heavy oil from 6.3 wt.% to 4.1 wt%, and reduced the vanadium from 195 ppm to 90 ppm.

Duong, A., et al. Also have applied the ultrafiltration process using an asymmetric, single-tube ceramic membrane for the upgrading of cold lake heavy oil [30]. The membrane that has been applied was of length 25 cm, o.d. 1 cm, average pore diameter 0.02µm - 0.1 µm, and the process was implemented under mild conditions of a transmembrane pressure 600 kPa and temperature about 110 °C. (T) in the range 80 °C - 160 °C and cross-flow velocities (v_{Tcf}) in the range 2 m s⁻¹- 10 m s⁻¹. The variation in both asphaltene content and the permeate flux as a function of time-on-stream was detected during the process. There was a notable drop in the permeate flux in a short period due to the fast fouling of the membrane. This issue results in raising the retention of asphaltene from 1% to 80%. It was found that the reduction of the asphaltene content depends on the density and viscosity of the permeate flux, in addition to the Ni and V content. Thus, both the membrane pore diameter and the cross-flow velocity are critical parameters that control the permeate flux and the asphaltene retention, and accordingly the membrane fouling. The main conclusions of this study that were confirmed by the authors are the ultrafiltration able to remove up to 90% of asphaltenes from the Cold Lake heavy oil under a permeate flux < 100kgm⁻²day⁻¹. The ultrafiltration process has limited commercial applications because of the high cost of the ceramic membrane which rapidly stains after a short time. So, to avoid the capital cost of the process to be applied in large-scale operations, employing higher permeate fluxes is a must.

Osterhuber, E.J. [31] have incorporated both the solvent dissolution and ultra-filtration methods under the effect of high pressure for the upgrading of heavy oil. The heavy oil in the first was completely diluted by applying the suitable solvent, then, the mixture exposed to ultra-filtration process through a proper membrane to separate the solvent from the oil. The most convenient

membranes that can be used are cellulose, polyvinylidene fluoride. It was demonstrated that The process has a high tendency for removing the trace metals, specifically, V and Ni with reducing the conrods on carbon residue of the resulting oil. The authors have tested the ultra-filtration process of Arabian heavy vacuum residue mixed with toluene with 1:1 ratio and they found that the amount of vanadium and nickel were decreased from 180 ppm and 43 ppm to 25.8 ppm and 7.1 ppm respectively.

Phosphoric acid was employed by Kukes, S.G. and D.R. Battiste for Ni and V removal from heavy crude oil [32]. Phosphoric acid reacts with metals forming oil inexplicable compounds that can be separated by any separation process. Kukes, S.G., and D.R. Battiste have investigated the removal of Ni and V from the Venezuelan crude oil at various acid concentrations and temperature for one hour in a stirred autoclave. After the reaction has completed, the product passed through a glass filter for separation. The Ni and V contents were detected using the atomic absorption spectrometry and the plasma emission spectrometry. It was found that H₃PO₃ is effectively excluded V and Ni from the heavy oil more than H₃PO₄. In the range concentration of 2 wt.% - 4 wt.%, the H₃PO₃ have Superiority over H₃PO₄ in V and Ni removal.

Eidem, P.K.[33] has employed the H₃PO₄ in the demetallization process of petroleum oil. A 250 g of residual oil was mixed with 1wt% of H₃PO₄ then the mixture exposed to stirring and heating to 150 °C under nitrogen gas blanket. The temperature increased gradually to 260 °C, after passing 44min the mixture was separated into maltenes fraction and asphaltenes. It was pronounced that the concentrations of Fe, Ni, and V in the original residual declined from 64, 101, and 63.3 to 0.06, 14.5, and 9.70 respectively.

Ni and V contaminants have also been removed by using SO₂ or SO₂ precursors at 93-232 °C and for 0.01h - 5h. The mixture is then exposed to a vacuum distillation process for separation into a distillate with boiling point 271°C and low metals content, and a residue with high metals concentration. The treatment of the heavy oil by the SO₂ or SO₂ precursors has successfully reduced the vanadium contamination from 1.70 wt.ppm to 1.36 wt.ppm[34].

Michlmayr demonstrated Another novel chemical method for the upgrading of metal-contaminated oil using ferric or stannic salt, M.J.,[35]. In this process, the oil stream exposed to an

extraction process using ferric or stannic chloride soluble in acidified water. The solution should be kept in acidic medium to prevent the precipitation of ferric or stannic in the form of hydroxide or a basic salt. It was confirmed that the ferric and stannic salts have a high ability for metal removal especially ferric nitrate in nitric acid recorded the greater effectiveness of removal. The main disadvantage of the process is the increase in the viscosity of the oil after the treatment because it might enhance the oxidation and/or the polymerization of the unsaturated components in the oil.

Garwood Eric P[36] has implemented a process for sulfur removal using H₂SO₄ and vanadium elimination by MgSO₄. An electric generating plant containing the residual oil was used and the oil mixed with 90 wt.% of H₂SO₄ by the ratio of 0.005-gallon acid/gallon of oil. The main findings of such process were the reduction of sulfur content from 2.6 wt.% to 0.02 wt.%.

The further treatment took place for the desulphurized oil using 20 wt.% an aqueous solution of MgSO₄. Accordingly, the vanadium content was reduced from 395 ppm to 24 ppm, and sodium was reduced from 21 ppm to 2 ppm. XU Zhen-hong et al. Have discovered a novel method for removal of metal salts from crude petroleum and petroleum fractions using a demetallization agent and demulsifying agent [37]. The metals in the feedstock are shifted to the aqueous phase by emulsifying the feedstock at 30 °C -140 °C for 0.5 s to 10 min. The demetallization agent that has been employed in this method is C1-4-fatty acid containing byproduct prepared by oxidation of paraffin waxes.

Demetallization process has been reached by employing an aqueous base from group IA and IIA hydroxides, carbonates, NH₄OH and (NH₄)₂CO₃, an oxygen-containing gas, and a phase-transfer agent. Metals were eliminated from the oil at 180 °C and after sufficient time for conveying to the aqueous phase. The authors have demonstrated that the process, fortunately, declined the amount of both Ni and V and valorized the oil for applying in further operations [38]. Several investigations have been performed for demetallization of petroleum oil by employing different acids such as hydrochloric, hydrobromic, polyphosphoric and sulphonic acids. Such acids have a lack of causing side reactions and product contamination. Hydrofluoric acid was found to be the best reagent that can be utilized in the demetallization process. Such acid can extract roughly 90% of metals with a high liquid yield of 85-90 wt.% [39].

Hurter, A.G. have used an aqueous solution of an anion for metal and ash removal from vacuum residue or used lubricating oil [40]. The aqueous solution reacted with the metal from the oil forming an aqueous salt such as NaCl and NH₄Cl. The reaction took place at a high temperature that equal or just below 100 °C and with a solution to oil ratio of 1:9. The process showed a notable drop in the concentration of Fe, Al, Ca, and Na in the oil phase after ash separation by centrifuge filter.

The oxidation process is a novel technique has applied by Gould, K. A. [41] for the demetallization of cold lake asphaltene, Arabian heavy asphaltene, and cold lake vacuum residuum. The method has been implemented by using different oxidizing agents such as air, NaOH/air, sodium hypochlorite, and peroxyacetic acid. The author declared that both sodium hypochlorite and peroxyacetic acid have high performance towards the removal process, while, air and NaOH/air are feeble oxidizing agents for demetallization. The major cons of the process are the ability of both sodium hypochlorite and peroxyacetic acid to remove and destroy the porphyrin rings. Additionally, sodium hypochlorite has the disadvantage of chlorine formation in the feed. Moreover, the process is suffering from the unselective elimination of metals, porphyrin ring removal, and consumption of the oxidant during the process which raise the cost.

Cumene hydroperoxide also was used in the demetallization process of the petroleum fraction at 80-250°C. The main disadvantage of such a process is the production of a high amount of asphaltene with 93-96% metals contaminants. It was investigated that increasing the asphaltene content is due to the polymerization, polycondensation, and oxidation by Cumene hydroperoxide[42].

Table 2.2 Efficiency of metal removal of some significant chemical methods (reprinted from [1])

Method	Removal efficiency %	Reference
Red phosphorus	72 % Ni and 100% V	[43]
Photochemical method for atmospheric residue	98% Ni and 93% V	[44]
Photochemical method for vacuum residue	85 % Ni and 73% V	[44]
Protonating agent	84 % VO-MTPP and 78% of VOOEP	[24]
HF as protonating agent	90% metal removal and 85-90% oil recovered	[45]
Peracetic acid as an oxidizing agent	80% V and 74% Ni	[41]
Organophosphate esters	99% V and 89.8% Ni	[46]
Oxidation using NaClO	78% V and 37% Ni	[41]

Table 2.3 Advantages and disadvantages of some demetallization method [1]

Method	Advantage	Disadvantage	Reference
Ultrasonic radiations with chemical reactions	High-efficiency metal removal	Can be applied only for mild and noncatalytic operations	[47]
Photochemical method	Solvent recovery, energy saving, safe demetallization method	Difficulty in removing bound-type metalloporphyrins without solvent addition	[44]
Micro-organisms	Good potential for metal removal	Long time-consuming process	[48]
Electrochemical MD	The high metal removal efficiency	High voltage required for high metal removal efficiency	[49]
Oxidation	By using the proper oxidant, the process has high metal removal efficiency with heavy feedstock	Consumption of the oxidant during the removal process	[41]
Nanosized catalyst	High selectivity in metal removal	The production of solid yield depends on the time of combustion, temp., and the catalyst activity	[50]

PROBLEM DEFINITION

Removal of metals and sulfur from the waste-derivative oil is indispensable since it would lead to avoiding most of the issues and limitations that impede its uses in a wide range of commercial applications. Although a considerable number of techniques have been developed and documented regarding such objective, only some of them have industrially been established. The main reason behind this aspect relates to the cons associated with each method. For instance, applying the solvent extraction method leads to remove the whole fractions that contain the metals, which declines the yield of the end-product. Distillation technique enhances the production of two grades of oils: (1) Light oil, which is the primary product and contains a very low concentration of metals; and (2) heavy oil, which contains a much higher concentration of contaminations that must go in a further upgrading process for metals removal. Fast catalyst deactivation needs for an emulsification process, high cost, and long processing time, among other factors, are additional aspects limit the performing of the developed techniques. Ultrafiltration technique is a capital cost affected due to the fast fouling of the membrane used in the process. So far, furthermore, no an industrial process has been designed to remove sulfur and metal in a single step. Kindly refer to section 2 (methods of demetallization) for further details.

CHAPTER 3 ARTICLE 1: ELECTRIFICATION OF DEMETALLIZATION AND DESULFURIZATION OIL PROCESSES: FUNDAMENTALS AND PROSPECTIVE APPLICATIONS

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Abstract

Even though the current noticeable pace of energy transformation paves the way for a more sustainable future, the aspirational goal to meet the Paris Agreement's Policy is unfortunately still far off. More innovative solutions for high energy and low carbon intensity processes are urgently needed to support accelerated progress toward that goal. Along with the innovation in renewable power generation technologies, innovation in the end-use sectors is nowadays among the most pressing needs. The results of such a roadmap include the prompt embedding of the electrification of end-use sectors and integrating high shares of renewable power into the existing systems.

The case studied in this work is the chemical and petrochemical industry. This industrial sector depends on oils for more than 50% of the total energy consumption, which must be electrified. Employing clean electricity with unconventional heating mechanisms has initiated a revolution in the industry during the last few years. The most common heating mechanisms that are being implemented include induction heating, plasma, ultrasound, and microwave heating. Herein, the fundamentals and applications of these techniques are demonstrated, and more attention is directed to the microwave-assisted demetallization and desulfurization of petroleum oils by removing sulfur and metals.

Keywords: Microwaves; demetallization; desulfurization; oil valorization; oil processing.

3.1 Unconventional heating mechanisms

The most common unconventional heating mechanisms are electromagnetic heating – including, induction heating and microwave heating - plasma, and ultrasound.

3.1.1 Induction heating

Induction heating is a mechanism comprising a complex interaction of electromagnetism, heat transfer, metallurgical phenomena, and circuit analysis. It is a non-linear heating mechanism since the aforementioned physics depend on the applied electric and magnetic field intensities, temperature, the microstructure of the target, and other factors. The theory of induction heating relies on Faraday's law of induction, which states that "circulating currents – also called eddy currents – are induced in bulk pieces of metal moving through a magnetic field." In the same manner, an electromotive force (emf) is induced in a circuit by a changing magnetic flux. If an alternating voltage is applied to an induction coil, an alternating current will flow in the coil circuit. The alternating coil current produces a time-variable magnetic field in its surroundings. The produced field has the same frequency as the coil current. If a workpiece is located inside or near the coil, the produced magnetic field will induce eddy-currents inside the workpiece. The produced eddy-currents have the same frequency as the coil current; however, they are in opposite directions. The induced eddy-currents produce heat by the Joule effect, which is simply presented by " I^2R ," where "I" is the electric current and "R" is the electric resistance. The current distribution within the inductor (coil current) and workpiece (induced eddy-currents) is not uniform because of the acts of several electromagnetic phenomena. The most important include the following:

- Skin effect: also called penetration depth represents the non-uniformity of the electrical current distribution within a conductor's cross section carrying current. The high concentration of eddy-current is located on the surface of the workpiece while zero is measured in the center of the conductor;
- Proximity effect: expounds the interaction between the fields produced by the conductor itself and the other nearby, which redistributes the induced current in the conductor; and
- Slot effect: explains the magnetic flux density in the gap between the inductor and the conductor.

Other effects, such as the ring effect, end and edge effects, also impact the distribution of electric current within the cross-section area of the conductor.

This heating mechanism leads the workpiece reaching a temperature of several hundred degrees in less than a second, although it is impacted by the aspects mentioned above. Induction heating has been well investigated at the lab-scale; however, it is still not in the commercialization track due to scale-up issues and limitations.

3.1.2 Ultrasound

Ultrasound is propagated via a series of compression and rarefaction waves at frequencies of around 20 kHz and continuing up to the order of MHz, induced at the molecule level in the medium, which it passes in. Cavitation bubbles are formed because of the attractive forces of the molecules at high power. The formed bubbles grow over a few cycles and take in some vapor from the medium. The frequency of the formed bubbles matches that of the applied sound frequency. At 20 kHz, the generated bubbles are relatively large, and their collapse results in strong shockwaves that can be used in emulsification and other applications. In the frequency range of 100 kHz to 1000 kHz, the generated bubbles are much smaller, and their collapse induces a more significant increase in temperature, which has been used in sonochemical applications. At frequencies above 1 MHz, the cavitation effects are much weaker and, therefore, commonly used for medical and industrial imaging purposes.

Under the effect of a sound field, the generated bubbles could trigger (1) coalescence – a bubble combines with another to form a larger one; (2) rectified diffusion – individual bubbles grow over several acoustic cycles at above a certain threshold pressure. Thereafter, degassing happens, which means the bubbles leave the system entirely due to buoyancy if they grow large enough, then collapse. Unstable bubbles at a certain point collapse, often violently. Bubbles below the threshold pressure for rectified diffusion can dissolve into the solution.

Two competing theories exist to explain the chemical effects due to cavitation:

- The hot-spot theory: Localized hot spots are formed, which leads to reaching temperatures and pressures in excess of 5000 K and 500 atm – when the bubbles cavitate.

- The electrical theory: On the surface of a cavitation bubble, an electrical charge is created and forms enormous electrical field gradients across the bubble, which are capable of bond breakage upon collapse.

A bubble grows until it reaches a critical size known as “resonance size,” which depends on the applied frequency of the sound waves. At the resonance size bubbles (1) may become unstable and collapse within a single or a small number of acoustic cycles (transient cavitation), and/or (2) oscillate for many cycles at or near the linear resonance size (stable cavitation). The terms transient and stable cavitation are used to define whether the bubbles are active in chemical reactions. The chemical effects of ultrasound are attributed to the collapse of both stable and transient cavitation events.

3.1.3 Plasma

Gaseous plasma contains a mixture of electrons, ions (which are the heavy particles), and neutral particles. The heavy particles might partially be excited for the high energy of plasma. The exciting part may return to its ordinary state by photon emission. Therefore, plasma consists of electrons, ions, neutrals in the ground state, excited species, and photons. Such a mixture is only called plasma if it is electrically in nature. The case of the positive and negative charges in balance is called quasi-neutrality.

Plasmas occur over a wide range of pressures and temperatures and, therefore, are classified according to the electron temperature and electron density, as follows:

- Extremely tenuous, such as solar corona, $T \sim 10^6$ K
- Ionosphere, similar electron density, $T \sim 10^3$ K.
- Flames show a bit higher electron densities and temperatures than ionosphere
- Glow discharges pressure, 10^{-4} to 1 kPa and $T \sim 10^4$ K
- Fluorescent lamp, $T_{\text{electron}} \sim 2.5 \times 10^4$ K, while $T_{\text{heavy-particle}} \sim 300$ K
- Thermonuclear fusion, $T \sim 10^6$ K to 10^8 K.
- Thermal plasmas, $T \sim 10^4$ K

Generally speaking, thermal plasma is generated by applying an electric current through a gas. Gases at room temperature are excellent insulators; thus, involving an electrical breakdown is essential. This is usually achieved by generating a number of charges to make the gas electrically conducting. Electrical breakdown creates a conducting path between a pair of electrodes. Passing an electric current through an ionized gas leads to gaseous discharge. There are various ways to produce plasmas, most commonly include Electrodeless RF discharges, Microwaves, Shock waves, High-energy particle beams, Laser, and Heating gases in a high-temperature furnace. Plasmas have been used in several industrial applications, such as coating and synthesis of ceramic powders, such as carbides, nitrides, oxides, and other applications.

3.2 Microwave heating

In 1831 the electromagnetic induction was discovered by Michael Faraday, and thereafter Faraday's law was documented. James Clerk Maxwell worked on Faraday's concept and in 1864 presented a mathematical framing of the combined impact of electric and magnetic fields. Later, it was known as electromagnetic theory. In 1865, Maxwell displayed the electromagnetic theory through 20 equations in his article "*A Dynamic Theory of the Electromagnetic Field – 1865.*" Those 20 equations were thereafter simplified into the forms known today as "Maxwell's four equations," which as fundamental to electromagnetic phenomena as Newton's laws are for mechanical phenomena. The equations are presented below.

1. Gauss's law for an electric field

$$\oint_S E \cdot dA = - \frac{q}{\epsilon_0} \quad (1)$$

The total electric flux through any closed surface (E) equals the net charge inside that surface (q) divided by the permittivity of free space (ϵ_0).

2. Gauss's law for a magnetic field

$$\oint_S B \cdot dA = 0 \quad (2)$$

The net magnetic flux through a closed surface (B) is zero; this implies that magnetic field lines cannot begin or terminate at whatever period.

3. Faraday's law of induction

$$\oint E \cdot ds = -\frac{d\phi_B}{dt} \quad (3)$$

The induced emf, which is the line integral of the electric field around any closed path, equals the rate of alteration of magnetic flux through any open area bounded by that path.

4. Ampère–Maxwell law

$$\oint B \cdot ds = \mu_0 I + \epsilon_0 \mu_0 \frac{d\phi_E}{dt} \quad (4)$$

It describes the generation of a magnetic field by an electric field and electric currents. The line integral of the magnetic field around any closed path is the sum of the magnetic permeability of free space (μ_0) times the net current through that path and $\epsilon_0 \mu_0$ times the rate of change of electric flux through any surface bounded by that path.

Electromagnetic radiation behaves like photons carrying radiated energy and waves moving at the speed of light. As depicted in Figure 3.1A, electromagnetic waves are comprised of an alternating electric field orthogonal to alternating magnetic field. The magnetic and electric fields propagate in the direction of oscillation. The frequency of the electromagnetic spectrum covers a wide range starting from 300 MHz and ending at 300 GHz. The corresponding wavelength of these frequencies is from 1 m to 1 mm. This frequency range includes a number of electromagnetic wave-based applications, such as radio waves, microwaves, infrared, visible light, ultraviolet radiation, X-ray, and gamma-ray, as shown in Figure 3.2. It should be known that each of these applications is restricted by a frequency range and corresponding wavelength to avoid overlapping each other.

Throughout the 20th century, microwaves have been established in several applications, e.g., communications, navigation, radar detection, power transmission, and microwave heating. These

noticeable and solid establishments are the result of the rapid development of the electromagnetic technology over the last few decades.

Recently, microwave heating (MWH) is being widely implemented in a number of industrial sectors, which is a result of the increased attention on the field by scientific research and development.

3.2.1 Polarization mechanisms of microwaves

Interaction between microwaves and target materials takes place at the molecular level, and is classified into four main polarization mechanisms:

- i. Electronic Polarization, which is a displacement of valence electrons around the nuclei, as depicted in Figure 3.1B;
- ii. Atomic or Ionic Polarization, which is a relative displacement of positive and negative ions or atoms from their equilibrium position, refer to Figure 3.1C;
- iii. Interfacial Polarization, which is an accumulation of charges at interfaces between components in heterogeneous systems, as shown in Figure 3.1D; and
- iv. Orientation or Dipolar Polarization, which is explained by the permanent dipole moments in molecules that tend to re-orientate under the influence of an alternating electric field, as demonstrated in Figure 3.1E.

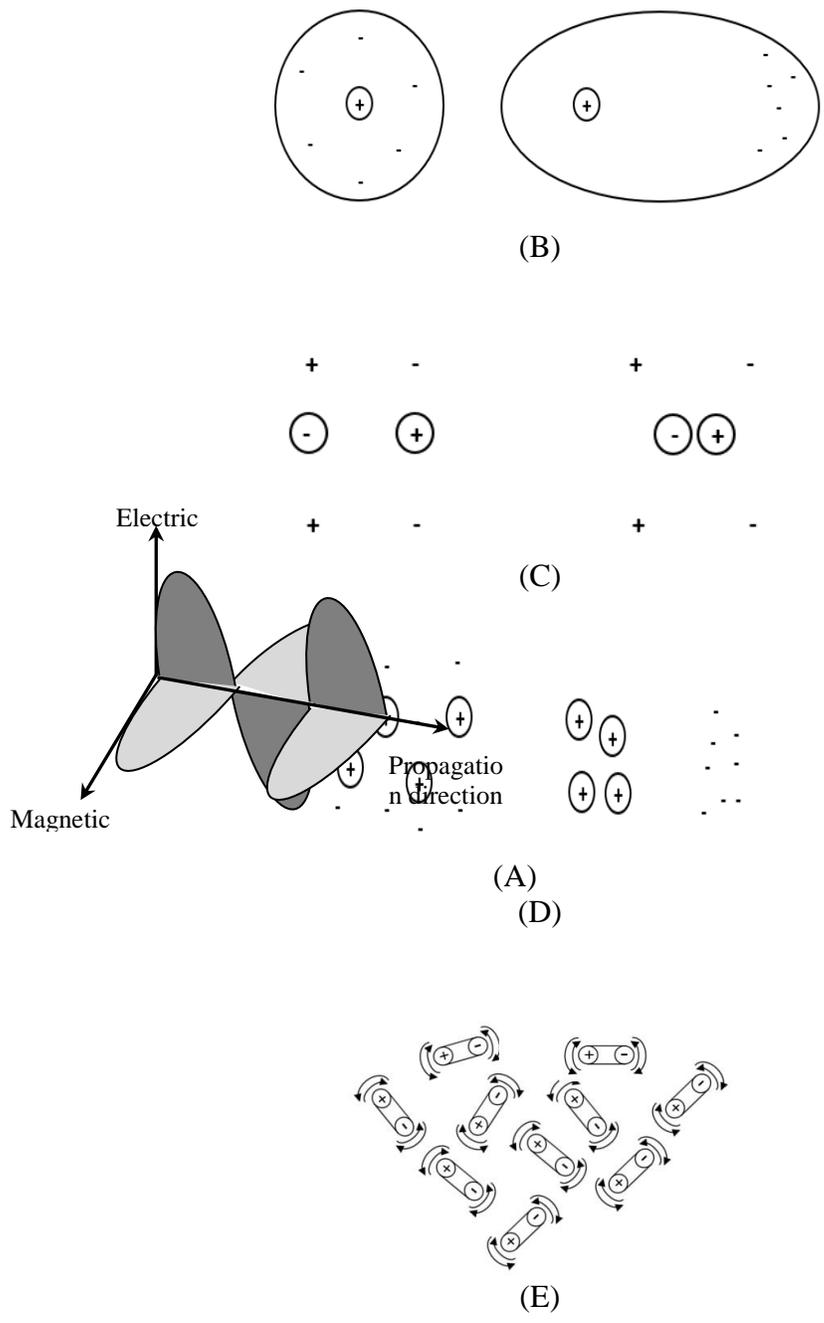


Figure 3.1 Polarization mechanisms of microwaves

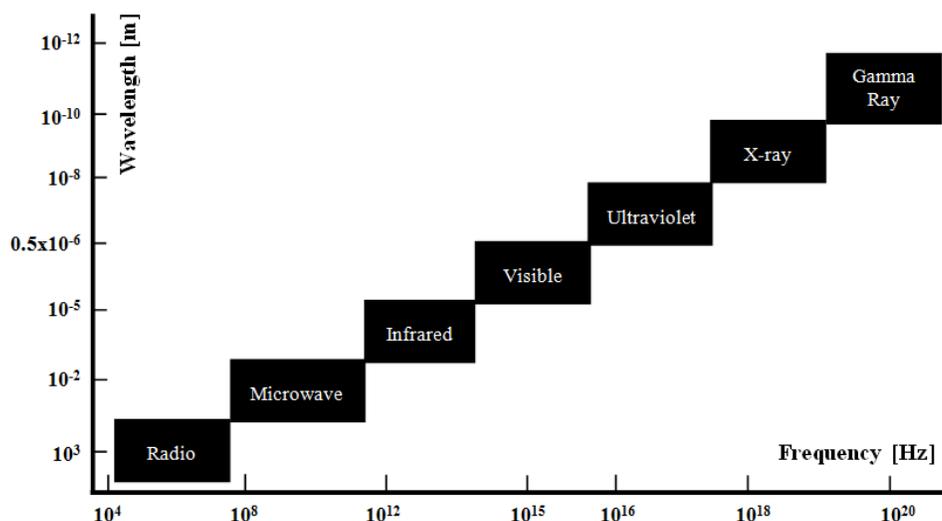


Figure 3.2 Electromagnetic spectrum (Reprinted from reference [51])

Dipolar polarization is the most dominant mechanism of microwave-induced heating. Materials contain permanent dipole moments that have randomly oriented molecules in the absence of an external alternating electric field. The reason is that there is no net dipole moment being presented. Application of an external alternating electric field leads to aligning the molecules with the oscillating field. This aligning (also known as reorientation) results in permanent dipoles parallel to the alternating field, which makes the aligned dipoles track the fluctuation of the electric field [51-54].

The oscillation frequency of the applied electric fields is in the order of GHz. This huge oscillation rate, fortunately, makes the agitated molecules unable to reorient themselves at that frequency rate. This aspect creates a phase shift between the orientation of the dipoles and the applied field, which, subsequently, creates random collisions between the re-oriented molecules. The created collisions are responsible for releasing heat energy from the irradiated material.

Due to the conversion of electromagnetic energy to heat taking place within the entire volume of the target material, respecting the penetration limits of the applied waves and the material, microwave heating is defined as a volumetric energy conversion mechanism [55-58]. This mechanism is fundamentally different from the superficial heat transfer of conventional heating

and, therefore, noticeable advantages of microwave heating have been highlighted during the last few years.

3.3 Microwave heating parameters

The main parameters governing the level of heat generation within the irradiated material are “complex permittivity” (ϵ) and “complex permeability” (μ). Complex permittivity is linked to the alternating electric field component of the microwaves. It represents the ability of the heated material to absorb and store electric potential energy, i.e., it defines the response of the payload to the applied electric field. As well, complex permeability is linked to the alternating magnetic field component of the microwaves. It represents the response of the heated material to the applied alternating magnetic field component. Complex permittivity and complex permeability are expressed by Equations (5) and (6), respectively.

$$\epsilon = \epsilon' - j \epsilon'' \quad (5)$$

$$\mu = \mu' - j \mu'' \quad (6)$$

The real part of Equation (5) – ϵ' – is called “dielectric constant” or “permittivity.” It measures the ability of the target material to pass microwaves, more specifically, electric field, through it. The imaginary part of the complex permittivity – ϵ'' – is called “dielectric loss factor.” It indicates the ability of the heated material to dissipate microwave energy; in other words, it measures the amount of electric energy that can be stored within the exposed material. Permittivity mathematically equals the product of the permittivity of free space, ϵ_0 : $8.854 \times 10^{-12} \text{ F/m}$, and the material relative permittivity (ϵ'_r).

The ratio between permittivity and the dielectric loss factor is called loss tangent ($\tan \delta$), Equation (7). Loss tangent represents the phase difference between the polarization of the target material and the oscillating applied electric field. It measures the ability of the exposed material to convert the absorbed microwave energy into heat energy.

$$\tan \delta = \epsilon'' / \epsilon' \quad (7)$$

where δ is the phase difference between the alternating applied electric field and the polarization of the exposed material [59].

The real part of Equation (6) – μ' – is called “magnetic permeability” and defines the amount of magnetic energy that can be stored within the heated material. Magnetic permeability equals the product of the permeability of free space (μ_0) – $4\pi \times 10^{-7} \text{ F/m}$ – and the relative permeability of the material (μ'_r) [52, 53, 60].

The imaginary part of complex permeability, μ'' , represents the magnetic energy that can be converted into thermal energy. The fraction between μ'' and μ' is called “magnetic loss tangent,” and can be expressed by Equation (8).

$$\tan \delta_{\mu} = \mu'' / \mu' \quad (8)$$

Most of the material processed in chemistry applications are non-magnetic materials, which means the microwave effects that convert microwave energy to heat energy within the target material are fundamentally due to the interaction with the electric field component of the applied microwaves.

It is important for the application to get full information about the dielectric properties of the reactants. Typical values of ϵ' and ϵ'' for the selected materials are tabulated in Table 3.1. It is critical to consider that the value of the dielectric properties is highly affected by the material temperature and the frequency of the applied alternating waves [51, 53, 54, 57].

Table 3.1 Dielectric constant, dielectric loss, and loss tangent of selected materials

Material	ϵ'	ϵ''	$\tan \delta$	T [°C]	f [GHz]
Vacuum ¹	1.00	0	0	25	NA
Air ¹	1.0006	0	0	25	NA
Glass (Pyrex) ¹	4.82	0.026	0.0054	25	3
Fused quartz	4	0.001	0.00025	20	2.45
Styrofoam ¹	1.03	0.0001	0.0001	25	3
PTFE ¹	2.08	0.0008	0.0004	25	10
Titanium oxide ¹	50	0.25	0.0050	25	NA
Magnesium oxide ¹	9	0.0045	0.0005	25	NA
Aluminum oxide ¹	9	0.0063	0.0007	25	NA
Zinc oxide ¹	3	3	1.0000	25	NA
Water, ice ²	0.003	0.001	0.3333	-12	2.45
Water, distilled ²	78	12	0.1538	25	2.45
Apple ²	57	12	0.2105	19	2.5
Beef, frozen ²	4.4	0.53	0.1205	-20	2.45
Beef, cooked ²	30.5	9.6	0.3148	30	2.45
Potato ²	15.7	0.27	0.0172	25	2.45
Paper ²	2.7	0.2	0.0741	NA	2.45
Paper ²	2.8	0.2	0.0714	NA	0.915
Polyethylene ²	2.26	0.002	0.0009	NA	0.915
Polyethylene ²	2.3	0.001	0.0004	NA	2.45
Methanol ¹	32.6	21.48	0.6589	25	2.45
Ethanol ¹	24.3	22.86	0.9407	25	2.45
Zirconium oxide ¹	20	2	0.1000	25	NA

NA: Not available

Adapted from references [51, 52, 59, 61]

Based on the dielectric properties of the target material, the interaction of materials with microwaves is classified into three main groups:

1. Absorbing materials, which are high-dielectric loss materials that highly absorb the applied microwaves and convert them to heat energy, e.g., silicon carbide and carbon;
2. Transparent materials, which allow electromagnetic waves to pass through them with little attenuation, e.g., ceramics, quartz, glass, and air; and
3. Impermeable materials, which reflect the applied electromagnetic waves, e.g., highly conductive materials, such as metals.

In addition, magnetic materials interact with the magnetic component of the applied electromagnetic field, e.g., typically ferrites.

3.4 Dissipated power and penetration depth

The rate of heat energy absorbed by the heated material (P_{av}), which is also called the heat energy generated or the microwave energy dissipated within the material, can be estimated using Equation (9). This equation is comprised of two terms:

1. the absorbed electric energy term, which is a function of the applied alternating electric field; and
2. the absorbed magnetic energy term, which relates to the oscillating magnetic field.

$$P_{av} = \omega \epsilon_o \epsilon_{eff}'' E_{rms}^2 V + \omega \mu_o \mu_{eff}'' H_{rms}^2 V \quad (9)$$

where P_{av} : average absorbed power [W]; ω : angular frequency [s^{-1}] = $2\pi f$; ϵ_{eff}'' : effective dielectric loss factor [-] and equals the losses due to conduction (ϵ_{cond}'') and polarization (ϵ_{polar}''), Equation (10); E_{rms} : root mean square of the electric field [V/m]; μ_{eff}'' : effective magnetic loss factor [-]; H_{rms} : root mean square of the magnetic field [A/m]; and V : volume of the target material [m^3].

$$\epsilon_{eff}'' = \epsilon_{polar}'' + \epsilon_{cond}'' \quad (10)$$

In most chemistry-based materials, the term that represents the conversion of magnetic energy into heat energy is neglected since the materials are non-magnetic. In the case of such materials,

decaying the applied electric field along the heated material is measured using the “electric field penetration depth” – also called “electric field skin depth” (D_E), Equation (11). It represents the depth at which the magnitude of the applied electric field drops by a factor of $1/e$ ($=1/2.7183$) of the surface’s value, Figure 3.3.

$$E = E_0 e^{-y/D_E} \quad (11)$$

The same definition is used to represent the dissipated microwave power inside the target material, which is called “power penetration depth” (D_p). It should be noted that $D_p = D_E/2$.

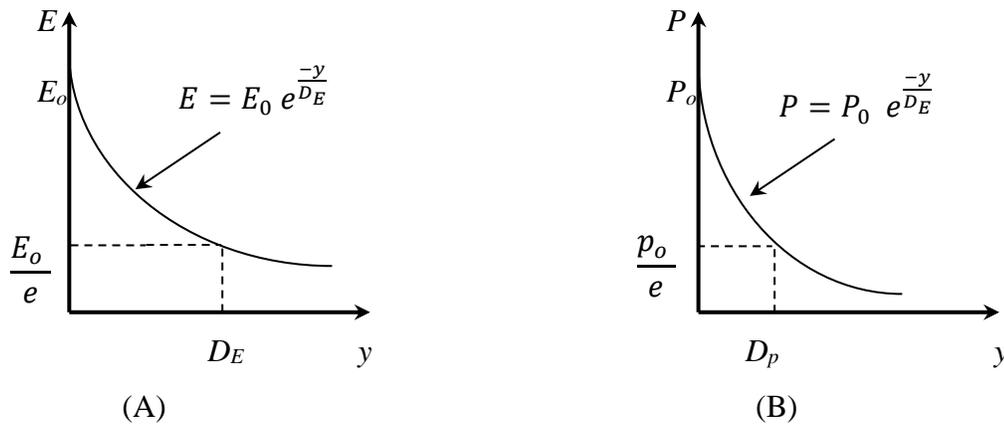


Figure 3.3 (A) electric field penetration depth, and (B) power penetration depth

3.5 Microwave heating vs. conventional heating

The unique advantages of MWH establish this heating mechanism as an alternative to conventional heating (CH) in a number of applications. The mechanism of MWH relies on direct volumetric energy conversion, i.e., direct conversion of electromagnetic energy to heat energy within the volume of the heated material. This mechanism is fundamentally different from the superficial heat transfer of CH and, thus, can avoid most of the issues and limitations associated with CH, which most importantly include the temperature gradient inside and outside the heated material. The interaction between microwaves and the heated material, which is mainly based on the

dielectric properties of the material, leads to selectively heating the target. This reduces the heat energy required to achieve a particular end, which consequently results in decreasing the operating costs as well as the potential of thermal hazards. In addition, it can restrict secondary reactions and might lead to (1) producing material with a novel microstructure, (2) initiating reactions that cannot be initiated when CH is applied, and (3) achieving the existing reactions under conditions that are different from those of traditional processing. Furthermore, numerous investigations have reported that MWH can save more in energy consumption and enhance product quantity and quality compared to the conventional processed materials [62-68].

Chandra Shekara et al. have documented that MWH achieves a better conversion compared to CH [62]. MWH modifies the porosity of the processed materials and leads to a faster reaction rate at less energy consumption compared to CH as claimed by Paixão, Monteiro et al. [63]. Patil, Gude et al. agree with Paixão, Monteiro et al. on the impacts of microwaves on the reaction rate [69]. A higher product yield in less reaction time has been reported by Zhang and Zhao [64]. Budarin, Clark et al. have investigated the influences of microwaves on the product quality compared with the conventional processes, which led to documenting that the obtained oil contains few impurities and is rich in aromatics [66]. Guiotoku, Rambo et al. tend to believe that MWH increases the carbonization yield [70]. MWH decreases catalyst loading and liquefaction according to Krzan and Zagar [71]. Dogan and Hilmioglu found that MWH significantly shortens the reaction time compared to the traditional methods [72]. Increasing the conversion that is compared was reported by Sithambaram, Nyutu et al. [73]. Orozco, Ahmad et al. are in agreement with the above-mentioned claims regarding the higher product yields, shorter reaction time, and higher reaction rate at moderate temperature [74]. The same conclusion was reached by Lucchesi, Chemat et al., and Menéndez, Domínguez et al. 2004 [68, 75]. Karthikeyan, Balasubramanian et al. believe that applying MWH leads to a faster extraction rate and produces different chemical components than CH [67]. Zhu, Wu et al. and Farag, S et al. have reported the noticeable impacts of MWH on enhancing product quality [57, 76]. Further details about the nature of MWH are demonstrated in the references [56, 77].

In summary, it is believed that applying MWH impacts reaction kinetics in addition to the noticeable effects on the product yield, product quality, and energy consumption. It should be

noted that these key conclusions highly depend on the dielectric properties of each component of the target(s) and other aspects.

3.6 Upgrading petroleum oil using microwaves

During the past few decades, substantial attention has been directed to petroleum heavy oils for use in several commercial applications. However, the demand for such oils is limited due to serious concerns. One of the decisive issues that face heavy oils is the inadmissible level of metals contamination. In fact, the problem places the refinery processes in jeopardy as a result of severe damage to the contact surfaces. Furthermore, it gives rise to numerous environmental issues for both humanity and the atmosphere. The most important include emissions into the environment as a poisonous gas in the form of SO_x and NO_x. Vanadium oxide reacts with mucus into the human body, causing irritation. Nickel in the form of nickel carbonyl is a carcinogenic matter resulting in numerous types of malignant neoplastic diseases. During the refinery processes, metals also play a hazardous role in enhancing the corrosion problems on the contact surfaces. Calcium and magnesium chlorides become hydrolyzed when they are subjected to temperatures of 170 °C, leading to the production of HCl, which is a highly corrosive agent. Furthermore, metals have an impediment impact on the efficiency of the catalyst during the refinery process. The main reason for this is due to the catalyst pores becoming rapidly plugged by minerals, which results in fast catalyst deactivation. Consequently, it elevates the rate of uptake of the catalyst during the process, which augments the monetary value of the technique. Also, the accumulation of metals on the surface of catalysts exhibits dehydrogenation activity as it intensifies the dehydrogenation reactions during the cracking operation. This issue raises the production of increased amounts of coke and dry gases at the expense of the liquid output. Additionally, if the product is used as fuel, the metals in the fuel oil will heighten the production of ash. When oil is burned, the ash deposits on the engines, causing significant abrasion in the moving parts.

For a better understanding about the principal obstacle that challenges heavy oils, considerable efforts have been made to specifically determine the main characteristics and the impurity content of the oils, refer to Figure 3.4. It has been demonstrated that the concentration of various metals existing in heavy oils varies from a few parts per million to higher than 1000 ppm, as shown in Table 3.2

Table 3.2 Actual concentration of metals in the crude oil (adopted from reference [1])

Petroleum feedstock	Concentration (ppm)
Extra light	Less than 10
Light	10-200
Heavy	50-500
Extra heavy	200-1000

Some of the most distinct elements that have been identified in the oil include cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), silver (Ag), sodium (Na), potassium (K), lithium (Li), calcium (Ca), and strontium (Sr) [1, 2].

Discovering the chemical structure of metals in heavy oil is essential for better estimating the ultimate metals removal process from heavy oils. In general, metals exist in an oil-soluble form of naphthenic acid or complex organometallic compounds, i.e., the structure of the metalloporphyrin ring [3, 4]. Both V and Ni can be present in the form of a porphyrin and nonporphyrin structure. Figure 3.5-A demonstrates the general form of a metalloporphyrin complex, Figure 3.5-B shows the structure of Ni tetraphenyl porphyrin, Figure 3.5-C depicts the structure of vanadyl octaethyl porphyrin, and Figure 3.5-D shows the general structure of nickel etioporphyrin [1]. Figure 3.6 displays the structures of different vanadium porphyrin species in Venezuela crude oil. Other metals, such as calcium, titanium, magnesium, and zinc, are found in combination with naphthenic acid, as in soaps. The porphyrinic form was in fact extensively investigated due to its hazardous impact and the role of its geochemical markers [5]. Similarly, the metallic elements in the shape of metalloporphyrins are difficult to withdraw due to the high stability of the ring. Moreover, the decomposition temperature of porphyrin compounds is usually more than 250 °C. For further literature about the processes that have been developed for the removal of metals from petroleum oils using different DMA, refer to Table 3.4

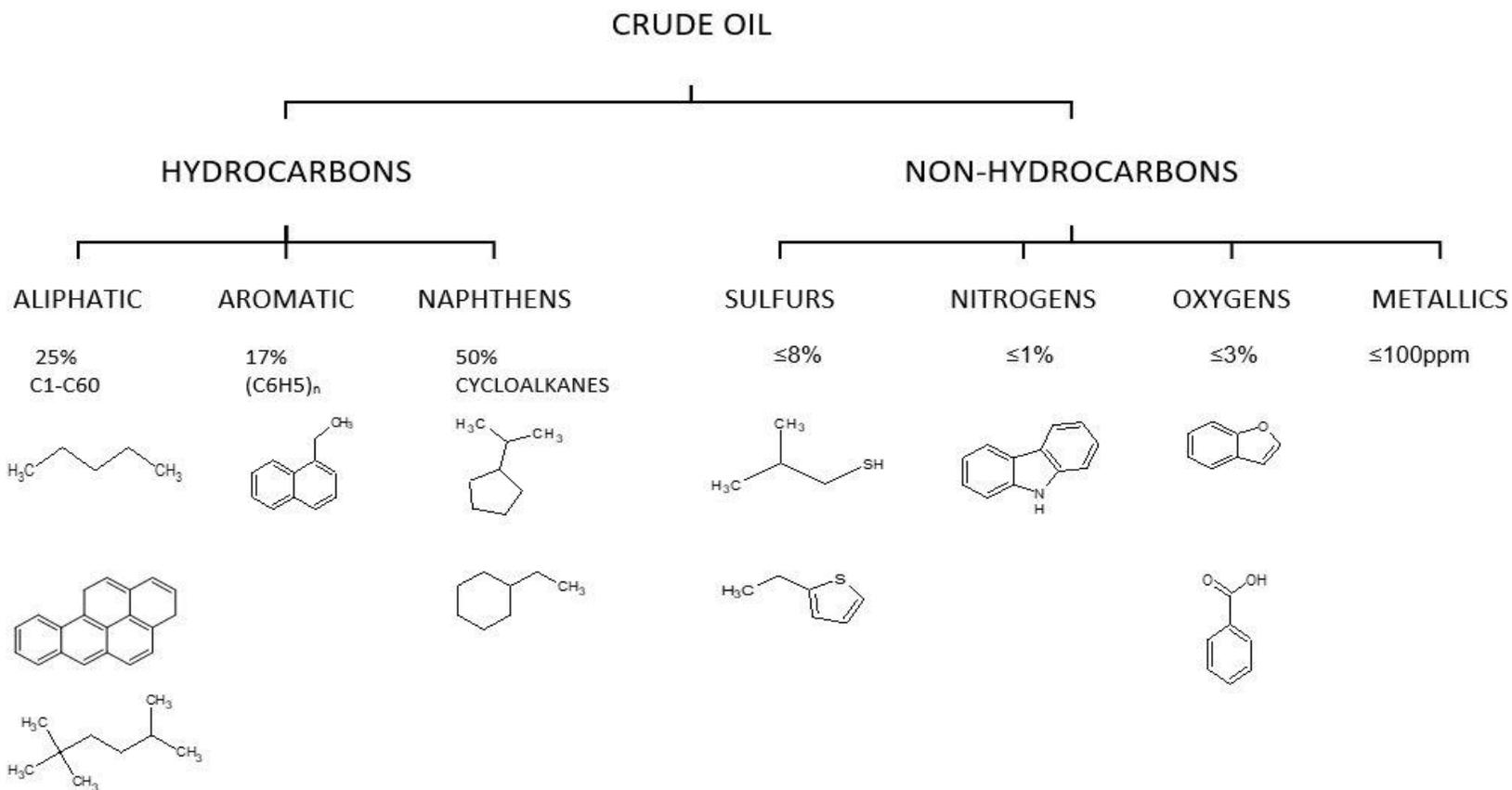


Figure 3.4 Composition of crude oil (reprinted from reference [78])

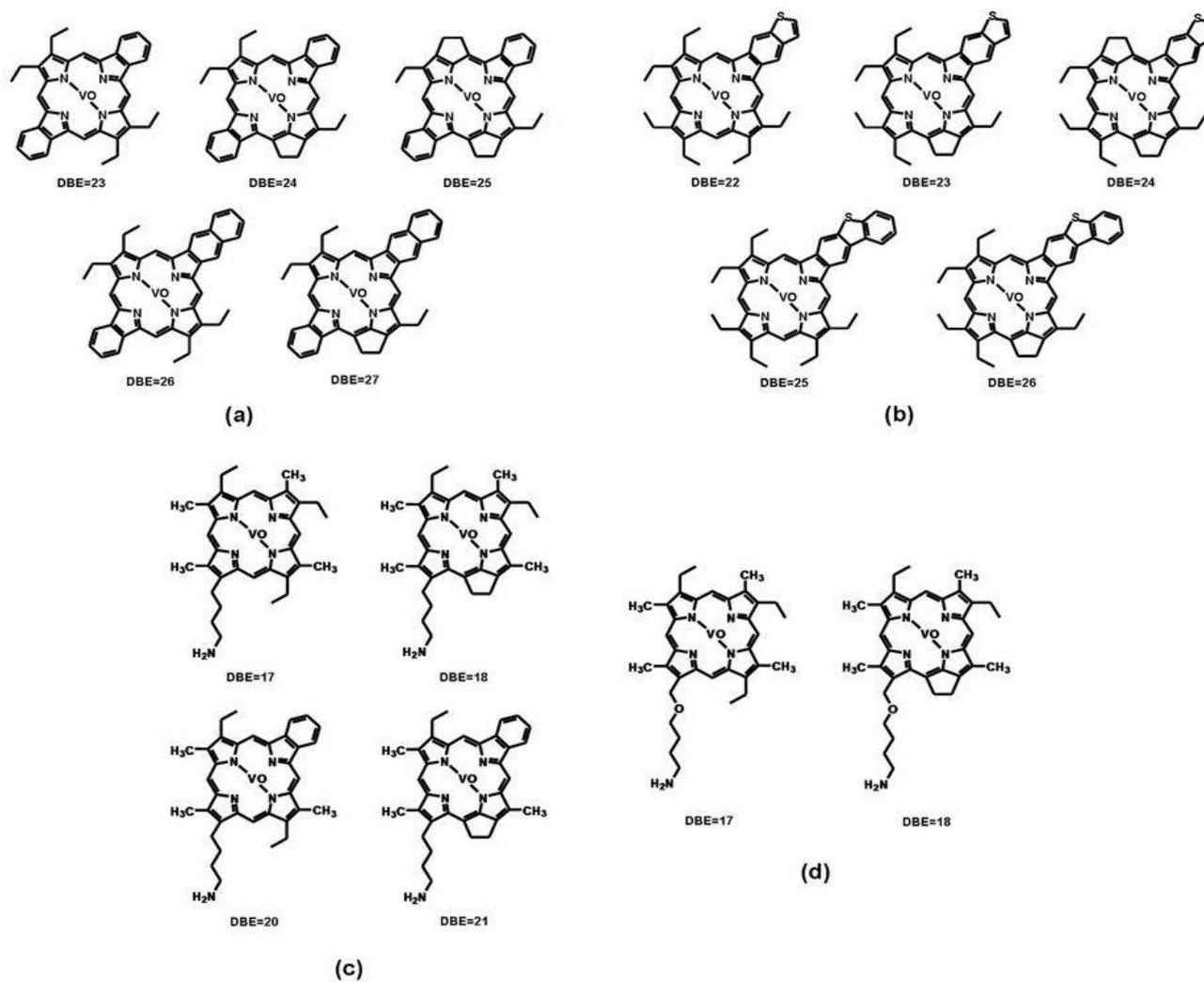


Figure 3.6 Detected structures of different vanadium porphyrin species in Venezuela crude oil (reprinted from reference [79])

In the case of dealing with heavy oil, which is a poor microwave-to heat convertor while metals are not, employing the microwave would lead to removing metals at a relatively low bulk temperature. Microwave metal interaction will lead to creating local hotspots at the metal bonds, which would lead to a weakening in the bond between the metals and the four nitrogen in the porphyrin ring. This, in turn, would enhance the easy and rapid breakdown of the metal bond and liberation of metals from the four N bonds. So, applying microwave heating will enhance the selective removal of metals from the network of the oils. As a result, the yield of the treated oil is not affected.

Theoretically, metals are perfect microwave reflectors, but in reality, they are not. In the case of a conductor, i.e., high loss medium, Equation (12) represents the penetration depth of the target.

$$D_E = \sqrt{\frac{\rho}{\pi f \mu' \mu_o}} \quad (12)$$

where ρ is the electric resistivity; it is a fundamental property that quantifies how strongly a given material opposes the flow of electric current. Decreasing the electric resistance of the heated material (decrease the resistivity or increase the conductivity) shortens the penetration depth of the applied microwaves. In the case of a perfect conductor, i.e., resistivity equals zero – penetration depth equals zero, refer to Equation (13). This means that the applied electromagnetic waves are totally reflected on the surface of the metals.

$$D_E = \sqrt{\frac{\rho}{\pi f \mu' \mu_o}} = 0 \quad (13)$$

However, in reality, the total reflection of microwaves is not possible for the limited resistance of the heated conductor materials due to defects and impurities. Furthermore, resistivity is directly proportional to temperature, according to Equation (14).

$$\rho = \rho_{amb} (1 + \alpha_R \Delta T) \quad (14)$$

where ρ_{amb} is the resistivity at room temperature; α_R is the temperature resistivity coefficient; and ΔT is the temperature change.

Temperature, impurities, defects, and other factors play a role in increasing the resistivity of a material. Increasing resistivity leads to increasing the penetration depth of the microwave, which promotes coupling with microwaves, as shown in the flowchart below.

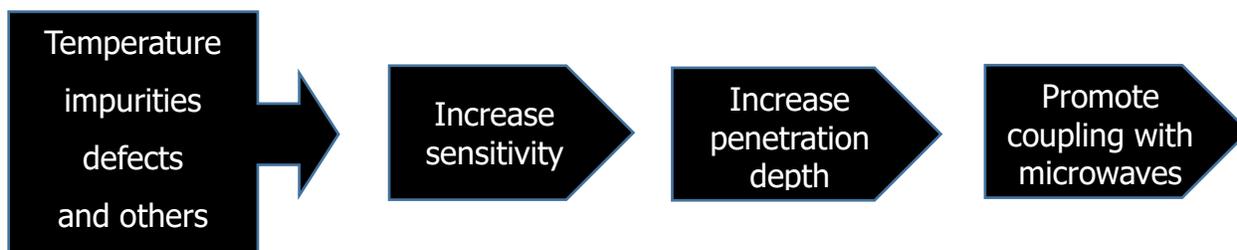


Table 3.3 demonstrates the penetration depth of selected metals at 2.45 GHz. It is clear that microwaves penetrate only a few micrometers of the material, which makes the interaction between metals in the form of small particles, such as powder, have a much higher interaction with microwaves than in the form of sheets.

