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**Process Development for Metal and Sulfur Removal from Crude Petroleum
Oil Utilizing Microwave Heating Technology**

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

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présentée par **Amin SOLOUKI**

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DEDICATION

To my beloved parents, brothers, Mobin & Mehdi, and my love Kobra.

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In the pursuit of knowledge, no accomplishment is achieved in isolation. This innovative journey of my