Table 3.3 Penetration depth of selected metals at 2.45 GHz

Pure metal	Penetration depth (μm)
Nickel	2.7
Iron	3.2
Mercury	10
Silver	1.3
Vanadium	4.6
Zinc	6.4
Zirconium	6.7

Better coupling between a metal and microwaves is achieved at a particle size equal to or less than the penetration depth of the target at the applied microwave frequency. It should be noted that exposing metals in the form of powder to the atmosphere forms a thin layer of metal oxide film, which consequently increases the effective power and penetration depth of the composite. Metal with increased power and a particle size in the order of microns could reach a penetration depth

during heating that is greater than the same size of the particle at ambient conditions. Charge buildup at the ends of the particles may affect the induced currents, which subsequently leads to noticeable changes in the scattering patterns. Irregularly shaped particles may cause changes to the current flux or direction, and the space between particles allows for deeper penetration of microwaves.

In summary, magnetic loss factor is the principal source leading to microwave absorption in most metals and some oxides, and not the dielectric loss.

Several techniques for upgrading petroleum crude oil have been reported in the literature. Depending on the nature of the process, the techniques are grouped into physical methods, which are mainly based on distillation or solvent extraction, and chemical, which refers to the use of demetallization agents, thermal processes, and hydrogenation. The above methods are the main technologies applied to extract Ni and V from crude oils. Coupling microwave heating with the demetallization technology would lead to taking advantage of this heating mechanism. Most importantly, it includes most of the demetallization agents (DMA), such as acids (e.g., sulfuric, hydrofluoric, hydrochloric, nitric, phosphorus acids, and/or their salts), aqueous base selected from Group IA and IIA (e.g., hydroxides, carbonates, NH_4OH and $(\text{NH}_4)_2\text{CO}_3$), salts (e.g., boron trifluoride), oxidative agents (e.g., sodium hypochlorite and peroxyacetic acid), and chlorine-containing compounds (e.g., Cl_2 , SOCl_2 , FeCl_2 , SnCl_2 , ZnCl_2 , TiCl_4 , RuCl_3 , CrCl_3 , and COCl_2), and the metal compounds contained in the oil are polar materials. This would act as a strong microwave-to-heat converter. On the other hand, petroleum oils have a relatively low interaction with microwaves, while the metals inside the oil have a high interaction, which means the generation of heat energy is performed locally where the reaction between DMA and metal bonds takes place. V and Ni among other metals exist in petroleum oil and are strong microwave receptors, as demonstrated in Figure 3.7.

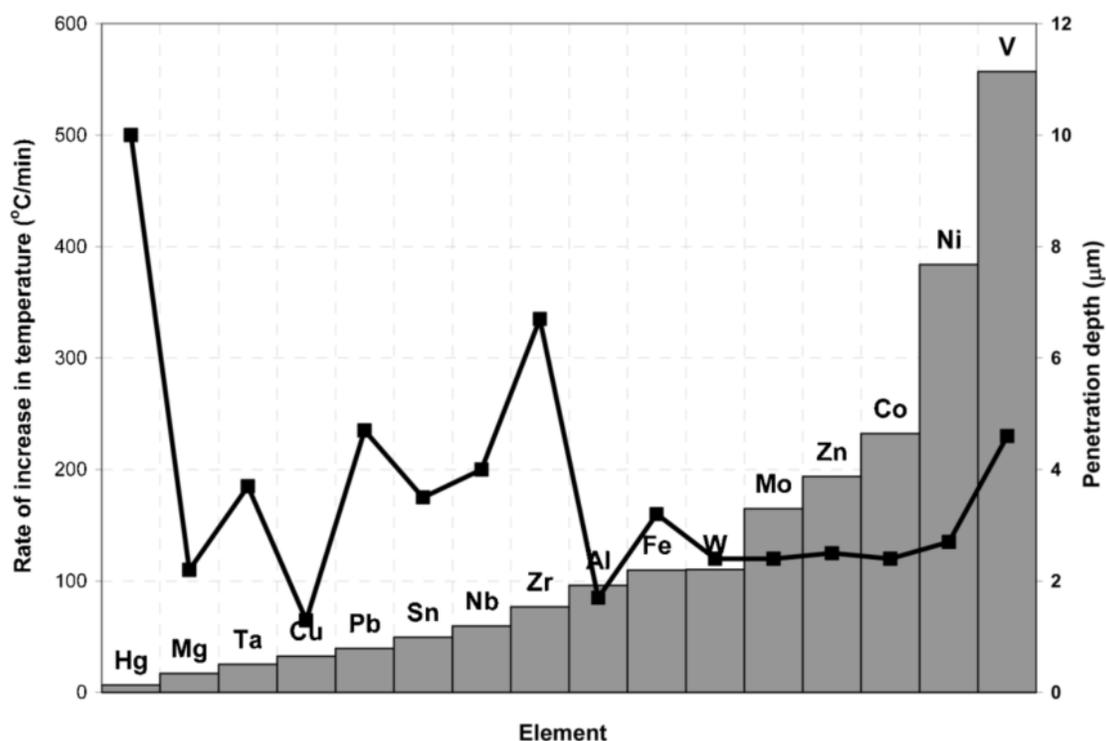


Figure 3.7 Penetration depth and heating rate of selected metals (Reprinted from (Gupta & Eugene, 2007))

Khan and Al-Shafei [80] have patented a hydrodesulfurization process that includes MW irradiation of a mixture of heavy crude oil with a catalyst and in the presence of hydrogen. The process is based on the conversion of sulfur compounds present in the crude oil into hydrogen sulfides. The method has been implemented under mild conditions, as the hydrogen was maintained in the microwave and the reaction was done at a pressure range from 1 atmosphere to 400 psi. The temperature of the reaction ranges from 80° C to 400° C, with the most preferable being 200° C to 250° C. In this process, crude oil was mixed with an iron powder catalyst, then the mixture was exposed to microwave heating in the presence of hydrogen. Microwaves have been used to increase the temperature of the crude oil to 200° C. The key findings of the process are that when the temperature of the oil remained at 200° C for twenty minutes, the sulfur concentration decreased in the treated oil by 25%. By increasing the temperature, the concentration was reduced by 2% more and reached 27%. By changing the catalyst to palladium oxide diethanolamine as a polar additive, and a sensitizer in the existence of hydrogen, the sulfur concentration decreased by 16-39% of hydrogen.

Chamorro et al. [81] applied the MWH technique to reduce the concentration of both metals and sulfur in a carbonaceous material. As the carbonaceous material was mixed with an acidic compound or a mixture of acids, such as HNO_3 , H_2SO_4 , HCl , HClO_4 , H_3PO_4 , HF , the mixture was then exposed to microwave irradiation. The process took place at a time between 10 s and 1 h, and at a pressure not exceeding 200 psi, in order to avoid the evaporation of the components of the reaction. The removal ration for both Ni and V reached 80% and 99%, respectively, in 15 min. Cationic starches have been tested as a demetallization agent for the removal of both Ni and V from crude oils using the MWH technique [82]. It was demonstrated that increasing the degree of cationic substitution of cationic starches, leads to increasing the removal efficiency of heavy metals. The optimum reaction conditions for the removal of both Ni and V are 200 mg/L of cationic starch 4 (CS4) with 300 W of microwave power for a residence time of 5 min. The removal efficiency when applying the above conditions on nickel from Iran and Shengli crude oil were 55% and 60%, respectively, and in the case of V were 76% and 79%, respectively.

3.7 Microwave prospective applications

The significant advantages of the energy conversion mechanism of the microwave heating have been underlined as volumetric, uniform – when the penetration and other limits of the applied waves and the target are respected, and selective – mainly when the payload composes of multiple components – heating technique; reduced energy consumption – the heated material must be a strong microwave receptor; high reaction selectivity – especially in multiple reactants applications; less heat transfer limitations – because it does not depend on the superficial heat transfer as the conventional processes; equipment portability – mainly for small and medium powers; high power density; process flexibility and robust; and instantaneous power control. Since microwave heating is correlated with the structure characteristics – in other words, the physical properties – of the target(s), the response of each heated material is different. This aspect leads to create a local temperature that is totally different from the bulk temperature of the multiphase/multi-component systems, which is exclusively associated with this heating mechanism.

In the oil industry, most common feedstocks – namely, crude oils and gaseous components – are not active microwave receptors and, in turn, fail to establish substantial interaction with electromagnetic microwaves. On the other hand, most metals, metal oxides and catalytic agents

are highly efficient microwave-to heat converters. This aspect, which is a rather complicated matter in several applications, can make a revolution in the industry. Having a high local temperature on the active site promotes the catalytic and non-catalytic reactions while the relatively low temperature of the bulk material(s) restricts the undesirable secondary reactions correspondingly. As a result, it is believed that the applications of the outstanding temperature gradient of microwave heating ameliorate not only the productivity but the selectivity of various reactions in the oil processing.

For example, conversion of methane to ethylene and acetylene is an endothermic process. The rate of product formation is much higher than that of the complete decomposition of the feedstock, which leads to the creation of carbon soot. Applying conventional heating in such reaction needs quenching or fast cooling of the products to avoid undesirable further decompositions. Taking advantage of the high interaction between microwaves and active catalytic agent in this reaction and the low response of the produced gases to the microwaves can noticeably enhance the reaction selectively. Microwave generates hotspots where the catalyst exists, leading to the decomposition of methane. Subsequently, once the products leave the catalytic material, they face much lower temperature, which avoids most issues and limitations associated with the conventional processes. Other methane conversion processes, such as steam reforming, partial oxidation, and CO₂ dry reforming processes as well as other gas, liquid and or solid reactions can take advantage of such outstanding selective heating of microwaves.

Although the vast interaction between microwaves and metals is well known, unfortunately, a little attention has been directed to upgrading petroleum oils through the removal of metals, specifically Ni and V; and S using microwaves. Therefore, the author of this work has invented three processes for the removal of V, Ni, and S in addition to the other metals by applying a novel DM-DSA and using the microwave heating technique. The process is green as no solvents are needed and, at the same time, cost-effective because no emulsification-processes are required for mixing the agent with the crude oil and other reasons. The process can reduce the concentration of almost all the contaminations, specifically Ni, V, and S by more than 90%.

The reason behind this outstanding result is because the invented processes take advantage of the non-uniform temperature distribution within the payload to enhance the removal efficiency of

metals and sulfur. The microwave receptors are the metals exist in the chemical network of the crude oils and the employed DM-DSA while the poor microwave-to-heat converter is the crude oil itself. The interaction between microwave and metals creates local hotspots at the metal bonds, which consequently leads to weakening the bond between the metals and the four nitrogen in the porphyrin ring. This aspect, in turn, enhances the easy and rapid breakdown of the metal bonds and the liberation of metals from the core of the metalloporphyrin ring. Also, the high interaction of the other metals in the form of polar salts exist in the oil boosts the removal of such metals from the crude oil significantly. The difference in the dielectric and magnetic properties of the heated components enhances the selective removal of metals from the network of the oils and keeps the main skeleton of the oil without further degradation. As a result, the yield of the treated oil is not affected compared to the other demetallization technologies.

Table 3.4 Selected literature on the demetallization of petroleum oil

Reference (Author, Date)	DMA	Method	Key findings	Important notes
Eidem 1988 [33]	H ₃ PO ₄	Stirring and heating under a nitrogen gas blanket to 150 °C, the temperature is gradually raised to 260 °C, the reaction time is 44 min.	Fe decreased from 64 to 0,06 ppm V decreased from 63,3 to 9,7 ppm Ni decreased from 101 to 14,5 ppm	
Michlmayr 1977 [35]	Ferric chloride and hydrogen chloride	Feedstock: Arabian crude oil (50ppm V and Ni) Rotary disk contactor (3 stages, 93 °C) Settling (oil phase and water phase) The oil phase is withdrawn, dried and freed of hydrogen chloride	metal content reduced by at least 20%.	Aqueous solutions of acid alone are not effective. pH must be acidic.
Kukes and Battiste 1985 [32]	Phosphorous acid (H ₃ PO ₃)	The reaction requires 2-4 wt.% of acid, reaction time between 1-2h.	The process removes from 49% to 99% of V and Ni respectively.	
P 1972 [83]	H ₂ SO ₄ for S removal and MgSO ₄ for V removal	The residual oils treated with sulfuric acid then each treated with a 20 wt.% aqueous solution of magnesium sulfate, the reaction temperature of about 120 F	S decreased from 2,6 to 0,02 wt.%, V from 395 to 24 ppm, and Na from 21 to 2 ppm.	
Marcusson and Eickmann 1917 [84]	Sulfuric acid	Treatment of the asphaltic materials with low boiling naphtha, followed by		Many side reactions with the hydrocarbons.

		fractionation of the naphtha-soluble material with concentrated sulfuric acid.		
Greaney and Polini 1999 [85]	NaOH, KOH, ammonium hydroxide and carbonate	400 g of water, 193 g of sodium hydroxide, 50 g of 40 wt.% tetrabutylammonium hydroxide (TBAOH) and 1 ml of Triton-X-100 surfactant. The temperature of the glass reservoir was 100° C.	vanadium decreased from 29.6 to 2.9 ppm and nickel from 16.5 ppm to 6.3 ppm.	The residuum phase was set apart by the addition of toluene to the sample followed by centrifugation,
Gould 1980 [41]	Oxydizing agents (air at 100 °C, NaOH/air, sodium hypochlorite and peroxyacetic acid	These DMA were tested on Cold Lake asphaltenes, Arabian Heavy asphaltenes and Cold Lake vacuum residuum.	Demetallization is proportional to the amount of oxidant used.	Air at 100 °C and NaOH/air does not have appreciable demetallization activity. Sodium hypochlorite and Peroxyacetic have high demetallization activity coupled with the ability to remove or destroy petroporphyrins, cause chlorine incorporation into the feed.
Kashima oil Co., Ltd. Japan. 1983 [86]	1,2,3,4-tetrahydroquinoline	A 20:60 g mixture of a vacuum-distillation residue (288 ppm of V) and 1,2,3,4-tetrahydroquinoline was autoclaved (5mL/min to 216 °C for 60 min) then cooled and filtered.	83% of V was removed	

D.A. Young 1979 [87]	ZnCl ₂ and TiCl ₄	Hydrocarbon feedstocks were blended with ZnCl ₂ and TiCl ₄ (2.0-4.5 lb/bbl oil). The resulting mixtures are treated with hydrogen at approximately 288-482 °C A heavy Iranian residue was hydrogenated at 343 °C, 1034-2500 kPa, for 2 h and 7000 rpm stirring rate in the presence of ZnCl ₂ (4.2 ppb)	70% of the Ni and V contaminants were converted to oil-insoluble forms	Coke formation being <3 wt.%
U.S. Patent Nos: -Young 1979 [88] - Siskin1977 [89] - Michlmayr 1977[35] - Nametkin, Gubin et al. 1976[90] -Gleim 1969)[91]	Chlorinating compounds (Cl ₂ , SOCl ₂) or inorganic salts (FeCl ₂ , SnCl ₂ , ZnCl ₂ , TiCl ₄ , RuCl ₃ , CrCl ₃ , COCl ₂) or their aqueous solutions.	Temperature ranging from 40 to 300 °C. Metals were converted into insoluble constituents and removed by filtration.	Up to 70% of Ni and V are reported to be removed.	Chlorine and metal incorporate into the production and degrades the quality of the oil
W. Baird, R. Bearden 1977 [92]	Sodamide +H ₂	On Safaniya atmospheric residue, 9.9% sodamide at pressure 3447.5 kPa and temp. 370 °C	Desulfurization reached to 68% and demetallization reached to 77%.	The reaction between heavy hydrocarbon and sodamide at elevated temperatures produce salt. This salt is separated by filtration.
Bearden (1978) [93]	Molten sodium+ H ₂	Hydrogen pressure between 1013 and 2026 kPa, with temp. Above 400 °C.	On Safaniya residue this treatment reduced sulfur to 0.2% and Ni+V to less than 1 ppm.	

Greaney et al. (1996) [94]	toluene is added to an aqueous solution of 40 wt.% tetra-butylammonium hydroxide (20mL)	The applied potential was set at 2.5 V. for 18h stirring.	Removal of 53% of V, 50% of Ni and 65% of Fe.	The demetallization and desulfurization were done by Electrolysis using electrochemical cell a commercially available coulometry cell consisting of a mercury pool cathode, a platinum wire anode, a standard calomel reference electrode and a glass stirring paddle.
S.R. Savel'ev, G.K.Azerbaeva, Y.P. Saltykov, N.F. Noskova (1996) [95]	TiCl ₄ , FeCl ₃ , ZnCl ₂ , CuCl ₂ , CuBr ₂ , CuSO ₄ or AlCl ₃	Temperature ranges from 30-90 °C for 5-60 min.	80-92% of vanadium was removed.	It was found that there was a correlation between the redox potentials of the ligands and their reactivities.
D.P. Mann, S.G. Kukes, D.M. Coombs (1985) [46]	Organophosphate esters + light solvents	Hot extraction temp. 210 °C and pressure 6205.5 kPa with n-pentane containing di-methyl phosphite.	Removal of 99.0% of V and 89.8% of Ni.	
S.G. Kukes, A.W. Aldag (1985) [96]	P ₄ S ₃	Monagas pipeline oil with 3% P ₄ S ₃ at 400 °C	Removal of 90% of V and 18% of Ni	Production of a variety of side reactions (element incorporation, cracking, polymerization..)

<p>Yan 1983 [97]</p>	<p>An aqueous solution containing chelating agent (EDTA, N-(hydroxyethyl)ethylenediamine triacetic acid, N-[2-(bi(carboxymethyl)amino)-ethyl]-N-(2-hydroxyethyl)glycine, diethylenetriamine pentaacetic acid or its salts.</p>	<p>A vacuum distillation residual oil was treated with 27% EDTA aqueous solution at pH 4.5</p>	<p>Removal percentages are 99% of Ca, 35% of Fe, 4% of Ni, 3% of V.</p>	
<p>Peifu, Zhang, T. Zhang (1991) [98]</p>	<p>An aqueous solution of chelating agent +phosphate salts such as $(\text{NH}_4)_3\text{PO}_4$</p>	<p>Dosing the feed with an aqueous solution of chelating agent containing phosphate salt, an emulsion breaker and solid wetting agents.</p>		<p>Applying an electrical field for liquid-liquid separation. Emulsification process is a must.</p>
<p>H. Miyadera, Y. Oguri, H. Ozaki, T. Suzuka, K. Nakamura, H. Yoshikai (1975) [99]</p>	<p>Sn or Sn alloys</p>	<p>650 g Sn was melted at 500°C in a reactor and was sprayed, at 1.6mL oil/min with 106 ml min/Ar (g) for 30min. The residual oil containing 100 ppm of V, 33ppm of Ni, 5ppm of S</p>	<p>The product was 8.7% gas, 14.8% coke, 76.5% oily material. The oily material contained 7ppm V, 3 ppm Ni and the by-product coke contained 177ppm V. When Pb was used the product was gas 8.4%, oily</p>	

			material 78.4% and 12.9% coke. The oily material contained 27ppm V and 10ppm Ni, and the coke contained V with 600 ppm.	
J.G. Reynolds (2004) [100]	Maleic acid in dimethylformamide, montmorillonite in 1-methyl naphthalene, CF ₃ SO ₃ H in 1-MN and FSO ₃ H in 1-MN.	Petroporphyrin from heavy crude oils were treated with chemicals agents and then washed with aqueous solutions to remove the metal.		
Wieckowska, E. Zienkiewicz, T. Lisik, T. Chrapek, J. Tomusiak (1988) [101]	SiO ₂ and/or Al ₂ O ₃ or silica gel-adsorbent activated with a mineral acid (H ₂ SO ₄) +Fe catalyst	Contacting the feed with SiO ₂ and/or Al ₂ O ₃ or silica gel-adsorbent (pore size 100-1000A) activated with a mineral acid (H ₂ SO ₄) followed by contacting the feed with an Fe catalyst at 249-397°C with simultaneous introduction of H ₂ at a flow rate equal to that of the feed. The contact time was 1.8x10 ³ s.	The product contained V, Ni, and Fe at 8 ppm in the total amount.	
Aldridge, R. Bearden, K. Riley (1991) [102]	Vanadium oxide supported on activated carbon.	Treatment of Arabian Heavy vacuum resid at 5268 kPa and 290 °C.	The activity of vanadium removal can be increased by increasing the percentage of vanadium on the activated carbon support.	The reaction is highly selective with minimal occurrence of other reactions.
Rankel, (1994) [103]	Activated carbon catalysts in the	An atmospheric residue containing 4.2 wt.% sulfur, 104 ppm vanadium, and 32 ppm	Significant reductions in the sulfur content, reduction of	Petrofarco A carbons seem to be the most efficient.

	presence of hydrogen	nickel was treated in a trickle bed micro unit reactor. The trickle bed was charged with different types of commercially activated carbon catalysts and operated at 400°C under hydrogen pressure.	23% of the original metal content (Ni and V content).	
J. Piskorz, D. Radlein, P. Majerski, D. Scott (1996)[104]	Supercritical fluids and activated carbon as a catalyst.	The ration of a mass mixture of bitumen and n-dodecane was 1:1. The hydrogen feed ration was 1220 m ³ hydrogen per m ³ of liquid feed.	Sulfur content was reduced from 5.44 wt.% to 1.16% with complete demetallization.	
K.L. Riley 1977 [105]	Hydrogen + catalyst containing CoO 4.5%, MoO ₃ 16.0% and Al ₂ O ₃ 79.5%	First stage treatment with hydrogen in the presence of a catalyst with fine pores, and a second stage in the presence of a catalyst with larger pores and a specified pore size distribution.	Removal of 60% of V with the catalyst with pore volume 0.525 mL/g and average pore radius 84 Å. Removal of 40% for a catalyst with pore volume 0.47 mL/g and average pore radius 35 Å.	
Mobil Oil Corp. 1979 [106]	Catalyst contained 1-10 wt.% of an Fe-group metal (Co or Ni) and 5-25 wt.% of a group VIB metal as the oxides or sulfides on a	An atmospheric residuum containing 235 ppm V and 2.12 wt.% S was treated over a catalyst that calcinated at various temperature ranges from 281 to 466 °C.	V removal was 56.6-71.1 wt.% and S removal 48.7-55.9 wt.%	The hydrocarbons were treated by catalytic cracking, hydrocracking or coking.

	calcined support containing 85% Al ₂ O ₃ and 0.5-7.0wt.% of a rare earth.			
Nippon Oil Co. (1982) [107]	Zeolite catalyst.	The heavy petroleum oils containing heavy metals and S compounds were catalytically hydrodesulfurized (300-450°C, 50-250 kg/cm ² , 0.1-4.0 h/l liquid space velocity, 200-1500:1 H-oil vol. Ration in a fluidized bed of zeolite catalyst and then demetallized in a magnetic field.	80% of the S compounds and 45% of the Ni were removed.	
J. Devanneaux, D. Laforgue, J.P. Gallez, J.C. Courcelle (1984) [108]	Hydrodemetallized in a bed of sulfurized Al ₂ O ₃ catalyst	Hydrodemetallization of a refining residue containing 5% of S, 120 ppm of V and 55 ppm of Ni at 410 °C. The catalyst was prepared by passing (CH ₃) ₂ S ₂ at 250 °C with 1h/l space velocity, through a bed of Al ₂ O ₃ granules (surface area 188 m ² /g, pore volume 0.77 cm ³ /g)	The removal of S, V and Ni reached 15%, 85%, and 68% respectively.	Hydrodemetallization process
H.J. Chen, F.E. Massoth 1988 [109]	sulfide cobalt-molybdenum/alumina catalyst in a batch stirred autoclave	Hydrodemetallization of vanadium and nickel porphyrin model compounds over sulfide cobalt-molybdenum/alumina catalyst in a batch stirred autoclave.	Both of reactants and products were adsorbed , which inhibited the reaction. The hydrodemetallization rates increased with temperature and hydrogen pressure and were very low	The reaction was done using model compounds

			without the catalyst of H present. The reaction order in porphyrin was less than unity at a lower temperature, increasing to first order above about >350°C.	
Gomez 2005 [110]	sulfuric acid	experiments were carried out in a 3L autoclave using sulfuric acid in a nitrogen atmosphere at a pressure of 8 bar.	Removal efficiency reaches to 86% for S, Ni, and V.	
Romano 2000 [81]	sulfuric and nitric acids	Two Coke samples from crude oil were applied: C1 with particle size 500 microns and C ₂ with 250 microns Operating conditions : HNO ₃ -HCL 2:1, pressure 100 psig, the frequency of the microwave 2450 MHz, and time of irradiation 15 min	the removal ratios in C1 for both Ni, V and S are 80, 99, and 55 respectively. For C2 are 43%, 62%, and 32% respectively.	
. Wen et al. 2009 [111]	Sodium dimethyldithiocarbamate in the presence of water	Temperature range of 80–90 °C, microwave power of 100–800 W, and a treatment time of 5–60 min.	Removal ratios of Ni in Iran and Shengli crude oils are 45% and 49% respectively, and for V are 70% and 87% respectively.	

Wang, Xu et al. 2011 [112]	carboxymethyl chitosan (CT)	A reaction temperature of 60 °C, a microwave power of 300 W, a microwave time of 2 min, and a CT-50 dose of 500 mg/L	Ni and V removal efficiencies reached up to 69.8% and 93.7%, respectively	
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CHAPTER 4 OBJECTIVES AND METHODOLOGY

The main purpose of this work is to investigate the potential of implementing electromagnetic waves at the frequency of microwaves for metal and sulfur removal from petroleum oil. In order to accomplish this, the following steps are taken:

- 1- Select a DM-DSA that fulfills the chemical and dielectric properties and can extract both metals and sulfur in a single step.
- 2- Develop a new process for the removal of metals and sulfur using the conventional heating mechanism to prove the performance of the selected agent.
- 3- Investigate the removal mechanism to better understand the chemistry behind the reaction.
- 4- Introduce microwaves as the central heating mechanism in the removal process.
- 5- Investigate the influence of the basic process parameters, such as DM-DSA dosage, irradiation power, residence time, and others on the removal efficiency of the developed technique.

Chapter 5, Chapter 6, and Chapter 7 present the achievements and scientific findings of these objectives. Chapter 5 first demonstrates the characteristic of the developed demetallization-desulfurization agent and its effect on the removal efficiency of the process. The impact of the process parameters in the case of conventional heating is then presented. Chapter 6 debates the effects of the energy conversion mechanism in contrast to the superficial heating transfer mechanism on the demetallization-desulfurization process. The invented methods in this work have been proven using five different oil samples received from different fields around the world. The processes invented in this work are listed in the appendices. Chapter 7 presents the conclusions of this work and the recommendations for future investigations.

CHAPTER 5 ARTICLE 2: METALS AND SULFUR REMOVAL FROM PETROLEUM OIL USING A DEVELOPED DEMETALLIZATION- DESULFURIZATION AGENT

Mai Attia, Sherif Farag, Shaffiq Jaffer, and Jamal Chaouki

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Abstract

Metals and sulfur in residual fuel oil are the major challenges behind restrictions facing fuel oil production. Both metals, particularly vanadium and nickel, and sulfur compounds reside in crude oil in complex stable forms yet are soluble and have a negative impact on machinery during the refinery processes and other aspects. This work was performed using an invented process capable of selectively extracting almost all the minerals, especially vanadium and nickel. Additionally, it eliminates the thiophene compounds, which are alongside the metals, with a different extraction mechanism under the same reaction conditions. The removal efficiency of both vanadium and nickel amounted to 90% and 79%, respectively, and reached up to 53% for S in the case of Basra oil. The process is green and cost-effective since no additional operations, such as an emulsification process, are required, and no solvents are consumed during the reaction.

Keywords: Demetallization; desulfurization; metalloporphyrin; upgrading of crude oil

5.1 Introduction

During the preceding few decades, considerable attention has been focused on petroleum heavy crude oil for use in several applications. The demand for the oil, however, has declined due to serious concerns, one of which is the unsatisfactory level of contamination by both metals and sulfur. The issue has an adverse effect throughout the refinery operations as a result of severe damage to the contact surfaces. Furthermore, it gives rise to diverse environmental issues that affect the surrounding area and society. Therefore, refining heavy crude oil is required to avoid the challenges facing crude oil and expand its commercial scale in various industrial applications.

Substantial numbers of metal contamination exist in oil, and their concentrations vary from a few parts per million (ppm) to higher than 1000 ppm. Some of the most distinct elements that have been identified in oil are cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), silver (Ag), sodium (Na), potassium (K), lithium (Li), calcium (Ca), strontium (Sr) and arsenic [1, 2]. Ni and V are the most abundant, and they reside predominantly in residual fuel oil fractions in an oil soluble form. The concentration of both Ni and V varied from a few ppm to 150 ppm and from less than 1 ppm to 1200 ppm, respectively [1, 2, 7].

Recently, all the attention has been directed to study the extraction of both Ni and V from crude oil. These elements exist in the core of stable organometallic compounds in the form of metalloporphyrinic and nonporphyrinic structures [3, 4]. The high stability of these compounds increases the difficulty of elimination of the above metals from heavy crude oil. The subsistence of such elements in crude oil produces high volumes of coke and dry gases and decreases the liquid output [7]. In addition, the two elements poison the catalyst in a short time, ranging from 10 years for light oil to approximately one year for heavy crude oil [6, 7], which is mainly due to the deposition of the two metal oxides formed on the pore of the catalyst and blocking the access site. Thus, the removal of both Ni and V from heavy oil becomes a vital objective of the crude oil industry.

Sulfur exists in crude oil as well in different forms, such as mercaptans, sulfides, disulfides, and thiophenes, refer to Figure 5.1. The detected percentage of sulfur in petroleum oil ranges from 0.1 wt.% to 15 wt.% and depends on several parameters, most importantly the origin of the extracted oil [8]. Sulfur is emitted to the atmosphere in the form of SO_x, causing acid rain formation through

its reaction with water, oxygen, and other chemicals exist in the atmosphere. The presence of sulfur in oil increases corrosion issues during the refinery process and helps in the deactivation of the catalyst in minimal time. Removal of dibenzothiophene and its alky derivatives is a big challenge, as the compounds can not be transferred into H₂S due to the steric hindrance adsorption on the surface of the catalyst. The existence of sulfur in various forms, specifically the thiophenic form, is a considerable challenge due to the difficult removal of the element from its complex structure.

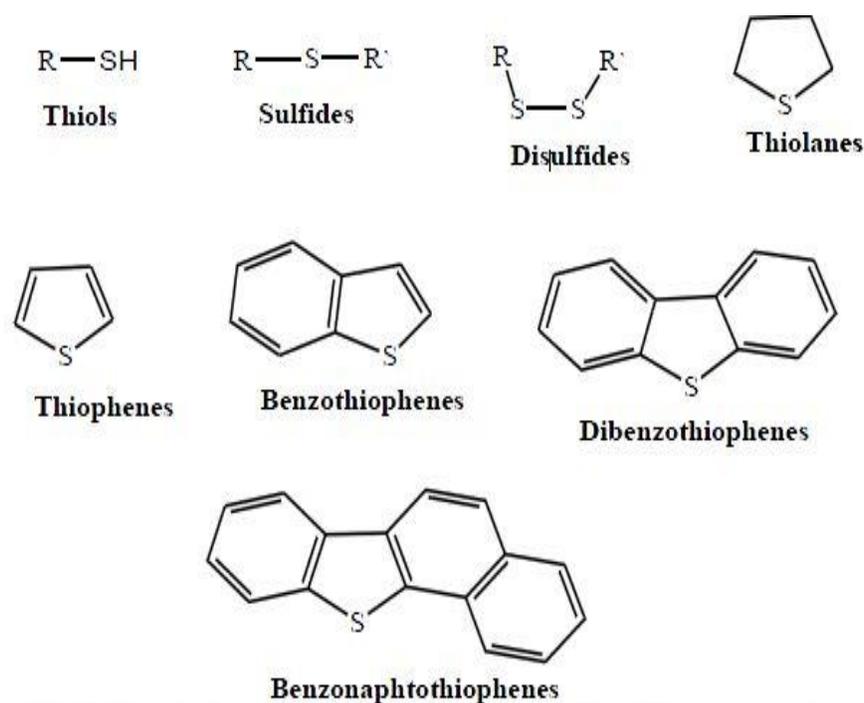


Figure 5.1 Different forms of sulfur in petroleum crude oil (reprinted from reference [9])

Although a large number of techniques have been developed to lessen or remove the metals and sulfur from crude oil, only a few of them have been industrially applied, the main reason being the disadvantages associated with each method. For instance, the process relies on solvent extraction, which leads to removing the whole fraction containing metals, thus reducing the yield of the end-product. The distillation technique enhances the production of two grades of oils: (1) light oil, which is the primary product and contains a shallow concentration of metals; and (2) heavy oil, which includes a much higher level of contaminants that must undergo a further upgrading process.

The fast catalyst deactivation, the need for an emulsification process, the high cost and long processing time are additional aspects that limit the performance of the developed demetallization and desulfurization techniques.

Ultrafiltration is a costly, value-intensive technique due to the fast fouling of the membrane used in the procedure. The bio-demetalization and bio-desulfurization processes are novel techniques for metals and sulfur removal from crude oil by the action of certain microorganisms. The process is applied directly after the burning of the fuel oil with keeping the calorific value without change. The main disadvantages of the process are the degradation of the crude oil which destroy the main skeleton of the oil. Also, the long processing time of the technique considers a big challenge. The hydrotreatment process for both metals and sulfur removal (HDM-HDS) is the only process widely used in the industrial sector. This technique can remove around 90% of the metals and sulfur content from the oil. Although the HDM-HDS process effectively removes a large portion of the metals and sulfur, it suffers from several issues. Most importantly, they include the fast catalyst deactivation, high hydrogen consumption, which reaches H_2/Oil , Scf/bbl 300-2000 for light oil and 2000-10,000 for heavy residual oil, an elevated temperature that ranges from 300 to 400 °C for light distillate and from 340 to 425 °C for heavy residual, and elevated pressure, which ranges from 30 to 130 atmosphere.

Several studies and efforts were performed on the removal of metals and sulfur from crude oil. Gould et al. developed a method for the demetallization of cold lake asphaltene, Arabian heavy asphaltene, and cold lake vacuum residuum [41]. Various oxidizing agents were tested to be demetallization agents, such as air at 100 °C, NaOH/air, sodium hypochlorite, and peroxyacetic acid. It was found that the demetallization process is proportional to the amount of oxidant used. Air at 100 °C and NaOH/air do not show any visible demetallization activity. Sodium hypochlorite and Peroxyacetic have high demetallization activity coupled with the ability to remove or destroy petroporphyrins and cause chlorine incorporation into the feed. D.A. Young proposed a new technique using $ZnCl_2$ and $TiCl_4$ for the demetallization of different hydrocarbon feedstocks [87]. The raw materials were blended with $ZnCl_2$ and $TiCl_4$ (2.0-4.5 lb/bbl oil), and the resulting mixtures were treated with hydrogen at approximately 288-482 °C. A heavy Iranian residue was hydrogenated at 343 °C, 1034-2500 kPa for 2h and a 7000 rpm stirring rate in the presence of $ZnCl_2$ (4.2 ppb). Seventy percent of the Ni and V contaminants were converted to oil-insoluble forms

with coke formation of less than 3 wt.%. Young [88], Siskin [89], Michlmayr [35], Nametkin, Gubin et al. [90], and Gleim [91] have patented techniques using different demetallization agents, such as chlorinating compounds (Cl_2 , SOCl_2), inorganic salts (FeCl_2 , SnCl_2 , ZnCl_2 , TiCl_4 , RuCl_3 , CrCl_3 , COCl_2) or their aqueous solutions. The reaction temperature ranged from 40 °C to 300 °C, and metals were successfully converted into insoluble constituents and removed by filtration. It was reported that the concentration of both Ni and V decreased by up to 70 wt.%. The main disadvantage of this process is the incorporation of chlorine and metal into the production and the degradation of the quality of the oil.

A novel technique has been applied by Greaney et al. [94] for demetallization and desulfurization by electrolysis using an electrochemical cell. The commercially available coulometry cell consisting of a mercury pool cathode, a platinum wire anode, a standard calomel reference electrode and a glass stirring paddle. The applied potential was set at 2.5 V. for 18 h stirring. In the process, toluene was added to an aqueous solution of 40 wt.% tetra-butylammonium hydroxide (20 mL). It was demonstrated that the removal percentages reached to 53% of V, 50% of Ni and 65% of Fe. Yan [97] has reported a demetallization method using an aqueous solution containing a chelating agent (EDTA, N-(hydroxyethyl) ethylenediamido triacetic acid, N-[2-(bi(carboxymethyl)amino)-ethyl]-N-(2-hydroxyethyl) glycine, diethylenetriamine pentaacetic acid or its salts as a demetallization agent. A vacuum distillation residual oil was treated with 27% EDTA aqueous solution at pH 4.5. It was found that the removal percentages reached up to 99% of Ca, 35% of Fe, 4% of Ni, and 3% of V. Aldridge, R. Bearden, K. Riley [102] used a vanadium oxide supported by activated carbon for the demetallization of Arabian heavy vacuum residue. The treatment process was done at 5268 kPa and 290 °C. It was noted that the activity of vanadium removal could be increased by increasing the percentage of vanadium on the activated carbon support. The reaction is highly selective with minimal occurrence of other reactions.

The removal of metals and sulfur from petroleum oil in a single step has received considerable attention as is evident in the scientific literature. Several techniques have also been developed to remove either sulfur or metals, but the scale-up limitation is a challenge for industrialization purposes. In addition, it is essential to propose a chemistry mechanism for the removal of metals and sulfur from crude oil, which would lead to deeper insights toward improving selective removal efficiency. Therefore, this work demonstrates a technique to remove both metals and sulfur in a

single step using a demetallization-desulfurization agent (DM-DSA). This technique is based on the authors invention “US Patent Pending Application: 62753071.” A removal mechanism was proposed and exhibited based on the obtained results. It is worth mentioning that the invented process is environmentally friendly, cost-effective and, moreover, successfully decreases the concentration of both metals and sulfur in a single step.

5.2 Experimental work

5.2.1 Materials

The invented demetallization-desulfurization process has been implemented on a number of petroleum crudes obtained from several countries. Iran and Basra oils were obtained directly from the tanks of the TOTAL refinery station in France with a high concentration of V, Ni, and S. Heavy aromatic naphthenic crude oil, light naphthenic crude oil, and Pennsylvania crude oil were purchased from the ONTA company, in Ontario. The concentrations of V, Ni and S vary from low to high in the ONTA samples, as it is indispensable to gain deeper insight into the removal efficiency using the DM-DSA for the high and low metal concentrations. All the other chemical agents, such as the DM-DSA and the solvents, were purchased from Sigma-Aldrich, Canada.

The concentration of metals and sulfur in all the oil samples has been determined by the neutron activation analysis technique (NAA) using the SLOWPOKE reactor at Polytechnique Montréal, QC, Canada. The other required information archived directly from the supplier, Iran and Basra oils, are tabulated in Table 5.1.

5.2.2 Experimental setup

The experimental setup shown in Figure 5.2 was employed to carry out the experimental work. The mixture of the raw oil and reactants was poured into a batch reactor equipped with a stirring technique. The reactor is attached to a water-cooled Liebig or Vigreux condenser fitted onto the top. The condensation system, in other words, reflux, works at a temperature of -5 °C and ambient pressure. The central role of the reflux is to condense the lower molecular weight compounds that might be vaporized during the reaction time due to increasing temperature. The reactor is heated conventionally to a temperature lower than the boiling point of the DM-DSA yet enough to perform

the elimination reaction. The temperature was controlled not only based on the electric oven temperature, but also as a direct measurement by using a thermometer immersed inside the oil. The experiment was carried out utilizing the conventional heating mechanism to control the reaction temperature and other aspects better.

Table 5.1 Characteristic of the processed oils

Property	Unit	Basra Oil	Iran Heavy	Light naphtha	Heavy aromatic naphtha
Density (15°C)	kg/m ³	886.8	881.2	873.5	953.0
API	-	27.98	28.99	30.0	16.4
Viscosity (10°C)	mm ² /s	23.8	18.4	-	-
Viscosity (37,8°C)	mm ² /s	9.32	10.6	-	-
Viscosity (50°C)	mm ² /s	6.79	8.67	-	-
S _{total}	mg/kg	26354	22795	33557	18385
Ni	mg/kg	12	25	61.1	35.3
V	mg/kg	40	85	331	383.1
CCR	%W	7.845	6.88	H/C= 1.668	H/C= 1.558

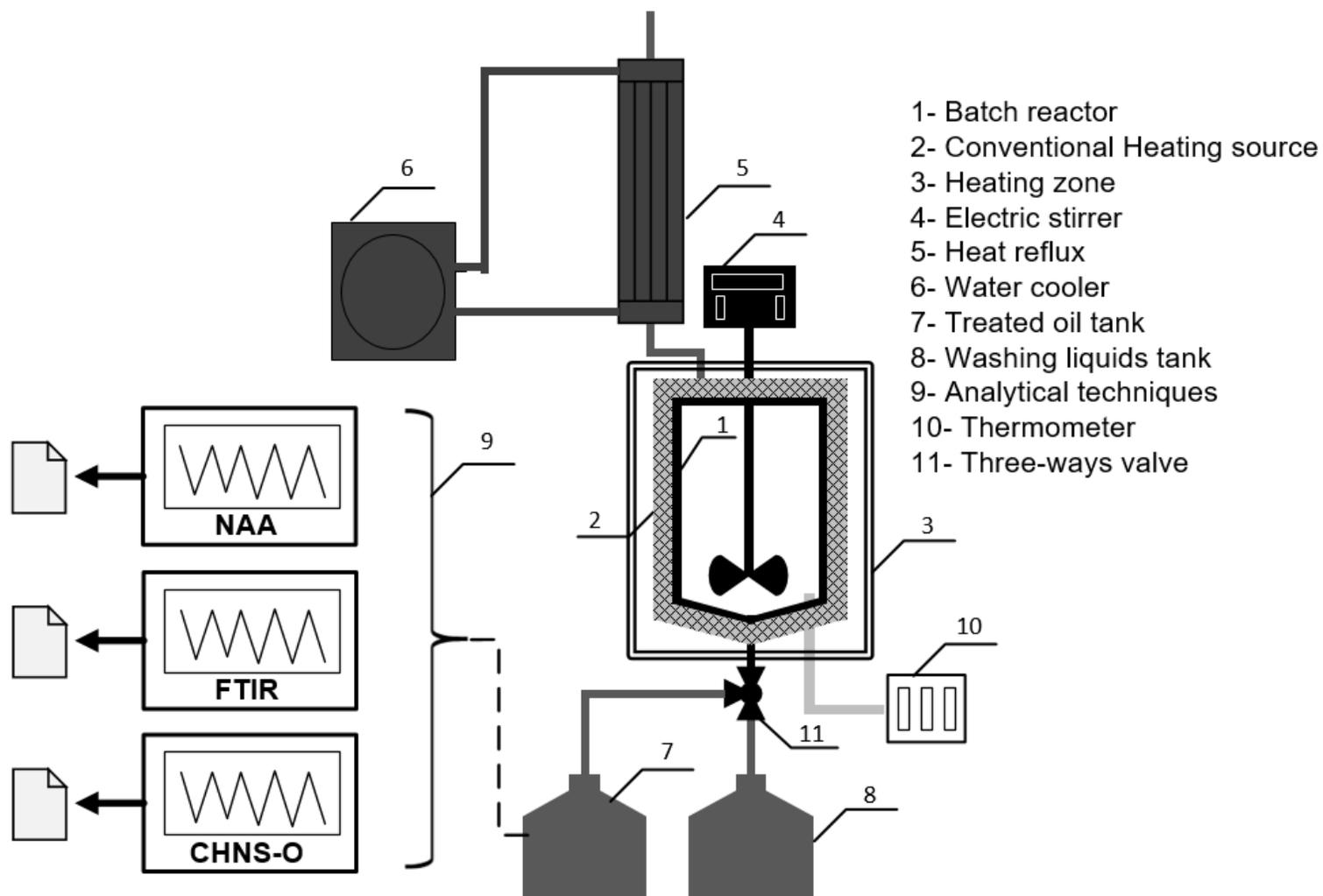


Figure 5.2 Experimental setup of the demetallization-desulfurization process by conventional heating mechanism

5.2.3 Experimental procedures

The invented process consists of three main stages: (1) reaction, which is between the oil and the DM-DSA; (2) washing the treated oil; (3) and separation, which is performed to separate the aqueous phase from the oil phase, as shown in Figure 5.3. The subsections below debate the three stages in full detail.

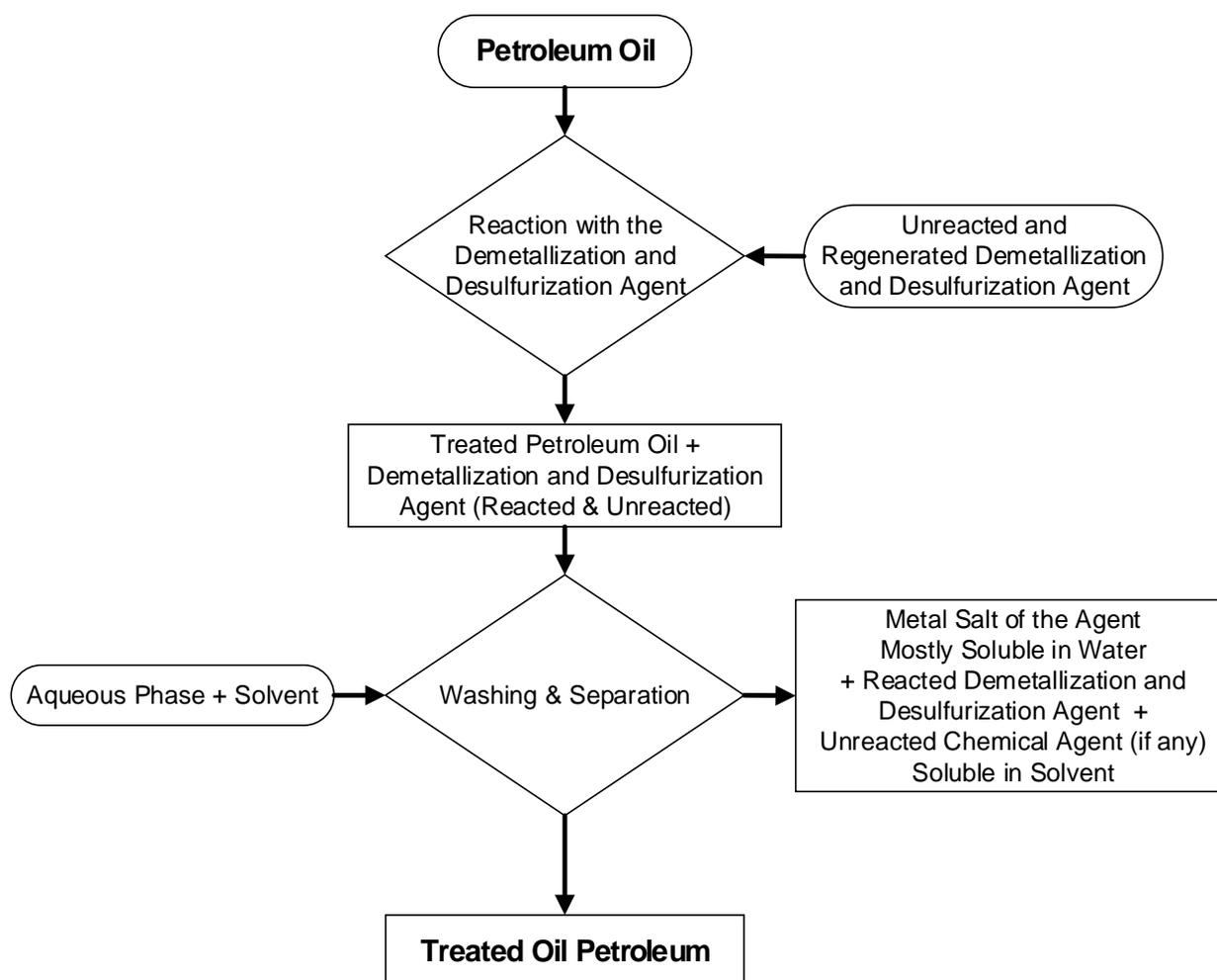


Figure 5.3 Flowchart of the invented process to remove metals and sulfur content in petroleum oil

5.2.4 Principal reaction of the DM-DSA with oil

A precise weight/volume of the untreated oil was mixed with a specific percentage of the DM-DSA – 2 wt.% and 5 wt.%. The mixture was poured into the reactor as demonstrated in Figure 5.2. It is worth mentioning that the described process does not need an emulsification process, which is contrary to most of the existing chemical demetallization techniques. The principal reason for this aspect is the complete miscibility of the employed DM-DSA with petroleum oil, which is a major advantage in the application. The electric stirring applied during the reaction is essential for mixing the reactants and to distribute the heat properly inside the oil better, which, in turn, enhances the replacement reaction taking place between the processed oil and the DM-DSA. The mixture is heated for a strategic residence time of about 1 hr at an actual temperature of up to 250 °C under stirring conditions up to 700 rpm.

5.2.5 Oil and DM-DSA separation

Several attempts were made to separate the treated oil from the reacted one efficiently and unreacted (if any) DM-DSA and its salts. This step is, in fact, critical because the processed oil after the reaction remains in the same vessel with both the metal salt of the formed DM-DSA and the unreacted DM-DSA (if any). The separation process was performed applying a mix of two different organic solvents. The first solvent was used mainly to dissolve the unreacted DM-DSA and separate it from the treated oil. The second solvent, an aqueous phase, was used to dilute the metal salt of the formed DM-DSA after the reaction. The mixture of the two solvents and the treated oil, which contains the DM-DSA and its salt, was then heated at a temperature of less than 100 °C under stirring conditions up to 700 rpm for the residence time mentioned above. The separation is always performed in a reflux system to avoid the evaporation of the solvent and precipitating the dissolved compounds again into the oil. After the separation time, a mixture of three phases appeared in the reactor; the upper phase was the treated oil while the lower phase contained both the metal salt of the DM-DSA dissolved in the aqueous phase and the unreacted part of the DM-DSA dissolved in ethanol. Eventually, the two obtained phases were separated by decantation and, then, centrifugation. The organic solvent phase with the dissolved DM-DSA has separated again from the aqueous phase to regenerate the unreacted DM-DSA. Figure 5.4 demonstrates a proposed

5.3.1 FTIR technique

Fourier transform infrared spectroscopy analysis was undertaken using a Perkin Elmer 65 FTIR-ATR instrument (PerkinElmer, Woodbridge, ON, Canada). A sum of 128 scans was accumulated for the signal averaging of each IR spectral measurement with a 4 cm^{-1} resolution. The spectra of the samples were recorded over a wavenumber range of $4000\text{-}650\text{ cm}^{-1}$ to detect the transformation of N-M bond to the N-H bond. FTIR can detect the characteristic vibration frequencies for each bond, functional group, side chain, and cross-link inside the molecule. It is evident that the demetallization reaction is primarily founded on the conversion of N-M bonds into the N-H bond. Therefore, the FTIR technique is one of the best candidates to observe the changes taking place in the N-M bond. Unfortunately, the FTIR instrument that is employed in the detection process cannot detect the peaks lower than 600 cm^{-1} ; consequently, the peaks of N-M bonds at less than 400 cm^{-1} have not been recorded.

5.3.2 Elemental analysis technique

It is indispensable to detect the sulfur concentration in the crude oil to record the change that should occur after the demetallization-desulfurization process. To observe the change, the elemental analysis technique is applied to find out the variation in sulfur concentration before and after the extraction process. The sulfur detection was performed using the Elemental Analyzer EA3000 (EuroVector) instrument. The data were processed using Callidus software interface version 5.1. Callidus. The 5.1 software fully controls the device, integrates peaks, reprocesses sample data, and reports result selecting one of the pre-arranged formats. The Callidus is based on the autorun concept as the samples cannot analyze in isolation but must be in association with standards (for calibration purposes), blanks (for the determination of potential trace contaminants) and bypasses (for conditioning purposes).

5.3.3 Neutron activation analysis

Neutron activation analysis is a nuclear technique used to determine the compactness of each element existing in vast numbers of chemical compounds. The analysis was performed in a slowpoke lab at Polytechnique Montréal, QC, Canada. In this technique, a neutron source is required for bombarding the sample with neutrons. Due to this bombardment, the element transfers

to its isotopic form. According to the radioactive emission and decay data known for each element, the spectra of emission of gamma rays for all the elements can be easily studied. Quantifying various metals in crude oil is indeed a challenge, due to the complex matrix of crude oil, which includes vast numbers of metals and different elements. In addition, the depressed concentration of each metal remains a considerable issue to be determined by most of the analytical techniques. Many of the metals and elements are interfering as well, which affects the accuracy of the measurements. The NAA technique is characterized by high accuracy in quantifying a wide assortment of metal elements in the complex matrix of crude oil. Its proficiency is indirectly dealing with the oil itself without any digestion process or dilution, such as the ICP-MS technique, which has several factors for error production in the measurements. The drawbacks, the uncertainty, and the limitations were precisely determined for the NAA measurements to heighten the accuracy of the technique. The most optimum method that can be used for metals quantification using the NAA technique is the k₀-Neutron Activation analysis (k₀-NAA). This method is a single-comparator standardized method used for high accuracy quantification of elements in any type of materials. By applying this method, the calibration of each element by changing the matrix or the detector is not required.

5.3.4 Quantification method

For the quantification of the metals and sulfur in the crude and treated oil, the extraction efficiencies in the case of each oil have been calculated. The extraction efficacy percentage has been determined using the following equation.

$$\text{Extraction efficacy (\%)} = \frac{((C_{\text{crude}} - C_{\text{treated}}))}{C_{\text{crude}}} * 100$$

Where the C_{crude} is the concentration of an element in the crude oil before the treatment process, C_{treated} is the concentration of the element in the treated oil after the demetallization process.

5.4 Results and discussion

The DM-DSA applied in the study has the ability to form an ionic liquid while it is present in oil at a lower temperature. The DM-DSA is not miscible with water, but it forms salts that are completely soluble in water. Thus, the unreacted part of the DM-DSA can be easily recycled. The

reason behind the immiscibility of the agent with water is the existence of the long side chains in the composition of the agent, which reduce its polarity.

The FTIR of the DM-DSA indicates that the DM-DSA has specific peaks appearing in regions that are different than what appeared in the treated oil, in particular, between 4000cm^{-1} and 3000cm^{-1} , which, in turn, can confirm that any peak appears in these regions after the elimination process was related to the treatment process.

The FTIR shows a difference in the absorption frequencies between the treated and untreated oil. It is supposed to transfer the metalloporphyrin ring into free based porphyrin; accordingly, new frequencies for the N-H bonds should appear instead of the N-M bonds.

Figure 5.5 shows the deviation in the IR absorption frequencies between the untreated and treated heavy aromatic naphthenic crude oil. There is a peak located at 3320cm^{-1} , which is attributed to the N-H bond stretching frequency. The peak located around 1600cm^{-1} is related to another vibrational mode of N-H [113]. There are two other peaks appearing at around 1110cm^{-1} and 740cm^{-1} in the treated oil, which are relative to in-plane N-H and out-of plane bending N-H, respectively [114]. It should be noted that these two peaks do not exist in the raw oil or the DM-DSA. The bands around 2922cm^{-1} were assigned to the C-H bond of the benzene ring and pyrrole ring. Bands at ~ 1458 and $\sim 1379\text{cm}^{-1}$ are attributed to the C=C stretching mode and the C=N stretching vibration, respectively. The bands at around 800cm^{-1} and 750cm^{-1} were respectively assigned to the C-H bond bending vibration of the para-substituted and molecule ortho-substituted phenyl ring.

Figure 5.6 shows precisely the same peaks appearing in Figure 5.5 but for light naphthenic crude oil. The FTIR results confirm that new peaks appeared in the processed oil related to the N-H bond. This key finding, in turn, confirms that the treatment process using the developed DM-DSA was successfully implemented and the N-M bond transferred to N-H bond. Since the same results were obtained in all processed oil samples and to minimize the number of figures in this manuscript, it was decided not to add the FTIR results of the other oils.

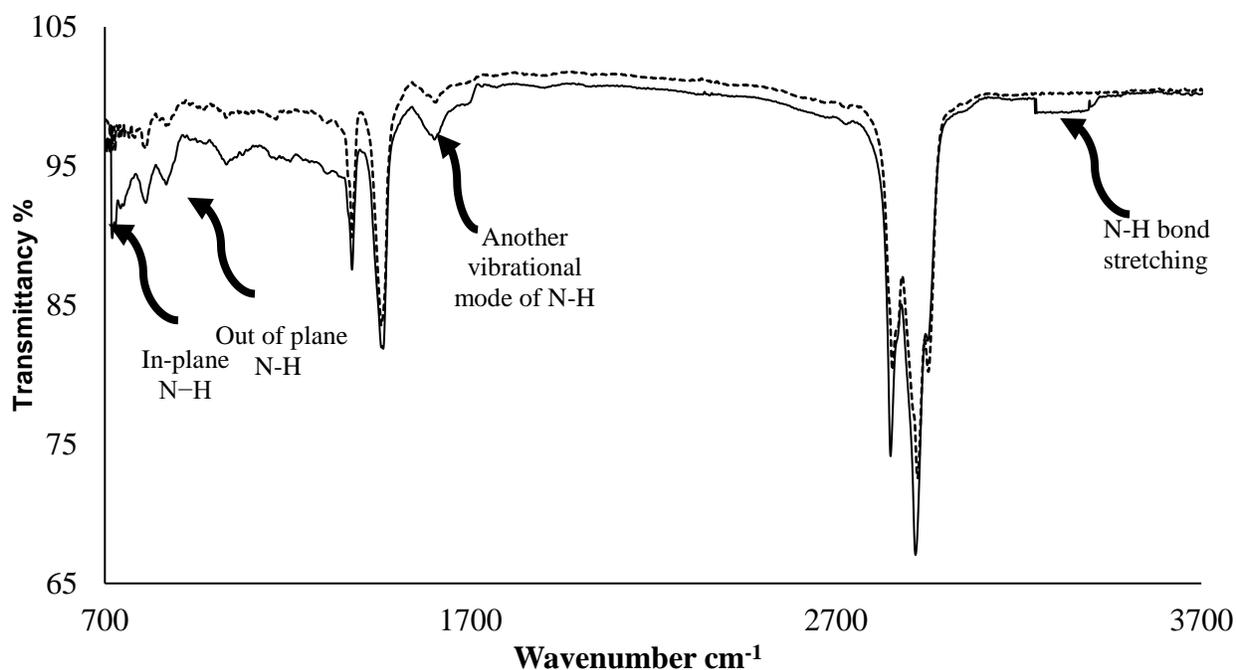


Figure 5.5 FTIR results of the raw heavy aromatic naphthenic crude oil (dotted line) and the treated oil by 2 vol.% DM-DSA (continuous line)

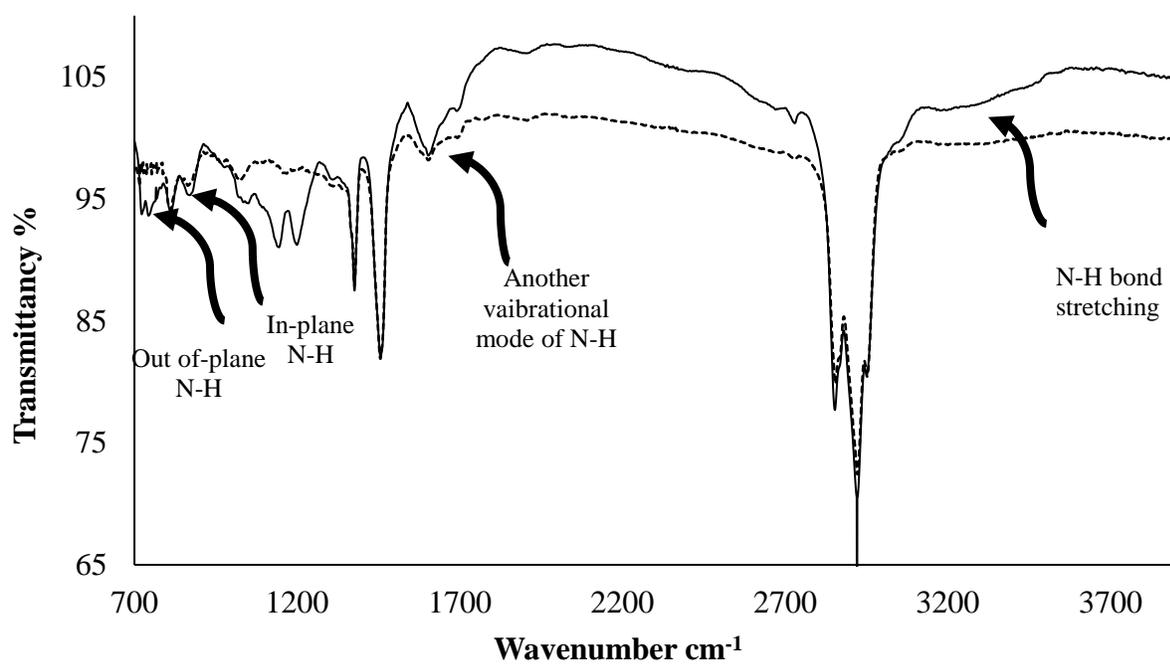


Figure 5.6 FTIR results of raw light naphthenic crude oil (dotted line) and treated oil by 2 vol.% DM-DSA (continuous line)

An increased concentration of DM-DSA, which reached to 5 vol.%, was also applied during the treatment process of both heavy aromatic naphthenic crude oil and light naphthenic crude oil. This experiment took place to detect the variation in the removal efficiency in the case of applying a higher dose of the DM-DSA. This difference can be detected by comparing the intensity of the peak for both 2 vol.% and 5 vol.% using the FTIR technique. It was found that there is no significant increase in the removal efficiency by applying 5 vol.% of DM-DSA during the treatment process, as presented in Figure 5.7 and Figure 5.8.

The elemental analysis was carried out to detect the variation in sulfur concentration before and after the treatment process, and to record the effect of the DM-DSA on sulfur removal. Figure 5.9 depicts a clear peak for sulfur in the region between 144 and 180 cm^{-1} on the heavy aromatic naphthenic crude oil and Figure 5.10 demonstrates the change performed for the sulfur peak after the remediation process, as the strength of the peak was reduced, which indicates the decrease in the concentration of sulfur in the treated oil.

This affirms that the DM-DSA successfully eliminated a portion of the sulfur compounds from the crude oil during the demetallization-desulfurization process. The same decrease in the sulfur content was obtained in the light naphthenic crude oil. Figure 5.11 and Figure 5.12 also confirms the reduction in sulfur concentration that took place after the demetallization-desulfurization process.

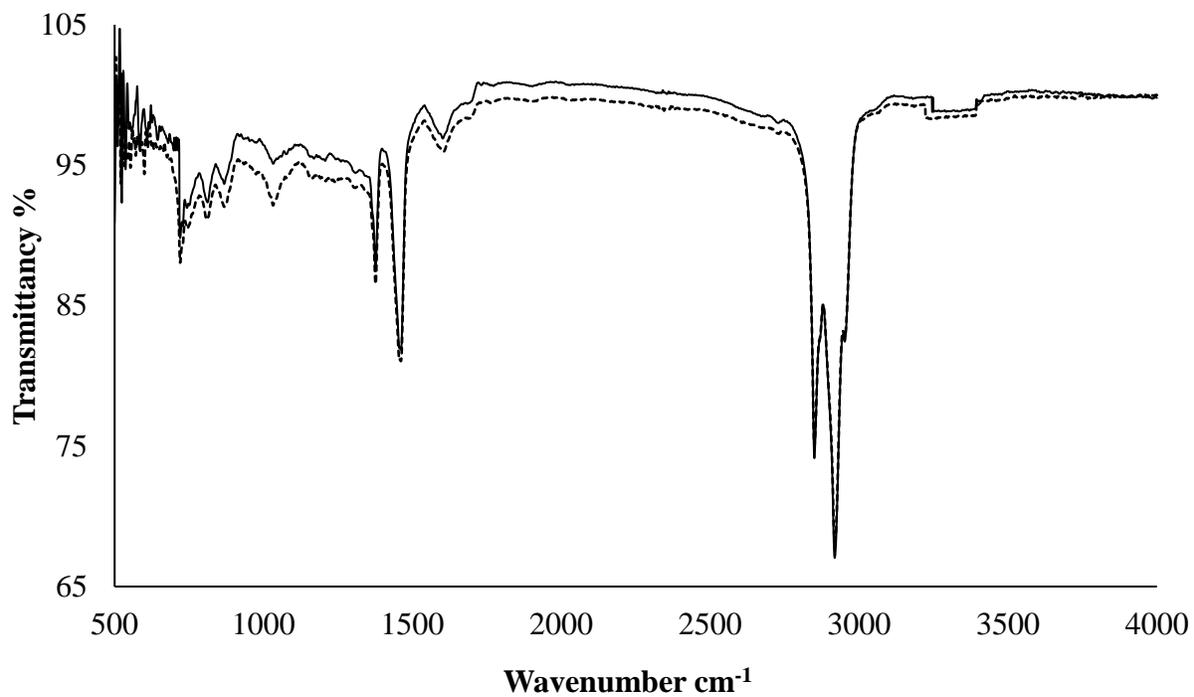


Figure 5.7 Treated heavy aromatic naphthenic crude oil with 2 vol.% (continuous line) and 5 vol.% DM-DSA (dotted line)

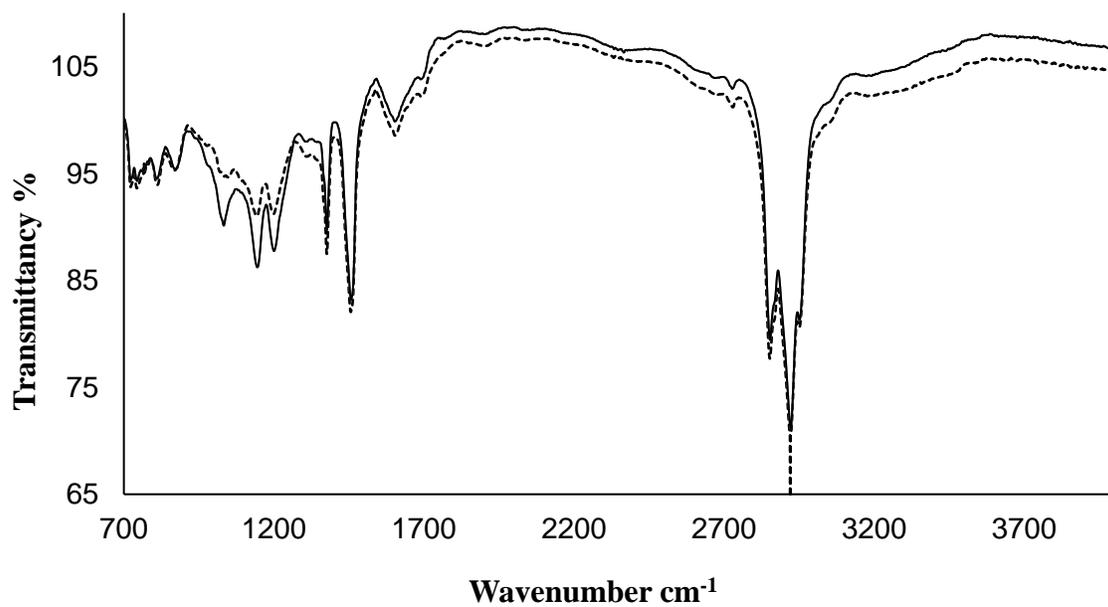


Figure 5.8 Treated light naphthenic crude oil with 2 vol.% (dotted line) and 5 vol.% DM-DSA (continuous line)

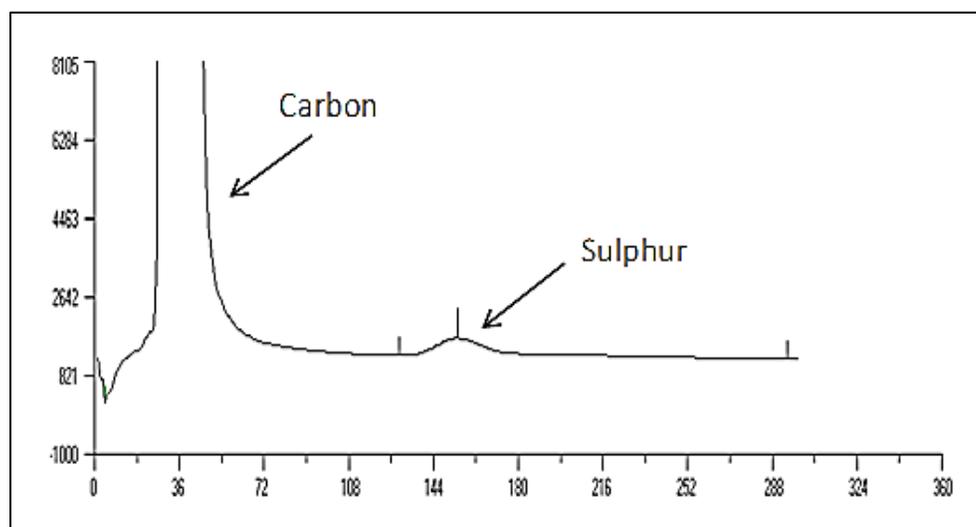


Figure 5.9 Sulfur detection in the raw heavy aromatic naphthenic crude oil using elemental analysis technique

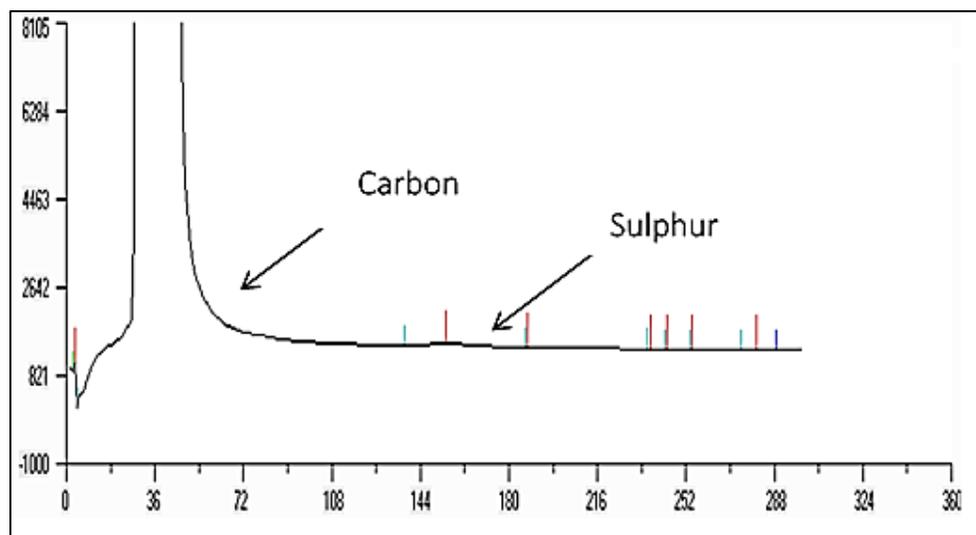


Figure 5.10 Sulfur detection in the treated heavy aromatic naphthenic crude oil by 2 vol.% DM-DSA using elemental analysis technique

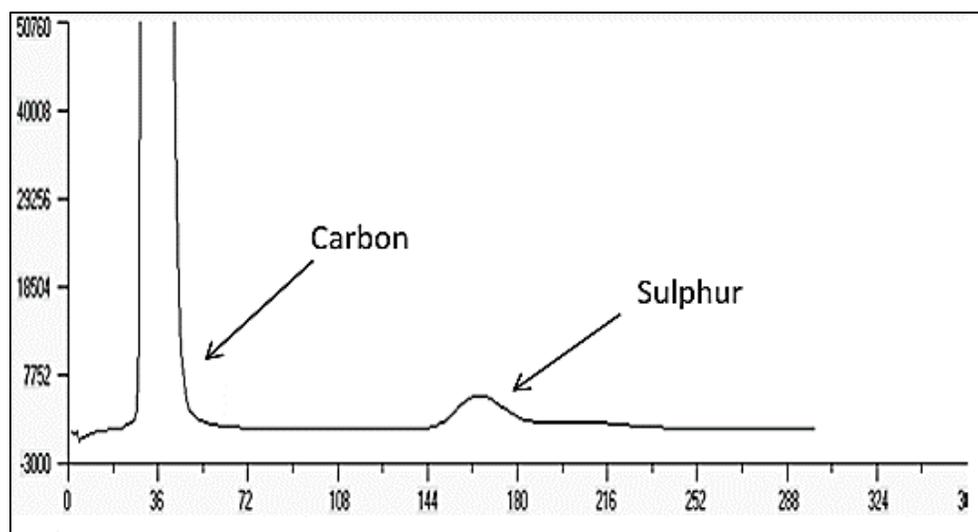


Figure 5.11 Sulfur detection in the raw light naphthenic crude oil using elemental analysis technique

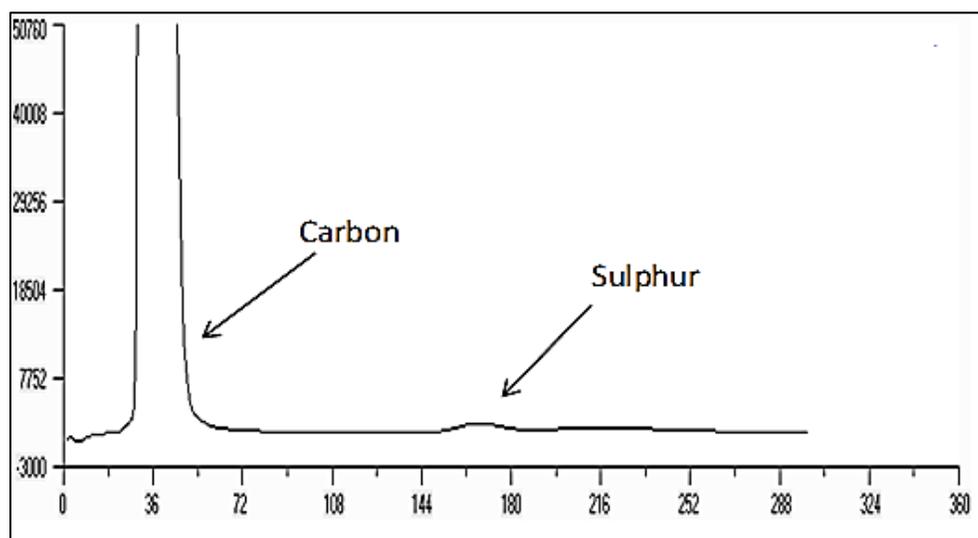


Figure 5.12 Sulfur detection in the treated light naphthenic crude oil by 2 vol.% DM-DSA using elemental analysis technique

To accurately determine the metal content in the oils, the NAA technique was performed. The analysis was carried out along with the raw oil, treated oil, and the aqueous phase produced after the rinsing step. A noticeable difference in the metal content between the raw oil and the treated oil was detected. In addition, the analysis of the aqueous phase showed the presence of metals in the aqueous phase after the washing step, which supports the validation of the invented process. It is worth mentioning that almost all the metals concentrations have been reduced compared to the virgin oils, specifically, V and Ni, which are difficult to eliminate. Pennsylvanian crude oil is a light oil with low metals concentrations. Thus, it was used to test the removal efficiency of the DM-DSA in the case of the lower levels of metals in crude oil. The NAA results are tabulated in Table 5.2 and Figure 5.13 confirm that the DM-DSA has a high removal efficiency in the case of Ti, I, Al, and Ca, which reaches more than 90 wt.%. The removal efficiency for both Br, Mg, V, and Cl was detected at higher than 70 wt.%. The treatment process included partial removal of sulfur alongside metals, which reached 27%.

The NAA results of the heavy aromatic naphthenic oil are tabulated in Table 5.3. Figure 5.14 displays the removal efficiency of the treated heavy aromatic naphthenic crude oil using 2 vol.% DM-DSA. All three of Ti, Mg, and Na have a higher removal efficiency, which reached more than 80%, followed by Cl and Ca with more than 65%. The concentration of S decreased as well with a removal efficiency of around 15%. Figure 5.15 and Table 5.4 demonstrate the results of the light aromatic naphthenic oil

The NAA analysis shows a high removal efficiency of both Iran and Basra oils in spite of the high complexity of the two oils. In the case of Iran oil, the removal efficiency presented in Figure 5.16 and Table 5.5. V, Ni, and S reached 33%, 73%, and 35%, respectively. For Basra oil, the removal efficiency was more prominent than in Iran oil, as all of V, Ni and S have been eliminated with 90%, 79%, and 63% efficiency, respectively, kindly refer to Table 5.6 and Figure 5.17.

It is essential to distinguish the variation that could take place for the metals and sulfur concentrations if the dosage of the DM-DSA rose to more than 2 vol.%. Therefore, another batch of experiments was carried out on the heavy aromatic naphthenic crude oil and light naphthenic crude oil applying 5vol.% DM-DSA, Figure 5.18, Table 5.7, Figure 5.19 and Table 5.8. It was found from the NAA analysis that there is an adequate discrepancy in the removal efficiency of some metals when raising the DM-DSA dosage, specifically Na and Mn. This reduction could be

due to the simple structure of the metals in the oil, which make them much smoother to attach to the DM-DSA than the other metals complexes. Concerning the S, it is reasonable to enhance the removal efficiency of S by increasing the DM-DSA dosage, because S compounds will encounter more ionic liquids with which to connect.

It is interesting to confirm that the decrease in metals concentrations after the treatment process was due to the reaction of the metals with the DM-DSA and not because of the washing step. A comparison between the treated oil with the invented technique and the same oil exposed only to the washing step was therefore carried out. Iran oil was used, and the results were analyzed by the NAA technique. Figure 5.20 illustrates the comparison in removal efficiency between the treated and washed Iran oil. It was noted that all the metals decreased due to the high removal efficiency reaching up to 100% for some metals, whereas employing just the washing step did not show any drop in the metals except those that can be extracted just by washing, such as Ca and Ba. This confirmed that the treatment process is only responsible for the decline that took place for all the metals concentrations.

Table 5.2 NAA results of Pennsylvania oil treated with 2 vol.% DM-DSA

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	7	0.3
I	0.6	0.03
Br	0.5	0.06
Mn	0.02	0.01
Al	12	0.50
Mg	15	1.6
Na	6	2.6
V	0.03	0.01
Cl	12	3.2
Ca	44	2.7
S	839	612

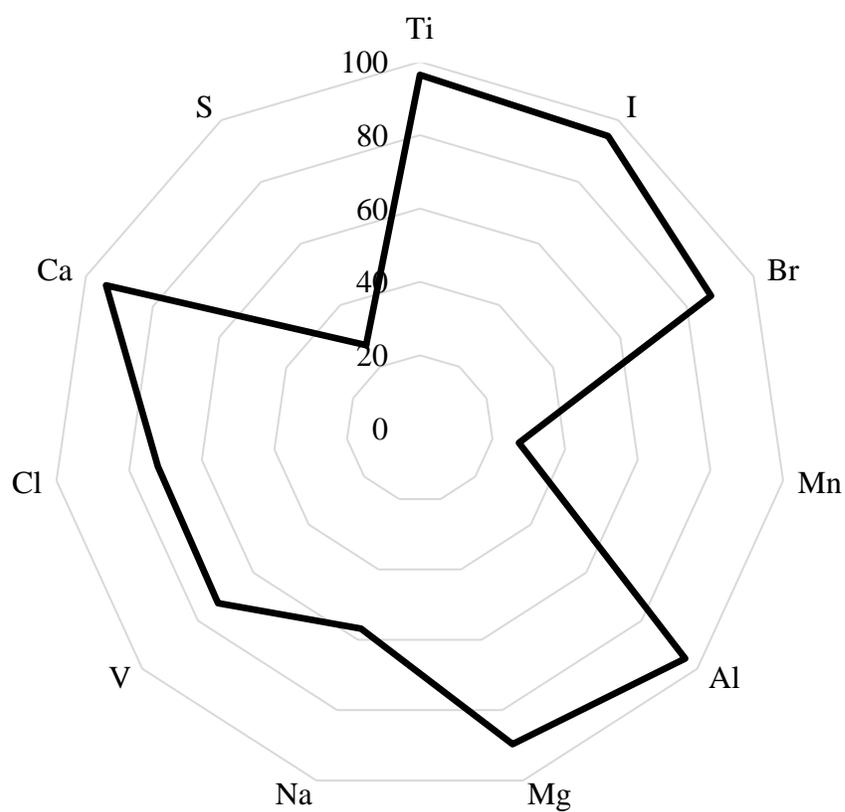


Figure 5.13 Removal efficiency of Pennsylvania oil treated with 2 vol.% DM-DSA

Table 5.3 NAA results of heavy aromatic naphthenic oil treated with 2 vol.% DM-DSA

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	20.4	2.05
Mn	0.23	0.15
Mg	41	3.37
Na	5.88	0.85
V	383.1	233.6
Cl	100.8	27.02
Ca	54.16	16.66
S	18385	15513.8

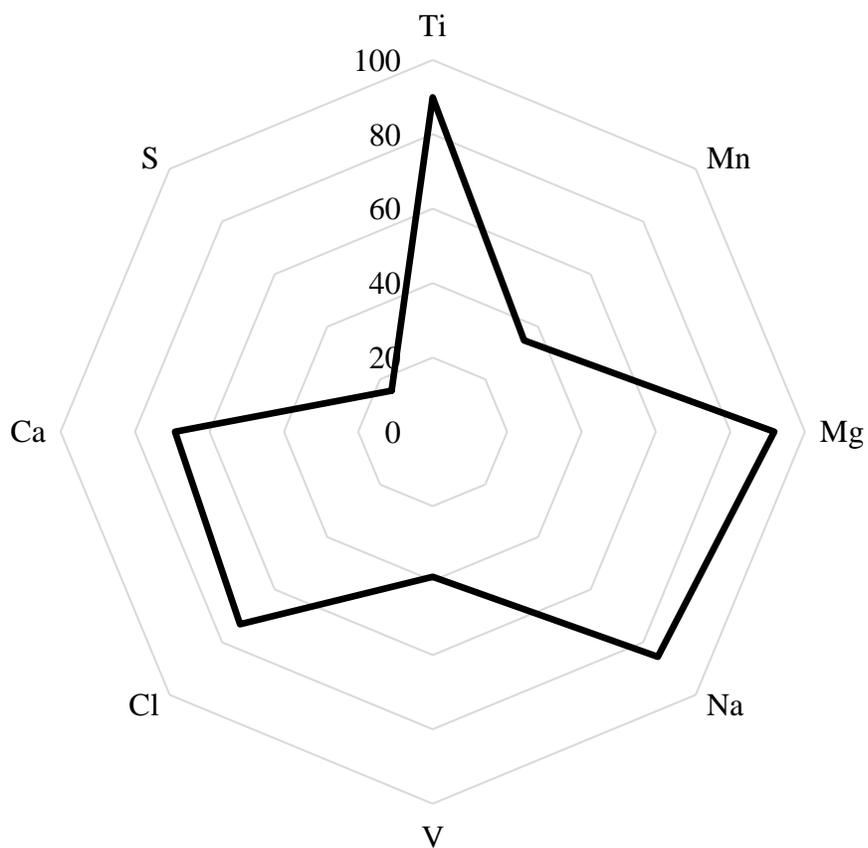


Figure 5.14 Removal efficiency of heavy aromatic naphthenic oil treated with 2 vol.% DM-DSA

Table 5.4 NAA results of light naphthenic oil treated with 2 vol.% DM-DSA

Element	Raw oil (ppm)	Treated oil (ppm)
Ti	34	3
Mn	0.2	0.1
Mg	74	10
Na	9	7
V	331	307
Cl	106	18
Ca	55	17
S	33557	23812

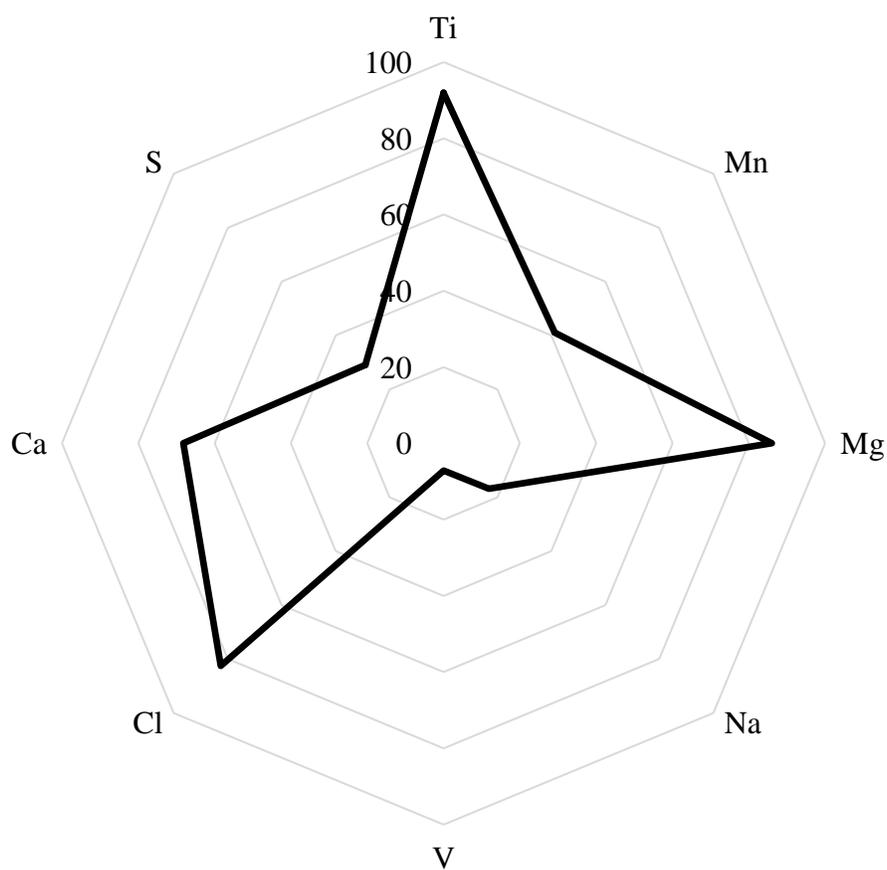


Figure 5.15 Removal Efficiency of light naphthenic oil treated with 2 vol.% DM-DSA

Table 5.5 NAA results of Iran oil treated with 2 vol.% DM-DSA

Metals	Raw oil (ppm)	Treated oil (ppm)
Ti	6	0.5
Mn	0.02	0.01
Mg	17	6
Na	13	0.1
V	88	59
Ni	30	8
Cl	22	17
Ca	5	0
S	22795	14816

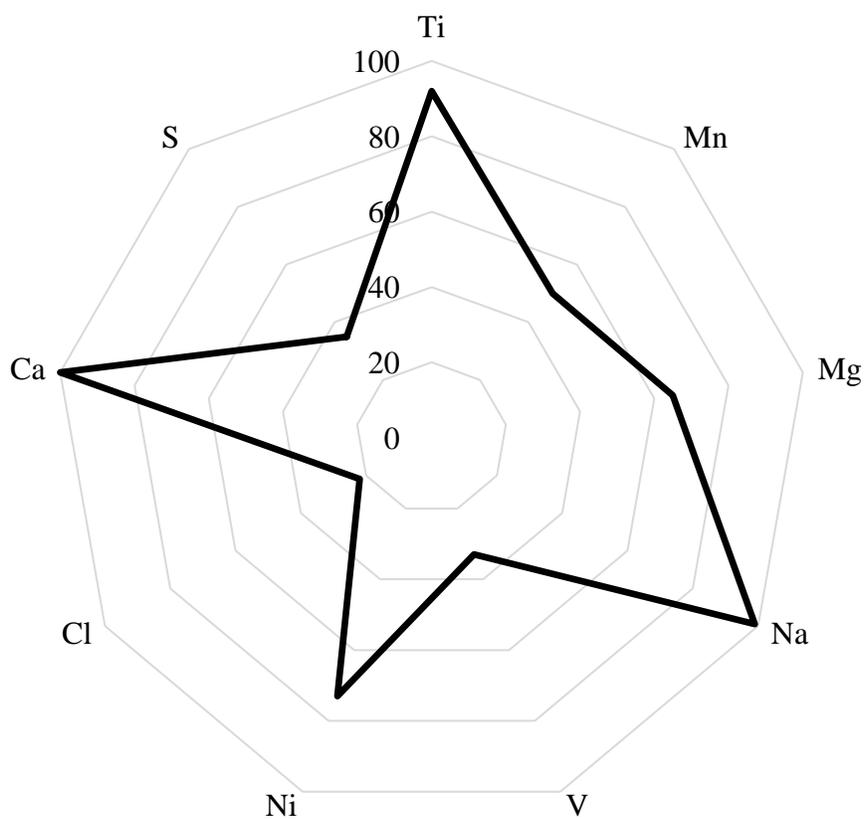


Figure 5.16 Removal Efficiency of Iran oil treated with 2 vol% DM-DSA

Table 5.6 NAA results of Basra oil treated with 2 vol.% DM-DSA

Metals	Raw oil (ppm)	Treated oil (ppm)
Ti	4	0.6
Mn	0.05	0.008
Mg	5	1
Na	14	5.5
V	37	3.6
Ni	10	2
Cl	25	10
Ca	8	2.6
S	26354	9751

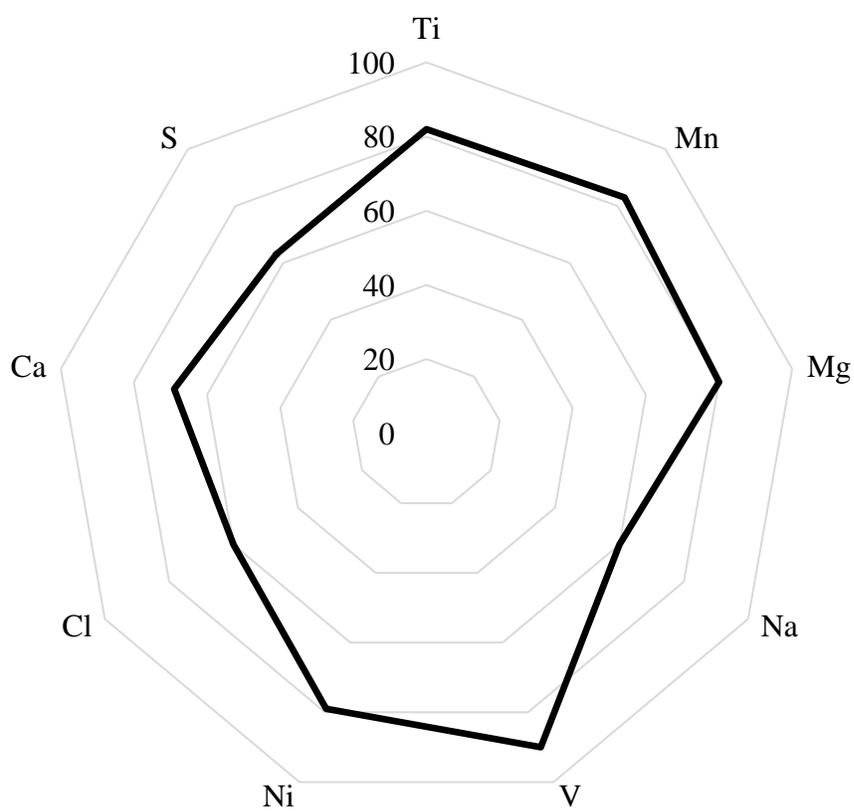


Figure 5.17 Removal efficiency of Basra oil treated with 2 vol.% DM-DSA

Table 5.7 comparison between heavy aromatic naphthenic crude oil and treated oils with 2 vol.% and 5 vol.% DM-DSA

Metal	Raw oil (ppm)	Treated oil 2 vol.-% (ppm)	Treated oil 5 vol.-% (ppm)
Ti	20.4	2.05	3.06
Mn	0.23	0.15	0.1
Mg	41	3.37	2.5
Na	5.88	0.85	2.24
V	383.1	233.6	222.6
Cl	100.8	27.02	26.76
Ca	54.16	16.66	14.72
S	18385	15514	10090

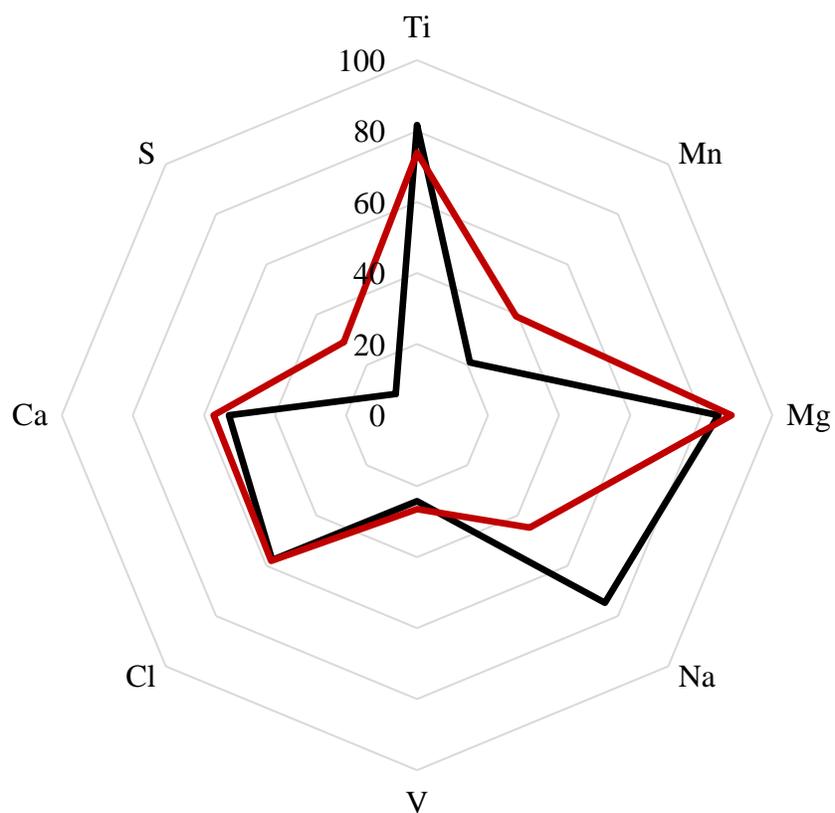


Figure 5.18 Removal Efficiency with 2 vol.% (black) and 5 vol.% (red) DM-DSA for heavy aromatic naphthenic oil

Table 5.8 NAA analysis of light naphthenic crude oil and treated oils with 2 vol.% and 5 vol.% of DM-DSA

Metal	Raw oil (ppm)	Treated oil 2 vol.% (ppm)	Treated oil 5 vol.% (ppm)
Ti	33.66	2.7	1
Mn	0.169	0.105	0.03
Mg	73.99	10.33	0.45
Na	9.4	7.82	2.85
V	331	307.26	300.15
Cl	100.8	18.46	44.68
Ca	54.955	17.48	8.88
S	33557	23812.9	23602.6

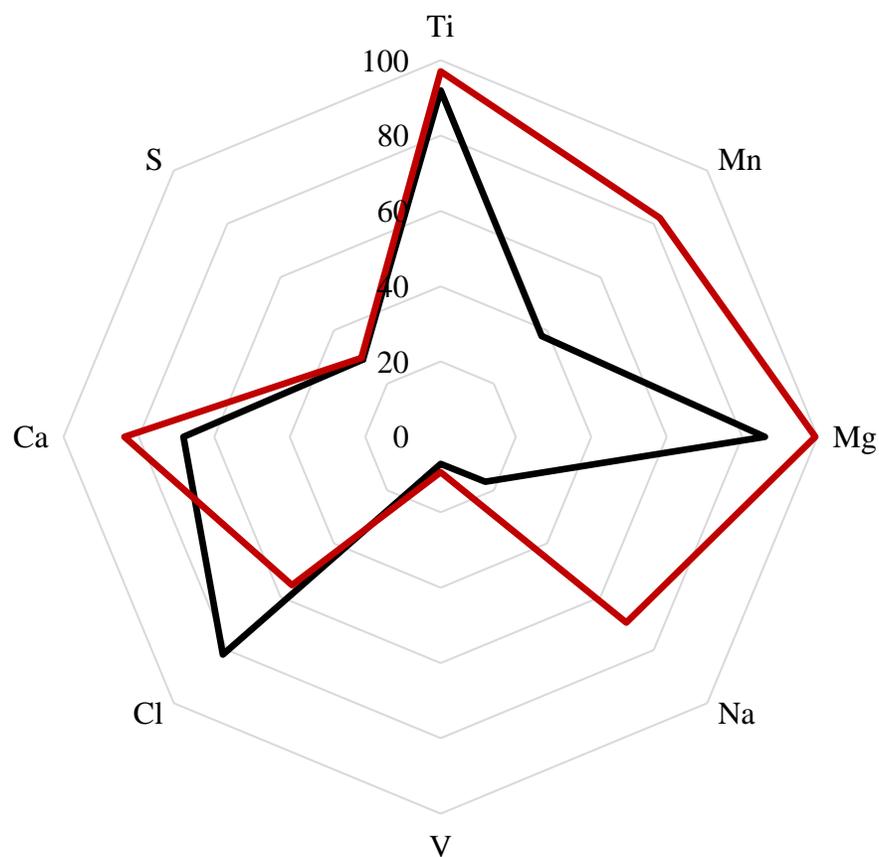


Figure 5.19 Removal Efficiency with 2 vol.% (black) and 5 vol.% (red) DM-DSA for light naphthenic oil

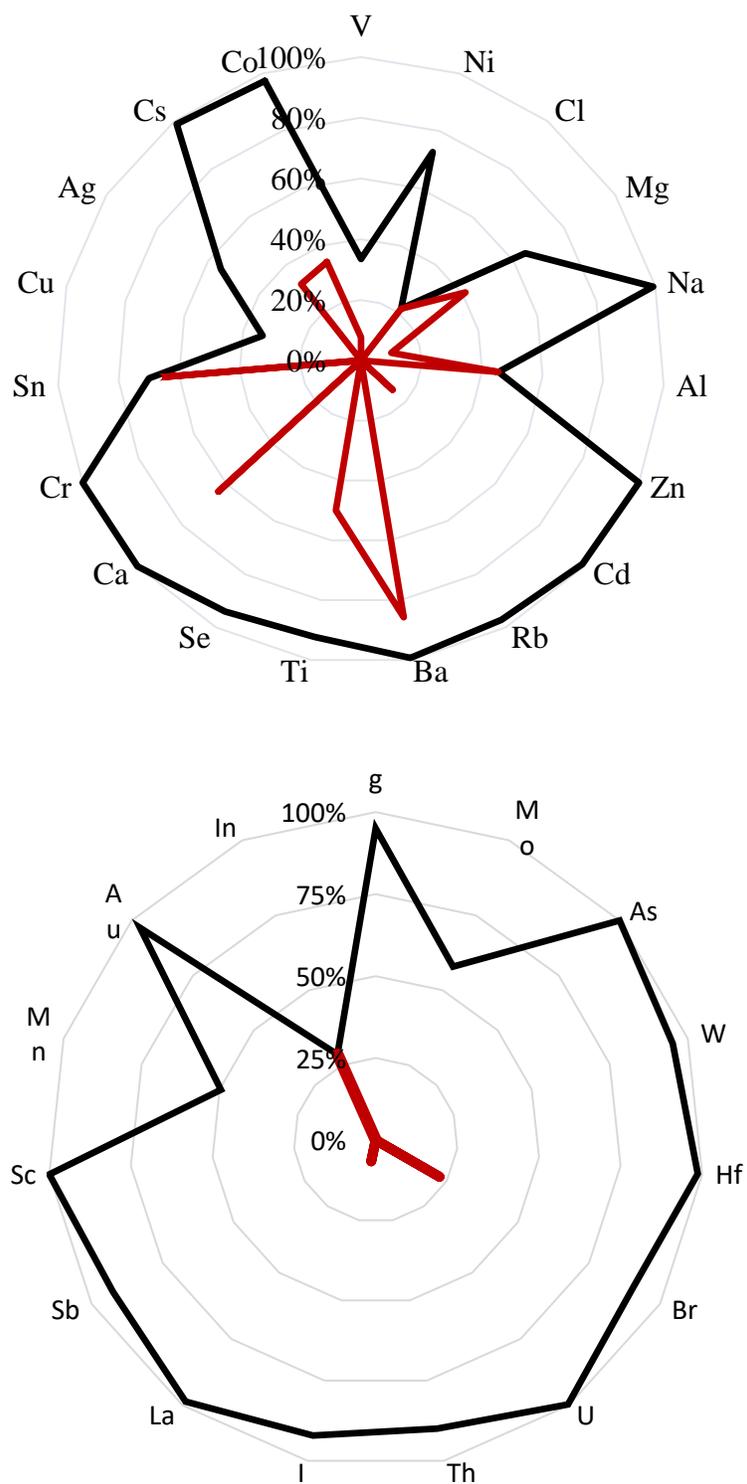


Figure 5.20 Removal efficiency of treated Iran oil with 2 vol.% DM-DSA (black color) against that only washed with aqueous solution (red color)

The employed DM-DSA in this study acts as a proton donor and, thus, provides the porphyrin ring with the needed hydrogen ions to occupy the vacancies created during the metal extraction reactions. The DM-DSA also helps to extract the metals from the porphyrin ring forming the metal salt of the agent. Behind the demetallization and desulfurization processes, there are a set of complex chemical reactions taking place. Significant effort has been made to better understand them and be able to present them based on a scientific interpretation.

The main idea behind the demetallization reaction is the ion exchange mechanism that happens very quickly in homogeneous solutions. In the reaction (cation exchanger), the agent acts as a proton donor for the metalloporphyrin ring after the four nitrogen atoms extract the electron bonds between the metals, due to the high electronegativity of the nitrogen atoms, which reaches up to 3.04 compared to 1.63 for the V atom. The high electronegativity of the four nitrogens plays an essential role in leaving the metal atom as a positive metal ion after the electron bond extraction. This, in turn, forms four negative nitrogen ions, which directly bond with the hydrogen protons from the agent forming the pure porphyrin ring. At the same time, the negative side of the agent robustly extracts the positive metal ion from the media creating the metal salt of the agent. The reaction of the demetallization process can be explained through the following mechanism, the arrows show the specific place of the reaction.

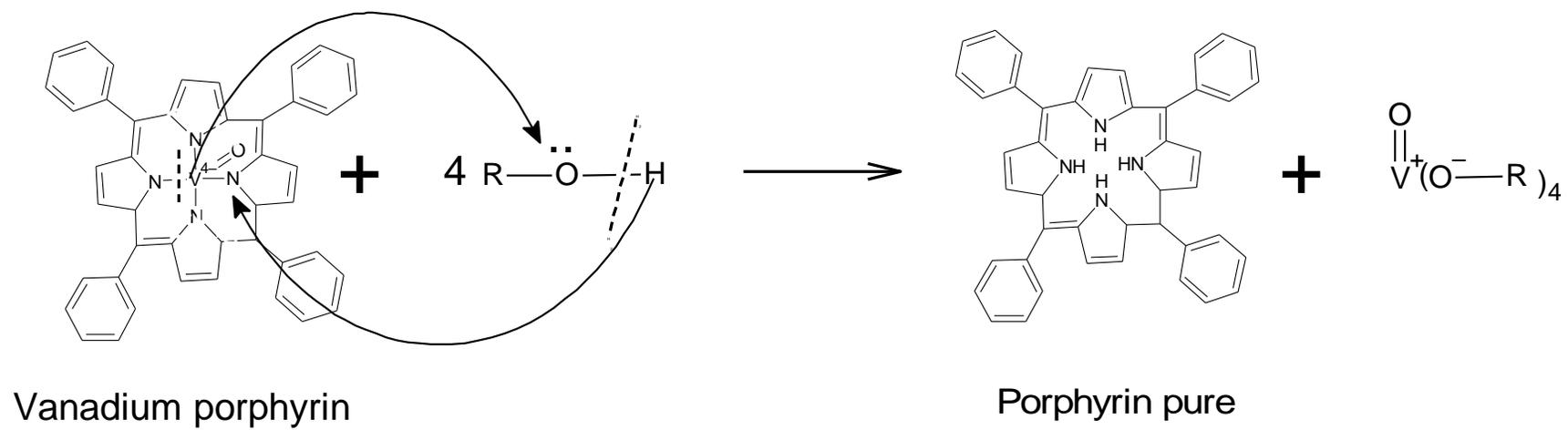


Figure 5.21 Mechanism of demetallization process

The DM-DSA used for the demetallization process is one of the most famous cations that can form ionic liquids with several anions. Both anion and cation species can interact forming an ionic liquid, or the cation can interact with a chloride anion from the oil medium forming another ionic liquid. The ionic liquid is formed by stirring both of the DM-DSA with the crude oil [115]. It was demonstrated that there are some factors strongly affected by the melting point and the physical state in general of the ionic liquid at room temperature, most importantly, the lengths of the alkyl chain and the central atom of the cation [116]. Platzer et al. have claimed that larger side chain cations tend to reduce the melting point of the ionic liquid [117]. This confirms that the ionic liquid formed during the process is a liquid.

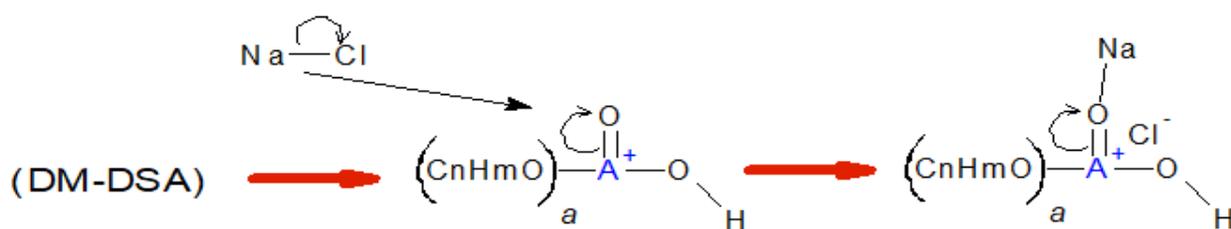


Figure 5.22 Ionic liquid formation

As soon as the ionic liquid formed, it bonded with the thiophen compounds [118] in the oil through two different bonds: (1) through the H-bond between the S and the H from the agent, and (2) the electrostatic force between the different charges of the high molecular weight part of both the agent and the thiophen compounds. The desulfurization process can be explained by the following mechanism.

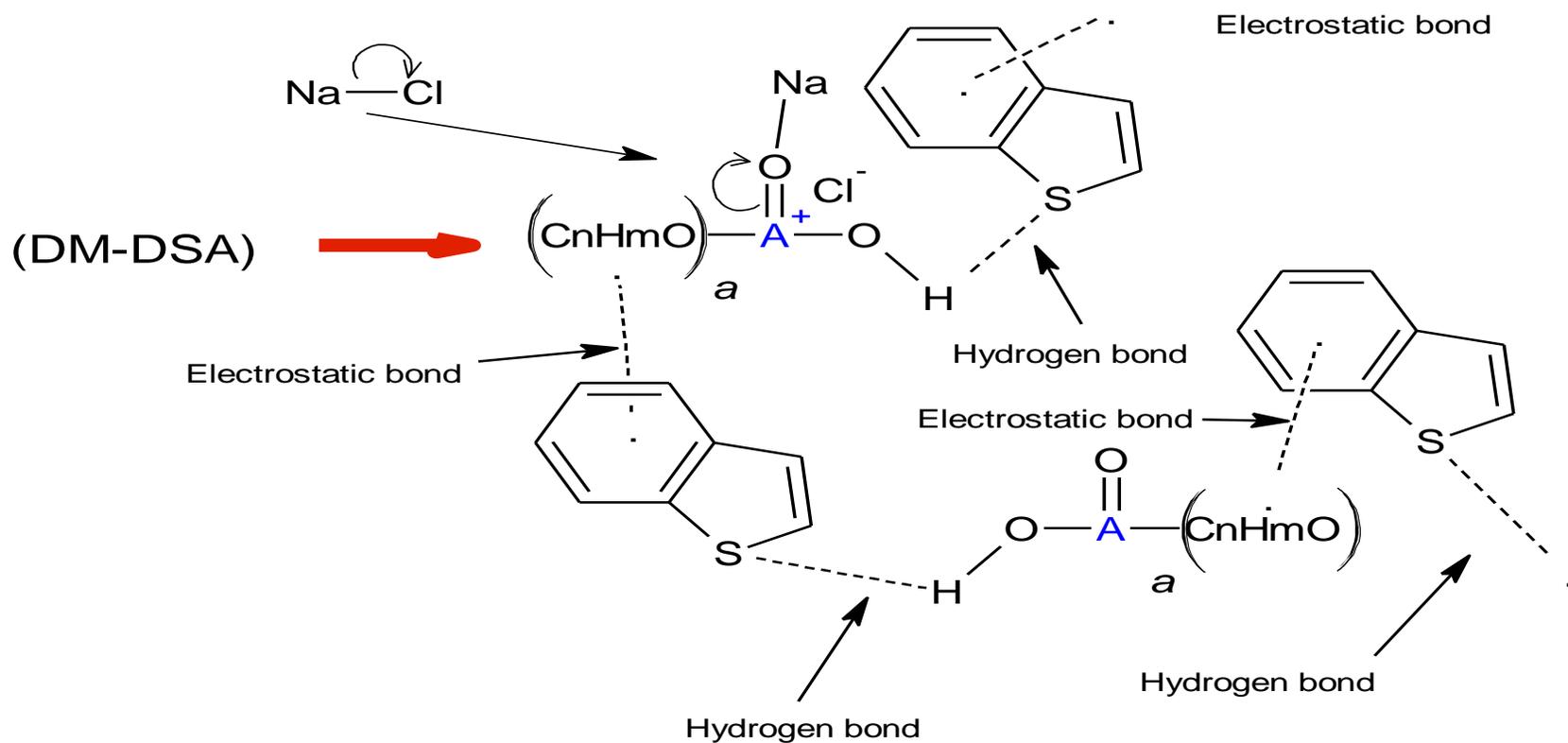


Figure 5.23 Desulfurization mechanism by ionic liquid

5.5 Conclusion

A novel demetallization agent successfully achieved the demetallization and desulphurization process of crude and petroleum oil. The invented technique is adequate in eliminating virtually all the metals and specifically V and Ni, without destroying the porphyrin ring. The agent selectively extracts the metals from the core of the porphyrin ring, forming the metal salts of the agent. The process also delivers a high capability for reducing the sulfur concentration, which exists in the form of thiophene compounds that are difficult to remove. This is a consequence of the ionic liquid formation by the DM-DSA in the crude oil, which induces a high tendency to withdraw the thiophene compounds through attaching to it by a hydrogen bond and electrostatic force. The conventional heating mechanism was used during the demetallization-desulfurization process for better controlling the reaction temperature, and thus far, a good removal efficiency for both V and Ni, which reached to 90% and 79%, respectively, and for S, which reached up to 53%, has been obtained in the case of Basra oil. Both Iran and Basra oils showed the highest removal efficiency for almost all the metals and sulfur, especially for V and Ni. It was found that by increasing the amount of DM-DSA, there was no efficient decrease observed in the metal contents, except for Ca and Ba, and S in the heavy aromatic crude oil.

CHAPTER 6 ARTICLE 3: METALS AND SULFUR REMOVAL FROM PETROLEUM OIL USING ELECTROMAGNETIC IRRADIATION

Mai Attia, Sherif Farag, Shaffiq Jaffer, and Jamal Chaouki

This article is based on the US Provisional Patent Applications:

- 1- **62758227** - **Mai Attia**, Sherif Farag, Jamal Chaouki (2018). Microwave process for the removal of metals from petroleum oil using a developed demetallization and related techniques.
- 2- **62758251** - **Mai Attia**, Sherif Farag, Jamal Chaouki (2018). Microwave process for the removal of sulfur from petroleum oil using a developed desulfurization agent and related techniques.

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Abstract

This work investigates the extraction of metals and sulfur from petroleum oil using a novel demetallization desulfurization agent. A microwave irradiation environment was created during the reaction to provide the required energy essential for separating such contaminations from the oil chemical network. Strategic reaction conditions were applied, and the obtained results were compared against those of a conventional heat process. The comparison showed a significant difference between the removal efficiencies of selected elements. More than 95% of the vanadium concentration in the raw oil was removed using the energy conversion mechanism of the microwave compared to 33% for the superficial heat transfer mechanism. The removal of sulfur showed a considerable deviation in the removal efficiency using the microwave, 99% compared to 60% for the traditional heat. The invented process is green and not costly and can thus compete well with the existing demetallization and desulfurization processes.

Keywords: Demetallization; Desulfurization; Metalloporphyrin; Oil Upgrading; Microwaves

6.1 Introduction

Petroleum crude oil is experiencing a considerable challenge due to the presence of metals and sulfur pollutants. Metals, especially vanadium (V) and nickel (Ni), are present in the oil in stable sets of organometallic compounds, called metalloporphyrines. Refer to Figure 6.1. The porphyrins exist in different patterns and are quite soluble in oil, which, in turn, augments the difficulty in eliminating them from crude oil. The presence of these impurities causes several health issues if the oil is used as fuel. One of the most harmful metals is V, which spreads to the surrounding area in the form of vanadium oxide and reacts with the mucus of the body causing various types of bodily irritations. Ni in the form of nickel carbonyl reacts in the body as well, causing numerous types of neoplastic diseases. Similarly, sulfur (S) has a catastrophic ecological impact, as SO_x is emitted into the ecosystem, causing acid rain formation. Acid rain is mainly owing to the reaction of SO_x with water forming sulfuric acid, which is carried away by air. The acid subsequently falls to earth in the form of rain, dust, snow, sleet, or hail. Minerals and sulfur compounds not only have a negative impact on the environment but they also affect the contact surfaces during the refinery processes, generating serious corrosion problems for the instruments and pipelines. Furthermore, they reduce the lifetime of the catalyst during the hydrodemetallization and hydrodesulfurization processes. Both metals and sulfur block the pores of the catalyst by the deposition of metal oxide, which leads to reducing the activity of the catalyst in an incredibly short time. This issue raises the cost of refining because using a fresh catalyst to obtain new active sites with high performance is a must.

Serious attempts have been carried out to upgrade petroleum crudes by extracting both metals and sulfur from the oil. Various approaches have been published in the literature, such as solvent extraction, distillation, visbreaking and coking, applying a demetallization agent, and hydrodemetallization/hydrodesulfurization. Indeed, each technique faces several issues that can impede its objective in the industrial sector. For example, the solvent extraction process demands an enormous amount of solvent and, on top of that, it discards the whole metalloporphyrin ring, which reduces the treated oil yield at the end of the process. Distillation produces oil with a lower concentration of impurities and another with a higher concentration. Most of the demetallization agents that have been applied are acids and not capable of removing the metals selectively. They remove the whole fraction containing the metals instead of only the metals.

Almost all the demetallization agents require an emulsification process to be blended well with the oil, which raises the cost of the operation. Hydrodemetallization and hydrodesulfurization techniques have been practiced in the industry. However, such processes are costly as extreme temperature and pressure conditions are required. In addition, an excessive volume of hydrogen is required for the reaction. The existence of the catalyst in this technique is a must, although it rapidly deactivates in a minimal period.

Applying microwave heating in the metals and sulfur removal from crude oil was discovered recently. It was noted that addressing the microwave heating techniques provided several advances, such as reaction acceleration, higher yield, and various selectivities. Microwave can also enforce some synthetic reactions that can not be achieved by superficial heating techniques [119-122]. It was announced further on in the research that employing microwave heating during the process demonstrates considerable superiority over the superficial heating technique, as it enhances the metals removal from the crude oil at a relatively significantly low bulk temperature compared to the superficial heating mechanism. Additionally, microwave heating reduces energy consumption due to the high heating selectivity [123-125], avoids heat transfer limitations, improves process flexibility and equipment portability, and is environmentally friendly, especially when clean electricity is used.

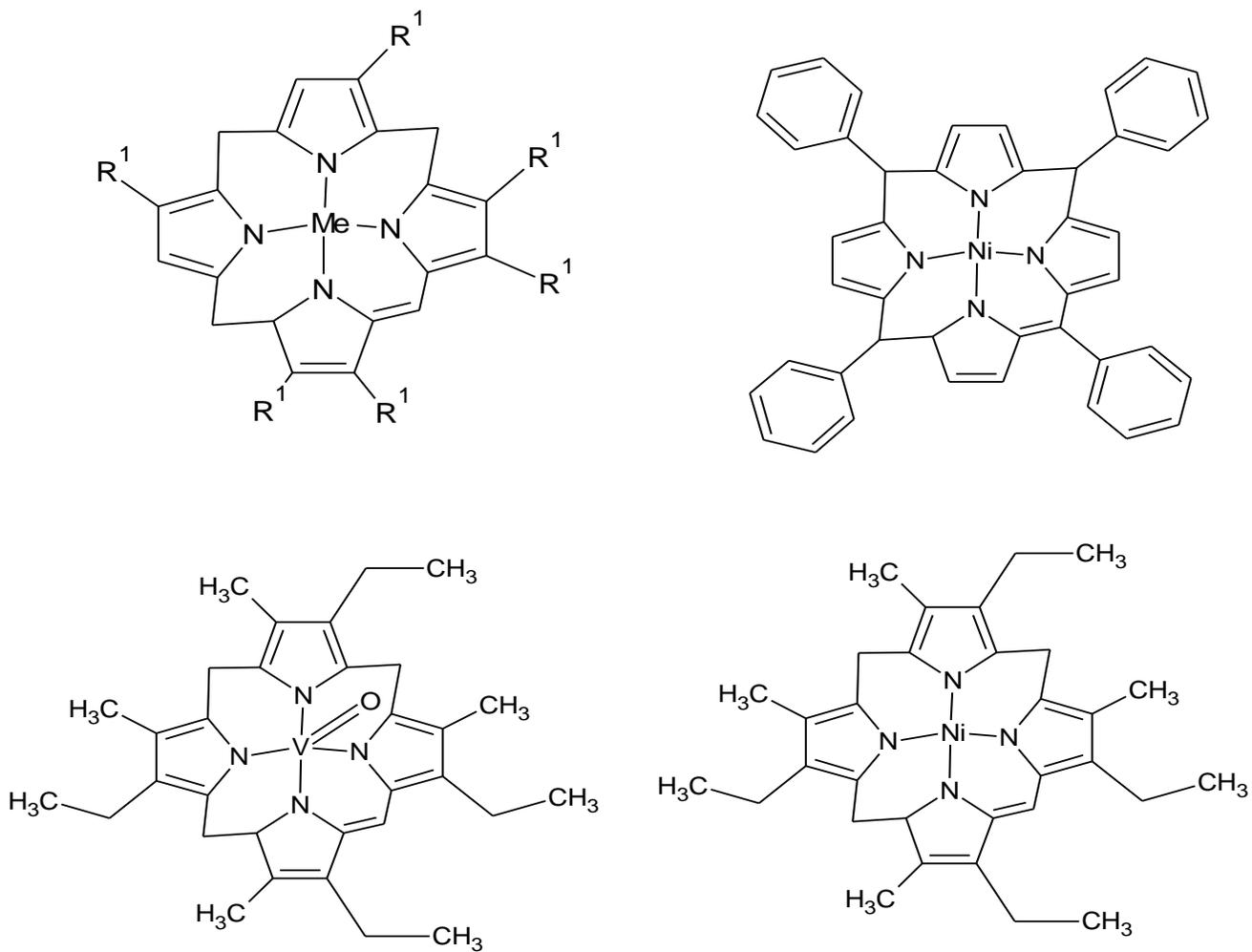


Figure 6.1. Different forms of a metalloporphyrin ring

6.2 Microwave heating mechanism

Electromagnetic waves are composed of both alternating electric and magnetic fields that are orthogonal to each other. The propagation of these fields is in the path that is perpendicular to the oscillation planes. Electromagnetic radiation behaves like waves, which flow at the velocity of light, and photons, which carry the radiated energy [51, 54]. For non-magnetic objects, when an external alternating electric field is employed, the molecules of the exposed material are aligned with the alternating field. In other words, they reorient themselves to try to be in phase with the externally applied alternating field. A phase shift is generated between the orientation of the dipoles and the externally applied electric field because the agitated molecules do not possess the ability to reorient themselves as swiftly as the reversing field. Random collisions between the oriented molecules and each other are generated and, as a result, heat energy is released from the irradiated material. Therefore, the mechanism of microwave heating is fundamentally characterized as “a volumetric energy transformation” due to the conversion of electromagnetic energy to heat energy within the exposed volume of the heated material [55, 58].

Based on the interaction between the exposed material and the applied electromagnetic waves, the heated materials can be classified into three major groups: (1) absorbing materials, such as carbon and silicon carbide; which absorb the applied microwaves and convert them into heat energy, (2) transparent materials, such as ceramics and quartz; which allow microwaves to pass through them without a noticeable interaction, and (3) impermeable materials, such as metals, which reflect microwaves on their outer services.

To successfully introduce microwave heating in a process, at least one of the target materials must be an excellent microwave receptor, i.e., it should be included in the first category, or under controlled conditions, in the third category. Fortunately, most of the materials involved in this study fall within these two groups, which should facilitate the use of technology in the demetallization and desulfurizing applications [54]. For non-magnetic materials, the central parameter that characterizes microwave propagation and the level of energy conversion inside the irradiated target is “complex permittivity” (ϵ). It measures the ability of the material to absorb and store electric potential energy and it is presented as:

$$\epsilon = \epsilon' - j \epsilon''$$

The real part of Equation – ϵ' – is called “dielectric constant” or “permittivity.” It measures the ability of the target material to pass the electric field, through it. The imaginary part of the complex permittivity – ϵ'' – is called “dielectric loss factor.” It measures the amount of electric energy that can be stored within the exposed material.

Various attempts have been made to introduce the microwave heating mechanism in the extraction of metals from crude oil. Khan and Al-Shafei have patented a hydrodesulfurization process that includes microwave irradiation of a mixture of heavy crude oil with a catalyst and in the presence of hydrogen [80]. The process took place through the transformation of sulfur compounds into hydrogen sulfides. The technique was operated under mild conditions as the hydrogen was maintained in the microwave and the reaction was kept at pressure ranges from 1 atmosphere to 400psig. The temperature of the reaction ranged from 80° C to 400° C and the most desirable was 200°C to 250°C. Crude oil was mixed with an iron powder catalyst, then the mixture was exposed to microwave heating in the presence of hydrogen. Microwave heating was applied to raise the temperature of the crude oil to 200°C. The key finding of the process was the reduction of sulfur concentration by 25% by maintaining the temperature of the oil at 200° C for 20 min. A further increase in the microwave energy application for 30 minutes while maintaining the temperature at 200°C led to a 27% reduction in sulfur concentration. The irradiation of crude oil when mixed with a palladium oxide catalyst and sensitizer resulted in a 16-39.4% reduction in sulfur concentration.

Chamorro et al. have used the microwave heating technique to reduce the concentration of both metals and sulfur in a carbonaceous material [81]. The material was blended with an acidic compound or a mixture of acids, such as HNO₃, H₂ SO₄, HCL, HCLO₄, H₃ PO₄, and HF, then the mixture was exposed to microwave irradiation. The process took place at a time between 10 sec. and 1 hour, and at a pressure not exceeding 200 psig, to avoid the evaporation of the reaction components. The removal ration for both Ni and V reached 80% and 99%, respectively, in 15 min.

Cationic starches have been tested as a demetallization agent for the removal of both Ni and V from crude oil under the effect of the microwave heating technique. It was demonstrated that increasing the degree of cationic substitution of cationic starches leads to enhancing the removal efficiency of heavy metals. The optimum reaction conditions for the removal of both Ni and V are

200 mg/L of cationic starch 4 (CS4) with a microwave power of 300 W for a residence time of 5 min. The removal efficiency of Ni when applying the above conditions for Iran and Shengli crude oil was 55% and 60%, respectively, and in the case of V, it was 76% and 79%, respectively.

In this study, the removal of approximately all the metals, particularly Ni and V, in addition to sulfur took place using a novel demetallization-desulfurization agent (DM-DSA) under the effect of the microwave heating mechanism. The technique is green since no consumption of solvents is required. The process is cost-effective because no alternative emulsification processes are needed, such as the emulsification process for mixing the agent with the crude oil, since the agent has an amphiphilic nature.

6.3 Experimental work

6.3.1 Processed materials

Two different petroleum oils received from the company TOTAL in France were processed in this work. The first oil is “Iran oil” with total V and Ni concentration of up to 110 ppm, and S concentration of 22,000 ppm. The second oil is the Basra oil with 40 ppm of V+Ni and 27,000 ppm of S concentration. DM-DSA and the alternative chemicals were purchased from Sigma-Aldrich.

The quantification of metals and sulfur in crude and treated oils is a challenge due to the excessive complexity of the oil and the low concentration of contamination [126]. The most common analytical techniques to precisely identify and measure low concentration elements include Inductive Coupled Plasma Mass Spectrometry (ICP-MS), Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Neutron Activation Analysis (NAA) [127-129]. In this work, NAA was performed to avoid the issues and limitations associated with the digestion and dilution of such complex materials. NAA analyses were carried out in the SLOWPOKE lab of Polytechnique Montréal, in Quebec, Canada, using the k0 NAA method [130]. The Fourier-transform infrared spectroscopy (FTIR) was also applied to detect the transformation of the nitrogen-metal (N-M) bond to the nitrogen-hydrogen (N-H) bond after the treatment process. The analysis was implemented using a Perkin Elmer 65 FTIR-ATR instrument (PerkinElmer, Woodbridge, ON, Canada).

6.3.2 Sample preparation for the NAA analysis

The analyzed samples in NAA were prepared by injecting about 1g of oil into a 10 mm diameter HDPE capsule. Consequently, the capsule is inserted into an 18 mm long polyethylene vial. The capsule and the vial were then properly heat sealed to avoid discharging into the nuclear reactor in case of leakage. Thereafter, the sample was inserted into the Slowpoke reactor for an irradiation period between 20 to 30 min, which was selected based on the matrix of crude oil. After the irradiation period, the radiation of the irradiated sample is counted on an HPGe detector with a 50% relative performance. All samples were counted at various distances of 1.6 mm (P1), 33 mm (P2) and 100 mm (P3) with regards to the detector [131]. École Polytechnique Montreal Activation Analysis (EPAA) software was, eventually, employed for processing the data and quantification of various minerals.

6.3.3 Dielectric properties of the processed materials

To better understand the interaction between the processed materials – i.e., oil, aqueous, and DM-DSA – the dielectric properties were measured and tabulated in Table 6.1. The measurements were done in the electrical department at École Polytechnique de Montreal.

Table 6.1 Dielectric properties of the processed materials

Material	Dialectic constant	Dielectric loss factor
Crude oil	1.6	0.013
Aqueous	79.7	7.5
DM-DSA	76	11

6.3.4 Experimental setup

The experimental setup that was built to carry out the experimental work is demonstrated Figure 6.2. It comprises a microwave generator, a microwave cavity, a batch reactor made of a material transparent to microwaves, an oil tank, an aqueous phase tank, a thermometer, a reflux to avoid the evaporation of the heated materials, a stirrer, and a water cooler. The batch reactor, which includes the heated materials, such as oil, DM-DSA, and/or the aqueous phase, was settled inside the irradiation cavity. The stirrer was utilized inside the reactor to better mix the reactants together.

The reactor connected with a reflux system composed of a set of condensers fitted onto the top of the reactor and linked with a water-cooler kept at $-5\text{ }^{\circ}\text{C}$. Using the reflux is essential for condensing the low molecular weight compounds that might evaporate from the heated materials.

6.3.5 Experimental procedure

The invented demetallization-desulfurization process implemented in this work comprises three primary stages. The initial stage is the reaction between the DM-DSA and the oil in the presence or absence of an aqueous phase. The primary task of the employed aqueous phase is to trap the metal salt of DM-DSA as soon as it forms during the extraction process. The reaction was performed under different microwave powers and irradiation times to investigate the effect of these parameters on the elimination performance. The second and third stages involved washing the treated oil and then separating the extracted metals from the washing mixture.

Different volumes of oil were mixed with a calculated percentage of DM-DSA in the reactor. There was no emulsification needed in this step because the oil and the agent were perfectly miscible. The employed agent is amphiphilic liquid and, thus, can easily be mixed with oil. The aqueous phase is then added to the mixture in the reactor. A stirrer is always essential for mixing the heated materials as well as reaching the uniform distribution of temperature. Different stirring speeds, microwave power, and various residence times were applied.

Once the desired temperature was reached and the irradiation time had passed, the mixture of oil, DM-DSA, and/or the aqueous phase was further processed to separate the aqueous phase that encompasses the soluble metal salts from the oil phase. This step was achieved using a setup similar to a separating funnel, which allows the mixture to settle for few minutes to attain almost a complete separation of the oil phase from the aqueous phase.

After the reaction step, both metals and sulfur were present in the oil in two different forms, the metal salt of DM-DSA and the ionic liquid attached to the sulfur compounds. Since both were still present in the oil phase, a specific number of washings were required to attain the most effective extraction efficiency. The washing step was performed using a mixture of 50% aqueous phase incorporated with few drops of organic solvent to dissolve and eliminate the metal salt of the agent and the unreacted part (if any) from the DM-DSA. The mixture was added to the oil phase and

vigorously shaken for a few minutes before being heated for a short time at less than 100 °C under reflux. The same separation setup mentioned above was used to separate the aqueous phase from the oil phase after each washing step. Finally, the collected treated oil was sent for the analysis purposes.

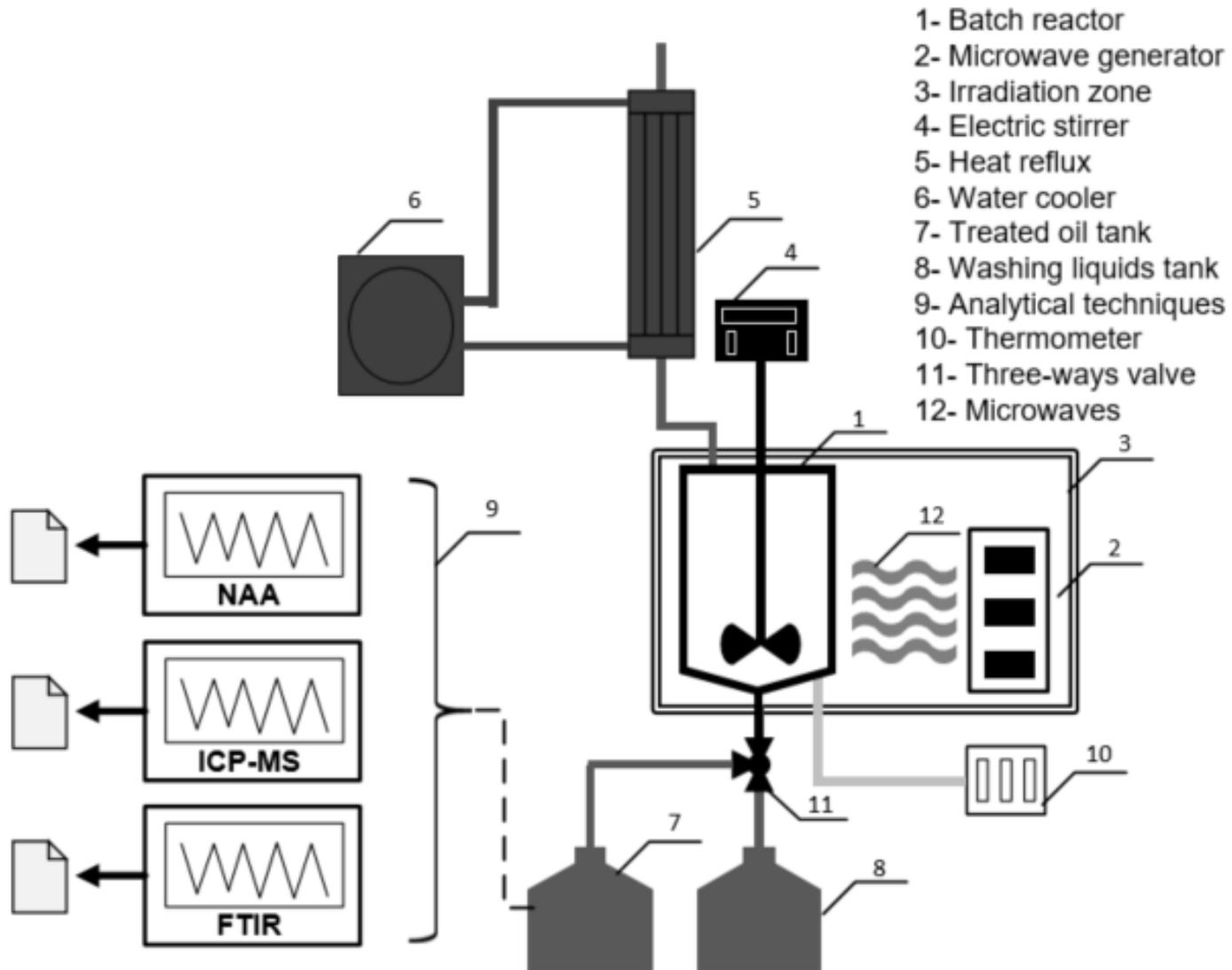


Figure 6.2 Microwave setup for metals and sulfur removal from oil

6.4 Results and discussion

The DM-DSA applied in this work exhibits the same behaviors as carboxylic acids in terms of the reception of microwave energy. When a mixture of oil and DM-DSA is exposed to the microwaves, the interaction of the mixture with the microwaves is improved compared to the oil alone. According to the microwave heating mechanism, polar compounds can effectively absorb microwave energy. On the other hand, nonpolar materials are not adequately able to convert the energy of the electromagnetic waves into heat. Thus, the interaction of crude oil with microwaves is almost negligible compared to that of the aqueous phase and the employed DM-DSA. This aspect affirms that the inclusion of the DM-DSA with oil enhances the interaction with microwave heating by creating hot spots in some specific sites [132, 133].

Petroleum oil contains a vast number of metals, the most abundant being V and Ni, which exist in relatively higher concentrations in the oil. V and Ni have significant interactions with microwaves, kindly refer to Table 6.2. The novelty of employing electromagnetic waves in such reactions is to focus the interaction with microwaves where the metals exist and, as a result, enhance the heat generation at the N-M bonds. This approach facilitates the dissociation or, in other words, break down of the metal bond, which reinforces the liberation of the metal from the core of the metalloporphyrin ring. The employed DM- DSA can then easily extract the metals from the surrounding porphyrin ring and provide the ring with the required protons that are essential for complete stability.

To sum up, DM-DSA plays several roles by interacting with microwaves, enhancing the heat generation in the reaction site, extracting the metal ions from the core of the porphyrin ring, providing the nitrogen ions by essential protons after the N-M bond dissociation, and extracting sulfur compounds from crude oil.

Table 6.2 Penetration depth and heating rates of various metals exposed to microwaves (adapted from reference [134])

Element	Penetration depth (μm)	Heating rate ($^{\circ}\text{C}/\text{min}$)
V	11.2	240
Ni	7.8	120
Co	4.8	110
Zn	4	115
Mo	3.1	110
W	2.1	110
Fe	2.1	155
Hg	0.2	500

Analyzing the crude and treated oil with FTIR technique shows a significant variation in the absorption frequencies between the processed and unprocessed oils. It is assumed that the metalloporphyrin ring is transferred into the free base porphyrin. Accordingly, new frequencies for the N-H bonds should appear instead of the N-M bonds. Figure 6.3 shows the deviation in the IR absorption frequencies between the treated and untreated Iran oil, and Figure 6.4 shows the same comparison for the Basra oil.

There is a weak band at 3430 cm^{-1} , which is attributed to the N-H bond stretching frequency [135-138]. There is also a peak located around 1600 cm^{-1} that is assigned to another vibrational mode of N-H [113]. The peaks appeared at around 1110 cm^{-1} and 740 cm^{-1} in the treated oil relative to in-plane N-H and out-of-plane bending N-H, respectively [114].

The bands around 2922 cm^{-1} referred to the C-H bond of the benzene ring and pyrrole ring. Bands at $\sim 1458\text{ cm}^{-1}$ and $\sim 1379\text{ cm}^{-1}$ are attributed to the C=C stretching mode and the C=N stretching vibration, respectively. The bands at around 800 cm^{-1} and 750 cm^{-1} were respectively appointed to the C-H bond bending vibration of para-substituted and ortho-substituted phenyl rings.

It should be noted from the FTIR graphs that the magnitude of the peaks related to the N-H bond increased compared to the oil treated with conventional heating. Due to the significant effect of the microwaves on the reaction mechanism, it was demonstrated that applying the microwaves enhances the removal efficiency. Accordingly, the elimination percentage of both metals and sulfur should be efficiently developed, which will positively influence the intensity of the peak.

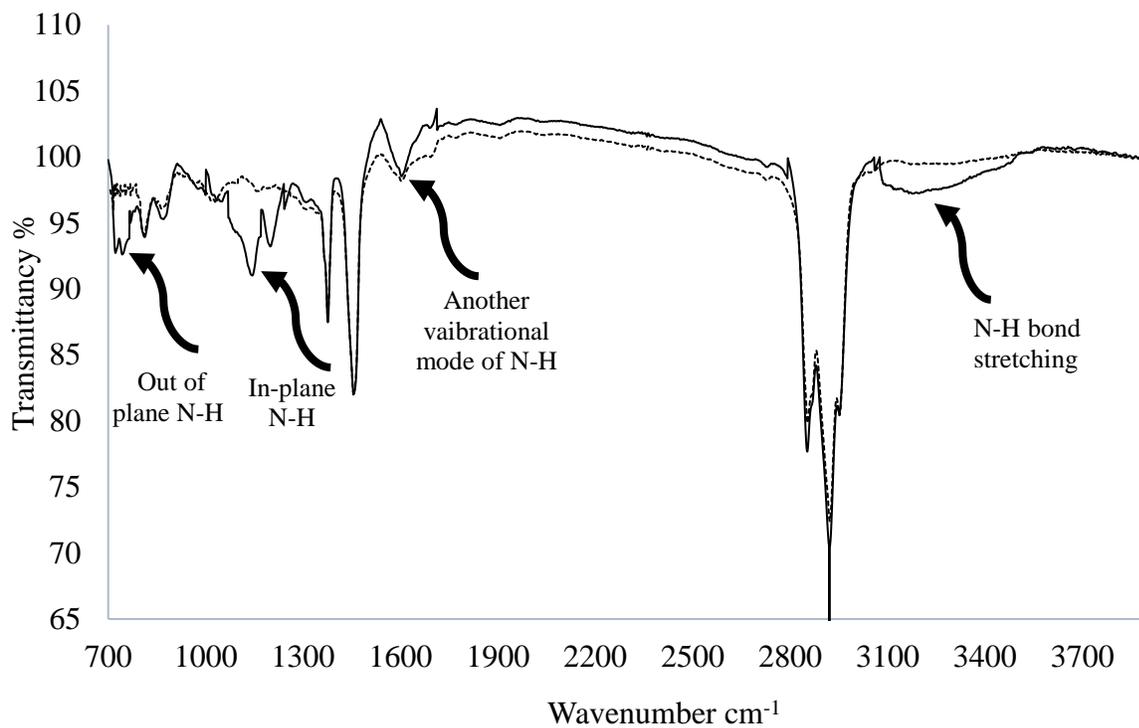


Figure 6.3 FTIR of raw (dotted line) and microwave treated Iran oil (continuous line)

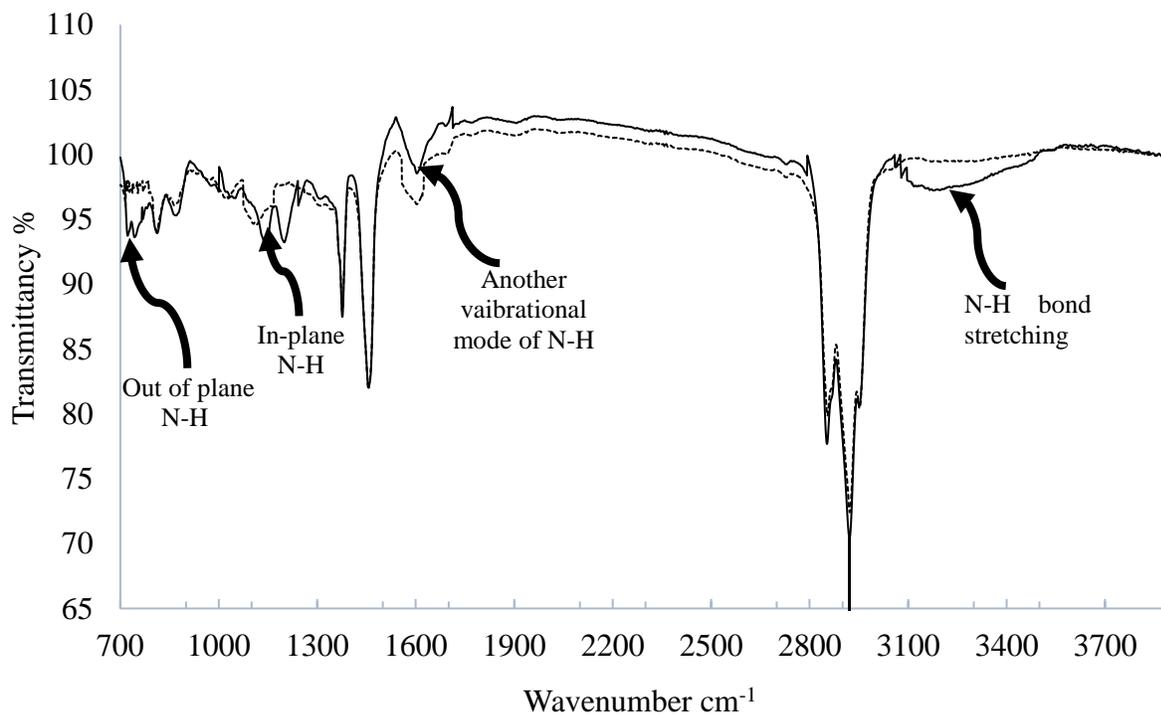


Figure 6.4 FTIR of raw (dotted line) and microwave treated Basra oil (continuous line)

The NAA technique was performed to quantify the metals and sulfur concentrations present in the raw and treated oils. The results of the microwave heating were contrasted against those of conventional heating. Figure 6.5 illustrates the removal efficiency comparison of both heating mechanisms in the case of Iran oil. The figure reveals a significant variation in approximately all the metals compared to that of conventional heating.

It is evident from Figure 6.5 and Figure 6.6 that the concentration of Ti considerably dropped using conventional heating only and the removal efficiency reached 92%. The concentration of V and Ni presented in Figure 6.5, Figure 6.8, and Figure 6.9 decreased with small amounts and the removal performance reached around 35% in the case of conventional heating. Although Ti, Ni, and V remain in the oil in the same chemical forms, the elimination efficiency using traditional heat is quite apparent in the results of Ti. The principal reason behind this attitude is linked to the deviation in the electronegativity difference between the N atoms and each metal in the metalloporphyrin ring. The electronegativity difference between N and Ti is more significant than that of V and Ni. Thus the N-Ti bond has more ionic character than that of V and Ni. Accordingly, N can withdraw the bond electrons easily, forming a negatively charged N and positively-charged Ti, which dramatically boost the liberation of Ti from the porphyrin ring and enhance the removal efficiency of Ni and V.

When using microwave heating, removal efficiency increased because microwaves generated hotspots near or entirely within the area where the reaction took place thanks to the interaction of the matter with microwaves. For this reason, the removal capability of both V and Ni is higher than that of Ti when using microwave heating compared to the reference case.

Figure 6.5 also demonstrates that both Mg and Cl have high removal efficiencies, 100%, and 80%, respectively, when applying microwave heating compared to 65% and 23% when using conventional heating due to the elements remaining in the oil as inorganic salts, mainly in the form of chloride or sulfate of Mg and other metals ions, such as Ca [24]. These salts are highly soluble in water because they are characterized by high polarity and, in turn, significant interaction with microwaves.

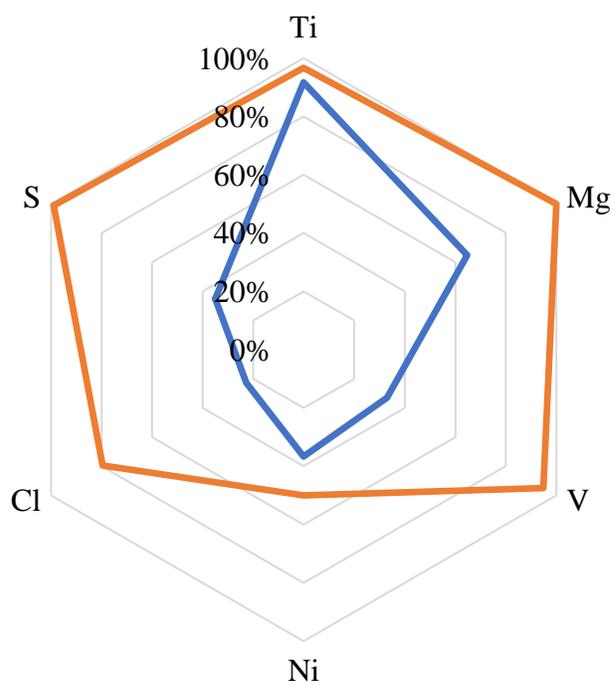


Figure 6.5 Removal efficiency of treated Iran oil using conventional (blue) and microwave heating (orange)

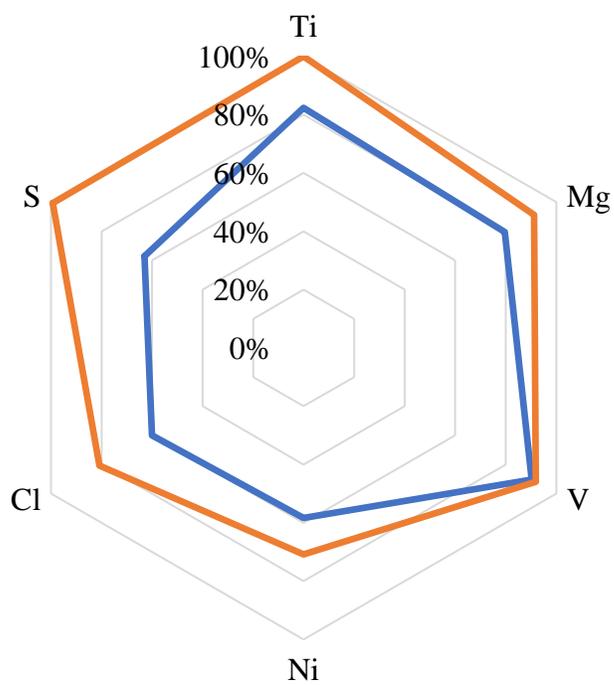


Figure 6.6 Removal efficiency of treated Basra oil using conventional (blue) and microwave heating (orange)

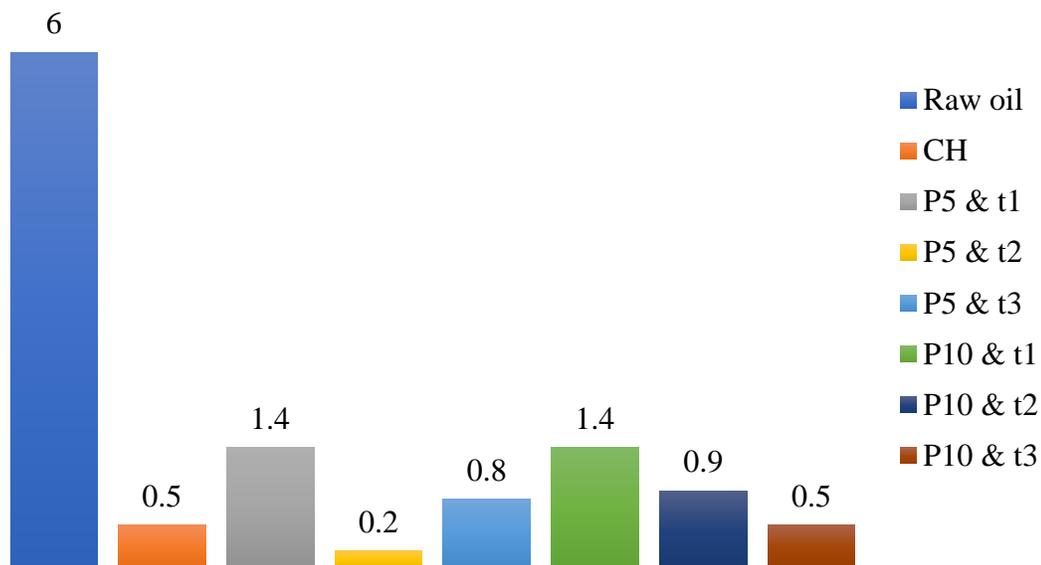


Figure 6.7 Concentrations of Ti in raw and treated Iran oil using conventional and microwave heating at different powers and residence times (ppm) – P is the microwave nominal setting power. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; t_1 = 1 min; t_2 = 2 min; and t_3 = 3 min

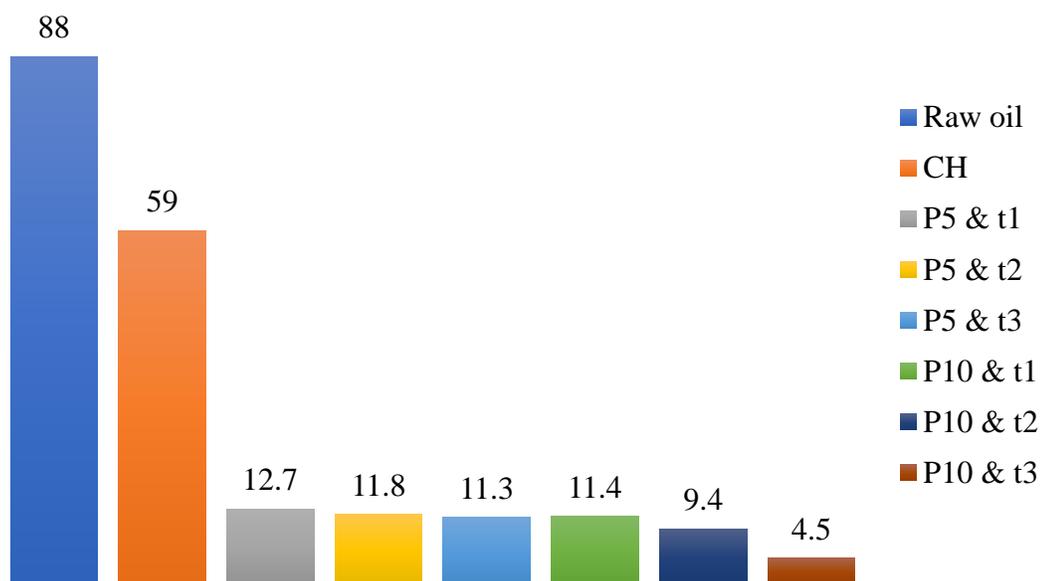


Figure 6.8 Concentrations of V in raw and treated Iran oil using conventional and microwave heating. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; t_1 = 1 min; t_2 = 2 min; and t_3 = 3 min

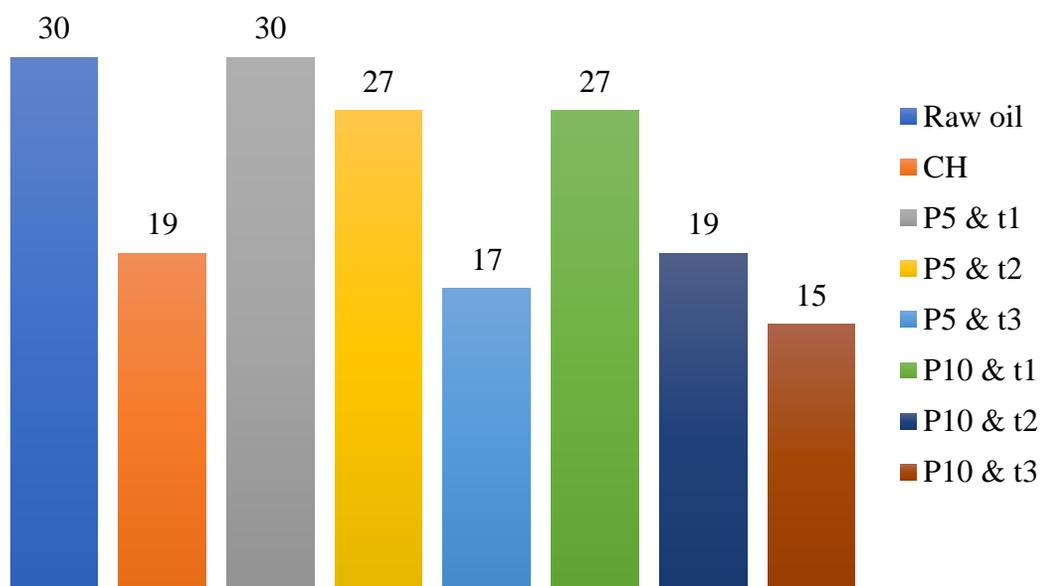


Figure 6.9 Concentrations of Ni in raw and treated Iran oil using conventional and microwave heating. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min

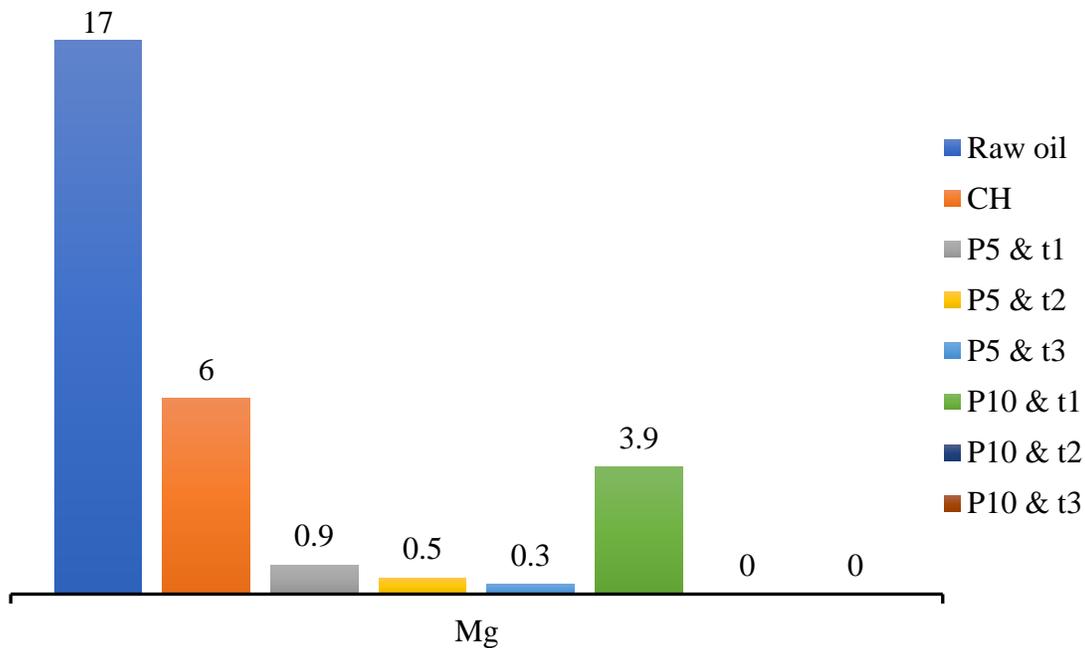


Figure 6.10 Concentrations of Mg in raw and treated Iran oil using conventional and microwave heating. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min

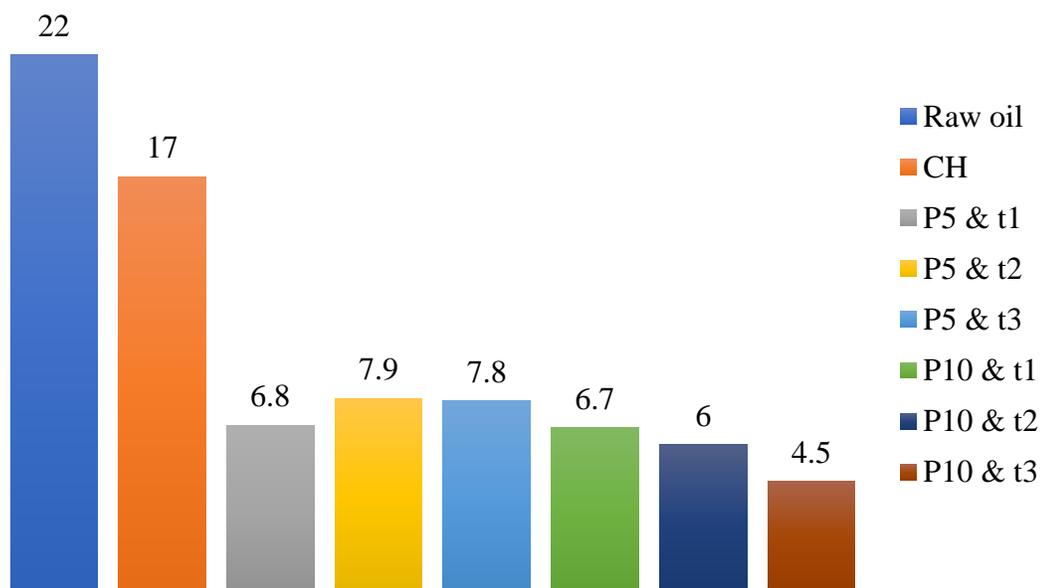


Figure 6.11 Concentrations of Cl in raw and treated Iran oil using conventional and microwave heating. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min

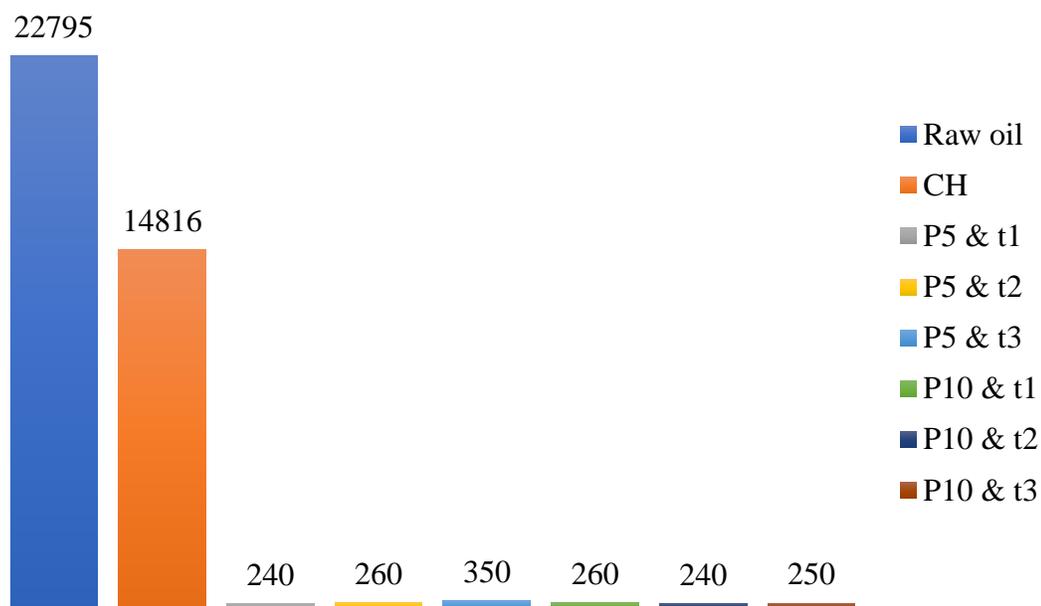


Figure 6.12 Concentrations of S in raw and treated Iran oil using conventional and microwave heating. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min

The better results of Mg compared to Cl are mainly due to the greater interaction of Mg with microwaves compared to that of Cl. Moreover, Mg is present in crude oil in another form, the metalloporphyrin structure [139]. As previously explained, the liberation of Mg from the ring is enhanced by applying microwave heating.

The removal efficiency of sulfur shows a high value, 99% when applying microwaves, compared to 30% using conventional heating. The considerable variation can be explained by the fact that it is essential to heat the entire oil until it reaches the local temperature of the reaction in the case of conventional heating. This, in turn, influences several aspects, most importantly the ionic liquid formed at a lower temperature. The ionic liquid might be exposed to decomposition at elevated temperatures, leading to the re-separation of some sulfur compounds in the oil. On the other hand, using microwaves generates a temperature much lower than the decomposition temperature of the ionic liquid. The formed liquid is highly polar, i.e., high microwave receptor, providing a boost to the chemistry between the ionic liquid and the sulfur compounds and, consequently, an excellent opportunity for more sulfur compounds to connect with the DM-DSA, which raises the removal efficiency of sulfur.

Basra oil was also processed to confirm the previous explanation for each metal as is evident in Figure 6.6. All the elements in Basra oil agree with those of Iran oil except V, which has the same removal efficiency for conventional and microwave heating possibly due to Basra oil being less complex than Iran oil. The removal of V in the case of conventional heating is therefore easier. However, other aspects, such as the lower bulk temperature of the payload and lower energy consumption, should be considered in the comparison.

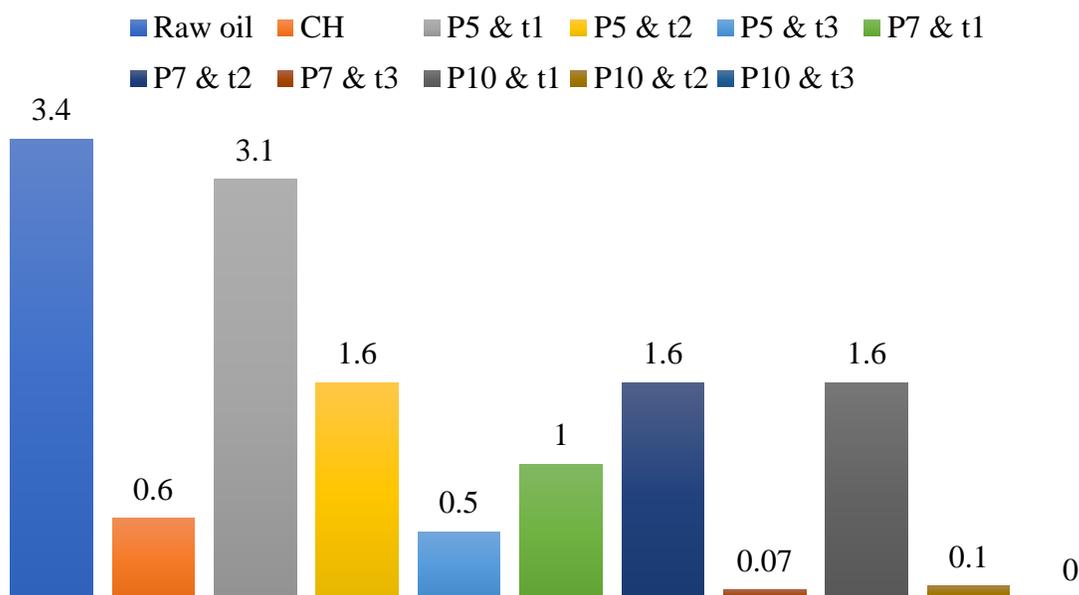


Figure 6.13 Concentrations of Ti in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm) – P is the microwave nominal setting power. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min

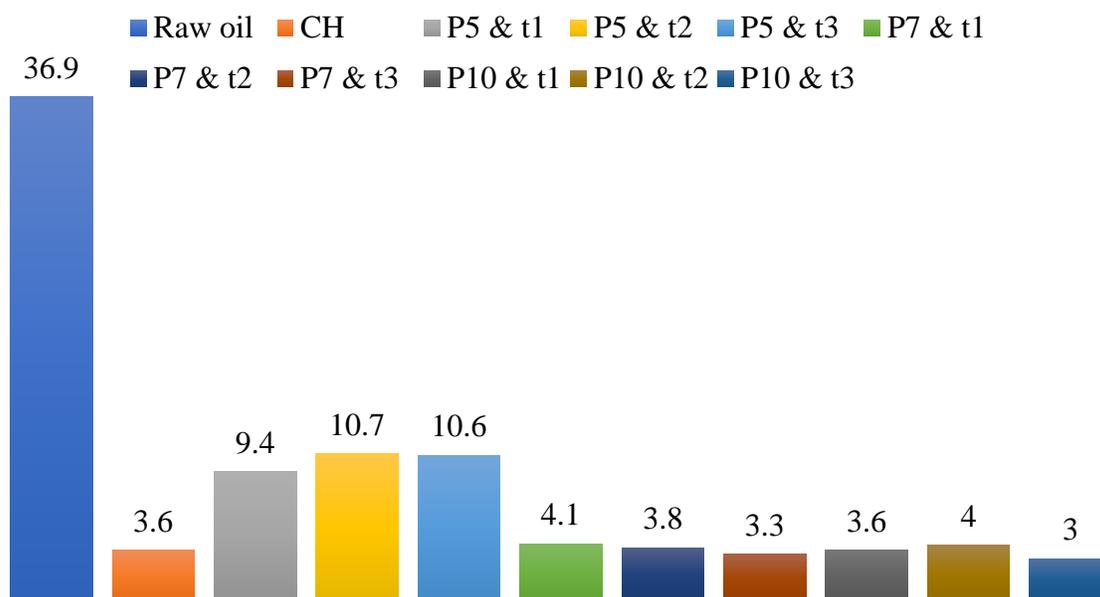


Figure 6.14 Concentrations of V in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm)

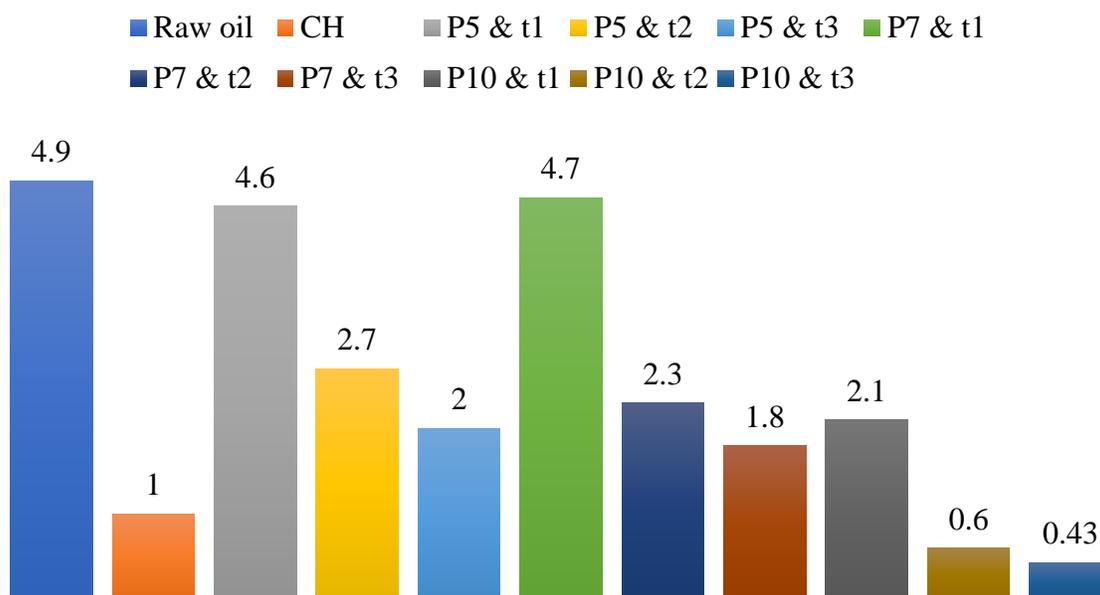


Figure 6.15 Concentrations of Mg in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm)

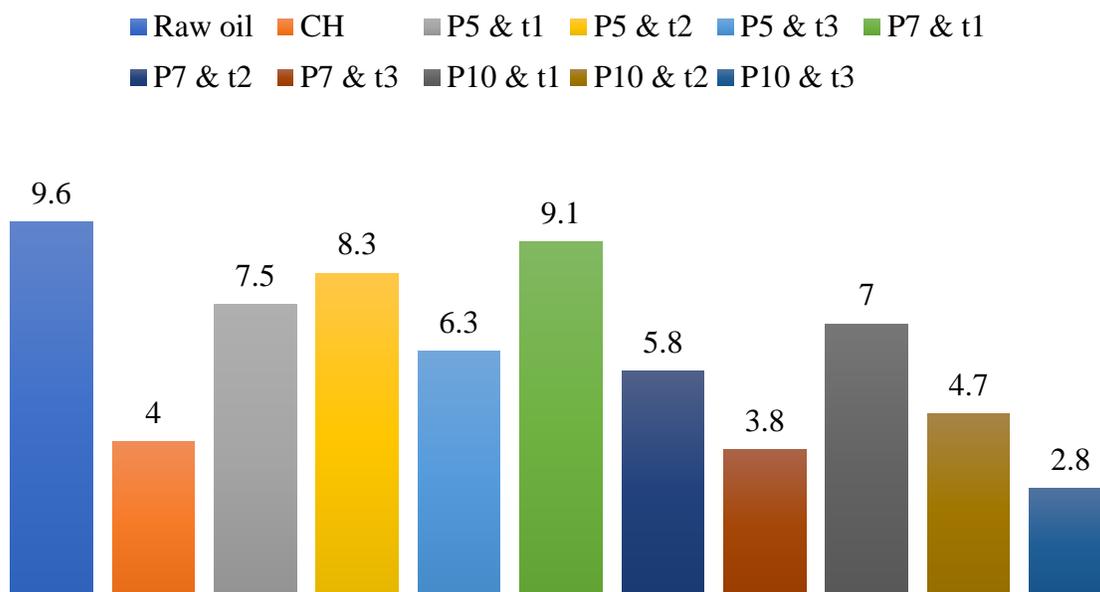


Figure 6.16 Concentrations of Ni in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm)

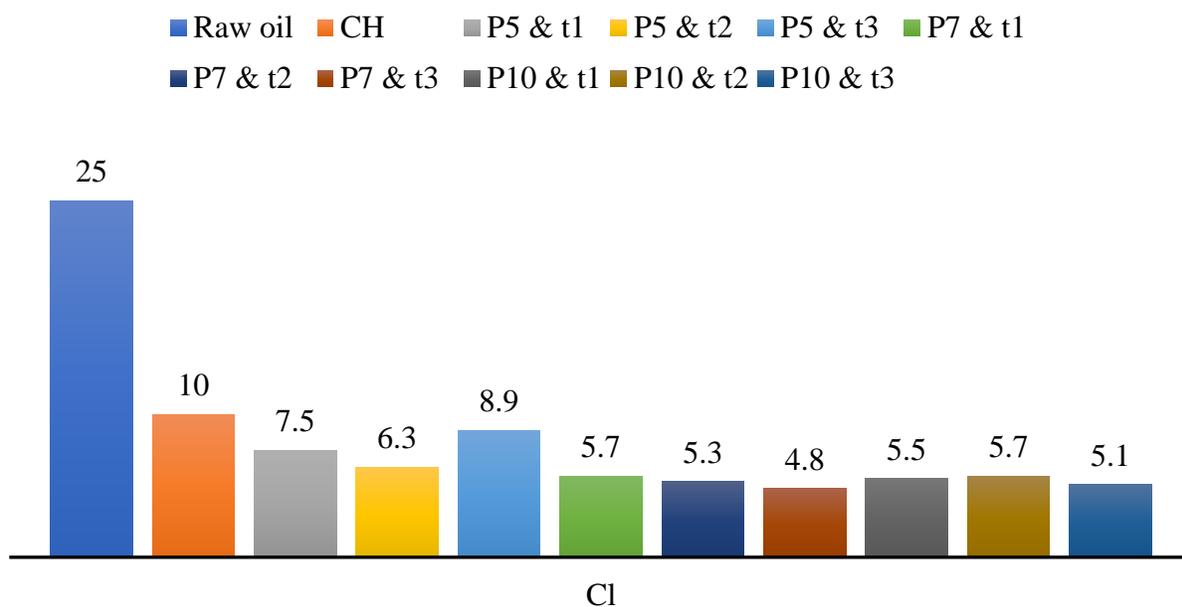


Figure 6.17 Concentrations of Cl in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm)

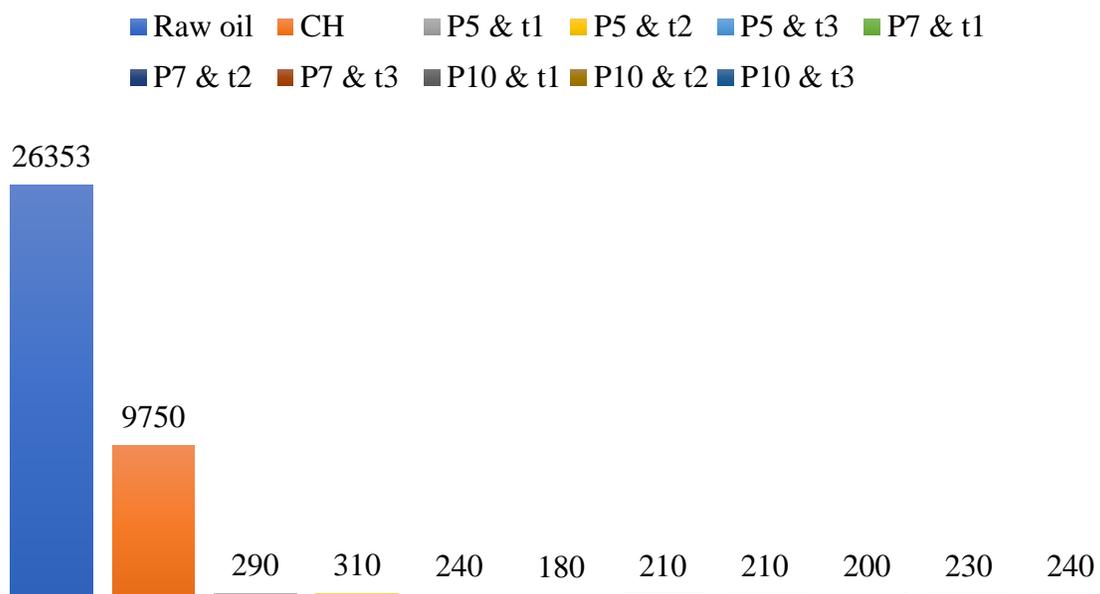


Figure 6.18 Concentrations of S in raw and treated Basra oil using conventional and microwave heating at different powers and residence times (ppm)

It was essential to examine the influences of the other process parameters that could impact the elimination performance of both metals and sulfur. There is significant interest in such an investigation to determine the most efficient value of the parameters, among the ones applied, to maximize removal efficiency. This step was implemented using different microwave powers: P5, P7, and P10, and various residence times: t_1 , t_2 , and t_3 .

It was found from the obtained NAA results of the treated Iran and Basra oils that the elimination capability of almost all the metals improved by raising the microwave power. For instance, at the time of t_3 Figure 6.7 and Figure 6.13 exhibit a decrease in the Ti concentration. It decreased from 0.8 ppm at P5 to 0.5 ppm at P10 in the case of Iran oil and from 0.5 ppm at P5 to 0.07 ppm at P7, and then 0 ppm at P10 for Basra oil.

The concentration of V was recorded in Figure 6.8 for Iran oil and Figure 6.14 for Basra oil. It decreased from 11.3 ppm at P5 to 4.5 ppm at P10 in the Iran oil. For Basra oil, the concentration of V decreased from 10.6 ppm at P5 to 3.3 ppm at P7; then the concentration showed a further decline to 3 ppm from increasing the P10. The other elements exist in Figure 6.9, Figure 6.10, and Figure 6.11 for Iran oil and Figure 6.13 and Figure 6.14 for Basra oil show the same gradual drop in the metals concentration.

The effect of advancing the microwave power and residence time together on the removal efficiency of some metals has been investigated using a set of surface plots. Figure 6.19 shows that at a higher residence time, a marginally inverse trend was observed as the removal efficiency slightly dropped from 75% to 71% when increasing the time from t_1 to t_2 at P5. No further decline in the removal efficiency was observed from t_2 to t_3 . There is no appreciable boost in efficiency recorded when increasing the residence time at P7 and P10. Therefore, the residence time does not influence the removal efficiency of V; however, the removal efficiency was proportional to the irradiation power of the applied microwave. To some extent, a considerable increase in removal efficiency was noted passing from P5 to P10.

There is a gradual increase in the removal efficiency of Ti that is displayed in **Error! Reference source not found.** as the residence time increases. The graph demonstrates that the irradiation power affects the elimination of Ti, as an increase in efficiency was noted as the power increased. The element was effectively 100% removed at maximum power and residence time. Although both

irradiation power and residence time affect the removal efficiency of Ti, power alone has a lower impact compared to that of the residence time.

The removal efficiency of Ni presented in Figure 6.20 shows a modest drop from t_1 to t_2 before a slight improvement was detected in the elimination of Ni after increasing the time from t_2 to t_3 . The same situation was noted when the irradiation power was increased. The removal efficiency slightly dropped from P5 to P7 followed by a continuous increase with a reduced percentage at time t_1 . At time t_2 and t_3 any increment in the power showed an increase in the removal efficiency. It was evident from the graph that increasing both power and the irradiation time dramatically improved the removal efficiency to the maximum amount at the applied conditions.

Figure 6.21 shows that the removal efficiency of Mg gradually rose by increasing the irradiation time. The efficiency did not show improvement when increasing the power from P5 to P7; however, it climbed when increasing the power to P10. The whole graph illustrates that the removal efficiency of Mg showed a significant improvement when increasing both irradiation power and residence time together.

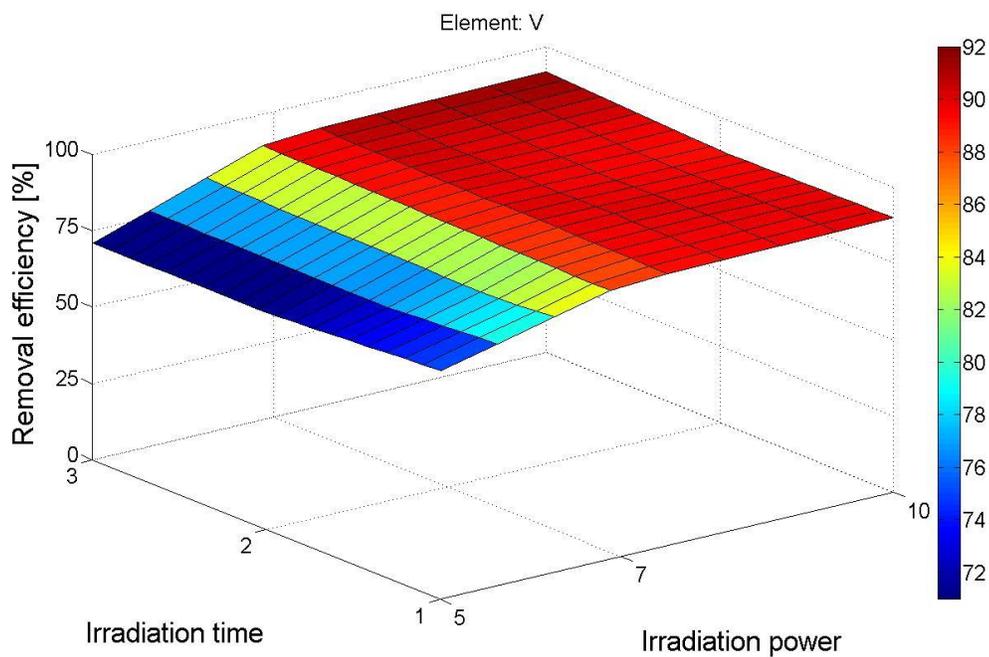
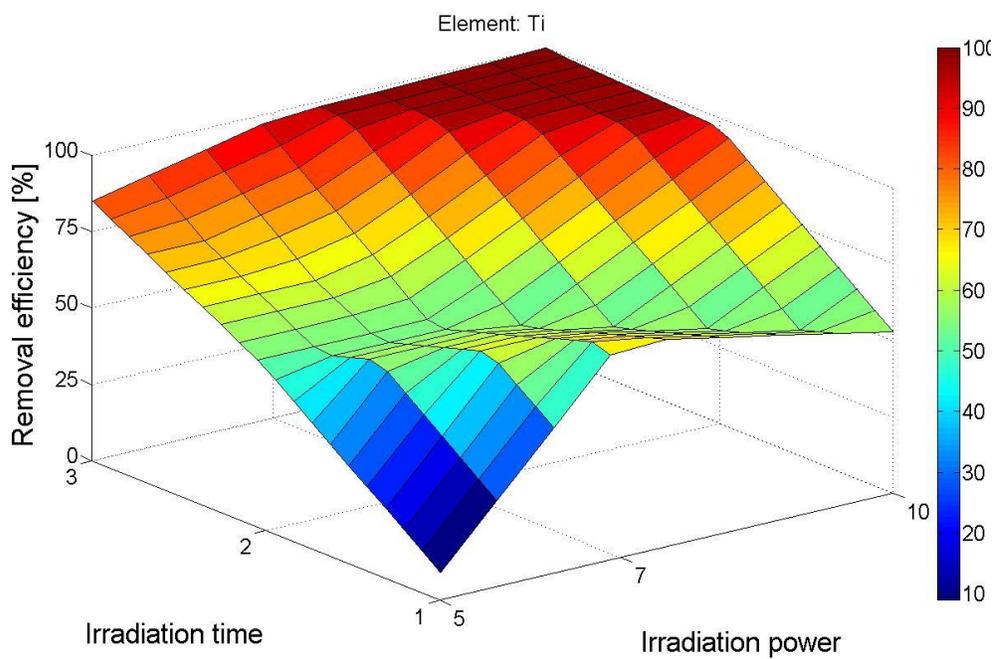


Figure 6.19 Removal efficiency of V in treated Basra oil at different microwave powers and residence times (ppm) – P is the microwave nominal setting power. P5 \approx 500 W; P7 \approx 700 W; P10 \approx 1000 W; $t_1 = 1$ min; $t_2 = 2$ min; and $t_3 = 3$ min



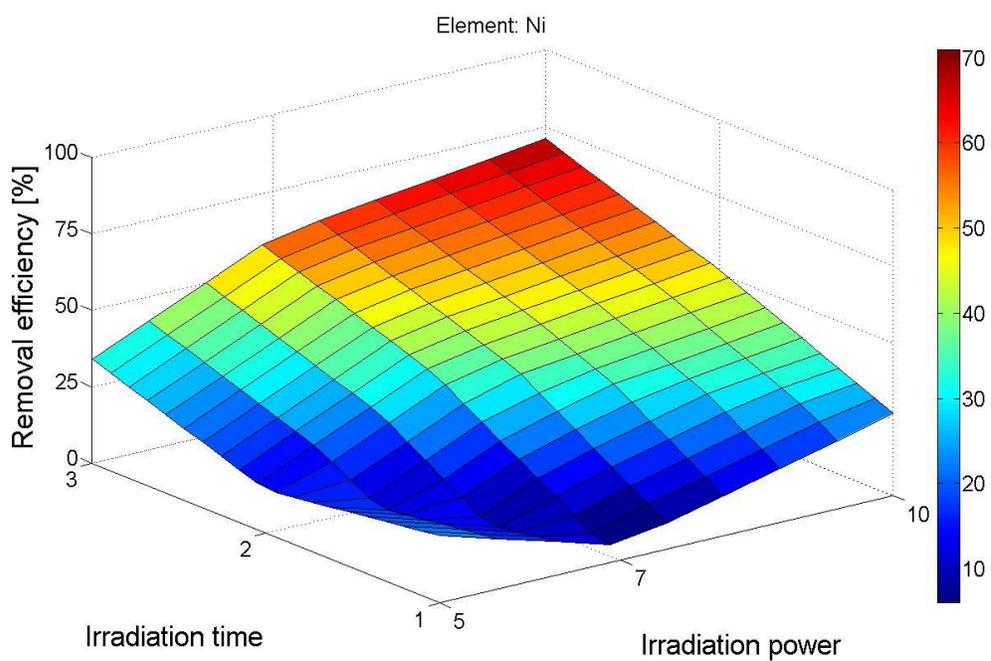


Figure 6.20 Removal efficiency of Ni treated Basra at different microwave powers and residence times (ppm)

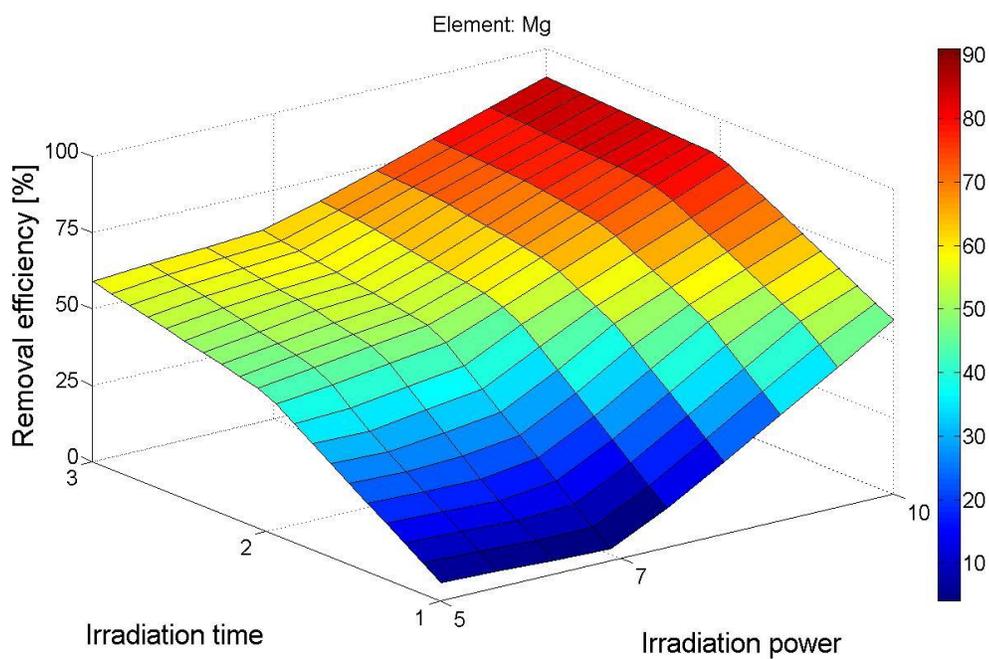


Figure 6.21 Removal efficiency of Mg in treated Basra at different microwave powers and residence times (ppm)

It can be concluded from the above-debated results that both irradiation power and residence time improve the removal efficiency of most metals. Increasing the microwave power improves the strength of the electric field, resulting in a stronger interaction of the reacted materials with the electromagnetic field. This interaction and the coupling of the elements with microwaves improved a rapid, efficient, and instantaneous heat generation process [7, 140]. Therefore, by increasing the microwave power, the interaction of each metal with microwaves improved, which in turn increased the heat generation in the N-M bond. Subsequently, the bond weakened, and the liberation of M from the porphyrin ring became much smoother, which intensified the removal efficiency.

Regarding residence time, the increase in the removal performance is due to the absorption of more microwave energy by the metals over a longer residence time, which leads to an increase in temperature where the metals remain. The removal efficiency of the metals is improved through a further weakness in the metal bond and greater liberation of metals. On the other hand, increasing the irradiation time did not strongly affect the metals V, Cl, and S, because they absorbed the maximum microwave energy in a shorter time. Therefore, increasing the residence time did not appear to improve removal efficiency.

6.5 Conclusion

A new approach has been investigated in this study for applying the microwave heating technique to remove metals and sulfur from Iran and Basra oils. The microwave heating mechanism seriously affects the removal efficiency of almost all metals, particularly V and S compounds when compared with conventional heating techniques. The removal efficiency of V using conventional heating is 33%, while the removal efficiency of the same element using microwave heating at a power 5 and after time t_1 , t_2 , and t_3 reached 87, 90, 95%, respectively. Sulfur as well showed a higher elimination efficiency when applying the microwave heating, which reached 99% compared with 60% for conventional heating. Investigating the effect of process parameters, such as microwave power and residence time, have been demonstrated as well and confirmed by a surface plot for some metals. It was found that changing the microwave power and residence time actively enforce the removal efficiency of almost all the metals, particularly Ni. Increasing the power and residence time enhances the heat generation and focuses on where the reaction takes place.

CHAPTER 7 GENERAL DISCUSSION

Removal of metals and sulfur from the waste-derivative oil is indispensable since it would lead to avoiding most of the issues and limitations that impede its uses in a wide range of commercial applications. Although a considerable number of techniques have been developed and documented regarding such objective, only some of them have industrially been established. The main reason behind this aspect relates to the cons associated with each method. For instance, applying the solvent extraction method leads to remove the whole fractions that contain the metals, which declines the yield of the end-product. Distillation technique enhances the production of two grades of oils: (1) Light oil, which is the primary product and contains a very low concentration of metals; and (2) heavy oil, which contains a much higher concentration of contaminations that must go in a further upgrading process for metals removal. Fast catalyst deactivation needs for an emulsification process, high cost, and long processing time, among other factors, are additional aspects limit the performing of the developed techniques. Ultrafiltration technique is a capital cost affected due to the fast fouling of the membrane used in the process. So far, furthermore, no an industrial process has been designed to remove sulfur and metal in a single step. Kindly refer to section 2 (methods of demetallization) for further details.

In the first stage of the project, a novel technique has been invented using a developed demetallization desulfurization agent and by applying the conventional heating technique. The process composed of three steps, the first step is the main reaction between the agent and the crude oil under specific temperature, residence time and stirring power. The second step is the washing step of the treated oil form the metal salt of the DM-DSA formed and the unreacted part of the agent. The washing step has been applied three times under reflux and at specific temperature stirring power and residence time. The third step is the separation of the treated oil from the other components using the decantation and the centrifugation.

Three different analytical techniques have been used for analyzing the treated oil and untreated oil. The process successfully declined the concentration of all the metals and sulfur in a single step specifically V that exist in the porphyrinc form. The chemistry behind the elimination reaction of both metals and sulfur has been studied. The agent acts as a proton donor for the metalloporphyrin ring after the four nitrogen atoms extract the electron bonds between the metals, due to the high electronegativity of the nitrogen atoms, which reaches up to 3.04 compared to 1.63 for the V atom.

The high electronegativity of the four nitrogens plays an essential role in leaving the metal atom as a positive metal ion after the electron bond extraction. This, in turn, forms four negative nitrogen ions, which directly bond with the hydrogen protons from the agent forming the pure porphyrin ring. At the same time, the negative side of the agent robustly extracts the positive metal ion from the media creating the metal salt of the agent.

In the second stage of the project, the microwave heating mechanism has been applied during the demetallization-desulfurization process. The interaction between microwave and metals creates local hotspots at the metal bonds, which consequently leads to weakening the bond between the metals and the four nitrogen in the porphyrin ring. This, in turn, enhances the easy and rapid breakdown of the metal bonds and the liberation of metals from the core of the metalloporphyrin ring. Also, the high interaction of the other metals in the form of polar salts exist in the oil boosts the removal of such metals from the crude oil. This means that applying microwave heating enhances the selective removal of metals from the network of the oils and keep the main skeleton of the oil without further degradation. As a result, the yield of the treated oil is not affected compared to the other demetallization technologies.

The invented process is green because there is no solvent consumption during the process compared with the other processes that require a significant amount of solvents for the extraction process. Moreover, both of the agent and the washing solvent can be regenerated and reused in the process; this will decline the waste production and decrease the cost dramatically. The invented technique is cost-effective, because there is no elevated temperature and/or pressure is required during the process. Also, there is no any other chemical additives or catalysts are a need for the elimination process if compared with the HDM-HDS process that currently applied in industry and requires a high hydrogen consumption, elevated temperature reaches up to 400 °C, and pressure amounted 100 atm. Furthermore, applying a catalyst is a must in the HDM-HDS process which deactivates in a short period, due to the deposition of the metal and sulfur oxides on the pore of the catalyst. This issue raises the cost of the process and give the chance to new technologies with low cost to replace the existing technology in industry. The invented technique does not require an emulsification process, because the agent is miscible with oil. Further, applying such heating mechanism improves the selective removal of the metals and sulfur compounds from the oil. The interaction of both metals exists in crude oil, the DM-DSA, the ionic liquid formed, and the aqueous

phase enhance the generation of local hot spots in the place where such elements and materials exist. Such hot spots significantly help in weakening the N-M bond and the liberation of the metal from the metalloporphyrin ring. Also, embedding the microwave enhances the interaction of both the DM-DSA and the ionic liquid formed with both metals and the sulfur compounds, which boosts the elimination reactions. By applying the microwave heating technique, the temperature of the whole oil increased by only one degree due to the low interaction of the oil with microwaves compared with the conventional heating which increases the temperature of the whole oil up to 170 °C to reach the reaction temperature. Further, Applying the microwave heating technique decreased energy consumption by 99%.

CHAPTER 8 CONCLUSION AND RECOMMENDATION

8.1 Conclusion

This work develops novel technology for the selective removal of metals and sulfur from petroleum oil in a single step using a novel demetallization-desulfurization agent (DM-DSA) and microwave heating technique. Conventional heating was applied as well and the results compared with that of microwave heating.

The first objective of the project was to select a DM-DSA that fulfills the chemical and dielectric properties and can extract both metals and sulfur in a single step. To achieve such goal, a set of chemical agents from a wide range of chemical families were selected. It was essential to choose an agent with specific characteristics, such as amphiphilicity, miscible with crude oil and does not require emulsification. For this reason, the physical and chemical properties of each tested agent were carefully studied.

The second objective was to develop a new process for the removal of metals and sulfur using a conventional heating mechanism to prove the performance of the selected agent. The first work was done by developing a technique for the removal of metals and sulfur using conventional heating. This heating method was used at the beginning to better control the reaction temperature and test the performance of the chosen DM-DSA. Five crude oils with different metals and sulfur concentrations were used to begin the work. All the oils had been tested under the same reaction conditions, such as temperature, pressure, residence time, stirring power, and DM-DSA dosage. The processed oil was then analyzed using different analytical techniques, such as Neutron activation analysis (NAA), Fourier transform infrared spectroscopy (FTIR), and elemental analysis. The results were compared with those of the raw oil to calculate the removal efficiency of each element. The comparison confirmed that almost all the metals and sulfur in the processed oil were reduced by considerable amounts.

It was essential to investigate the removal mechanism to better understand the chemistry behind the reaction and this was the third objective. Therefore, the chemistry of the reaction was well studied to propose a mechanism for the elimination reaction and explain the way the DM-DSA extracted the metals and sulfur from the composition of the crude oil. It was found that the agent acted as a proton donor for the four N negative ions present in the metalloporphyrin ring and

extracted the metals as a metal salt of the agent. For sulfur extraction, the agent formed an ionic liquid when mixed with the oil, and this liquid had a high tendency to extract the sulfur compounds through a hydrogen bond and electrostatic force.

The principal objective – which includes the originality of the project – was the embedding of the microwaves as the central heating mechanism in the removal process with the novel DM-DSA. This objective was achieved by applying the electromagnetic irradiation during the removal process to take the advantages of the interaction between DM-DSA and metals present in the oil with the applied microwaves. The work was done using Iran and Basra oils received from TOTAL France directly from their tanks. The removal efficiency of both metals and sulfur was compared for conventional and microwave heating. A significant improvement in removal efficiency by applying microwaves was noted. The concentrations of all the elements were reduced, specifically for V, 90% removal efficiency, which is difficult to eliminate from the metalloporphyrin ring. The elimination efficiency of sulfur also dramatically increased and reached 99%.

The last objective was to investigate the influence of the basic process parameters, such as DM-DSA dosage, irradiation power, residence time, and others on the removal efficiency of the developed technique. To improve the removal efficiency of both metals and sulfur, we tested the effects of different process parameters, such as microwave power and residence time. The test was implemented at irradiation powers P5, P7, and P10 and at residence times t1, t2, and t3. The effect of changing both the irradiation power and residence time on the removal efficiency of each element was also studied. It was found that both parameters enhance the removal efficiency of some elements, and the maximum removal efficiency of most elements at the applied conditions was reached at P10 and time t3.

8.2 Recommendations for future work

It is recommended to develop a technique to regenerate the reacted DM-DSA. It may decrease the cost of the process and help to recycle the agent and the aqueous phase consumed during the removal process. Developing a synthesizing process for the DM-DSA and comparing the cost against the market price is recommended as well. It is essential to create a kinetic model to predict the metals, especially V & Ni, and sulfur concentration in the treated oil. Carrying out a full study of the process design and simulation based on the invented techniques and considering the

economic aspects are recommended. Finally, a scale-up of the invented process using the lab-scale results is also important to apply the designed technique on an industrial scale.

REFERENCES

- [1] A. C. Jenifer, P. Sharon, A. Prakash, and P. C. Sande, "A Review of the Unconventional Methods Used for the Demetallization of Petroleum Fractions over the Past Decade," *Energy & Fuels*, vol. 29, no. 12, pp. 7743-7752, 2015/12/17 2015.
- [2] M. F. Ali and S. Abbas, "A review of methods for the demetallization of residual fuel oils," *Fuel Processing Technology*, vol. 87, no. 7, pp. 573-584, 7// 2006.
- [3] V. Valkovic, *Trace elements in petroleum*. 1978, p. Medium: X; Size: Pages: 279.
- [4] T. F. Yen, "Role of trace metals in petroleum," 1975.
- [5] M. F. Ali, H. Perzanowski, A. Bukhari, and A. A. Al-Haji, "Nickel and vanadyl porphyrins in Saudi Arabian crude oils," *Energy & fuels*, vol. 7, no. 2, pp. 179-184, 1993.
- [6] G. R. Dedeles *et al.*, "Microbial demetallization of crude oil: nickel protoporphyrin disodium as a model organo-metallic substrate," *Journal of bioscience and bioengineering*, vol. 90, no. 5, pp. 515-521, 2000.
- [7] H. Shang, Y. Liu, J.-C. Shi, Q. Shi, and W.-H. Zhang, "Microwave-assisted nickel and vanadium removal from crude oil," *Fuel Processing Technology*, vol. 142, pp. 250-257, 2016/02/01/ 2016.
- [8] A. Miadonye, S. Snow, D. Irwin, M. R. Khan, and A. Britten, "Desulfurization of heavy crude oil by microwave irradiation," *Computational Methods in Multiphase Flow V*, vol. 63, p. 455, 2009.
- [9] H. Hosseini and A. Hamidi, "Sulfur Removal of Crude Oil by Ultrasound-Assisted Oxidative Method," in *International Conference on Biologi-cal, Civil and Environmental Engineering (BCEE-2014) March*, 2014, pp. 17-18.
- [10] R. E. Overfield, "Method for extracting nickel and vanadium compounds from oils," ed: Google Patents, 1986.
- [11] J. G. Speight, "Visbreaking: A technology of the past and the future," *Scientia Iranica*, vol. 19, no. 3, pp. 569-573, 6// 2012.
- [12] R. E. Brown, R. J. Hogan, D. M. Coombs, and S. G. Kukes, "Process for demetallizing and desulfurizing heavy crude oil," ed: Google Patents, 1989.
- [13] R. Magomedov, A. Popova, T. Maryutina, K. M. Kadiev, and S. Khadzhiev, "Current status and prospects of demetallization of heavy petroleum feedstock (Review)," *Petroleum Chemistry*, vol. 55, no. 6, pp. 423-443, 2015.
- [14] J. G. Speight, *The chemistry and technology of petroleum*. CRC press, 2014.
- [15] M. A. Rodríguez, I. Elizalde, and J. Ancheyta, "Modeling the performance of a bench-scale reactor sustaining HDS and HDM of heavy crude oil at moderate conditions," *Fuel*, vol. 100, pp. 152-162, 2012.
- [16] D.-I. S. Kim, Pin Tu; Teh, Fu Yen; , " Evaluation of Versatile Ultrasonic Effects on Degradation of Organometallics from Petroleum., " *Environmental Engineering Research*, vol. 8, no. 2, p. 59–71, 2003.
- [17] H. Salehizadeh, M. Mousavi, S. Hatamipour, and K. Kermanshahi, "Microbial demetallization of crude oil using *Aspergillus* sp.: vanadium oxide octaethyl porphyrin (VOOEP) as a model of metallic petroporphyrins," *Iranian Journal of Biotechnology*, vol. 5, no. 4, pp. 226-231, 2007.
- [18] L. Beach and J. Shewmaker, "The Nature of Vanadium in Petroleum. Extraction and Volatility Studies," *Industrial & Engineering Chemistry*, vol. 49, no. 7, pp. 1157-1164, 1957.
- [19] P. C. Mandal, M. Sasaki, and M. Goto, "Non-catalytic vanadium removal from vanadyl etioporphyrin (VO-EP) using a mixed solvent of supercritical water and toluene: A kinetic study," *Fuel*, vol. 92, no. 1, pp. 288-294, 2012.
- [20] L. Sombrol, A. C. Pickler, J. R. Aires, and C. A. Riehl, "Study on nickel and vanadium removal in thermal conversion of oil sludge and oil shale sludge," in *Journal de Physique IV (Proceedings)*, 2003, vol. 107, pp. 1255-1258: EDP sciences.

- [21] K. N. Awokoya, B. A. Moronkola, S. Chigome, D. A. Ondigo, Z. Tshentu, and N. Torto, "Molecularly imprinted electrospun nanofibers for adsorption of nickel-5, 10, 15, 20-tetraphenylporphine (NTPP) in organic media," *Journal of Polymer Research*, vol. 20, no. 6, pp. 1-9, 2013.
- [22] R. A. Ware and J. Wei, "Catalytic hydrodemetallation of nickel porphyrins: I. Porphyrin structure and reactivity," *Journal of catalysis*, vol. 93, no. 1, pp. 100-121, 1985.
- [23] P. C. Mandal, M. Sasaki, and M. Goto, "Nickel removal from nickel-5, 10, 15, 20-tetraphenylporphine using supercritical water in absence of catalyst: A basic study," *Journal of hazardous materials*, vol. 187, no. 1, pp. 600-603, 2011.
- [24] K. Welter, E. Salazar, Y. Balladores, O. Márquez, J. Márquez, and Y. Martínez, "Electrochemical removal of metals from crude oil samples," *Fuel Processing Technology*, vol. 90, no. 2, pp. 212-221, 2009.
- [25] M. F. Ali, A. Bukhari, and M. Saleem, "Trace metals in crude oils from Saudi Arabia," *Industrial & engineering chemistry product research and development*, vol. 22, no. 4, pp. 691-694, 1983.
- [26] S. M. Y. Yamada, H. Kakiyama, H. Honda,, Japan, 1979.
- [27] O. R. Koseoglu, A. Al-Hajji, and H. Muller, "Process for demetallization of whole crude oil," ed: Google Patents, 2015.
- [28] O. Kutowy, T. A. Tweddle, and J. D. Hazlett, "Method for the molecular filtration of predominantly aliphatic hydrocarbon liquids," ed: Google Patents, 1989.
- [29] J. Arod *et al.*, "Process for the treatment of a hydrocarbon charge by high temperature ultrafiltration," ed: Google Patents, 1983.
- [30] A. Duong, G. Chattopadhyaya, W. Y. Kwok, and K. J. Smith, "An experimental study of heavy oil ultrafiltration using ceramic membranes," *Fuel*, vol. 76, no. 9, pp. 821-828, 1997.
- [31] E. J. Osterhuber, "Upgrading heavy oils by solvent dissolution and ultrafiltration," ed: Google Patents, 1989.
- [32] S. G. Kukes and D. R. Battiste, "Demetallization of heavy oils with phosphorous acid," ed: Google Patents, 1985.
- [33] P. K. Eidem, "Reducing the metals content of petroleum feedstocks," ed: Google Patents, 1988.
- [34] G. F. S. R. Bearden, USA, 1985.
- [35] M. J. Michlmayr, "Upgrading metal-contaminated petroleum oils containing vanadium and/or nickel," ed: Google Patents, 1977.
- [36] "On-site purification of problem petrolic liquid fuels," ed: Google Patents, 1972.
- [37] "Method for removing metal from hydrocarbon oil by using by product generated in producing fatty acid through oxidizing paraffin," ed: Google Patents, 2003.
- [38] P. J. P. M.A. Greaney, "Demetalation of petroleum streams," USA, 1999.
- [39] J. Maxwell, C. T. Pillinger, and G. Eglinton, "Organic geochemistry," *Quarterly Reviews, Chemical Society*, vol. 25, no. 4, pp. 571-628, 1971.
- [40] A. G. Hurter, "Removal of metal contaminants from oil," ed: Google Patents, 1989.
- [41] K. A. Gould, "Oxidative demetallization of petroleum asphaltenes and residua," *Fuel*, vol. 59, no. 10, pp. 733-736, 1980/10/01/ 1980.
- [42] E. G. A. Bukowski, M. Gardzinski, K. Wawszczak, , "Removal of heavy metals from petroleum fractions," Poland, 1979.
- [43] F. Samedova, A. Kasumova, S. Y. Rashidova, and G. Bakhshesh, "Dehydration and desalination of oils using supercritical carbon dioxide," *Russian Journal of Physical Chemistry B*, vol. 5, no. 7, pp. 1076-1079, 2011.

- [44] Y. Shiraishi, T. Hirai, and I. Komasaawa, "A novel demetalation process for vanadyl-and nickelporphyrins from petroleum residue by photochemical reaction and liquid-liquid extraction," *Industrial & engineering chemistry research*, vol. 39, no. 5, pp. 1345-1355, 2000.
- [45] J. R. P. Maxwell, C. T.; Eglinton, G.. Q. , , . " Organic geochemistry," *Rev., Chem. Soc.*, vol. 25, p. 571-628, 1971.
- [46] D. P. Mann, S. G. Kukes, and D. M. Coombs, "Metals removal with a light hydrocarbon and an organophosphorous compound," ed: Google Patents, 1985.
- [47] K. S. Suslick *et al.*, "Acoustic cavitation and its chemical consequences," *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 357, no. 1751, pp. 335-353, 1999.
- [48] S. Le Borgne and R. Quintero, "Biotechnological processes for the refining of petroleum," *Fuel Processing Technology*, vol. 81, no. 2, pp. 155-169, 2003.
- [49] C. Ovalles *et al.*, "Upgrading of Orinoco Belt crude oil and its fractions by an electrochemical system in the presence of protonating agents," *Fuel processing technology*, vol. 48, no. 2, pp. 159-172, 1996.
- [50] S. M. Rao and M.-O. Coppens, "Increasing robustness of deactivating nanoporous catalysts by optimizing the pore network—application to Hydrodemetalation," *diffusion-fundamentals.org*, vol. 16, pp. 1-2, 2011.
- [51] S. Farag and J. Chaouki, "Microwave Heating Assisted Biorefinery of Biomass," in *Innovative Solutions in Fluid-Particle Systems and Renewable Energy Management*, T. Katia, Ed. Hershey, PA, USA: IGI Global, 2015, pp. 131-166.
- [52] S. Farag, "Production of Chemicals by Microwave Thermal Treatment of Lignin," *Philosophiae Doctor Ph.D. Thesis, Chem. Eng., University of Montreal: École Polytechnique de Montréal*, December 2013.
- [53] S. Farag and J. Chaouki, "A modified microwave thermo-gravimetric-analyzer for kinetic purposes," *Applied Thermal Engineering*, vol. 75, pp. 65-72, 1/22/ 2015.
- [54] S. Farag, A. Sobhy, C. Akyel, J. Doucet, and J. Chaouki, "Temperature profile prediction within selected materials heated by microwaves at 2.45GHz," *Applied Thermal Engineering*, vol. 36, no. 0, pp. 360-369, 4// 2012.
- [55] S. Farag, D. Fu, P. G. Jessop, and J. Chaouki, "Detailed compositional analysis and structural investigation of a bio-oil from microwave pyrolysis of kraft lignin," *Journal of Analytical and Applied Pyrolysis*, vol. 109, no. 0, pp. 249-257, 9// 2014.
- [56] S. Farag, L. Kouisni, and J. Chaouki, "Lumped Approach in Kinetic Modeling of Microwave Pyrolysis of Kraft Lignin," *Energy & Fuels*, vol. 28, no. 2, pp. 1406-1417, 2014/02/20 2014.
- [57] S. Farag, B. P. Mudrabovina, P. G. Jessop, and J. Chaouki, "Impact of the Heating Mechanism on the Yield and Composition of Bio-oil from Pyrolysis of Kraft Lignin," *Biomass and Bioenergy*, 2016.
- [58] S. Samih, M. Latifi, S. Farag, P. Leclerc, and J. Chaouki, "From complex feedstocks to new processes: the role of the newly developed micro-reactors," *Chemical Engineering and Processing - Process Intensification*, 2018/07/07/ 2018.
- [59] T. Durka, T. Van Gerven, and A. Stankiewicz, "Microwaves in Heterogeneous Gas-Phase Catalysis: Experimental and Numerical Approaches," *Chemical Engineering & Technology*, vol. 32, no. 9, pp. 1301-1312, 2009.
- [60] J. Doucet, J.-P. Laviolette, S. Farag, and J. Chaouki, "Distributed Microwave Pyrolysis of Domestic Waste," (in English), *Waste and Biomass Valorization*, vol. 5, no. 1, pp. 1-10, 2014/02/01 2014.
- [61] M. Gupta and W. W. L. Eugene, *Microwaves and metals*. Singapore: John Wiley & sons (Asia) Pte Ltd 2007, p. 256.

- [62] B. M. Chandra Shekara, B. S. Jai Prakash, and Y. S. Bhat, "Microwave-induced deactivation-free catalytic activity of BEA zeolite in acylation reactions," *Journal of Catalysis*, vol. 290, no. 0, pp. 101-107, 2012.
- [63] V. Paixão *et al.*, "Desilication of MOR zeolite: Conventional versus microwave assisted heating," *Applied Catalysis A: General*, vol. 402, no. 1–2, pp. 59-68, 2011.
- [64] Z. Zhang and Z. K. Zhao, "Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid," *Bioresource Technology*, vol. 101, no. 3, pp. 1111-1114, 2010.
- [65] R. Pan, Y. Wu, Q. Wang, and Y. Hong, "Preparation and catalytic properties of platinum dioxide nanoparticles: A comparison between conventional heating and microwave-assisted method," *Chemical Engineering Journal*, vol. 153, no. 1–3, pp. 206-210, 2009.
- [66] V. L. Budarin *et al.*, "The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw," *Bioresource Technology*, vol. 100, no. 23, pp. 6064-6068, 2009.
- [67] S. Karthikeyan, R. Balasubramanian, and S. W. See, "Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter," *Talanta*, vol. 69, no. 1, pp. 79-86, 2006.
- [68] M. E. Lucchesi, F. Chemat, and J. Smadja, "Solvent-free microwave extraction of essential oil from aromatic herbs: comparison with conventional hydro-distillation," *Journal of Chromatography A*, vol. 1043, no. 2, pp. 323-327, 2004.
- [69] P. Patil, V. G. Gude, S. Pinappu, and S. Deng, "Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions," *Chemical Engineering Journal*, vol. 168, no. 3, pp. 1296-1300, 2011.
- [70] M. Guiotoku, C. R. Rambo, F. A. Hansel, W. L. E. Magalhães, and D. Hotza, "Microwave-assisted hydrothermal carbonization of lignocellulosic materials," *Materials Letters*, vol. 63, no. 30, pp. 2707-2709, 2009.
- [71] A. Krzan and E. Zagar, "Microwave driven wood liquefaction with glycols," *Bioresource Technology*, vol. 100, no. 12, pp. 3143-3146, 2009.
- [72] H. Dogan and N. D. Hilmioglu, "Dissolution of cellulose with NMMO by microwave heating," *Carbohydrate Polymers*, vol. 75, no. 1, pp. 90-94, 2009.
- [73] S. Sithambaram, E. K. Nyutu, and S. L. Suib, "OMS-2 catalyzed oxidation of tetralin: A comparative study of microwave and conventional heating under open vessel conditions," *Applied Catalysis A: General*, vol. 348, no. 2, pp. 214-220, 2008.
- [74] A. Orozco, M. Ahmad, D. Rooney, and G. Walker, "Dilute Acid Hydrolysis of Cellulose and Cellulosic Bio-Waste Using a Microwave Reactor System," *Process Safety and Environmental Protection*, vol. 85, no. 5, pp. 446-449, 2007.
- [75] J. A. Menéndez, A. Domínguez, M. Inguanzo, and J. J. Pis, "Microwave pyrolysis of sewage sludge: analysis of the gas fraction," *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 2, pp. 657-667, 2004.
- [76] S. Zhu, Y. Wu, Z. Yu, J. Liao, and Y. Zhang, "Pretreatment by microwave/alkali of rice straw and its enzymic hydrolysis," *Process Biochemistry*, vol. 40, no. 9, pp. 3082-3086, 2005.
- [77] F. Motasemi and M. T. Afzal, "A review on the microwave-assisted pyrolysis technique," *Renewable and Sustainable Energy Reviews*, vol. 28, no. 0, pp. 317-330, 12// 2013.
- [78] T. A. Dickneider. (2019). *Petretec – Dupont's Technology For Polyester Regeneration*. Available: <https://www.scranton.edu/faculty/cannm/green-chemistry/english/industrialchemistrymodule.shtml>
- [79] X. Zhao, Q. Shi, M. R. Gray, and C. Xu, "New vanadium compounds in venezuela heavy crude oil detected by positive-ion electrospray ionization fourier transform ion cyclotron resonance mass spectrometry," *Scientific reports*, vol. 4, 2014.

- [80] R. M. Khan and E. N. Al-Shafei, "Microwave-promoted desulfurization of crude oil," ed: Google Patents, 2013.
- [81] M. D. L. M. De Chamorro and M. C. Romano, "Simultaneous demetallization and desulphuration of carbonaceous materials via microwaves," ed: Google Patents, 2000.
- [82] S. Wang, J. Yang, and X. Xu, "Effect of the cationic starch on removal of Ni and V from crude oils under microwave irradiation," *Fuel*, vol. 90, no. 3, pp. 987-991, 2011/03/01/ 2011.
- [83] G. E. P, "On-site purification of problem petrolic liquid fuels," ed: Google Patents, 1972.
- [84] H. Loebell, J. Marcusson, R. Eickmann, A. Scheller, E. Pailler, and D. Holde, "Über die Untersuchung von Asphalten Untersuchung von Asphalten," *Zeitschrift für analytische Chemie*, vol. 56, no. 3, pp. 157-159, 1917.
- [85] M. A. Greaney and P. J. Polini, "Method for demetallating petroleum streams (LAW772)," ed: Google Patents, 1999.
- [86] L. J. Kashima Oil Co., "Removal of heavy metals from heavy petroleum oil.," Japan, 1983.
- [87] D. A. Young, "Demetalization of petroleum feedstocks with zinc chloride and titanium tetrachloride catalysts," United States, 1979. Available: <https://patents.google.com/patent/US4148717A/en#patentCitations>.
- [88] D. A. Young, "Demetallization of petroleum feedstocks with zinc chloride and titanium tetrachloride catalysts," ed: Google Patents, 1979.
- [89] M. Siskin, "Hydrodesulfurization with a metal halide-hydrogen halide catalyst," ed: Google Patents, 1977.
- [90] N. S. Nametkin *et al.*, "Method of purifying crude petroleum and primary refining products," ed: Google Patents, 1976.
- [91] W. K. Gleim, "Hydrorefining of metal-containing black oils with a molten lewis acid and a molybdenum halide," ed: Google Patents, 1969.
- [92] W. C. Baird Jr and R. Bearden Jr, "Combined desulfurization and hydroconversion with alkali metal oxides," ed: Google Patents, 1977.
- [93] R. Bearden Jr, "Combined disulfurization and conversion with alkali metals," ed: Google Patents, 1978.
- [94] M. A. Greaney, M. C. Kerby Jr, W. N. Olmstead, and I. A. Wiehe, "Method for demetallating refinery feedstreams," ed: Google Patents, 1996.
- [95] S. Savel'ev, G. Azerbaeva, Y. Saltykov, and N. Noskova, "Binding of petroleum metals into insoluble complexes," *Izvestia Ministerstva Nauki Akademii Nauk Respubliki Kazahstan, Seria Khimicheskaya*, vol. 1, pp. 40-45, 1996.
- [96] S. G. Kukes and T. Davis, "Demetallization of heavy oils," ed: Google Patents, 1983.
- [97] T. Y. Yan, "Demetalation of heavy hydrocarbon oils," ed: Google Patents, 1983.
- [98] Z. Peifu, T. Zhang, "Removal of metals from hydrocarbon raw material with chelating agent.," China, 1991.
- [99] Y. O. H. Miyadera, H. Ozaki, T. Suzuka, K. Nakamura, H. Yoshikai, " Removal of metal from waste petroleum residual oils with molten tin," Japan, 1975.
- [100] J. G. Reynolds, *Removal of nickel and vanadium from heavy crude oils by exchange reactions*. United States. Department of Energy, 2003.
- [101] E. Z. J. Wieckowska, T. Lisik, T. Chrapek, J. Tomusiak, "Method of removing metallic compounds from petroleum and its fractions and distillation residues.," Polish 1988.
- [102] C. L. Aldridge, R. Bearden Jr, and K. L. Riley, "Removal of metallic contaminants from a hydrocarbonaceous liquid," ed: Google Patents, 1991.
- [103] L. A. Rankel, "Process for treating heavy oil," ed: Google Patents, 1994.
- [104] J. Piskorz, D. S. A. Radlein, P. Majerski, and D. S. Scott, "Hydrotreating of heavy hydrocarbon oils in supercritical fluids," ed: Google Patents, 1996.

- [105] K. L. Riley, "Two-stage hydrodesulfurization of oil utilizing a narrow pore size distribution catalyst," ed: Google Patents, 1977.
- [106] Mobil Oil Corp. USA, "Catalyst for demetalizing and desulfurizing hydrocarbons.," Netherland, 1979.
- [107] L. Nippon Oil Co., "Heavy petroleum oil treatment," Japanese, 1982.
- [108] D. L. J. Devanneaux, J.P. Gallez, J.C. Courcelle, , "Catalyst and methods for hydrodemetallation of hydrocarbon charges.," France, 1984.
- [109] H. J. Chen and F. Massoth, "Hydrodemetalation of vanadium and nickel porphyrins over sulfided cobalt-molybdenum/alumina catalyst," *Industrial & engineering chemistry research*, vol. 27, no. 9, pp. 1629-1639, 1988.
- [110] R. A. M. Gomez, "Treatment of crude oils," ed: Google Patents, 2005.
- [111] J. Y. Y. Z.C.Wen, X.R. Xu, B.C. Cao, J.S. Gao, "Microwave chemistry method removal of nickel and vanadium in crude oil," 2009.
- [112] S. Wang, X. Xu, J. Yang, and J. Gao, "Effect of the carboxymethyl chitosan on removal of nickel and vanadium from crude oil in the presence of microwave irradiation," *Fuel Processing Technology*, vol. 92, no. 3, pp. 486-492, 3// 2011.
- [113] K. A. Castro *et al.*, "Galactodendritic porphyrinic conjugates as new biomimetic catalysts for oxidation reactions," *Inorganic chemistry*, vol. 54, no. 9, pp. 4382-4393, 2015.
- [114] P. Sen *et al.*, "Fluorescence and FTIR Spectra Analysis of Trans-A (2) B (2)-Substituted Di-and Tetra-Phenyl Porphyrins," *Materials*, vol. 3, no. 8, pp. 4446-4475, 2010.
- [115] D. Kogelnig *et al.*, "Greener synthesis of new ammonium ionic liquids and their potential as extracting agents," *Tetrahedron Letters*, vol. 49, no. 17, pp. 2782-2785, 2008/04/21/ 2008.
- [116] P. Pirkwieser, J. A. Lopez-Lopez, W. Kandioller, B. K. Keppler, C. Moreno, and F. Jirsa, "Novel 3-Hydroxy-2-Naphthoate-Based Task-Specific Ionic Liquids for an Efficient Extraction of Heavy Metals," (in eng), *Front Chem*, vol. 6, p. 172, 2018.
- [117] S. Platzer *et al.*, "Task-specific thioglycolate ionic liquids for heavy metal extraction: Synthesis, extraction efficacies and recycling properties," *Journal of Hazardous Materials*, vol. 324, pp. 241-249, 2017/02/15/ 2017.
- [118] S. A. Dharaskar, K. L. Wasewar, M. N. Varma, D. Z. Shende, K. K. Tadi, and C. K. Yoo, "Synthesis, characterization, and application of novel trihexyl tetradecyl phosphonium bis (2,4,4-trimethylpentyl) phosphinate for extractive desulfurization of liquid fuel," *Fuel Processing Technology*, vol. 123, pp. 1-10, 2014/07/01/ 2014.
- [119] B. L. Hayes, *Microwave synthesis: chemistry at the speed of light*. Cem Corporation, 2002.
- [120] C. O. Kappe, "Controlled microwave heating in modern organic synthesis," *Angewandte Chemie International Edition*, vol. 43, no. 46, pp. 6250-6284, 2004.
- [121] C. O. Kappe, A. Stadler, and D. Dallinger, *Microwaves in organic and medicinal chemistry*. John Wiley & Sons, 2012.
- [122] X. Jiayi, "Microwave irradiation and selectivities in organic reactions," *PROGRESS IN CHEMISTRY-BEIJING-*, vol. 19, no. 5, p. 700, 2007.
- [123] G. B. Dudley, R. Richert, and A. Stiegman, "On the existence of and mechanism for microwave-specific reaction rate enhancement," *Chemical science*, vol. 6, no. 4, pp. 2144-2152, 2015.
- [124] P.-K. Chen, M. R. Rosana, G. B. Dudley, and A. Stiegman, "Parameters affecting the microwave-specific acceleration of a chemical reaction," *The Journal of organic chemistry*, vol. 79, no. 16, pp. 7425-7436, 2014.
- [125] M. R. Rosana *et al.*, "Microwave-specific acceleration of a Friedel–Crafts reaction: Evidence for selective heating in homogeneous solution," *The Journal of organic chemistry*, vol. 79, no. 16, pp. 7437-7450, 2014.

- [126] W. F. McDonough and S. s. Sun, "The composition of the Earth," *Chemical Geology*, vol. 120, no. 3, pp. 223-253, 1995/03/01/ 1995.
- [127] E. Bulska *et al.*, "Inductively coupled plasma mass spectrometry in comparison with neutron activation and ion chromatography with UV/VIS detection for the determination of lanthanides in plant materials," *Talanta*, vol. 97, pp. 303-311, 2012/08/15/ 2012.
- [128] J. A. D'Angelo, L. D. Martinez, S. Resnizky, E. Perino, and E. J. Marchevsky, "DETERMINATION OF EIGHT LANTHANIDES IN APATITES BY ICP-AES, XRF, AND NAA," *Journal of Trace and Microprobe Techniques*, vol. 19, no. 1, pp. 79-90, 2001/03/28 2001.
- [129] R. S. Dyczyński, E. Czerska, B. Danko, K. Kulisa, and Z. Samczyński, "Comparison of performance of INAA, RNAA and ion chromatography for the determination of individual lanthanides," *Applied Radiation and Isotopes*, vol. 68, no. 1, pp. 23-27, 2010/01/01/ 2010.
- [130] C. Chilian and G. Kennedy, "The NAA method at Polytechnique Montreal: an efficient alternative way to use the k0 NAA models," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 300, no. 2, pp. 533-538, 2014/05/01 2014.
- [131] M. Abdollahi Neisiani, M. Latifi, J. Chaouki, and C. Chilian, "Novel approach in k0-NAA for highly concentrated REE Samples," *Talanta*, vol. 180, pp. 403-409, 2018/04/01/ 2018.
- [132] S. Horikoshi and N. Serpone, "Role of microwaves in heterogeneous catalytic systems," *Catalysis Science & Technology*, vol. 4, no. 5, pp. 1197-1210, 2014.
- [133] N. F. K. Kaiser, U. Bremberg, M. Larhed, C. Moberg, and A. Hallberg, "Fast, Convenient, and Efficient Molybdenum-Catalyzed Asymmetric Allylic Alkylation under Noninert Conditions: An Example of Microwave-Promoted Fast Chemistry," *Angewandte Chemie International Edition*, vol. 39, no. 20, pp. 3595-3598, 2000.
- [134] M. Gupta and E. W. W. Leong, *Microwaves and metals*. John Wiley & Sons, 2008.
- [135] M. Asemani and A. R. Rabbani, "Oil-oil correlation by FTIR spectroscopy of asphaltene samples," *Geosciences Journal*, journal article vol. 20, no. 2, pp. 273-283, April 01 2016.
- [136] M. R. Derrick, D. Stulik, and J. M. Landry, *Infrared spectroscopy in conservation science*. Getty Publications, 2000.
- [137] D. W. Mayo, F. A. Miller, and R. W. Hannah, *Course notes on the interpretation of infrared and Raman spectra*. John Wiley & Sons, 2004.
- [138] D. L. Pavia, G. M. Lampman, G. S. Kriz, and J. A. Vyvyan, *Introduction to spectroscopy*. Cengage Learning, 2008.
- [139] M. Khuhawar, M. A. Mirza, and T. Jahangir, "Determination of metal ions in crude oils," in *Crude oil emulsions-Composition stability and characterization: InTech*, 2012.
- [140] X. Li and J. Xu, "Effects of the Microwave Power on the Microwave-assisted Esterification," *Current Microwave Chemistry*, vol. 4, no. 2, pp. 158-162, 2017.
- [141] B. Knight and A. Westwood, "World biomass review: Biomass as a global power source," *Refocus*, vol. 5, no. 6, pp. 42-44, 2004.
- [142] G. Berndes, M. Hoogwijk, and R. van den Broek, "The contribution of biomass in the future global energy supply: a review of 17 studies," *Biomass and Bioenergy*, vol. 25, no. 1, pp. 1-28, 2003.
- [143] F. Sherif and C. Jamal, "Energy and chemicals from biomass & waste: the state of the art," *Submitted for publication*.
- [144] J. S. Tumuluru, S. Sokhansanj, C. T. Wright, R. D. Boardman, and N. A. Yancey, "A Review on Biomass Classification and Composition, Co-Firing Issues and Pretreatment Methods," Idaho National Laboratory (INL)2011.
- [145] G. Tao, T. A. Lestander, P. Geladi, and S. Xiong, "Biomass properties in association with plant species and assortments I: A synthesis based on literature data of energy properties," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 5, pp. 3481-3506, 2012.

- [146] J. M. F. Johnson, A. J. Franzluebbbers, S. L. Weyers, and D. C. Reicosky, "Agricultural opportunities to mitigate greenhouse gas emissions," *Environmental Pollution*, vol. 150, no. 1, pp. 107-124, 2007.
- [147] P. McKendry, "Energy production from biomass (part 1): overview of biomass," *Bioresource Technology*, vol. 83, no. 1, pp. 37-46, 5// 2002.
- [148] G. Tao, P. Geladi, T. A. Lestander, and S. Xiong, "Biomass properties in association with plant species and assortments. II: A synthesis based on literature data for ash elements," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 5, pp. 3507-3522, 2012.
- [149] C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, and Y. Y. Lee, "Coordinated development of leading biomass pretreatment technologies," *Bioresource Technology*, vol. 96, no. 18, pp. 1959-1966, 2005.
- [150] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, and D. B. Levin, "Biomass pretreatment: fundamentals toward application," *Biotechnology advances*, vol. 29, no. 6, pp. 675-685, 2011.
- [151] A. R. Womac *et al.*, "Shearing characteristics of biomass for size reduction," in *ASAE Annual International Meeting*, 2005.
- [152] S. Sokhansanj, S. Mani, X. Bi, P. Zaini, and L. Tabil, "Binderless pelletization of biomass," in *2005 ASAE Annual Meeting*, 2005, p. 1: American Society of Agricultural and Biological Engineers.
- [153] P. D. Grover and S. K. Mishra, *Biomass briquetting: technology and practices*. Food and Agriculture Organization of the United Nations, 1996.
- [154] M. J. C. Van der Stelt, H. Gerhauser, J. H. A. Kiel, and K. J. Ptasinski, "Biomass upgrading by torrefaction for the production of biofuels: a review," *Biomass and bioenergy*, vol. 35, no. 9, pp. 3748-3762, 2011.
- [155] O. Hjelm, "Disposal strategies for municipal solid waste incineration residues," *Journal of Hazardous Materials*, vol. 47, no. 1-3, pp. 345-368, 1996.
- [156] T. Sabbas *et al.*, "Management of municipal solid waste incineration residues," *Waste Management*, vol. 23, no. 1, pp. 61-88, 2003.
- [157] A. A. Zorpas *et al.*, "Compost produced from organic fraction of municipal solid waste, primary stabilized sewage sludge and natural zeolite," *Journal of hazardous materials*, vol. 77, no. 1, pp. 149-159, 2000.
- [158] I. Déportes, J.-L. Benoit-Guyod, and D. Zmirou, "Hazard to man and the environment posed by the use of urban waste compost: a review," *Science of the Total Environment*, vol. 172, no. 2, pp. 197-222, 1995.
- [159] V. N. Gunaseelan, "Anaerobic digestion of biomass for methane production: a review," *Biomass and bioenergy*, vol. 13, no. 1, pp. 83-114, 1997.
- [160] X. Tong, L. H. Smith, and P. L. McCarty, "Methane fermentation of selected lignocellulosic materials," *Biomass*, vol. 21, no. 4, pp. 239-255, 1990.
- [161] D. Das and T. N. Veziroğlu, "Hydrogen production by biological processes: a survey of literature," *International Journal of Hydrogen Energy*, vol. 26, no. 1, pp. 13-28, 2001.
- [162] R. Datar, J. Huang, P.-C. Maness, A. Mohagheghi, S. Czernik, and E. Chornet, "Hydrogen production from the fermentation of corn stover biomass pretreated with a steam-explosion process," *International Journal of Hydrogen Energy*, vol. 32, no. 8, pp. 932-939, 2007.
- [163] Y. Lin and S. Tanaka, "Ethanol fermentation from biomass resources: current state and prospects," *Applied microbiology and biotechnology*, vol. 69, no. 6, pp. 627-642, 2006.
- [164] F. W. Bai, W. A. Anderson, and M. Moo-Young, "Ethanol fermentation technologies from sugar and starch feedstocks," *Biotechnology advances*, vol. 26, no. 1, pp. 89-105, 2008.
- [165] F. Orecchini and E. Bocci, "Biomass to hydrogen for the realization of closed cycles of energy resources," *Energy*, vol. 32, no. 6, pp. 1006-1011, 2007.

- [166] S. Farag and J. Chaouki, "Economics evaluation for on-site pyrolysis of kraft lignin to value-added chemicals," *Bioresource Technology*, vol. 175, no. 0, pp. 254-261, 1// 2015.
- [167] R. C. Saxena, D. K. Adhikari, and H. B. Goyal, "Biomass-based energy fuel through biochemical routes: A review," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 1, pp. 167-178, 1// 2009.
- [168] R. C. Saxena, D. Seal, S. Kumar, and H. B. Goyal, "Thermo-chemical routes for hydrogen rich gas from biomass: A review," *Renewable and Sustainable Energy Reviews*, vol. 12, no. 7, pp. 1909-1927, 9// 2008.
- [169] H. B. Goyal, D. Seal, and R. C. Saxena, "Bio-fuels from thermochemical conversion of renewable resources: A review," *Renewable and Sustainable Energy Reviews*, vol. 12, no. 2, pp. 504-517, 2// 2008.
- [170] A. V. Bridgwater, D. Meier, and D. Radlein, "An overview of fast pyrolysis of biomass," *Organic Geochemistry*, vol. 30, no. 12, pp. 1479-1493, 12// 1999.
- [171] A. V. Bridgwater and G. V. C. Peacocke, "Fast pyrolysis processes for biomass," *Renewable and Sustainable Energy Reviews*, vol. 4, no. 1, pp. 1-73, 3// 2000.
- [172] A. Bridgwater, "Thermal conversion of biomass and waste: the status," *Birmingham (UK): Bio-Energy Research Group, Aston University*, 2001.
- [173] A. Bridgwater, Peacocke, GVC. , "Fast pyrolysis processes for biomass," *Renew Sustain Energy* vol. 4, pp. 1-73, Rev 2000.
- [174] A. Q. Desmond Radlein, "A short historical review of fast pyrolysis of biomass," *Oil and Gas Science and Technology, Institut Fran cais du P etrole*, vol. 68 no. 4, pp. 765-783, 2013.
- [175] !!! INVALID CITATION !!! [1, 32-36].
- [176] P. Basu, *Biomass gasification and pyrolysis: practical design and theory*. Academic press, 2010.
- [177] B. V. Babu, "Biomass pyrolysis: a state-of-the-art review," vol. Birla Institute of Technology and Science, Pilani, India.
- [178] G. Varhegyi, M. J. Antal, E. Jakab, and P. Szabó, "Kinetic modeling of biomass pyrolysis," *Journal of analytical and Applied Pyrolysis*, vol. 42, no. 1, pp. 73-87, 1997.
- [179] P. Wang, S. Hedges, K. Chaudharib, and R. Turtonb, "Kinetic study of coal and biomass co-pyrolysis using thermogravimetry," National Energy Technology Laboratory-In-house Research 2013.
- [180] A. W. C. A. J. P. REDFERN, "Thermogravimetric Analysis - A Review," vol. Chemistry Department, Battersea College of Technology, London, S. W. 11.
- [181] K. Raveendran, A. Ganesh, and K. C. Khilar, "Pyrolysis characteristics of biomass and biomass components," *Fuel*, vol. 75, no. 8, pp. 987-998, 1996.
- [182] A. O. Oyedun, C. Z. Tee, S. Hanson, and C. W. Hui, "Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends," *Fuel Processing Technology*, vol. 128, pp. 471-481, 12// 2014.
- [183] A. Demirbaş, "Biomass resource facilities and biomass conversion processing for fuels and chemicals," *Energy Conversion and Management*, vol. 42, no. 11, pp. 1357-1378, 7// 2001.
- [184] A. V. Bridgwater, "Principles and practice of biomass fast pyrolysis processes for liquids," *Journal of Analytical and Applied Pyrolysis*, vol. 51, no. 1-2, pp. 3-22, 7// 1999.
- [185] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68-94, 3// 2012.
- [186] S. Czernik and A. V. Bridgwater, "Overview of Applications of Biomass Fast Pyrolysis Oil," *Energy & Fuels*, vol. 18, no. 2, pp. 590-598, 2004/03/01 2004.
- [187] J. Yanik, C. Kornmayer, M. Saglam, and M. Yüksel, "Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products," *Fuel Processing Technology*, vol. 88, no. 10, pp. 942-947, 10// 2007.

- [188] W. T. Tsai, M. K. Lee, and Y. M. Chang, "Fast pyrolysis of rice husk: Product yields and compositions," *Bioresource Technology*, vol. 98, no. 1, pp. 22-28, 1// 2007.
- [189] H. S. Heo *et al.*, "Fast pyrolysis of rice husk under different reaction conditions," *Journal of Industrial and Engineering Chemistry*, vol. 16, no. 1, pp. 27-31, 1/25/ 2010.
- [190] S. Farag and J. Chaouki, "Technical and Economical Feasibility of Pyrolysis of Kraft Lignin," in *Materials for Oil, Gas & Biofuels Chapter 4, Materials for Energy, Efficiency and Sustainability: TechConnect Briefs*, Washington, DC, 2015, pp. 168 - 171.
- [191] J. Shabanian and J. Chaouki, "Influence of interparticle forces on solids motion in a bubbling gas-solid fluidized bed," *Submitted for publication publication. Powder Technol.*
- [192] M. Balat, M. Balat, E. Kirtay, and H. Balat, "Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems," *Energy Conversion and Management*, vol. 50, no. 12, pp. 3147-3157, 12// 2009.
- [193] W. N. R. W. Isahak, M. W. M. Hisham, M. A. Yarmo, and T.-y. Yun Hin, "A review on bio-oil production from biomass by using pyrolysis method," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 5910-5923, 10// 2012.
- [194] E. M. Rubin, "Genomics of cellulosic biofuels," (in eng), *Nature*, vol. 454, no. 7206, pp. 841-5, Aug 14 2008.
- [195] P. J. de Wild, W. J. J. Huijgen, and H. J. Heeres, "Pyrolysis of wheat straw-derived organosolv lignin," *Journal of Analytical and Applied Pyrolysis*, vol. 93, no. 0, pp. 95-103, 2012.
- [196] W. Mu, H. Ben, A. Ragauskas, and Y. Deng, "Lignin Pyrolysis Components and Upgrading—Technology Review," (in English), *BioEnergy Research*, pp. 1-22, 2013/02/27 2013.
- [197] J. Zakzeski, P. C. Bruijninx, A. L. Jongerius, and B. M. Weckhuysen, "The catalytic valorization of lignin for the production of renewable chemicals," *Chemical Reviews*, vol. 110, no. 6, p. 3552, 2010.
- [198] J. Kibet, L. Khachatryan, and B. Dellinger, "Molecular Products and Radicals from Pyrolysis of Lignin," *Environmental Science & Technology*, vol. 46, no. 23, pp. 12994-13001, 2012/12/04 2012.
- [199] T. Dickerson and J. Soria, "Catalytic fast pyrolysis: a review," *Energies*, vol. 6, no. 1, pp. 514-538, 2013.
- [200] D. Vamvuka, "Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—An overview," *International Journal of Energy Research*, vol. 35, no. 10, pp. 835-862, 2011.
- [201] J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius, and B. M. Weckhuysen, "The Catalytic Valorization of Lignin for the Production of Renewable Chemicals," *Chemical Reviews*, vol. 110, no. 6, pp. 3552-3599, 2010.
- [202] G. Jiang, D. J. Nowakowski, and A. V. Bridgwater, "Effect of the temperature on the composition of lignin pyrolysis products," *Energy & Fuels*, vol. 24, no. 8, pp. 4470-4475, 2010.
- [203] F. S. Chakar and A. J. Ragauskas, "Review of current and future softwood kraft lignin process chemistry," *Industrial Crops and Products*, vol. 20, no. 2, pp. 131-141, 9// 2004.
- [204] C. Liu, H. Wang, A. M. Karim, J. Sun, and Y. Wang, "Catalytic fast pyrolysis of lignocellulosic biomass," *Chemical Society Reviews*, 10.1039/C3CS60414D vol. 43, no. 22, pp. 7594-7623, 2014.
- [205] D. Fu, S. Farag, J. Chaouki, and P. G. Jessop, "Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent," *Bioresource Technology*, vol. 154, no. 0, pp. 101-108, 2// 2014.
- [206] B. P. Mudraboyina, S. Farag, A. Banerjee, J. Chaouki, and P. G. Jessop, "Supercritical Fluid Rectification of Lignin Pyrolysis Oil Methyl Ether (LOME) and Its Use as a Bio-derived Aprotic Solvent," *Green Chemistry*, 10.1039/C5GC02233A 2015.

- [207] V. K. Guda, P. H. Steele, V. K. Penmetsa, and Q. Li, "Chapter 7 - Fast Pyrolysis of Biomass: Recent Advances in Fast Pyrolysis Technology," in *Recent Advances in Thermo-Chemical Conversion of Biomass*, A. P. B. S. K. Sukumaran, Ed. Boston: Elsevier, 2015, pp. 177-211.
- [208] S. Beis *et al.*, "Fast pyrolysis of lignins," *BioResources*, vol. 5, no. 3, pp. 1408-1424, 2010.
- [209] V. B. F. Custodis, P. Hemberger, Z. Ma, and J. A. van Bokhoven, "Mechanism of Fast Pyrolysis of Lignin: Studying Model Compounds," *The Journal of Physical Chemistry B*, vol. 118, no. 29, pp. 8524-8531, 2014/07/24 2014.
- [210] M. Balat, "Mechanisms of Thermochemical Biomass Conversion Processes. Part 1: Reactions of Pyrolysis," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 30, no. 7, pp. 620-635, 2008/03/03 2008.
- [211] P. Patel, T. R. Hull, R. W. McCabe, D. Flath, J. Grasmeyer, and M. Percy, "Mechanism of thermal decomposition of poly(ether ether ketone) (PEEK) from a review of decomposition studies," *Polymer Degradation and Stability*, vol. 95, no. 5, pp. 709-718, 5// 2010.
- [212] H. S. Choi and D. Meier, "Fast pyrolysis of Kraft lignin—Vapor cracking over various fixed-bed catalysts," *Journal of Analytical and Applied Pyrolysis*, vol. 100, no. 0, pp. 207-212, 2013.
- [213] D. Lin, W. Ze, L. Songgeng, S. Wenli, and L. Weigang, "A Comparison of Monomeric Phenols Produced from Lignin by Fast Pyrolysis and Hydrothermal Conversions," *International Journal of Chemical Reactor Engineering*, vol. 11, p. 85 (11 pp.), 05/ 2013.
- [214] D. Klemm, B. Heublein, H. P. Fink, and A. Bohn, "Cellulose: fascinating biopolymer and sustainable raw material," (in eng), *Angew Chem Int Ed Engl*, vol. 44, no. 22, pp. 3358-93, May 30 2005.
- [215] D. Shen, R. Xiao, S. Gu, and H. Zhang, "The Overview of Thermal Decomposition of Cellulose in Lignocellulosic Biomass," *Edited by Theo van de Ven and John Kadla*, p. 193, 2013.
- [216] D. Shen, R. Xiao, S. Gu, and K. Luo, "The pyrolytic behavior of cellulose in lignocellulosic biomass: a review," *RSC Advances*, 10.1039/C1RA00534K vol. 1, no. 9, pp. 1641-1660, 2011.
- [217] S. Omori, M. Aoyama, and A. Sakakibara, "Hydrolysis of Lignin with Dioxane-Water XIX. Reaction of β -O-4 Lignin Model Compounds in the Presence of Carbohydrates," *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood*, vol. 52, no. 4, pp. 391-397, 1998.
- [218] P. R. Patwardhan, R. C. Brown, and B. H. Shanks, "Product distribution from the fast pyrolysis of hemicellulose," (in eng), *ChemSusChem*, vol. 4, no. 5, pp. 636-43, May 23 2011.
- [219] Q. Bu *et al.*, "A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis," *Bioresource Technology*, vol. 124, pp. 470-477, 11// 2012.
- [220] S. Wan and Y. Wang, "A review on ex situ catalytic fast pyrolysis of biomass," (in English), *Frontiers of Chemical Science and Engineering*, vol. 8, no. 3, pp. 280-294, 2014/09/01 2014.
- [221] J. Wildschut, F. H. Mahfud, R. H. Venderbosch, and H. J. Heeres, "Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts," *Industrial & Engineering Chemistry Research*, vol. 48, no. 23, pp. 10324-10334, 2009/12/02 2009.
- [222] R. Venderbosch, A. Ardiyanti, J. Wildschut, A. Oasmaa, and H. Heeres, "Stabilization of biomass-derived pyrolysis oils," *Journal of chemical technology and biotechnology*, vol. 85, no. 5, pp. 674-686, 2010.
- [223] D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness, and A. H. Zacher, "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products," *Environmental progress & sustainable energy*, vol. 28, no. 3, pp. 441-449, 2009.
- [224] A. Gutierrez, R. Kaila, M. Honkela, R. Slioor, and A. Krause, "Hydrodeoxygenation of guaiacol on noble metal catalysts," *Catalysis today*, vol. 147, no. 3, pp. 239-246, 2009.

- [225] K. Wang, K. H. Kim, and R. C. Brown, "Catalytic pyrolysis of individual components of lignocellulosic biomass," *Green Chemistry*, 10.1039/C3GC41288A vol. 16, no. 2, pp. 727-735, 2014.
- [226] S. D. Stefanidis, K. G. Kalogiannis, E. F. Iliopoulou, C. M. Michailof, P. A. Pilavachi, and A. A. Lappas, "A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin," *Journal of Analytical and Applied Pyrolysis*, vol. 105, pp. 143-150, 1// 2014.
- [227] M. Syamsiro *et al.*, "Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors," *Energy Procedia*, vol. 47, pp. 180-188, // 2014.
- [228] G. Yildiz *et al.*, "Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading," *Journal of Analytical and Applied Pyrolysis*, vol. 103, pp. 343-351, 2013.
- [229] P. R. Patwardhan, J. A. Satrio, R. C. Brown, and B. H. Shanks, "Influence of inorganic salts on the primary pyrolysis products of cellulose," *Bioresource Technology*, vol. 101, no. 12, pp. 4646-4655, 6// 2010.
- [230] J. D. Adjaye and N. N. Bakhshi, "Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts," *Fuel Processing Technology*, vol. 45, no. 3, pp. 161-183, 12// 1995.
- [231] S. P. Katikaneni, J. D. Adjaye, and N. N. Bakhshi, "Conversion of canola oil to various hydrocarbons over Pt/HZSM-5 bifunctional catalyst," *The Canadian Journal of Chemical Engineering*, vol. 75, no. 2, pp. 391-401, 1997.
- [232] A. Aho, N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D. Y. Murzin, "Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure," *Fuel*, vol. 87, no. 12, pp. 2493-2501, 9// 2008.
- [233] P. A. Horne, N. Nugranad, and P. T. Williams, "Catalytic coprocessing of biomass-derived pyrolysis vapours and methanol," *Journal of Analytical and Applied Pyrolysis*, vol. 34, no. 1, pp. 87-108, 6// 1995.
- [234] X. Li *et al.*, "Catalytic fast pyrolysis of Kraft lignin with HZSM-5 zeolite for producing aromatic hydrocarbons," (in English), *Frontiers of Environmental Science & Engineering*, vol. 6, no. 3, pp. 295-303, 2012/06/01 2012.
- [235] J. Encinar, J. Gonzalez, G. Martínez, and S. Roman, "Catalytic pyrolysis of exhausted olive oil waste," *Journal of Analytical and Applied Pyrolysis*, vol. 85, no. 1, pp. 197-203, 2009.
- [236] S. Boust, M. Green, and S. Machi, "Fluidized Catalytic Cracking to Convert Biomass to Fuels," 2015.
- [237] I. Babich, M. Van der Hulst, L. Lefferts, J. Moulijn, P. O'Connor, and K. Seshan, "Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels," *Biomass and bioenergy*, vol. 35, no. 7, pp. 3199-3207, 2011.
- [238] P. U. Karanjkar *et al.*, "Production of aromatics by catalytic fast pyrolysis of cellulose in a bubbling fluidized bed reactor," *AIChE Journal*, vol. 60, no. 4, pp. 1320-1335, 2014.
- [239] C. Mukarakate *et al.*, "Catalytic fast pyrolysis of biomass: the reactions of water and aromatic intermediates produces phenols," *Green Chemistry*, vol. 17, no. 8, pp. 4217-4227, 2015.
- [240] V. L. Budarin *et al.*, "The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw," *Bioresource Technology*, vol. 100, no. 23, pp. 6064-6068, 2009.
- [241] B. K. Adnadjević and J. D. Jovanović, "Kinetics of Isothermal Ethanol Adsorption onto a Carbon Molecular Sieve under Conventional and Microwave Heating," *Chemical Engineering & Technology*, vol. 35, no. 4, pp. 761-768, 2012.
- [242] Z. Li, L. Han, and W. Xiao, "Influence of microwave heating on the liquefaction kinetics of corn stover in ethylene glycol," *BioResources*, vol. 8, no. 3, pp. 3453-3460, 2013.

- [243] B. a. Temur Ergan and M. Bayramoğlu, "Kinetic Approach for Investigating the "Microwave Effect": Decomposition of Aqueous Potassium Persulfate," *Industrial & Engineering Chemistry Research*, vol. 50, no. 11, pp. 6629-6637, 2011/06/01 2011.
- [244] G. D. Yadav and I. V. Borkar, "Kinetic modeling of microwave-assisted chemoenzymatic epoxidation of styrene," *AIChE Journal*, vol. 52, no. 3, pp. 1235-1247, 2006.
- [245] B. K. Adnadjevic and J. D. Jovanovic, "A comparative kinetics study on the isothermal heterogeneous acid-catalyzed hydrolysis of sucrose under conventional and microwave heating," *Journal of Molecular Catalysis A: Chemical*, vol. 356, no. 0, pp. 70-77, 2012.
- [246] B. Adnađević, M. Gigov, M. Sindjic, and J. Jovanović, "Comparative study on isothermal kinetics of fullerol formation under conventional and microwave heating," *Chemical Engineering Journal*, vol. 140, no. 1-3, pp. 570-577, 2008.
- [247] J. Fukushima *et al.*, "In-situ kinetic study on non-thermal reduction reaction of CuO during microwave heating," *Materials Letters*, vol. 91, no. 0, pp. 252-254, 2013.
- [248] J. Sun, W. Wang, Z. Liu, Q. Ma, C. Zhao, and C. Ma, "Kinetic Study of the Pyrolysis of Waste Printed Circuit Boards Subject to Conventional and Microwave Heating," *Energies*, vol. 5, no. 9, pp. 3295-3306, 2012.
- [249] F. Chen *et al.*, "Kinetics of glycolysis of poly(ethylene terephthalate) under microwave irradiation," *Journal of Applied Polymer Science*, vol. 127, no. 4, pp. 2809-2815, 2013.
- [250] W. Yan, X. Hu, G. Zhang, M. Deng, C. Yi, and Z. Xu, "Microwave assisted preparation of monodisperse polymeric microspheres and its morphologies and kinetics," (in English), *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, vol. 27, no. 6, pp. 1100-1104, 2012/12/01 2012.
- [251] P. Max, T. Klaus, and W. Ronald, *Plant Design and Economics for Chemical Engineers*. New York, USA: The McGraw Hill Companies, 2012.
- [252] K. Vanreppelen, T. Kuppens, T. Thewys, R. Carleer, J. Yperman, and S. Schreurs, "Activated carbon from co-pyrolysis of particle board and melamine (urea) formaldehyde resin: A techno-economic evaluation," *Chemical Engineering Journal*, vol. 172, no. 2-3, pp. 835-846, 8/15/ 2011.
- [253] Y. Zhang, T. R. Brown, G. Hu, and R. C. Brown, "Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose," *Bioresource Technology*, vol. 127, pp. 358-365, 1// 2013.
- [254] R. P. Anex *et al.*, "Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways," *Fuel*, vol. 89, Supplement 1, pp. S29-S35, 11/1/ 2010.
- [255] A. V. Bridgwater, A. J. Toft, and J. G. Brammer, "A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion," *Renewable and Sustainable Energy Reviews*, vol. 6, no. 3, pp. 181-246, 9// 2002.
- [256] D. Brown, A. Rowe, and P. Wild, "A techno-economic analysis of using mobile distributed pyrolysis facilities to deliver a forest residue resource," *Bioresource Technology*, vol. 150, pp. 367-376, 12// 2013.
- [257] T. R. Brown, R. Thilakaratne, R. C. Brown, and G. Hu, "Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing," *Fuel*, vol. 106, pp. 463-469, 4// 2013.
- [258] B. Li *et al.*, "Techno-economic and uncertainty analysis of in situ and ex situ fast pyrolysis for biofuel production," *Bioresource Technology*, vol. 196, pp. 49-56, 11// 2015.
- [259] S. Shabangu, D. Woolf, E. M. Fisher, L. T. Angenent, and J. Lehmann, "Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts," *Fuel*, vol. 117, Part A, pp. 742-748, 1/30/ 2014.
- [260] M. B. Shemfe, S. Gu, and P. Ranganathan, "Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading," *Fuel*, vol. 143, pp. 361-372, 3/1/ 2015.

- [261] R. Thilakaratne, M. M. Wright, and R. C. Brown, "A techno-economic analysis of microalgae remnant catalytic pyrolysis and upgrading to fuels," *Fuel*, vol. 128, pp. 104-112, 7/15/ 2014.
- [262] A. Uslu, A. P. C. Faaij, and P. C. A. Bergman, "Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation," *Energy*, vol. 33, no. 8, pp. 1206-1223, 8// 2008.
- [263] M. M. Wright, D. E. Dagaard, J. A. Satrio, and R. C. Brown, "Techno-economic analysis of biomass fast pyrolysis to transportation fuels," *Fuel*, vol. 89, Supplement 1, pp. S2-S10, 11/1/ 2010.

**APPENDIX A US PATENT 1: REMOVAL OF METALS AND SULFUR
FROM PETROLEUM OIL USING A DEVELOPED DEMETALLIZATION
DESULFURIZATION AGENT AND RELATED TECHNIQUES**

US Provisional Patent Application Number: 62753071

INVENTORS

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FIELD OF THE INVENTION

The present invention generally relates to purification techniques and more particularly to techniques for removing or decreasing the metals and sulfur content in petroleum oil.

ABSTRACT

Techniques to extract metals and sulfur from petroleum oil are provided. The techniques described herein are not limited to the extraction of metals and sulfur but may also retrieve other impurities that may be present in petroleum oil. The techniques described herein may be applied to any form or phase of petroleum oil. The techniques described herein can be integrated into the current oil processing processes and/or performed as a separate process.

**APPENDIX B US PATENT 2: MICROWAVE PROCESS FOR THE
REMOVAL OF METALS FROM PETROLEUM OIL USING A
DEVELOPED DEMETALLIZATION AND RELATED TECHNIQUES**

US Provisional Patent Application Number: 62758227

INVENTORS

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APPLICANT

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FIELD OF THE INVENTION

The present invention generally relates to purification techniques and more particularly to techniques for removing or decreasing the metals content in petroleum oil using microwaves.

ABSTRACT

A microwave process for the extraction of metals from petroleum oil is provided. The techniques described herein are not limited to the extraction of metals but may also retrieve other impurities that may be present in petroleum oil. The techniques described herein may be applied to any form or phase of petroleum oil. The techniques described herein can be integrated into the current oil processing processes and or performed as a separate process.

**APPENDIX C US PATENT 3: MICROWAVE PROCESS FOR THE
REMOVAL OF SULFUR FROM PETROLEUM OIL USING A
DEVELOPED DESULFURIZATION AGENT AND RELATED
TECHNIQUES**

US Provisional Patent Application Number: 62758251

INVENTORS

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FIELD OF THE INVENTION

The present invention generally relates to purification techniques and more particularly to techniques for removing or decreasing the sulfur content in petroleum oil using microwaves.

ABSTRACT

A microwave process for the extraction of various sulfur derivatives from petroleum oil is provided. The techniques described herein are not limited to the extraction of sulfur but may also retrieve other impurities that may be present in petroleum oil. The techniques described herein may be applied to any form or phase of petroleum oil. The techniques described herein can be integrated into the current oil processing processes and or performed as a separate process.

APPENDIX D US PATENT 4: REMOVAL OF CADMIUM FROM PHOSPHATE USING A DEVELOPED DECADMIATION AGENT AND RELATED TECHNIQUES

US Provisional Patent Application Number: 62692669

INVENTORS

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APPLICANT

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FIELD OF THE INVENTION

The present invention generally relates to purification techniques and more particularly to techniques for removing or decreasing the cadmium content in phosphate.

ABSTRACT

Techniques to extract cadmium from phosphate are provided. The techniques described herein are not limited to the extraction of cadmium but may also retrieve other impurities that may be present in phosphate. The techniques described herein may be applied to any form or phase of phosphate, including – but not limited to – phosphate rocks, phosphate slurry, and phosphoric acids. The techniques described herein can be integrated into the current phosphate processing processes and/or performed as a separate process. On top of that, it can be applied during the transportation of the materials in pipelines or tanks, and/or in storage reservoirs. Consequently, it would lead to opening the door in front of the phosphate that contains trace metals and impurities for potential marketing in several counties.

APPENDIX E US PATENT 5: REMOVAL OF ZINC, SULFUR, AND OTHER METALS AND IMPURITIES FROM PYROLYSIS CHAR USING AND RELATED TECHNIQUES

US Provisional Patent Application Number: 62703421

INVENTORS

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APPLICANT

Mai Attia, Sherif Farag, and Jamal Chaouki

FIELD OF THE INVENTION

The present invention relates to techniques for removing or decreasing the zinc, sulfur, and other metals and impurities content in pyrolysis char.

ABSTRACT

Techniques to extract zinc from pyrolysis char are provided. The techniques described herein are not limited to the extraction of zinc but also can extract or remove sulfur, and other metals and impurities that may be present in pyrolysis char. The techniques described herein may be applied on any form or phase of pyrolysis char. It can be integrated into the current pyrolysis processes and/or performed in a separate process. Such techniques, consequently, open the door to employ pyrolysis char in a wide range of applications.

APPENDIX F ARTICLE 4: FAST PYROLYSIS OF LIGNOCELLULOSIC BIOMASS FOR THE PRODUCTION OF ENERGY AND CHEMICALS: A CRITICAL REVIEW

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Abstract

As a consequence of the shortage of traditional resources and escalating environmental constraints, the feedstocks for the production of energy and chemicals are swiftly changing. Biomass has received remarkable attention from both academia and industries as it is the most promising feedstock for these applications. Understanding the conversion mechanisms of such renewable low-value material to value-added products would lead to providing insights to enhance the product yield and/or quality and, in turn, help the new products compete with the traditional ones. In this regard, this paper provides an updated review on the processing of biomass for the production of valuable-products that could replace a part of the fossil fuel-based energy and chemicals. The common technologies that are performed in the conversion processes are demonstrated, and the thermochemical technique is emphasized. Several chemical reactors and their processes for fast pyrolysis applications are presented. The organic chemistry of pyrolysis of a biomass plant and its three constituents (i.e., cellulose, hemicellulose, and lignin) is debated. The effect of the heating

mechanism, process parameters, loading of catalyst and other aspects are discussed. Eventually, the economics aspect of fast pyrolysis of biomass is evaluated.

Keywords: Fast pyrolysis; pyrolysis of biomass; biomass processing; pyrolysis technologies; pyrolysis processes; bio-products; microwave pyrolysis; techno-economic analyses.

1. Introduction

The scarcity of sustainable oil resources combined with the rapid depletion of available reserves has prompted the chemical industry to pursue alternative resources for essential chemical production. Moreover, the environmental concerns associated with the application of conventional fossil fuels have compelled the energy sector to develop renewable alternative resources. In 2010 a 5.6% increase in global energy consumption was reported by British Petroleum (BP), the highest increase since 1973, with China singled out as the greatest contributor with 20.3%. BP has estimated the total discovered oil reservoirs at 1383.2 thousand million barrels worldwide. Considering the current production rate, capacity, and global energy demands based on the available reserves to production rate, the existing reservoirs will only cover worldwide energy requirements for the next 45 years (BP Report 2011). Meanwhile, biomass material has been widely acclaimed as potential solutions to deliver raw feedstock to address global energy requirements and develop novel methods to produce value-added chemical products [52, 60, 141-143]. Biomass, the biological components derived from the living feedstock or recently living organisms, such as plants and animals, have been historically proven as the primary energy production resource through the combustion of forestry materials. Although the application of biomass as the leading energy source has significantly declined with the escalation in fossil fuel exploration, it still contributes to approximately 14% of the global annual energy consumption, the third major energy resource trailing oil and coal [144].

In general different types of biomass have been classified under the following categories [143-145]:

- *Agricultural residues*: The remaining of cultivated nutritional and industrial crops consisting of dry lignocellulosic residues and livestock waste, such as straws, crop residues and liquid and solid manure;
- *Energy crops*: High yield crops specifically cultivated for energy purposes, namely dry lignocellulosic woody energy crops, oil energy crops, dry lignocellulosic energy crops and starch energy crops;
- *Forestry residues*: The residuals of the forest or wood processing plants, such as bark, wood blocks, wood chips and log residues; and

- *Industrial residues*: Industrial and manufacturing residues, undesired by-products or secondary products, including wood, food and petrochemical residues.
- The major advantages of the application of biomass for energy and value-added chemical production are highlighted as follows [52, 145, 146]:
- *Renewability*: The feedstock is naturally reproduced and replenished simultaneously facilitating the regeneration of the raw material;
- *Carbon neutrality*: In the long-term life cycle foresight aspect, the amount of carbon produced during manufacturing and processing is neutralized by the amount absorbed and consumed through the cultivation period associated with the forestry and agricultural biomass;
- *Feasible economy*: In general, biomass material possesses extremely low or even negative initial value, which maintains the feedstock economy significantly supportive;
- *Versatility*: Biomass material can be transformed into energy or recovered as valuable chemical components through numerous methods enabling dynamic conversion methods based on the economy and local requirements; and
- *Environmental impacts*: Due to the chemical composition of the biomass material, namely low sulphur, chlorine and metal free composition, the application of biomass reduces the environmental impacts drastically specifically compared with fossil fuels and petroleum based products.

However, in spite of all the advantages of the application of biomass, extremely high investment costs for biomass conversion plants, uncertainty over the feedstock supply levels due to seasonal production variations, and limited infrastructure for biomass production in various countries have globally restricted its commercial applications.

Biomass properties principally dictate the application of the feedstock for further conversion or treatment purposes. Essential characteristics of biomass material for consideration as energy or chemical feedstock material have been highlighted as moisture content (intrinsic and extrinsic), fixed and volatile carbon ratio, heating value, ash and other residual content, alkali and heavy metal content and lignocellulosic composition [147]. The carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S) and ash (A) content of the biomass material, further referred as CHONSA, has a substantial effect on energy and chemical characteristics [145]. Table 1 has summarized the

CHONSA data for multiple popular biomass materials. The analysis of typical biomass properties has been thoroughly presented in the available literature [55, 56, 145, 147, 148].

Table 1 Typical CHONSA analysis for different biomass materials (wt. %) [53, 56, 147]

Material	C	H	O	N	S	A
Ash	49.7	6.9	3.0	-	-	0.3
Beech	51.6	6.3	41.4	-	-	-
Sawdust	48.3	6.22	45.2	0.22	0	2.9
Barley Straw	45.7	6.1	38.3	0.4	0.1	6
Bituminous	73.1	5.5	8.7	1.4	1.7	9
Coal						
Cypress	55.0	6.5	38.1	-	-	0.4
Kraft lignin	63.3	5.8	29.2	0.1	1.6	1
Miscanthus	48.1	5.4	42.2	0.5	<0.1	2.8
Rice Straw	41.4	5	39.9	0.7	0.1	-
Wood	51.6	6.3	41.5	-	0.1	1
Wheat Straw	48.5	5.5	3.9	0.3	0.1	4

* Combined for N and S

Biomass pre-treatment is an essential step in increasing the economic feasibility and process efficiency of biomass conversion into energy and chemical products by reducing transportation expenses, boosting the quality of the feedstock, maximizing the loading capacity of the reactor and modifying the structure of the biomass material [149]. Major biomass pre-treatment methods have been listed as follows:

- *Washing/leaching*: Reduction of alkali metal compounds using water, acid or ammonia. The presence of alkali metals in the feedstock reduces the reaction yield and damages the reactor through corrosion or blockage build-up [150];
- *Grinding*: Reducing the size of the biomass particles to increase the efficiency of the gasification process by increasing the surface area and minimizing the heat and mass transfer limitations using grinding or hammer mills for particles < 5 mm, drum chippers or disk chippers for particles 5-50 mm and chunkers for particles > 50 mm [151];
- *Pelletizing*: Compacting the low bulk density biomass particles to very high energy density cylinders 6-8 mm in diameter in order to reduce transportation costs and deal with the limited capacity of the reactors, hence maximizing the feedstock loading [152];

- *Briquetting*: Converting the biomass particles into briquettes to increase the bulk density (from 60-180 kg/m³ for loose biomass to 800-1200 kg/m³) in order to address transportation, storage and feeding issues [153]; and
- *Torrefaction*: Treatment of biomass by the thermo-chemical method at 200-300 °C and the absence of oxygen to increase the uniformity of the feedstock and other purposes [154].

The available pre-treatment methods and their advantages and drawbacks have been thoroughly investigated in the available literature [149, 150].

Due to the diversity in the biomass feedstock, various recovery techniques have been implemented to eliminate or convert the material into fuel and value-added chemicals. However, each method has its unique advantages and drawbacks associated with economic and environmental impacts. The available biomass treatment methods have been classified as follows:

- *Incineration*: Generally regarded as an alternative waste disposal method to landfills in geographical locations with restrictions on availability or accessibility of space. Although it deemed as a feasible technique to minimize the material volume by 90% and recovers a significant margin of the waste material energy, the environmental threats in the form of air pollution and treatment of the ash residues, with a long term leaching risk, have sparked a high level of controversy on the general implementation [155, 156].
- *Compost production*: A duplication of the mineralization of material as the natural recycling process, compost production is a rapidly emerging method as an alternative to landfills for yard waste and agricultural residues. The advantages of composting over conventional landfilling are reduced volume of the material by up to 50%, termination of contagious pathogens during the thermophile phase and production of value-added chemicals, soil conditioners and fertilizers, from negative value feedstock. On the contrary, the prospect of the presence of hazardous microorganisms and heavy metals, namely arsenic, asbestos, chromium and nickel classified under carcinogens, may potentially contaminate the soil and penetrate the water reservoirs [157, 158].
- *Biological Treatment*: The biological conversion of biomass to liquid and gaseous fuels, primarily methane [159, 160], hydrogen [161, 162] and ethanol [163, 164] through anaerobic digestion and fermentation methods, has gained growing attention due to the environmental

impact compared to petroleum based fuels. Moreover, the biological conversion of biomass reduces the disposal problems while contributing to the regional sustainable development by providing alternative substrates to agro-industrial residues.

- *Thermochemical treatment*: The conversion of biomass material into energy, liquid and gaseous fuels, and chemical products with the application of thermal treatment or chemical reactions has been regarded as an optimistic resolution to address associated concerns with fossil fuels and waste management [60, 165, 166].

Generally speaking, energy and chemicals can be produced from biomass via thermo-chemical and/or biological processes [167, 168]. In general, thermo-chemical processes demonstrated a superior ability to destroy most of the organic compounds. Lignin materials, which are typically considered to be non-fermentable and thereby cannot be completely decomposed via biological approaches, are however decomposable via thermo-chemical techniques [52, 55, 56, 166, 169]. Furthermore, the thermo-chemical process can be implemented with a lower reaction time, i.e., a few seconds or minutes for thermo-chemical processes vs. several days, weeks or even longer for biological processes [170, 171].

The main factor controlling the thermochemical conversion mechanism is the percentage of oxygen in the environment where the target is treated. Based on this factor, the process can be named as combustion, gasification, or pyrolysis [52, 60, 172, 173]. Combustion is normally an exothermic reaction, which is performed in a rich-oxygen environment. This process is mainly applied for energy production purposes and, therefore, produces exhaust gases and water. It is not recommended at all to directly burn the raw biomass due to several environmental constraints. Instead, the feedstock can be converted to a liquid and/or gas product and then dealt with. Gasification is a thermochemical conversion technique that is accomplished in presence of oxygen at a concentration less than that of the combustion processes. Heating a material in a partial oxidation environment will lead to breakdown the target material's network at a temperature higher than that of pyrolysis. The main product from gasification processes is syngas, which has a potential of several applications. In addition, a by-product that contains extremely heavy molecular weight aromatics, known by "tar", is also produced. Gasification processes can be designed so that the system receives the needed heat energy from an external heating source or by burning a part of the feedstock/product. Pyrolysis is specified as a set of chemical reactions that take place when an

adequate amount of heat energy is supplied to the target in an oxygen-free environment. The primary products from pyrolysis are condensable gas, which is mostly chemicals and water, permanent gasses, such as carbon monoxide, carbon dioxide, methane hydrogen, etc., and solid, which is mostly carbon [52, 55, 56]. The yield and quality of the pyrolysis products are influenced by the applied technology, process parameters, characteristics of the feedstock, and other factors [52, 174].

The present study reviews the available technologies for processing biomass for the production of energy and chemicals, emphasizing the pyrolysis technique. In the sections below, the popular chemical reactors employed in the thermochemical treatment are demonstrated. Then, the organic chemistry of pyrolysis of the biomass plant and its three constituents is discussed. Subsequently, the effect of the heating mechanism, process parameters, loading the catalyst among other aspects is debated. Finally, strategic procedures to investigate the technical and economic aspects of a proposed process are demonstrated.

2. Fast pyrolysis of biomass

Pyrolysis is the thermal cracking of carbonaceous material into lower density components in the absence of oxygen. The thermal degradation of biomass leads to the production of char, oil and syngas products [175-177]. Thermal gravity analysis (TGA) of biomass revealed that there are three stages for a typical pyrolysis process [178-180]. The first stage accompanied by a slight weight loss takes place between 120 °C and 200 °C. This is due to the internal rearrangements, such as bond breakage, appearance of free radicals, and the formation of carbonyl groups, as well as a resulting release of small amounts of H₂O, CO, and CO₂. Next or in the second stage, with an increase in temperature the main pyrolysis process occurs leading to solid decomposition. This is demonstrated by a significant weight loss from the initially-fed biomass. Finally, further cleavage of C–H and C–O bonds causes continuous char devolatilization [181, 182].

Pyrolysis can be divided into fast, intermediate, and slow processes based on the reaction temperature and residence time. Generally speaking, fast pyrolysis has an extremely short residence time, less than a second; the reaction temperature is approximately 100 °C higher than that of slow pyrolysis [171]. Moreover, short reaction times associated with a high temperature result in a greater yield of liquid product, whereas slow pyrolysis with relatively lower reaction temperatures and longer residence times would produce fairly equal amounts of liquid, solid char, and gas

products. Therefore, to maximize the charcoal yield, a low temperature and low heating rates are necessary, whereas if liquid is the desired product, a combination of moderate temperature, short pyrolysis vapor residence time, and a high heating rate are required [183]. Table 2 illustrates a comparison between the pyrolysis conditions (maximum temperature range, residence time, and heating rate) and the product yields of different pyrolysis modes. As can be seen, fast pyrolysis produces the maximum liquid yield and minimum solid residue compared to the other techniques at almost the same average temperature. In fact, this aspect shows that the process fulfills the economics and product yields and quality requirements for the production of bio-oil and, therefore, receives noticeable interest from industries [171, 184]. In the next section, we will elucidate the features of fast pyrolysis, which predominantly shapes the frame of this review article.

Table 2 Applied conditions and product distribution of different pyrolysis modes (wt. %) [52, 185]

Process	Process parameters			Liquid	Solid	Gas
	Temperature °C	Residence time	Heating rate			
Torrefaction	200 - 300	~10-66 min	Slow	0 - 5%	~ 80%	~ 20%
Slow Pyrolysis	400 - 500	hours	Slow	~ 30%	~ 35%	~ 35%
Intermediate pyrolysis	450 - 500	~10-30 s	Medium	~ 50%	~ 25%	~ 25%
Fast pyrolysis	400 - 650	~ 1 s	High	~ 75%	~ 12%	~ 13%

A high heating rate (as high as thousands of °C/min) and a short hot vapor residence time in the reaction zone are required to implement the fast pyrolysis process [171, 186]. It is a more advanced process that can be carefully controlled to give high yields of liquid, but inhibit the formation of solid chars [169]. This dark brown mobile liquid product is composed of an aqueous phase containing several organo-oxygen compounds of low molecular weight, and a non-aqueous phase (tar) encompassing a variety of insoluble aromatic organic compounds of high molecular weight. The major product from fast pyrolysis is a potential liquid fuel that can be readily stored and transported. This is beneficial when biomass resources are at a distance from where the energy is required. The physical properties of the bio-oil are comparable with the properties of a typical

heavy fuel oil [186]. Specifically, bio-oil has a high water content (15–30 wt.%), a low corrosive pH (<3), a much higher oxygen content (35–40 wt.%) as well as a higher heating value (HHV) of 16–19 MJ/kg compared to around 44 MJ/kg for conventional fuel oil. In addition, high-quality fuels can be produced by a further upgrade of bio-oils as a feedstock for chemical production [171]. The main applications of the fast pyrolysis products are presented in Figure 1.

Liquid yield in a fast pyrolysis process can be improved up to 80 wt.% on dry feed by controlling either the material characteristics or operating conditions of the process. For instance, a finer particle size (smaller than 1 mm) can increase the liquid production. In addition, the temperature of the process must be controlled; it has been reported that optimal temperatures should be in the range of 450° C to 550° C to obtain the highest bio-oil yield of several biomass types [185, 187]. A higher heating rate (>200° C/s), a shorter hot vapor residence time (<4 s with a typical value of 1 s), and rapid cooling of the vapours are other determining factors that result in higher liquid yields [188, 189].

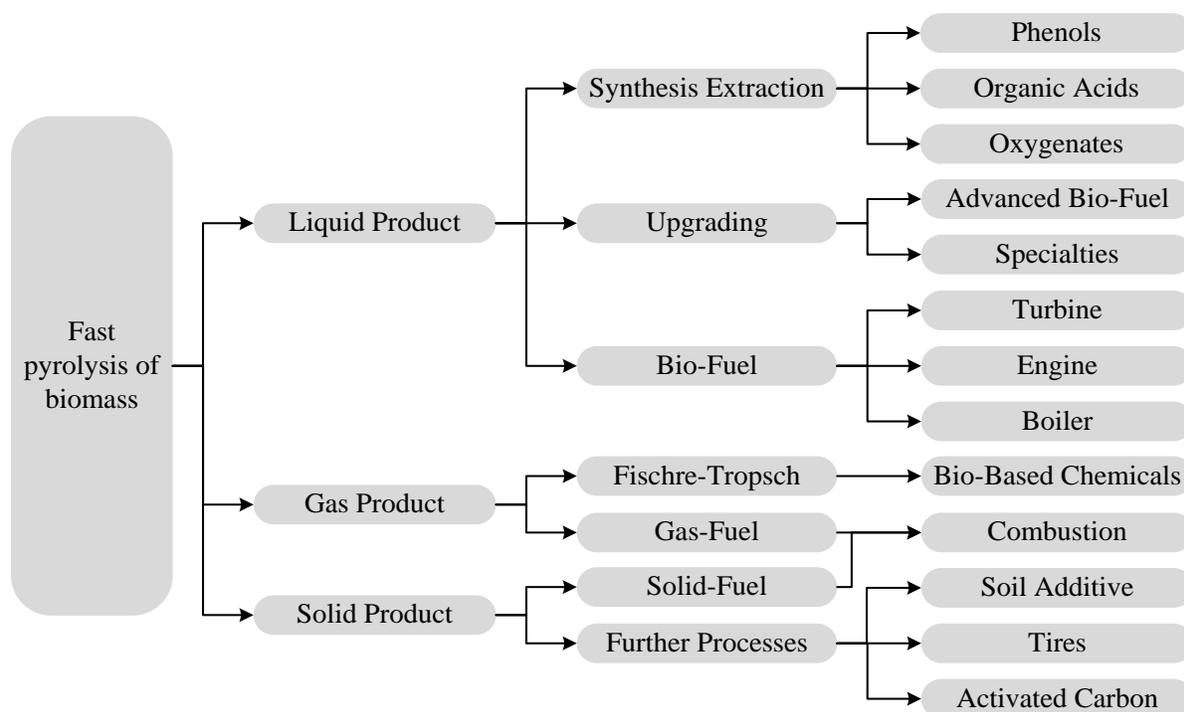


Figure 1 Applications for fast pyrolysis products [52, 56, 57, 143]

1.1 Industrial processes of fast pyrolysis

In pyrolysis processes, fast/slow techniques, industrial processes include four main steps: (1) pre-treatment, (2) thermal decomposition, (3) condensable gas recovery, and (4) heating generation. The pre-treatment step is essential to avoid any drawbacks that could negatively impact the yield and/or the quality of the pyrolysis products. The physical and chemical characteristics of the feedstock are the key parameters for selecting the appropriate and optimal technique for this assignment. Chopping and/or milling are the most commonly used techniques that are applied to reduce the average particle size of the processed material to the desirable range. This aspect dramatically reduces most of the heat and mass transfer limitations common in pyrolysis applications. In the case of processing a heterogeneous feedstock that includes a considerable concentration of metals or inorganics, a separation technique is a must to remove such materials from the feeding stream. Dealing with a wet-feedstock, such as wet biomass, sewage sludge, domestic waste, etc., requires a drying step to be constantly performed before the pyrolysis reactor. Decreasing the water content in the feedstock is definitely essential for increasing the quality of the liquid product and reducing the energy required for the decomposition reactions. The capacity of the selected drying system absolutely depends on the maximum operating flow rate of the plant and the maximum expected water content in the raw material, in addition to other factors.

Since the pyrolysis reactor is the main component of the process, it has received considerable attention from researchers to improve their understanding of its design, scale-up, and optimization. To design a pyrolysis reactor, it is necessary to know the kinetic parameters associated with the reactions taking place during the decomposition of the feedstock. In most cases, these parameters are estimated by performing a kinetic study on a laboratory scale. In some cases, the yield of the pyrolysis products obtained from lab works is also useful to achieve this aim. Together with the previous two factors, the capacity of the pyrolysis plant is the most important key for calculating the reactor volume and its total energy needs. It is worth noting that if enough heat energy is not provided for the pyrolysis reaction, the feedstock could form an extremely sticky block that once cooled becomes exceedingly difficult to break down [52, 55, 56, 166, 190]. Therefore, to ensure fully decomposing the feedstocks' network and unblocking the flow stream, the operating temperature of the pyrolysis reactor must meet the requirements at which the materials are decomposed [52, 55, 56, 190].

In order to not affect the yield and/or quality of the liquid product as a consequence of further undesirable reactions, the produced pyrolysis vapour must be quenched as soon as it exits the reactor. On an industrial or even laboratory scale, a multi-step condensation technique is employed to split the liquid phase into different portions based on the condensation temperature [56]. This technique decreases the effort made to extract/separate individual chemicals from the pyrolysis oil in the downstream processes. After collecting these liquids, careful handling and storage procedures must be followed to ensure the products are in compliance with the safety instructions as well as the technical guidelines.

In most pyrolysis plants, the heat energy required to break down the network of the raw material is provided by burning non-condensable gases. In this approach, pyrolysis gas is sent to a combustor to react with air, the result of which heats the pyrolysis reactor. To ensure enough oxygen is available to react with the hydrocarbon molecules in the combustible gases, 20% excess air is usually applied. For process integration, the exhaust gases from the combustion reactor, which is mostly carbon dioxide, could be used to dry the feedstock or in auxiliary processes, such as acidification in lignin precipitation from the pulp and paper industry. Nowadays, electromagnetic radiation is beginning to be applied in pyrolysis applications as it enhances the quality and in some cases the yield of the obtained products [60]. However, as a consequence of the high capital cost of the technology and the exponential increase of cost with the increase in plant size, MWH has not been industrialized yet for the pyrolysis of biomass/waste, even though remarkable findings have been reported [51, 190].

Occasionally, torrefaction is applied to decompose the side-chains of the feedstocks' network, which leads to significantly reducing the formation of water during the pyrolysis process. This aspect dramatically enhances the quality of the produced oil and, in turn, increases its commercial value [55]. Torrefaction is generally accomplished by heating the material to a temperature less than that of the decomposition point (200 °C - 300 °C) to avoid starting the pyrolysis step. Such a process can considerably help produce a product of high quality that could be used for a secondary process, such as liquid in the case of pyrolysis, syngas in the case of gasification, and energy in the case of combustion.

1.2 Fast pyrolysis reactors

Fast pyrolysis reactors are designed as to perfectly address two aspects, a high heating rate of the raw material and a low residence time of the pyrolysis vapour. In particular, a heating rate up to 10,000 °C/s and a residence time around less than a second is commonly applied. The maximum temperature of fast pyrolysis is close to that of slow pyrolysis, which is 400 °C - 600 °C. However, the key parameter that distinguishes between slow and fast pyrolysis is the time spent to reach the target temperature and that to remove the pyrolysis vapour from the reaction zone. Providing an intensive heat flux to a material that is a small particle size within a very short residence time is the chief factor behind enhancing the liquid product yield from fast pyrolysis processes. Rapidly cooling/quenching the pyrolysis vapour to condense the condensable-gas phase is also a key to increasing the liquid yield and avoiding undesirable reactions. It should be noted that the yield and composition of the liquid product are highly obscured by the nature of the feedstocks and the applied pyrolysis technology among other factors. In a few cases, decreasing the residence time of the pyrolysis vapour is a noteworthy matter since it might produce a liquid product with a considerable concentration of heavy molecular weight compounds. Actually, this aspect decreases the commercial value of the end-product and, accordingly, impacts the investment in the project. Therefore, it is highly recommended to consider this issue during the design of the pyrolysis reactors.

When selecting a fast pyrolysis technology, many aspects should be considered. The most important ones include the nature of the feedstock, the feeding rate of the raw material, the handling technique(s) of the pyrolysis products, target product yield and quality, cost-effectiveness, and other factors. Above all, the proposed reactor must meet the requirements of the fast pyrolysis technology for the high heating rate and short residence time.

1.2.1 Bubbling and circulating fluidized bed reactors

The most common reactor used in fast pyrolysis applications is the “bubbling fluidized bed.” In this technology, a gas phase, which is inert, is injected upward to fluidize the payload. The gas velocity at which the payload starts to fluidize and behave as a fluid phase is called minimum fluidization velocity. This velocity highly depends on the characteristics of the feedstock, the properties of the carrier gas, and the operating conditions. The gas phase is always injected at high

temperature and as a result it works as a heat carrier to heat up the target material to the decomposition point. As shown in Figure 2A, a bubbling fluidized bed pyrolysis reactor process consists of the pre-treatment, pyrolysis reactor, condensable gas recovery, and combustor. In addition, a cyclone is added to separate the solid particle suspended in the pyrolysis vapour. In some processes, the solid product collected from the cyclone is combusted and then recycled back to the reactor. The process in this case is called “circulating fluidized bed reactor,” which is demonstrated in Figure 2B.

The excellent heat and mass transfer of this technology is the key factor for dramatically increasing the heating rate of the feedstock. The high velocity of the injected gas is responsible for shortening the residence time of the pyrolysis vapour. These two aspects together are considered the main reasons behind successfully achieving the main objective of fast pyrolysis technology using this system. In addition, the high velocity of the carrier gas improves the char/vapour separation efficiency at the cyclone unit and, in turn, enhances the commercial value of the produced oil as a result of improving its quality. Moreover, the simple construction, ease of operation, and low maintenance cost are other advantages of the technology [191].

In contrast, bubbling fluidized bed reactors need a feedstock in the form of fine particles to be easily fluidized, the average size not greater than 2 mm, and at the same time a high surface area to achieve good heat transfer and a fast reaction. The bed height-to-diameter ratio is critical and must be carefully respected; otherwise, low thermal efficiency due to temperature gradients would take place inside the reaction zone. The high level of solid particles in the vapour products, the moderate level of tar, and the carefully controlled strategy to achieve the desired temperature are additional disadvantages for this technology.

1.2.2 Ablative pyrolysis reactors

The “ablative pyrolysis reactors” are quite different than the bubbling fluidized bed reactors in many respects, most importantly, the feeding mechanism and how the target material is heated, as shown in Figure 2C. In this technology, the payload is forced tangentially against a hot rotating disk, using a stream of gas. The disk is heated using an external source and then it heats the payload. Providing a high heat flux for the target and a short residence time for the pyrolysis vapour in the reaction zone are a must for achieving a high liquid yield.

The main advantages of this technology include the independence of the feedstock particle size and the good heat transfer to the target as a consequence of the direct contact between the hot surface and the decomposed material. In addition, the char layer formation common in traditional pyrolysis is avoided as a result of the material continuously corroding under thermal decomposition. This aspect actually allows the unreacted biomass to be heated directly and, in turn, avoids most of the issues regarding heat transfer limitations.

Complications associated with performing this technology, which includes heating the rotating disk, measuring the pyrolysis temperature, and other aspects, are the main issues for operating ablative pyrolysis reactors. The high particle surface to the relative velocity causes excessive wearing on the reactor internals, which leads to increases in maintenance expenditures and, therefore, the total operating cost of the system.

1.2.3 Twin screws reactors

The “twin screws reactor” is another technology for fast pyrolysis, which does not use carrier gas to fluidize the target material. It consists of two offset screws rotating in the same direction, as illustrated in Figure 2D. These screws are responsible for fluidizing the feedstock and transporting it through the reactor. Herein, heat is transferred from a heating source to the material via a heating carrier, which in most cases is sand. The high shear mixing of the biomass and continuous eroding of the char layer formatted on the surface of the heated material are the main advantages of this technology. The needs for feedstock with a small particle volume-to-surface ratio of less than 0.5 mm and a suitable technique to separate the particulates that are contained in the pyrolysis liquid are considered the main disadvantages of the technology.

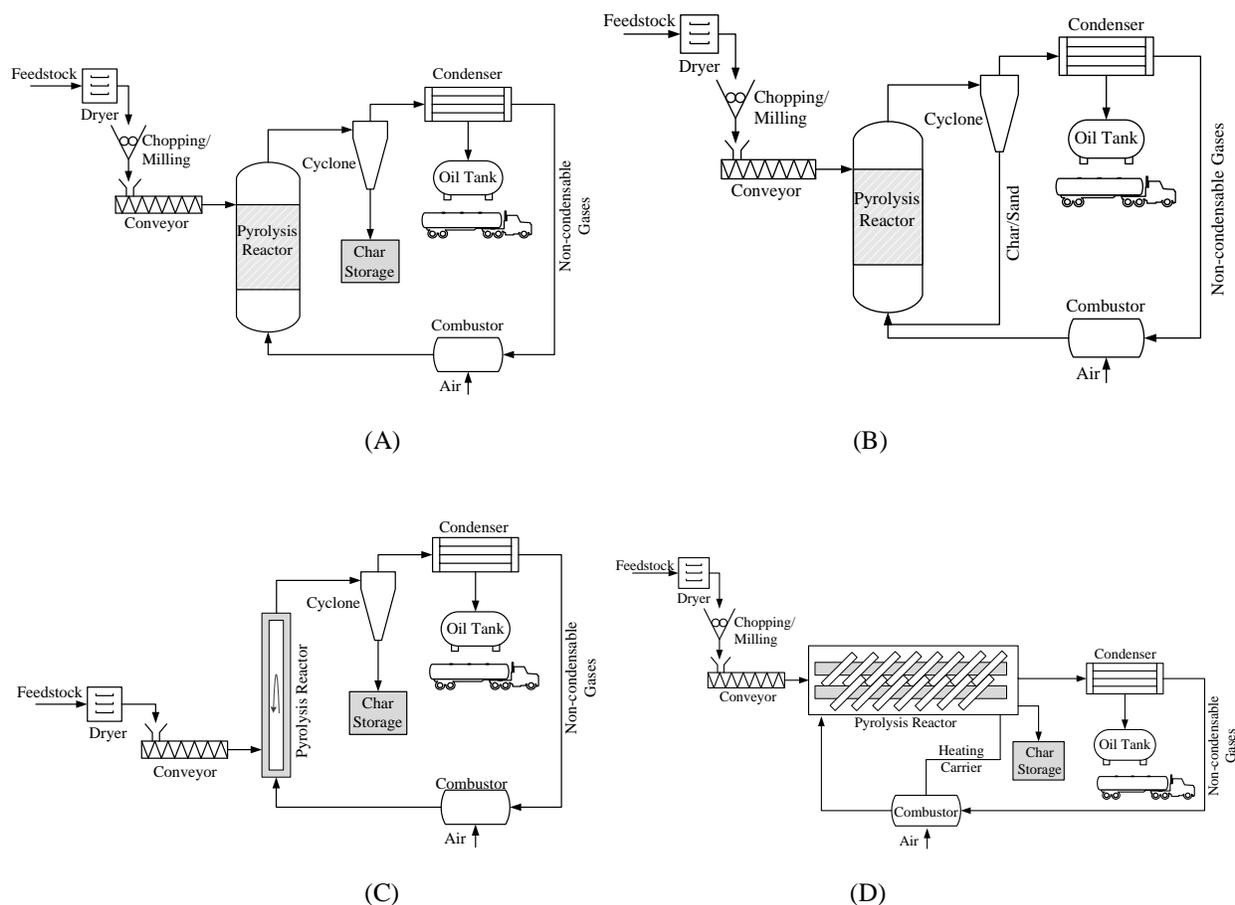


Figure 2 Common fast pyrolysis reactors in industrial processes: (A) bubbling fluidized bed, (B) circulating bubbling fluidized bed, (C) ablative, and (D) twin screw

2. Organic chemistry of fast pyrolysis of biomass

The persistent needs to develop new processes that can accept the intrinsic variability of feedstocks and fulfill the environmental constraints make it easy to understand why fast pyrolysis of biomass is receiving considerable attention in both academia and industry. Fast pyrolysis is mainly applied for the production of a liquid product and achieved by applying a high heating rate to the raw material and short residence time for the pyrolysis vapour [174, 185]. Accordingly, the main barriers that distinguish between the different pyrolysis modes, as shown in Table 1, are the heating

rate and the residence time [171, 185, 186, 192]. In addition, the nature of the feedstock and its chemical structure are other key factors that affect the yield and quality of the pyrolysis products. Thus, understanding the microstructure of the processed feedstock would lead to providing insights for producing an end-product with a desirable yield and properties.

A biomass plant mainly consists of three intertwined components: cellulose, hemicellulose, and lignin [52, 193, 194]. The distribution and characteristics of each component depend on many factors, such as the species, the plant age, the environment where the plant was grown, etc. [52]. The reported dry weight basis of each is 35-45% cellulose, 25–30% hemicellulose, and 20–35% lignin [52, 195-197]. Chemical structure is the key to distinguishing between these three components and to determine the resistance to degradation. Since hemicellulose is rich in branches, it is the weakest component compared to the other ones. Cellulose consists of long polymers of glucose without branches; thus, it is stronger than hemicellulose. The structure of lignin is completely different than cellulose and hemicellulose; it is mainly formed of aromatics with various branches, and the activity of bonds covers a wide range. This complex structure makes lignin the strongest component in a biomass plant and, therefore, the one with the highest resistance to decomposition [52, 55, 56, 166, 190].

Yang, H., et al. 2007 have individually investigated the thermochemical decomposition of cellulose, hemicellulose, and lignin over a temperature range of 25 °C to 900 °C in an inert environment, using a TGA. The decomposition of hemicellulose starts at 220 °C and the maximum solid residue is 20 wt. % at 900 °C. Between 360 °C and 400 °C, cellulose loses 93% of its initial mass, which is mainly due to its relatively simple chemical structure. Pyrolysis of lignin covers a temperature range of 100 °C - 900 °C, with a minimum solid residue of 45 wt. %. The structure of lignin is a three-dimensional, highly cross-linked amorphous polymer and, thus, it is considered one of the most complex organic aromatic polymers in nature. Therefore, its decomposition covers a wide temperature range with the maximum percentage of solid residue compared to cellulose and hemicellulose [196-198].

Pyrolysis, as a thermochemical process, contains a set of different reactions, including dehydration, dehydrogenation, polymerisation, depolymerisation, cracking, isomerization, fragmentation, rearrangement, and/or aromatization. Figure 3 shows some of the common reactions that are taking place during the process, which could be done in a forward and/or backward direction. Controlling

the reactions is intricate, or even, in some cases, impossible. Consequently, developing a method that can guarantee a desirable end-product is rather complex [199, 200]. Indeed, due to this aspect in addition to the complexity of the nature of the feedstock, the liquid product from the pyrolysis of biomass contains hundreds of fragments that are in different concentrations and properties. Figure 4 demonstrates some of the identified chemicals in a bio-oil from the fast pyrolysis of biomass.

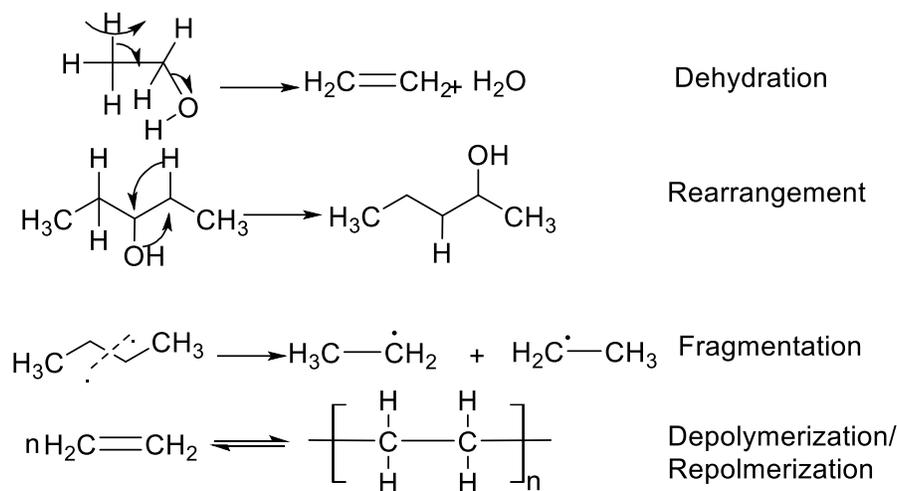


Figure 4 Different reactions take place during a pyrolysis process [199]

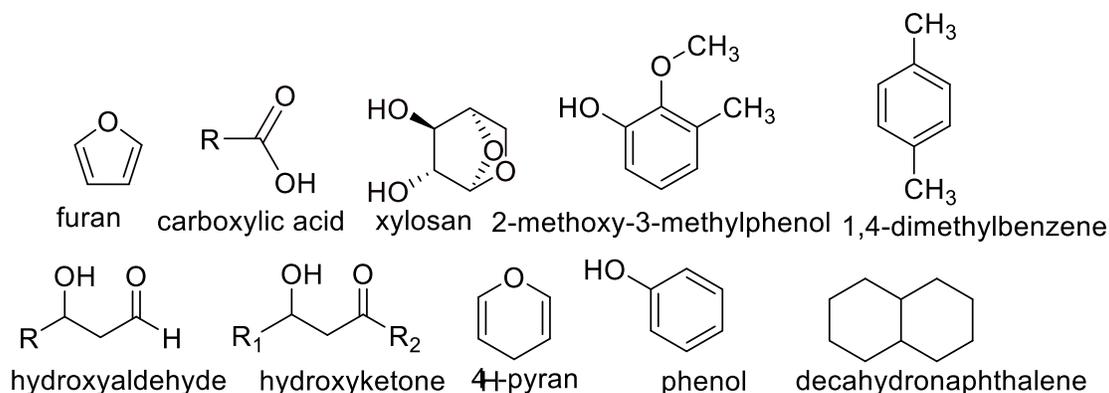


Figure 4 Chemical compounds identified in oils from the pyrolysis of biomass [52, 55, 56, 199]

In conclusion, the nature of the raw material together with the complexity of the reactions that are happening during the thermochemical decomposition of a material highly affect the yield and

chemical structure of the products and, as a result, the composition of the obtained liquids from the pyrolysis of biomass are extremely complex.

2.1 Degradation pathways of different materials

Biomass consists of long chain polymers of carbon atoms that are a combination of various chemical bonds between carbon and other elements, such as oxygen, hydrogen. While the long chain polymer is exposed to diverse ranges of temperatures during the pyrolysis process, it decomposes into smaller fragments due to bond cleavage. The amount of heat energy and heating rate, the bond nature, in addition to other factors control the rate of decomposition of the material network. To explain this aspect in detail, the three main compounds of biomass will be studied in the following sections of this chapter.

Although lignin is the only renewable resource of aromatics in nature, the exact structure of the untreated material is unknown [196-198]. The major building blocks of a lignin network are believed to be three aromatic alcohols: p-coumaryl, coniferyl, and sinapyl alcohol, as shown in Figure [195, 198, 201, 202]. These basic units are linked together through different positions to form diverse bonds, such as C-C and C-O bonds, as shown in Figure 6. Moreover, there are many side chains that are varied between long and short, e.g., hydroxy, methoxy, and sulfide groups. The type and concentration of each depends on the nature of the wood, soft/hard, the extraction process, kraft/organosolve, and other factors.

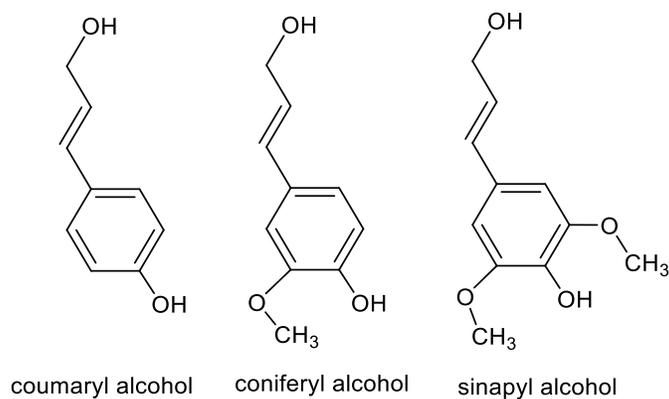


Figure 5 Main building blocks of lignin [52, 55]

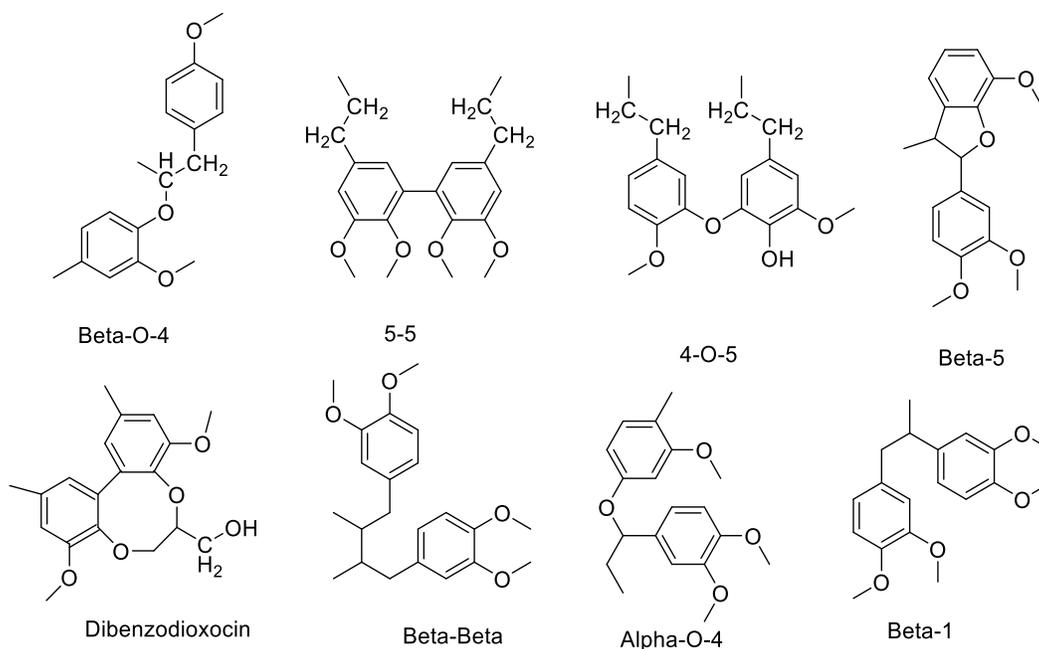


Figure 6 Common phenylpropane units in a lignin structure [52, 55, 203, 204]

Lignin is a complex heterogeneous aromatic polymer with many functional groups that make it look suitable for the production of many chemical compounds. Accordingly, modest efforts have been made over the last few years to provide a suite of technologies for developing high-value lignin-based products. This strategy, consequently, would benefit traditional paper mills by diversifying the range of products they can produce [52, 55-57, 166, 190, 205, 206]. Pyrolysis is the most promising technique that can deal with the huge amount of lignin produced worldwide [173, 185, 199, 207-209]. During the pyrolysis process, the lignin network decomposes through a set of reactions ranging from dehydration, rearrangement, radical, and elimination reactions. The process first occurs by bond cleavage between the phenyl propane units. Dehydration by the withdrawing of water molecules occurs due to a C-O bond break forming the guaiacol and di and tri methoxyacetophenone. This process is followed by the bond break of α and β -aryl-alkyl ether, then the liberation of the aliphatic side chains from the lignin structure. A relatively higher temperature is needed to the later bond break between the aromatic moiety and the side chain α -C atom [210]. Custodis, Hemberger et al. have studied the prospective pyrolysis pathways of lignin through the most common subunits diphenylether and guaiacole present in its structure [209]. As shown in Figure 7, the diphenylether unit decomposed through two different pathways “a” and “b”. In pathway “a”, the diphenylether underwent a bond cleavage between the oxygen and the phenyl

moiety forming phenyl and phenoxy radicals 1 and 2, respectively. Due to the high reactivity of both of the last two radicals, a recombination reaction between the diphenylether and the 1 and 2 radicals occurred. This reaction resulted in the formation of new compounds, such as 1,2-diphenoxybenzene, 3; 3,3'-diphenoxy-1,1'-biphenyl, 4; and 3-phenoxy-1,1'-biphenyl 5. A new compound 1,1'-biphenyl, 6, was produced through a combination of two phenyl radicals of 1 and 2 with water molecule formation. Benzene, 7, and phenol, 8, are also formed from phenyl and phenoxy radicals, respectively, as a result of the combination with two hydrogen radicals. A 6-membered ring opening followed by a 5-membered ring closure have taken place due to a carbon monoxide liberation from the phenoxyradical, 2, forming cyclopenta-1,3-diene, 9. The second pathway "b" of diphenylether was identified by the formation of dibenzofuran, 11, from the ring formation between diradicals, 10, [211].

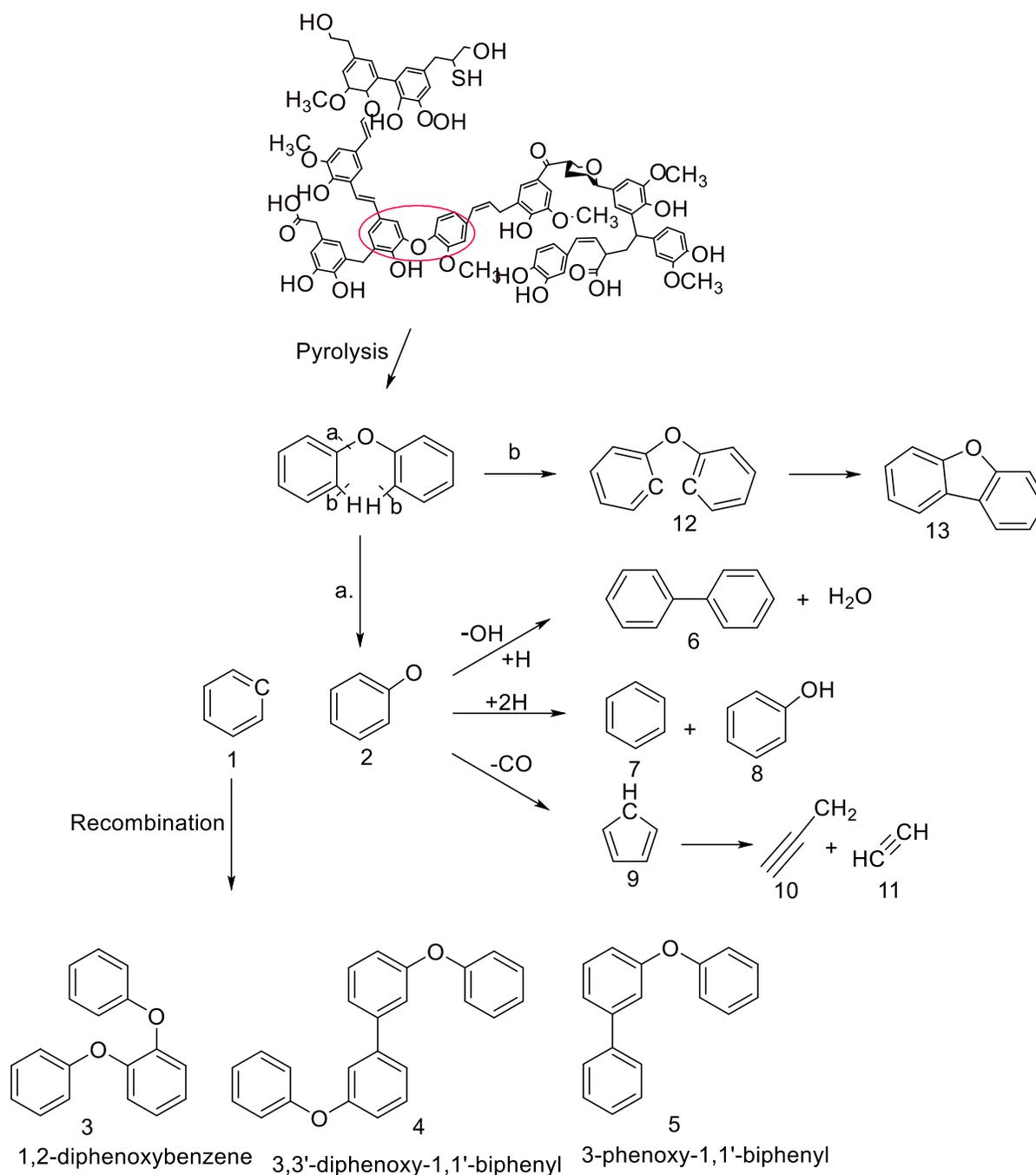


Figure 7 Suggested mechanisms of decomposition of diphenylether (Adapted with permission from Custodis, Hemberger et al. 2014 [209]. Copyright (2014) American Chemical Society)

Meanwhile, the pyrolysis process of guaiacole forms various chemical compounds, mostly phenolics, through several pathways of free radical reactions, as shown in Figure 8. The first

pathway “a” starts with bond cleavage between the methoxygroup and hydroxyphenyl moiety forming hydroxyphenyl radical. The formed radical, in turn, combined with the hydrogen radical forming the phenol compound, 1, that was exposed to liberation of the hydroxy radical and followed by the formation of the benzene ring, 2, and water. The bond between the methyl group and the 2-hydroxyphenoxy group were cleaved in pathway “b” forming the 2-Hydroxyphenoxy radical, which after further reaction gave a catechol compound. Further degradation occurred for catechol by the elimination of the carbon monoxide forming cyclopenta-2,4-dien-1-ol radical. Cyclopenta-2,4-dien-1-one, 5, is formed and, then, followed by the liberation of another carbon monoxide molecule resulting in a 5-membered ring opening to form the aliphatic but-1-en-3-yne compound, 6.

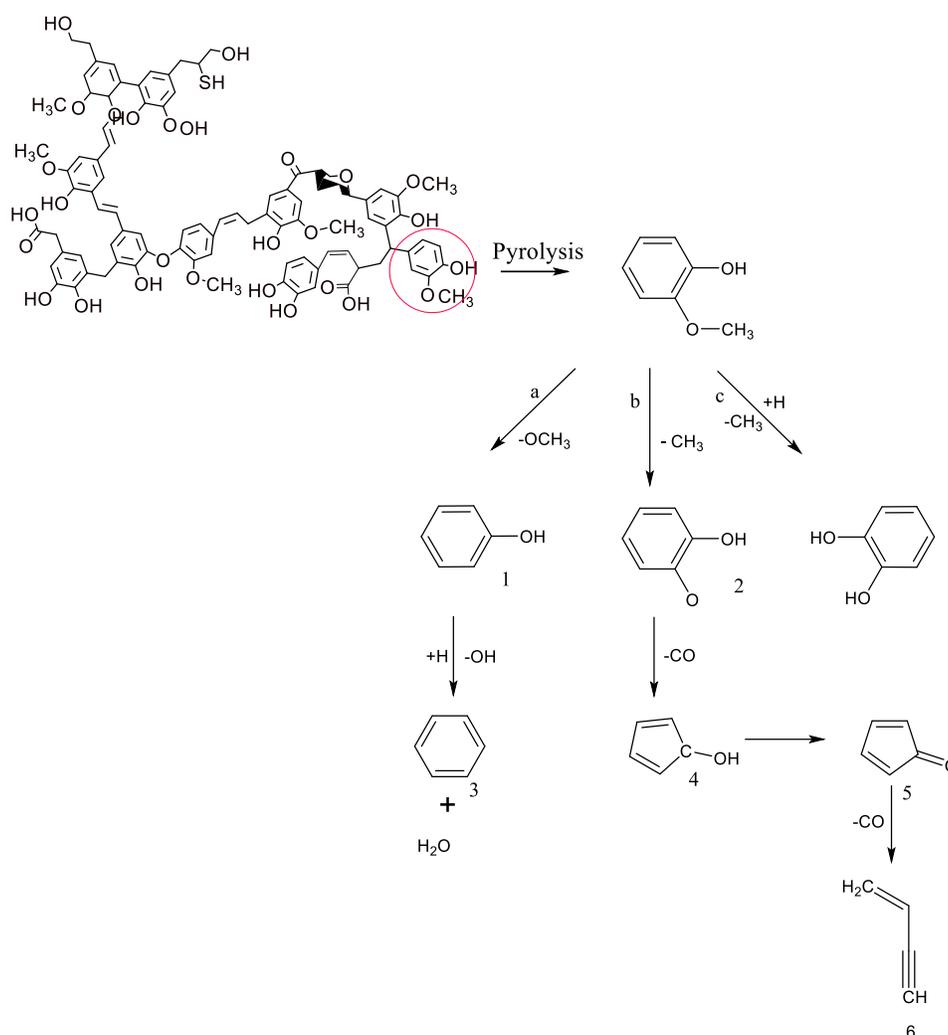


Figure 8 Suggested mechanisms of decomposition of guaiacol (Adapted with permission from Custodis, Hemberger et al. 2014 [209]. Copyright (2014) American Chemical Society)

Farag, Fu et al. 2014 have documented a detailed compositional analysis and structural investigation of a bio-oil from the pyrolysis of kraft lignin. One of the key conclusions stated that increasing the pyrolysis temperature augments the liquid product. A yield of 32 wt.% - 40 wt.% was obtained, which confirms the results reported by Choi and Meier. 2013 [212]. GC-MS analysis is inadequate to fully describe the composition of such liquids and, thus, a concentration up to 600 mg/g could not be identified using this technique. Up to 80% of the identified carbons in the oil phase using a Quantitative ^{13}C NMR spectroscopy are aromatic carbons, which is due to the chemical structure of the lignin network that is totally aromatics. The Quantitative ^{31}P NMR spectroscopy results show that the measured concentration of aliphatic hydroxyl groups in the oil phase is lower than the raw material by 90%, with respect to the virgin material. This decrease could refer to the swift decomposition of the raw material side chains, which might be attributed to forming water and/or unsaturated sites during the pyrolysis process, as presented in Figure 9-A. Farag and his co-authors tend to believe that the decomposition of the carboxyl group of a lignin network could be the source for the creation of carbon dioxide and/or unsaturated sites according to Figure 9-B. The identified concentration of aliphatic and C5 substituted/condensed phenolic hydroxyl groups in the oil phase is less than that in the virgin material. These decreases might be attributed to the increase in the concentrations of guaiacyl, *p*-hydroxyphenyl, and catechol hydroxyl groups in the oil phases compared to the raw lignin. Figure 10 demonstrates the suggested decomposition pathways by Farag, Fu et al. for the β -5 bond, the 4-O-5 bond, and the 5-5 bonds [55].

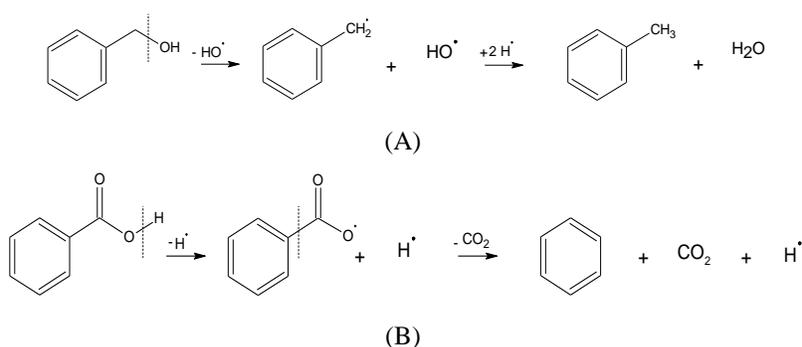


Figure 9 Possible degradation pathways for: (A) aliphatic hydroxyl group, and (B) carboxyl acid (Reprinted with permission from Farag, Fu et al. 2014 [55]. Copyright (2014) Elsevier B.V.)

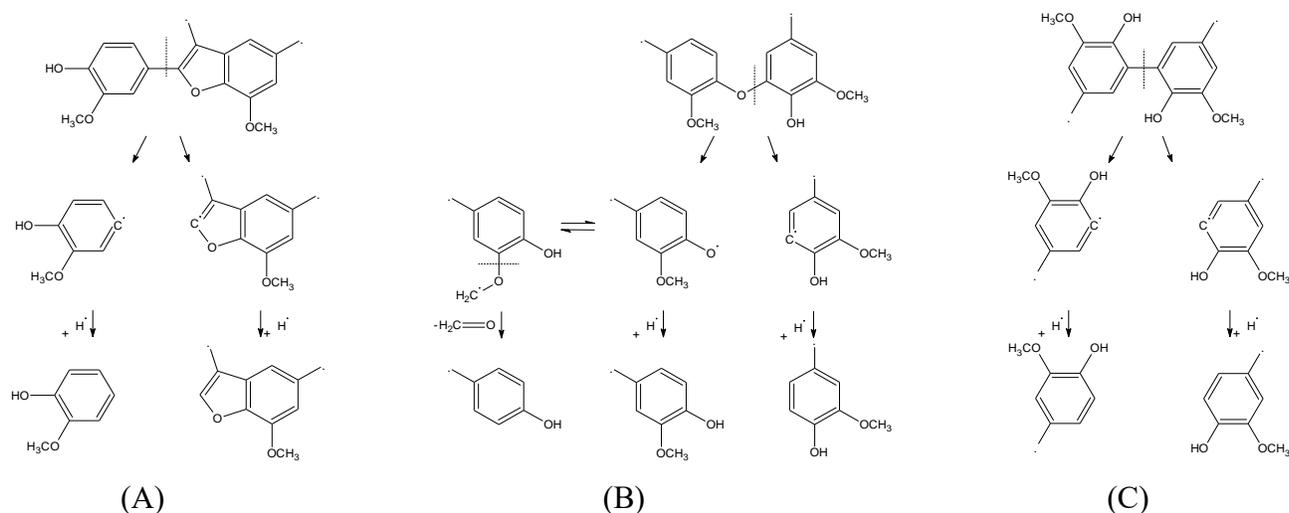


Figure 10 Possible degradation pathways of C5 substituted/condensed phenolic hydroxyl group: (A) β-5, (B) 4-O-5, and (C) 5-5 (Reprinted with permission from Farag, Fu et al. 2014 [55].

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A novel kinetics model to predict not only the yield of the pyrolysis products but also the composition of the liquid phase was documented by Farag, Kouisni et al. [56]. The model considers that the raw material is converted into seven products: (1) remaining solid, the produced bio-char; (2) non-condensable gases, which is the gas phase; (3) phenolics, the identified phenolic compounds using a GC-MS analysis; (4) ASR-Non-Ph, the identified single ring aromatics that are not phenols; (5) aliphatics, the identified aliphatic compounds using GC-MS analyses; (6) HMWC, the un-identified chemicals using GC-MS analysis, which might be heavy molecular weight compounds; and (7) water, which is formatted during the pyrolysis processes and probably from the decomposition of the aliphatic hydroxyl groups, as explained in Figure 9A. The summation of products 3, 4, 5, and 6 equals the oil phase yield, and if the water yield is taken into consideration, the result will be the total liquid yield. The reactions that are responsible for producing these seven products are considered a set of parallel reactions, as follows, which are governed by Equation (15). The kinetic parameters associated with the reactions presented in Equation (15) were estimated and tabulated in Table 2..

$$\begin{aligned}
\frac{dS}{dt} &= -k_{o_s} \left(e^{\frac{-E_{a_s}}{RT}} \right) (S - S_{\infty})^{n_s} \\
&= -k_{o_{Ph}} \left(e^{\frac{-E_{a_{Ph}}}{RT}} \right) (S - S_{\infty})^{n_{Ph}} \\
&\quad - k_{o_{ASR-Non-Ph}} \left(e^{\frac{-E_{a_{ASR-Non-Ph}}}{RT}} \right) (S - S_{\infty})^{n_{ASR-Non-Ph}} \\
&\quad - k_{o_a} \left(e^{\frac{-E_{a_a}}{RT}} \right) (S - S_{\infty})^{n_a} - k_{o_{HMWC}} \left(e^{\frac{-E_{a_{HMWC}}}{RT}} \right) (S - S_{\infty})^{n_{HMWC}} \\
&\quad - k_{o_w} \left(e^{\frac{-E_{a_w}}{RT}} \right) (S - S_{\infty})^{n_w} - k_{o_g} \left(e^{\frac{-E_{a_g}}{RT}} \right) (S - S_{\infty})^{n_g}
\end{aligned} \tag{15}$$

Table 2 Estimated kinetic parameters of the kinetic model developed by Farag, Kouisni et al.

2014 [56]

Product	ko [min-1]	Ea [kJ/mol]
Remaining Solid	7	19
Phenolics	21	38
ASR-Non-Ph	1	40
Aliphatics	20	47
HMWC	22	35
Water	9	27
Non-Condensable Gas	6	22

First order of reaction rate was considered (i.e., in Equation (15) all ns=1)

The authors have claimed that at any temperature up to 725 K, the obtained gas phase yield is slightly higher than that of the liquid phase, while beyond this temperature the result is the reverse. The authors have interpreted this as most of the decomposition reactions at a temperature less than 725 K are for the swift split of the raw material site chains and, consequently, increase the water yield more than that of the oil. On the other hand, at temperatures above 725 K, the reactions are mostly for decomposing the strong chemical bonds of the material network, which mostly produces the oil phase and, accordingly, the yield of the oil phase is higher than water. This conclusion could point to developing a two-step pyrolysis process: the first step would be to produce most of the non-condensable gases and water products while the second would be for the production of the oil phases. Developing such a process would lead to reducing the need for complicated downstream processes that are basically for separation purposes.

The above kinetic model is essential as the obtained information herein is the basis for designing, developing and scaling-up pyrolysis processes. Moreover, it can be employed to improve the current pyrolysis processes by optimizing the parameters to reach an end-product at the desired yield and composition. In that regard, for example, the estimated kinetic parameters that are presented in Table 2 were used to simulate the phenolics yields under different pyrolysis heating rates and maximum temperatures. Increasing the heating rate to 110 °C/min enhances the phenols yield because it decreases the chance of further decomposition when the products are being formed. However, the phenols yield decreases at any heating rate higher than this limit, for it could not enable the molecular bonds to be fully decomposed and, consequently, the HMWC's yield is increased. Therefore, performing the pyrolysis process at the optimum conditions reported in the investigation is highly important for both the technical and economic aspects.

Cellulose and hemicellulose have been employed in broad industrial applications, such as paper, fibres, consumables, etc.; therefore, they received less attention in fast pyrolysis applications compared to lignin. The relatively simple structure of cellulose and hemicellulose makes them readily convertible over a tight range of temperatures. The higher reactivity of cellulose and hemicellulose than lignin is the key factor that affects the conversion process [213]. Cellulose is a linear polymer of both amorphous and crystalline structures, and its basic unit is glucan, which is exemplified in a glucose unit as the elimination of water molecules; as presented in Figure 11 [171, 214]. The common identified chemicals inside the bio-oil composition from the pyrolysis of cellulose are pyruvic aldehyde, furfural, levoglucosan, hydroxyacetone, 5-hydroxymethyl-furfural, hydroxyacetaldehyde and glyceraldehyde, as depicted in Figure 12 [215]. As in the case of the other biomass components, the structure of a cellulose network highly affects its properties. The three hydroxyl groups present in its structure have the possibility to form intermolecular or intramolecular hydrogenbonds, as presented in Figure 13. Both intra and intermolecular hydrogen bonds play a significant role inside the conformation of cellulose. In fact, they are behind its rigidity and single-chain structure [204].

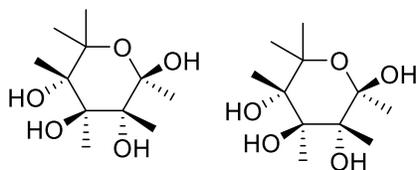


Figure 11 Building blocks of cellulose

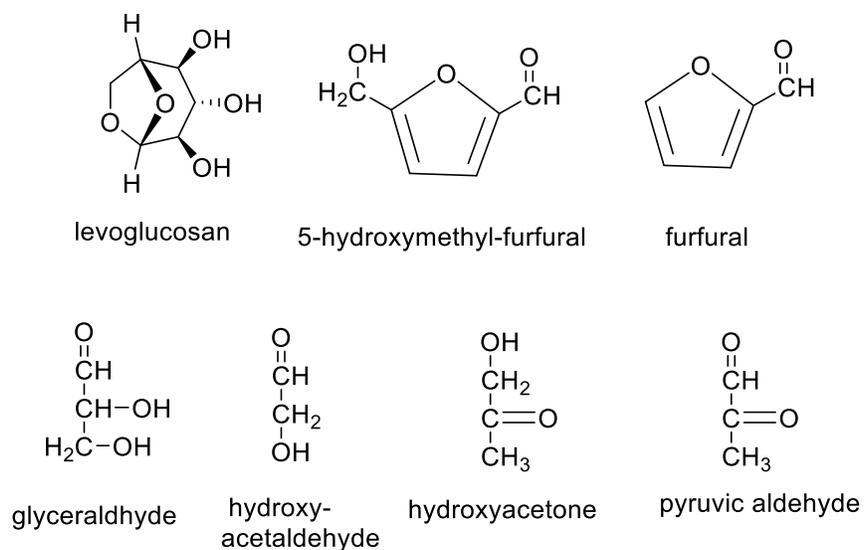


Figure 12 Typical chemical structures of a bio-oil from the pyrolysis of cellulose (Adapted with permission from Shen, Xiao et al. 2011[216]. Copyright (2011) Royal Society of Chemistry)

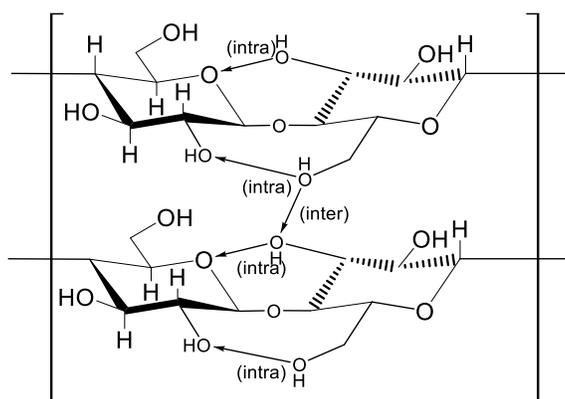


Figure 13 Intra and intermolecular hydrogen bonds of cellulose structure reported by Omori, Aoyama et al. 1998 [217]

The decomposition of cellulose gives two sets of products: the first set includes the monomers with low molecular weight, while the second one contains oligomers with high molecular weight, as shown in Figure 14. The pyrolysis of cellulose produces various products through five different ways of the free radical mechanism. The first pathway, a, is the formation of levoglucosan, 2, from the combination of the hydroxyl radical with the radical 1. Hydroxyacetaldehyd, 3, first formed in pathway b with a di-radical intermediate, 4, which was unstable and rapidly underwent a further rearrangement to give 4-hydroxy-3-oxobutanal, 5. The liberation of carbon monoxide occurred in the last step giving the hydroxyaceton product, 6. Two possible di-radical intermediates, 7 and 9, were formed in pathway c. The intermediate 7, was finally decomposed and gave the same last product of pathway b, hydroxyaceton (6), and the intermediate 9 gave hydroxyacetaldehyde, 11, and 3-oxobutanal, 12, which decomposes again by carbon monoxide liberation and acetone, 13, formation. Pathway c shows the formation of ethandial, 12, which underwent an ionic mechanism for carbon monoxide liberation giving a formaldehyde compound, 15. Compound 16 underwent a dehydration process through water molecule elimination and the formation of compound 17. A ring closure has occurred for compound 17 that finally gave 5-hydroxymethyl-furfural product 18.

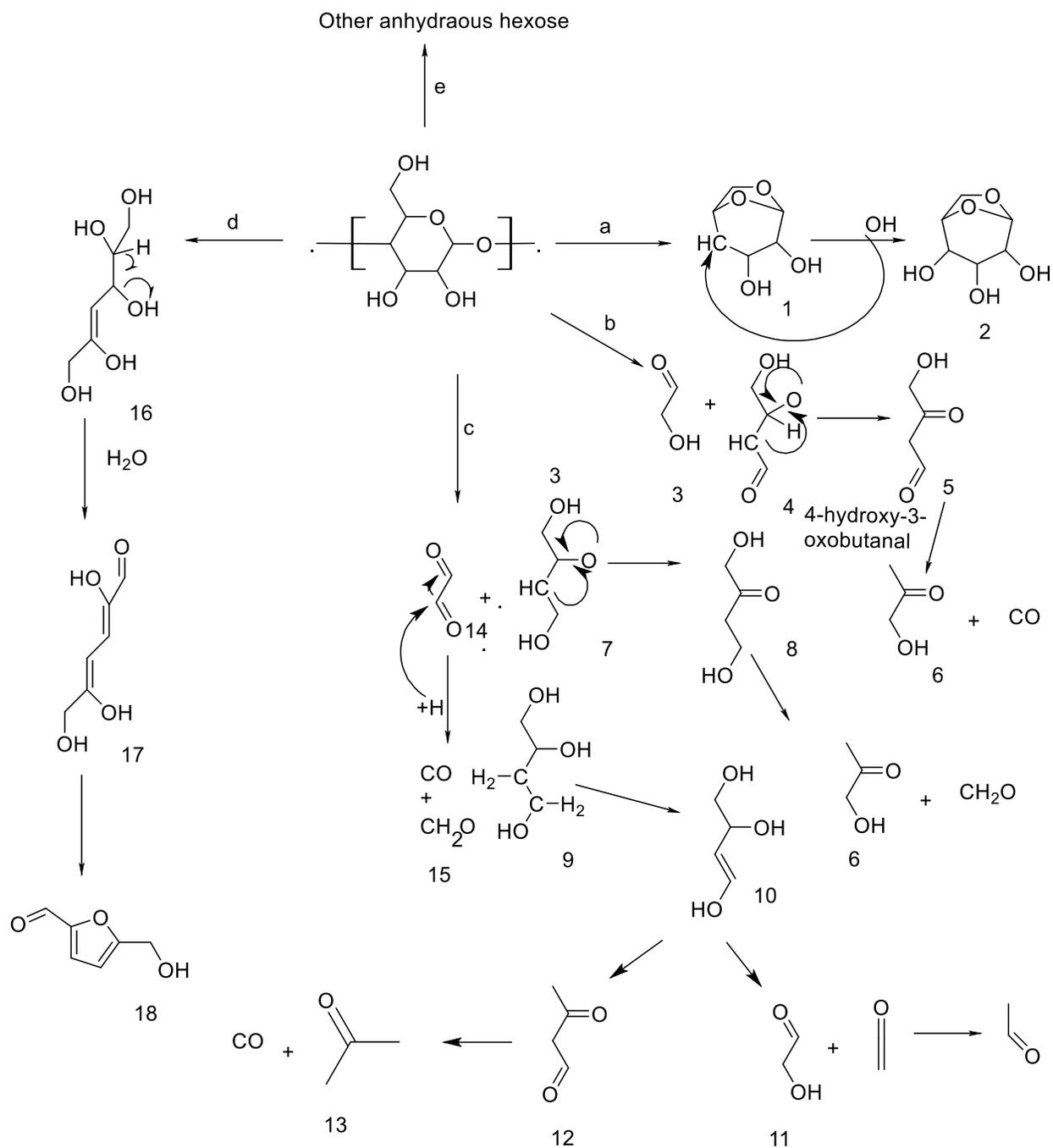


Figure 14 Suggested degradation pathways of cellulose (Adapted with permission from Shen, Xiao et al. 2011[216]. Copyright (2011) Royal Society of Chemistry)

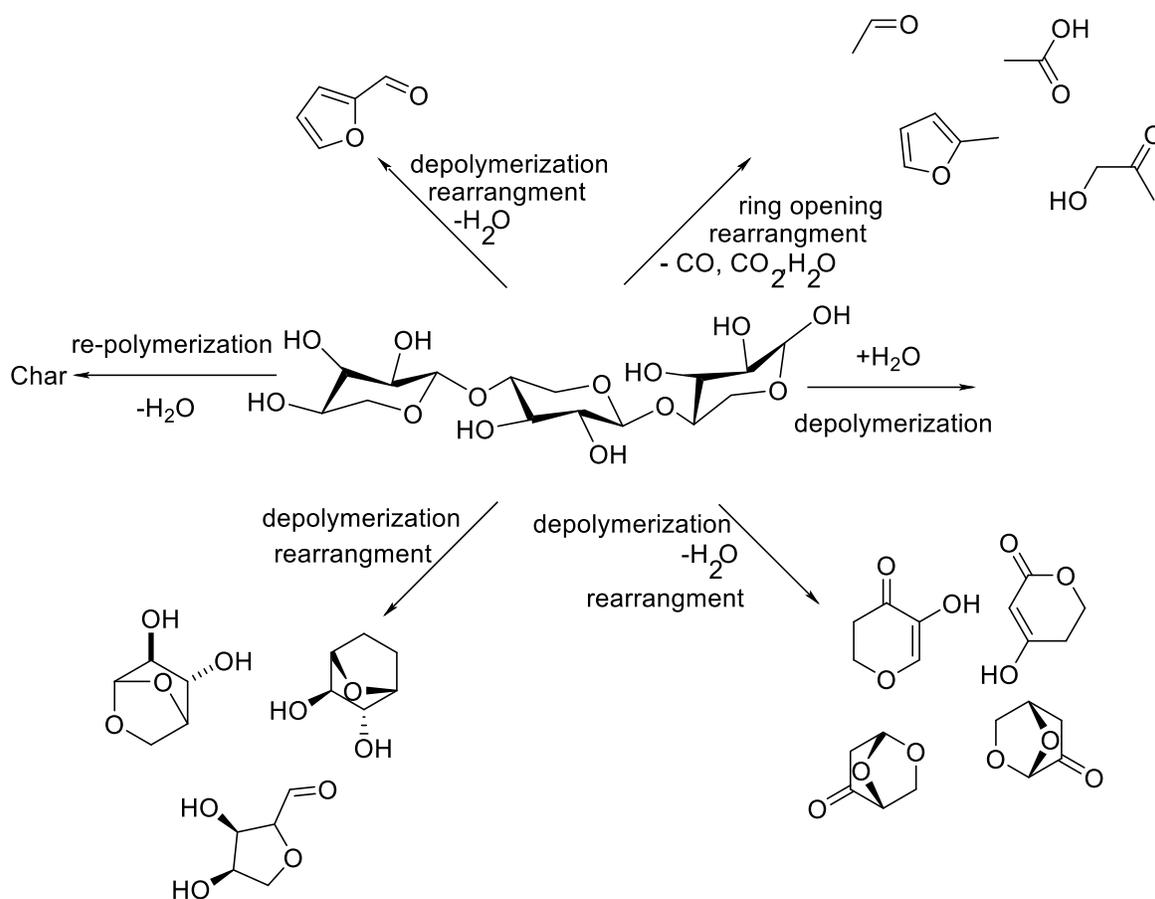


Figure 16 Possible decomposition pathways of hemicellulose reported by Patwardhan, Brown et al. 2011, and Liu, Wang et al. 2014 [204, 218]

Comparing the pyrolysis behaviour mechanisms and the pathways of hemicellulose and cellulose can elucidate that the major product from cellulose dehydration is levoglucosan; on the other hand, the main product formed from hemicellulose pyrolysis is di-anhydro xylose 2. As shown in Figure 17, Patwardhan et al. 2011 have investigated this aspect and their key conclusions include that pyrolysis of cellulose first forms a glucosyl cation as a result of the bonds between the pyranose rings breaking down. Since the formed cation is unstable, it tends to form 1, 6 anhydride, which undergoes further degradation to form levoglucosan. In contrast, hemicellulose first produces a xylose cation, which differs from the above-mentioned one as it does not contain the sixth carbon and the oxygen on the fourth position. Thus, the xylose cation of hemicellulose cannot form the anhydride product that has been formed in the case of cellulose. As a result, the xylose cation will

follow a different pathway through further degradation that can occur by combining with $-OH$ and $+H$, which could lead to xylose formation [218].

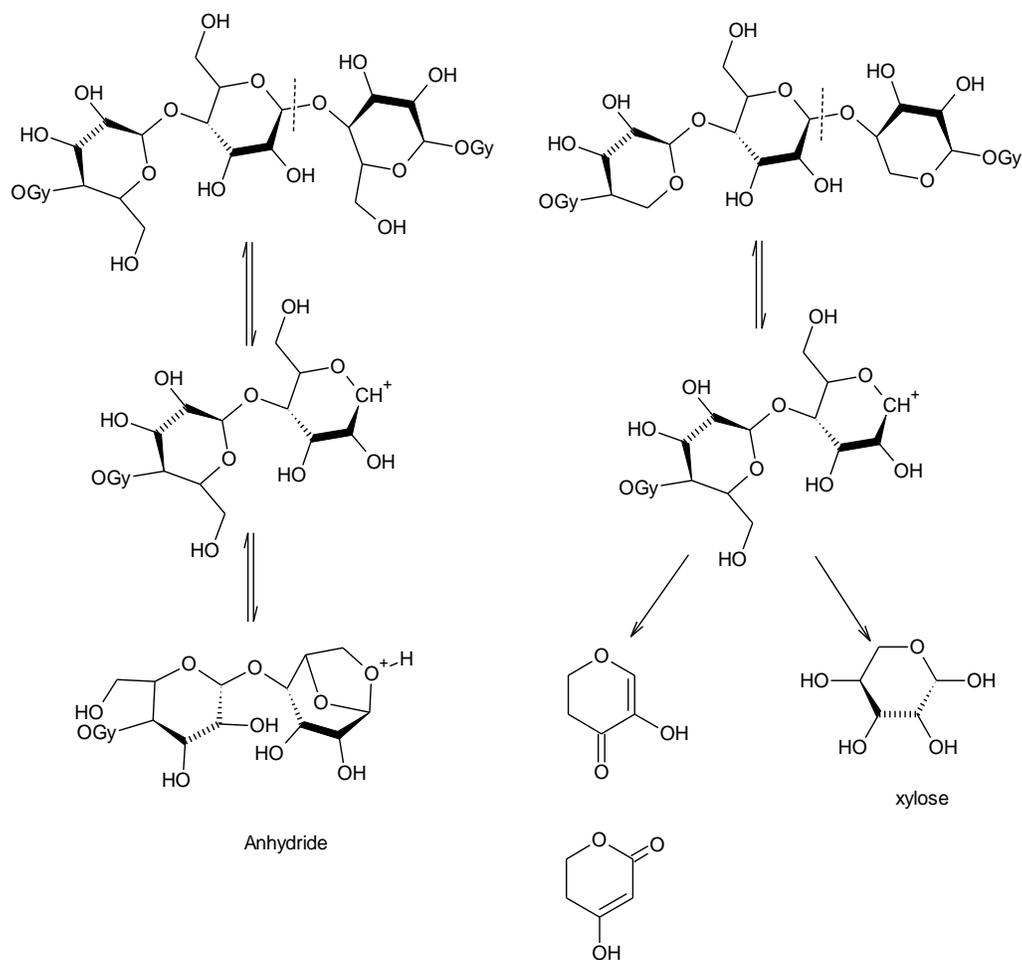


Figure 17 Decomposition pathways of cellulose against that of hemicellulose reported by Patwardhan, Brown et al. 2011 [218]

2.2 Effect of loading a catalyst on the pyrolysis products

Liquid phases produced from pyrolysis of lignocellulosic biomass are complex mixtures of hundreds of highly oxygenated compounds, such as aldehydes, ketones, aromatics, alcohols, and carbohydrates, etc. [219, 220]. The common reported characteristics about such oils include low heating value, low vapor pressure, and high viscosity [204, 220]. These properties together with the high corrosive liquid, which results from its acidity due to the high formic and acetic acid content, prompt the reactivity for further reactions, such as polymerization. These instability

properties actually reduce the ability to distill and/or store and, consequently, decrease the commercial-value of the end-product [204, 220]. To valorize such a product, a catalytic agent is commonly used after collecting the liquid product. Using a catalyst to upgrade a pyrolysis product is referred to as catalytic upgrading. On the other hand, using a catalyst in-situ or ex-situ during a pyrolysis process is called catalytic pyrolysis. The upgrading process uses a catalytic agent for removing high oxygen content that is in the oil product. This approach enhances the reactions of cracking, decarbonylation, hydrodeoxygenation, decarboxylation, hydrocracking and hydrogenation, as shown in Figure 18 [199]. Accordingly, the excess of oxygen content in the structure of the pyrolysis oil is converted into a form of water and/or carbon dioxide liberation, and the percentage of the heavy molecular weight compounds is decreased.

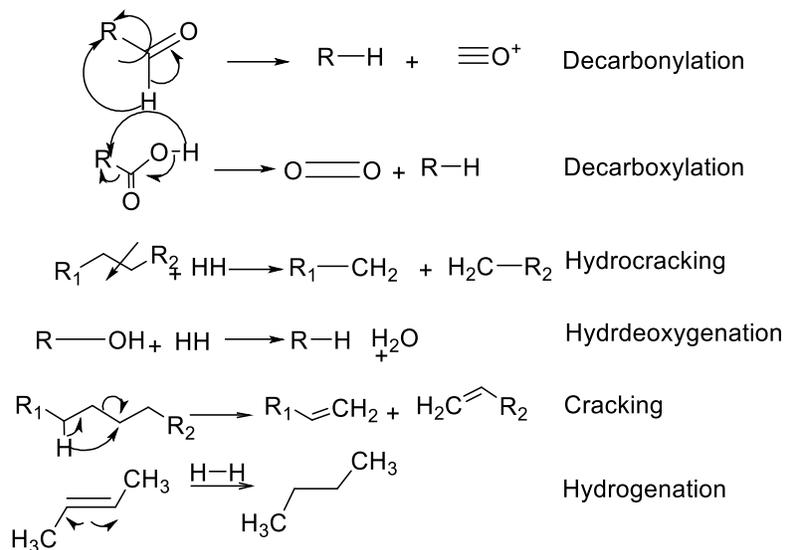


Figure 18 Different catalytic upgrading reactions reported by Dickerson and Soria 2013 [199]

Among the catalytic upgrading techniques, the hydrodeoxygenation (HDO) method is commonly used for removing the oxygen atoms from the oil phase. In fact, hydrogen atoms are soluble in oil and act as a hydrogenating agent when there is pressure and an appropriate catalyst. Raising the reaction pressure increases the solubility of the hydrogen in the oil, which in turn enhances the hydrogenation rate. Different types of catalysts, such as transition metal and molybdenum sulphide, are used and a pressure of up to 300 bar is normally applied [199, 204]. This method has actually

been extensively performed on oil under several conditions from different sources. Wildschut, Mahfud et al. have investigated upgrading a pyrolysis oil from beech wood using the catalyst Co–MoS₂/Al₂O₃ at 350 °C and 300 bar [221]. A yield of 26 wt% at a 0.8 oxygen to carbon ratio and a 1.3 hydrogen to carbon ratio were obtained. Venderbosch, Ardiyanti et al. and Wildschut, Mahfud et al. have applied the same method on pyrolysis oils from forestry residues and beech wood, respectively [221, 222]. The authors have used Ru/C and Ni–MoS₂/Al₂O₃ as catalytic agents under 230 bar/350–400 °C and 200 bar/350 °C of upgrading conditions, respectively. A 0.1 oxygen to carbon ratio and a 1.5 hydrogen to carbon ratio were reported for 38 wt. % and 28 wt.% yields, respectively. Elliott, Hart et al. have performed the same method on bio-oil from the pyrolysis of corn stover using Pd/C as the catalytic agent under 140 bar and 340 °C [223]. The authors reached the same oxygen to carbon and hydrogen to carbon ratios that were reported by Venderbosch, Ardiyanti et al., and Wildschut, Mahfud et al., respectively, while the obtained yield was 48 %. Baldauf, Balfanz et al. reached 0 oxygen to carbon and 1.8 hydrogen to carbon ratios using Co–MoS₂/Al₂O₃ at 370 °C and 300 bar [224].

The advantages of this method include producing non-corrosive oil with a high H/C ratio, which makes the product acceptable in a broad range of applications. The main disadvantage is the high cost of the operation due to the requirements for a high operating pressure [199].

Zeolites, aluminum silicate compounds in a three-dimensional structure, are wide and porous, which can trap several elements, such as sodium, calcium, and even molecules of water. Catalytic upgrading using zeolites has also been applied because it gives a chance for the oxygenated compounds to be adsorbed on the acid site of the catalyst. Both a dehydration or decomposition process can take place depending on the size of the pore.

Catalytic pyrolysis is another approach for upgrading pyrolysis oils. It has the ability to produce highly deoxygenated compounds from biomass conversion during the pyrolysis process [225]. In this technique, the pyrolysis vapour undergoes a treatment process using a catalyst prior to the quenching step. There are two different methods for loading the catalytic agent: (1) in-situ catalytic pyrolysis, where the catalyst is co-fed at the beginning of the process with the feedstock into the pyrolysis reactor, and (2) ex-situ catalytic pyrolysis, where the catalyst is placed in the path of the pyrolysis vapour.

Wang, K., et al. have studied the in-site catalytic pyrolysis of switchgrass and its components (cellulose, hemicellulose, and lignin) using the H-ZSM5 catalyst [225]. The key findings of their work include 15% @ 400 °C and 30 % @ 700 °C more in the aromatic yield were obtained from cellulose. The increasing percentages of hemicellulose and lignin were 20% and 9% at 700 °C, respectively. Wang, K. and his co-authors believed that the deficiency in aromatic yields from lignin catalytic pyrolysis is possibly due to the non-reactivity of phenolic compounds towards the H-ZSM5 catalyst. Phenolic compounds produced from the thermal decomposition of lignin underwent dehydration on the external surface of the zeolite used. Subsequently, it formed a layer of coke on the catalyst surface before penetrating the catalytic pores. This aspect, in turn, will prevent the catalyst from working efficiently during the pyrolysis process and will make the carbon conversion process incomplete. Accordingly, they concluded that the H-ZSM5 catalyst does not work effectively for oxygen atom removal during the catalytic pyrolysis of biomass.

Stefanidis, S.D., et al. examined pyrolysis of cellulose, hemicellulose and lignin using the catalyst ZSM-5 to decrease the liquid yield and increase the water and gas products [226]. The authors reported that removing oxygen in the form of H₂O, CO, and CO₂ from the pyrolysis vapour decreased the liquid yields and thus increased the water product. The same result was reported by Syamsiro, M., et al. in the catalytic pyrolysis of plastic waste using zeolites [227]. Loading the catalyst decreased the liquid yield and increased the gas yield, which might be due to the decomposition of the long chain hydrocarbons into smaller gaseous fragments. Moreover, the natural zeolite catalyst with a lower BET surface of 91 m²/g produced a higher liquid yield than that of the Y zeolite with the BET surface area 780 m²/g. Syamsiro, M., et al. believed that the more contact the pyrolysis gas has with the higher BET surface area increases the cracking of gas into small fragments. The above-three examples show the positive and negative impacts of the catalytic agent on the yield and/or composition of pyrolysis oil. Further information regarding this aspect is tabulated in Table 3.

Table 3 Catalytic pyrolysis of different feedstocks

Authors	Feedstock	Temperature	Catalyst	Key findings
Yildiz, Pronk et al. 2013 [228]	Pine wood	600 °C	Heterogeneous ZSM-5	Catalytic effect resulted in producing high quality oil with low oxygen content and acidity; Higher carbon yield was produced, and the sugars and aldehydes were removed by catalytic pyrolysis; Higher yield of aromatic and phenolic compounds was obviously noticed; and A drop in the liquid yield was observed: 50 wt.% for both in-situ and ex-situ processes compared to 59 wt.% for non-catalytic fast pyrolysis.
Patwardhan, Satrio et al. [229]	Cellulose	≤ 400 °C and 600 °C	Inorganic salts and switchgrass ash	0.005 mmole/g of inorganic salts are sufficient to change the composition of the pyrolysis oil; Formation of lower molecular weight species, in particular formic acid, glycolaldehyde and acetol, resulted from the catalytic pyrolysis of cellulose in the presence of inorganic salts/ash; At a temperature of ≤ 400 °C the major product from the pyrolysis of cellulose was anhydrous sugars, while at 600 °C the majority were levoglucosan and formic acid; and In the presence of ash and at similar temperatures, glycolaldehyde was the main product, besides levoglucosan and formic acid.
Adjaye and Bakhshi [230]	Maple wood	290 - 410 °C	HZSM-5, H-Y, H-mordenite, silicalite	Formation of organic distillate fraction (ODF) with 22-89 wt.% hydrocarbon content from the catalytic upgrading of bio-oil; More aromatics of ODF, mainly toluene, xylenes and trimethylbenzenes, were produced by HZSM-5 and H-mordenite; and H-Y silicalite and silica alumina produced aliphatic hydrocarbons, mainly cyclopentene, cyclopropane, pentane and hexane.

(Katikaneni, Adjaye et al. [231])	Canola oil	400 - 500 °C	Pt/HZSM-5 and HZSM-5	Using HZSM-5 increases the liquid oil product from 55 wt.%, in the absence of the catalyst, to 63 wt.%; and Incorporation of the Pt metal with HZSM-5 enhances the isomerization of the catalyst to raise the isobutane and isobutylene production.
Aho, Kumar et al. [232]	Pine wood	450 °C	H-Beta-25, H-Y-12, H-ZSM-5, and H-MOR-20. Quartz sand as a reference	The highest liquid yield was produced using H-ZSM-5-23 with a higher water content compared to the quartz sand that gave approximately the same percentage of liquid yield; Chemical composition of the obtained oils produced from Beta, Y and Mordenite catalysts is similar to each other; and The catalyst ZSM-5 increased the production of ketons more than the other catalysts; however, it decreased the amounts of alcohols and acids.
Horne, Nugrand et al. [233]	Wood waste	500 °C	ZSM-5	An obvious increase in the aromatic hydrocarbon formation in the presence of the catalyst compared to the case of the non-catalytic pyrolysis; and The presence of methanol with the pyrolysis vapor enhanced the production of alkylated phenolic and aromatic, increased the deoxygenation process through the liberation of water rather than carbon dioxide, and decreased the formation of polycyclic aromatics.
(Li, Su et al. 2012) [234]	Kraft lignins	500 – 650 °C	HZSM-5 (SiO ₂ /Al ₂ O ₃)	The presence of the HZSM-5 catalyst enhanced the production of valuable chemicals, such as benzene, toluene, xylenes, ethane and propene; and Less aromatic yield from lignin catalytic fast pyrolysis was produced.
Encinar, Gonzalez et al. [235]	Exhausted olive waste	500 – 800 °C	Dolomite	The amount of dolomite catalyst had a negative impact on the liquid yield; Liquid yield was dropped dramatically by increasing the quantity of the catalyst, while the gas yield was increased;

Boust, Green et al. [236]	Sawdust	600 °C	Zsm-5	<p>The produced hydrogen was increased by increasing the amount of the catalyst; due to the high cracking impact caused by the action of the catalyst on the heavy molecular weight compounds.</p>
Babich, Van der Hulst et al. [237]	Chlorella algae	300–450 °C	Na ₂ CO ₃	<p>The catalytic reaction did not impact the bio-oil yield; and Pyrolysis in presence of the catalyst resulted in the production of bio-oil with a higher quality, lower acidity, higher aromatics and higher heating values compared to the non-catalytic one.</p>
Karanjkar, Coolman et al. [238]	Cellulose	500 °C	ZSM-5 catalyst	<p>The maximum carbon yield obtained during the catalytic fast pyrolysis using ZSM-5 catalyst was 39 wt.% from cellulose compared to 16 wt.% produced from pine wood; Using different catalyst bed heights influenced the composition and selectivity of the yield; The aromatic yield was increased from 28 wt.% carbon at a height of 6.4 cm to 32 wt.% for a bed height of 17.6 cm; and The monocyclic aromatic products were formed at lower bed heights.</p>
Mukaraker, McBrayer et al. [239]	Avicel cellulose, lignin and pine wood	500 °C	HZSM-5	<p>Higher aromatic hydrocarbon content was produced, i.e., the catalyst upgraded the biomass pyrolysis vapors.</p>

2.3 Effects of the heating mechanism on the pyrolysis products

Over the last few decades, different technologies for providing the heat energy required to perform the thermal decomposition process have been developed to fulfill the demands for product quality and quantity as well as meet society's needs to protect the environment and reduce energy consumption. Microwave-assisted thermochemical decomposition of biomass is the most important technology that has been established in pyrolysis applications. Heating by exposure to electromagnetic irradiation can avoid most conventional heating (CH) issues and limitations [51, 53, 54], most importantly the temperature gradients inside and outside the heated material and the char layer formation that begins in conventional pyrolysis (CP), which is considered one of the most critical problems in the field.

Farag has schematically diagrammed a comparison between the effect of CH and microwave heating (MWH) on temperature gradients and the direction of heat and mass transfer, as shown in Figure 19. In CH processes, heat transfers from a heating source to the outer surface of the target via conduction, convection, and/or radiation. The temperature of the outer surface, heat capacity, thermal conductivity, and dimensions of the workload are the most important factors affecting the temperature gradients within the heated material. These factors together with the nature of the MWH mechanism create temperature gradients that represent a core colder than a surface, as presented in Figure 19A. On the outer surface of the heated material, consequently, a layer of char starts and grows toward the core. This "char layer formation" boosts the thermal barrier within the target and, as a result, dramatically increases the temperature difference between the surface and the core. As the pyrolysis vapour escapes the decomposed material flowing through this thermal barrier, undesirable degradations might take place and, in turn, negatively affect the quantity and/or quality of the final product. In microwave-assisted pyrolysis, on the other hand, electromagnetic waves penetrate the entire target at almost the same time. Thus, a uniform temperature distribution within the heated material should be found. However, when the penetration depth is respected, the result is a core that is hotter than the surface. This temperature gradient leads to the creation of the char layer in the core that grows in the direction of the surface, which is the opposite direction of that of CH, as shown in Figure 19B. This characteristic makes heat and mass transfer take the same direction and, consequently, preserves the structure of the pyrolysis vapour. As a result, there is a tendency to believe that applying electromagnetic waves in the pyrolysis application would enhance product selectivity and other advantages.

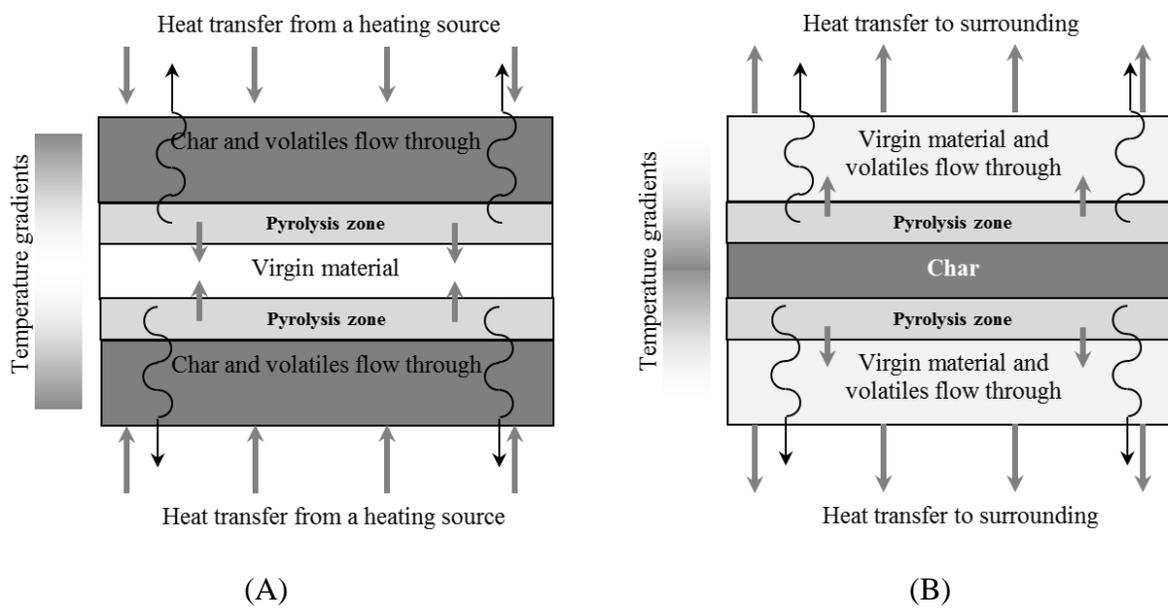


Figure 19 Schematic diagram of (A) conventional pyrolysis and (B) microwave pyrolysis in one direction (reprinted from Farag 2013 [52])

Remarkable efforts have been made to better understand the effects of electromagnetic radiation on the conversion of biomass. Farag et al. have finalized a study to compare the composition and yield of CP with microwave pyrolysis (MWP) of Kraft lignin [57]. One of the key conclusions from that work is that the difference between the liquid yield of both cases is slight; however, the effect on the composition is noticeable. Microwave-assisted pyrolysis produces less water content in the pyrolysis liquid compared to that of CP. This is due to the unification of heat and mass transfer directions that might preserve the structure of the side-chains of the lignin pyrolysis vapour. In CP, increasing the temperature and/or residence time, which is due to the thermal barriers that take place within the heated material, would create secondary reactions in the pyrolysis vapour. Such undesirable reactions, in turn, produce radical aromatic rings that would eventually be converted to polycyclic aromatics and others. Budarin, Clark et al. have reported that employing electromagnetic radiation in pyrolysis produces oils that are rich in aromatics compared to that of conventional processes [240]. Zhang and Zhao tend to believe that the exposure to microwaves leads to an increase in the product yield and a decrease in the reaction time in the production of 5-hydroxymethylfurfural and furfural from corn stalk, rice straw, and pine wood [64]. In a study by Krzan and Zagar, they concluded that MWH decreases the reaction time and loading of catalyst in

the liquefaction of wood with glycols using p-toluene sulfonic acid as a catalyst [71]. A faster reaction rate and a higher liquid yield were found compared to the CP of sewage sludge as reported by Menéndez, Dominguez et al. [75]. Solvent-free microwave extraction of oil from basil, garden mint, and thyme was examined by Lunches, Cheat et al. and the key findings state that microwaves decrease the reaction time and energy consumption more than that of CP [68]. The extraction of polycyclic aromatic hydrocarbons from airborne particles was achieved in minutes using MWH compared to hours for CH, as well as the high quality of the product as reported by Karthikeyan, Balasubramanian et al. [67]. Similar conclusions were reached by Orozco, Ahmad et al., Sithambaram, Nyutu et al., and Chandra Shekara, Jai Prakash et al., [62, 73, 74]. Adnadjević and Jovanović, Li, Han et al., Temur Ergan and Bayramoğlu, and Yadav and Borkar believe that molecular mobility in MWH is higher than that in CH, which is mainly due to the nature of the MWH mechanism [241-244]. Adnadjevic and Jovanovic, Adnađević, Gigov et al., Fukushima, Kashimura et al., Sun, Wang et al., Chen, Wang et al., Yan, Hu et al., Adnadjević and Jovanović, and Li, Han et al. have concluded that reaction activation energy decreases when electromagnetic waves are applied compared to CH [241, 242, 245-250]. Indeed, the last-mentioned interpretation is doubtful since the wavelength of microwaves, 12.24 cm @ 2.45 GHz, is much longer than the intermolecular distance of the target. Further review regarding this aspect can be found in [51-53]. To summarize, applying MWH in the field of biomass processing produces remarkable findings on the quality and yield of the products, energy consumption, loading the catalyst, and other aspects compared to CH. Such investigations would provide insights for a better understanding of the MWP mechanism, leading to the production of high-value products from biomass.

3. Economics feasibility of pyrolysis of biomass

Before scaling-up a pyrolysis process, examining the technical and economic aspects is essential as it is the basis for deciding whether to keep the project as is or make changes. To accomplish such an assignment, strategic procedures should be followed. First, a preliminary design of the proposed process, taking into account the nature of the feedstock and its requirements for successful feeding, is accomplished. Afterwards, mass and energy needed for operating the plant are calculated and, then, the annual expenditures are taking into account salaries and any other outlays. Based on the collected data from the local market, previous works, and/or the scientific literature, the purchased cost of the equipment and its requirements are valued. Thereafter, the total

capital investment of the project is evaluated using the corresponding information. Eventually, one of the common methods for estimating the profitability of a project, such as the rate of return on investment, discounted cash flow-based valuation, full-life performance, net present worth, capitalized costs or payout period, is applied. At this point, the minimal selling price of the end-product can be assessed and, subsequently, the cumulative cash flow at the end of the investment period can be calculated. It is also recommended to perform a sensitivity analysis to improve the understanding of the effects of key variables on net profitability. The analysis would indicate the optimum conditions that would establish the price that can guarantee a target profit and at the same time keep the product competitive among traditional products.

When little information about the proposed process is known, a preliminary economic estimation is often used. This approach will evaluate the profitability of the project, which consequently becomes the basis for making a decision whether to select or reject the investment. “Net Present Worth” (also is known by “Net Present Value” (NPV)) is one of the criterion methods applied for this purpose since it outputs the most realistic expectation for the profitability compared to the other methods. This method considers the time value of money, including present worth and discounted cash flow-rate of return, in addition to all the pertinent information about the other methods. NPV equals the outcome of subtracting the present capital investments from the present worth of the cash flows, as shown in Equation (16).

$$NPV = \sum_{i=1}^n F_{cf,i} [(R_i - E_i - D_i)(1 - T) + Rec_i + D_i] - \sum_{i=-b}^n F_{v,i} I_o \quad (16)$$

$F_{cf,i}$ is the selected present worth factor for the net cash flow in year i , R_i the value of sales in year i , E_i the total product cost not including depreciation in year i , D_i the depreciation in year i . T refers to the applied tax, Rec_i the money recovered from the working capital and the sales of physical assets, $F_{v,i}$ the appropriate present worth factor for investment occurring in year i , which equals 1 when all the investments are made at time zero. I_o is the total capital investment in year i . If the outcome of Equation (16) is a positive value, it means the investment should be accepted. However, in case of negative or zero value the investment should be rejected. Herein, zero value means that the present value of the expected cash outflows of the project equals the present value of the expected cash inflows from the project. This scenario is commonly applied for presenting the return

that can be expected for a given level of risk. Further information regarding the other profitability evaluation methods for a proposed project can be found in this reference [251].

The total capital investment of a project is defined as the money that is needed for building an industrial facility and putting it in operating condition. It can be classified into “fixed capital investment”, which includes direct and indirect costs, and “working capital”, which is the total money required for stock, the raw material, and cash kept on hand. The most important items included in the direct plan costs are land on which the buildings will be installed, purchased equipment and its installation, instrumentation, controls, piping, and electrical systems. In addition, service facilities, which encompass the utilities for supplying steam, water, fuel, etc., and yard improvements are considered under direct costs. The engineering and supervision, construction expenses, legal expenses, and contractor fees are the main sections of the indirect costs.

One of the most excessive methods used for estimating the initial capital investment of a project is the “Percentage of Delivered-Equipment Cost” method. It includes a multiplying factor of the purchased equipment cost for each of the above-mentioned investment costs. The suggested value for the working capital is commonly considered as 15 % of the total capital investment. It is important to know that as long as precise information about the above-mentioned aspects is collected, the developed economic analysis will produce accurate results. Generally speaking, an accuracy of 20-30% should be expected for this method [251-253].

Since the investment costs are only valid at the time they were developed, the "Cost Indexes Method" or any other method should be applied for updating all the costs, as defined in Equation (17) [251, 252]. C_p is the present cost of the equipment; C_Y is the equipment cost at year Y , in which the information is available. I_p and I_y are the index values of the present and that of year Y , respectively.

To overcome the matter regarding the size/capacity of the purchased equipment, the “Six-Tenths Factor” rule is widely used, which is defined in Equation (18). C_a and C_b refer to the cost of the new equipment and the reference one, respectively. P_a and P_b refer to the capacity of the new equipment and the reference one, respectively. In pyrolysis applications, 0.6 - 0.8 is the suggested range for the capacity exponent factor “ z ” [251, 252].

$$C_p = C_y \frac{I_p}{I_y} \quad (17)$$

$$C_a = C_b \left(\frac{P_a}{P_b} \right)^z \quad (18)$$

Pyrolysis of biomass for the production of energy and/or valuable-chemicals has been extensively studied over the last few decades [253-263]. The critical factors impacting the investment on the project include the transportation expenses, feedstock cost, product utilizations, end-product commercial value, and its competitiveness with traditional products.

The costs needed to collect the feedstock from widespread areas, such as the case biomass, is actually considerable. In addition, the subsequent emissions from the vehicles used to move the feedstocks are also a concern. Increasing the “value-to-volume ratio” of the transported materials could be one solution to minimize the effect of this aspect. Developing on-site pyrolysis systems could be an option to achieve this aim, which would lead to transporting pyrolysis products instead of feedstocks. A pyrolysis product, such as the liquid phase, weighs less and is higher in commercial value compared to the raw material from which it was produced. Therefore, transporting the oil product will have a much higher value-to-volume ratio compared to transporting biomass.

Pyrolysis of a feedstock that has a high purchase cost, such as lignin, the most abundant by-product from papermaking processes, always leads to an increase in the minimal selling price of the product. Such a feedstock should be employed in niche applications, which would accept the high selling price of the end-product. Processing feedstocks that have a negative value, such as domestic waste, agriculture residue, etc., would dramatically enhance this aspect. Employing the pyrolysis products to synthesize high-value intermediate/end-products would also add value to the pyrolysis applications. For example, using pyrolysis oil in the production of chemicals instead of considering it as a source of energy would offer a great profit, as in the case of the petrochemical industry.

Competing with the traditional products is the most important aspect affecting the success of the investment in the pyrolysis industry. Farag and Chaouki 2015 have investigated a first step economics evaluation for converting lignin into value-added chemicals [166]. A total capital investment of \$11.3MM and annual operating cost of \$8.3MM were estimated for an on-site

pyrolysis plant at a capacity of 100 t/d. The NPV method was performed to estimate the minimum selling price of the oil phase and evaluate the expected profit. The remarkable finding of that work includes the estimated price of the dry-oil from the pyrolysis of lignin, 3100 \$/t, which cannot compete with the price of fossil fuel based chemicals. The main reason for this is the high cost of the purchased raw material. To overcome this issue, lignin at a cost not higher than 200 \$/t should be found. Furthermore, starting with another feedstock that is similar, to some extent, to the structure of lignin, such as birch-wood, would be a good idea. In this case, the selling price of the obtained oil would be less than 900 \$/t, and therefore, could compete with the petrochemical products.

4. Conclusions

The key conclusions of this review paper include processing low-value renewable materials to high-value intermediate/end-products is a new approach to address the issues of the energy crisis and chemical costs. Thermochemical conversion, including pyrolysis, gasification and combustion are the promising techniques for converting non-fermentable feedstocks to energy and chemicals. Fast pyrolysis of biomass is the most promising technique for biomass processing for the production of fuels and chemicals as it can deal with a huge quantity of feedstock and other reasons. High heating rate of feedstocks along with short residence time of produced vapor result in fast pyrolysis process. Fluidized bed, ablative and twin screw reactors have been commonly employed in the fast pyrolysis process. To ensure the success of a pyrolysis plant, technical and economic aspects should first be evaluated and the effect of the critical factors on profitability is highly recommended to be well understood. Starting with a feedstock that has a low-value will dramatically decrease the minimal selling price of the end-product. This aspect, in addition to others, will lead to the pyrolysis product being in a competitive position among the traditional products.

APPENDIX G MECHANISTIC LIGNIN PYROLYSIS MODEL TO PREDICT THE PRODUCT YIELD AND COMPOSITION OF THE LIQUID PHASE

Abstract

Organic phase obtained from the pyrolysis of lignin contains several highly-functional chemical families. Those families make the lignin-based oil suitable to produce a number of end-products. The composition and quality of the liquid phase are crucial to identify the downstream process, which are impacted by few factors. Most importantly include the precipitation process of the feedstock, pyrolysis conditions, and presence of an in-situ or ex-situ catalytic agent. In this regard, this work aims to predict the yield of the pyrolysis products from Kraft lignin and the composition of the liquid phase at different conditions. A kinetic model based on lumped approach is employed. A temperature-range from ambient to 1100 K and a heating rate from 2 to 200 °C min⁻¹ are applied. The predicted results from the study are compared at selected conditions against a lab-scale experimental data, which shows the high capability of the employed model.

Keywords: Kinetics; Pyrolysis; Kraft Lignin; Oil Composition.

APPENDIX H CALCIUM OXIDE CATALYSED MICROWAVE PYROLYSIS OF PAPER CUPS: ANALYSIS OF OIL QUALITY

Abstract

Microwave pyrolysis (MWP) of household waste in generation sites is an attractive opportunity to considerably reduce waste nuisance and its negative impact on the environment. While most gaseous and solid products are suitable enough for fossil gas and char substitution, pyrolytic oils are generally inadequate for direct integration into existing processes. In this study, the effect of calcium oxide as an additive to microwave pyrolysis of paper cups is examined. The oil acidity is reduced by 54% when calcium oxide is present. The GCMS analysis shows that long chain sugars are substituted by lower molecular weight compounds and anhydrous sugars. Glycolaldehyde production and 5-hydroxymethylfurfural are observed, consistent with existing studies' findings. Lower carbon number chains replace higher ones. Acetic and propionic acids content diminish by 30% and 65% respectively. And higher value chemicals were produced when calcium oxide was added such as glycolaldehyde. This compound did not appear in oil from the non-catalytic reaction and was produced with a mass content up to 12 wt.% when CaO was present. Hence, pyrolytic oil could be used as a source of added-value chemicals. Calcium oxide is a cheap catalyst, and the process modification consisted of simply adding quantities of it inside the pyrolysis compartment.

Keywords: Microwave Pyrolysis; Catalytic Pyrolysis; Household Waste; Oil Upgrading.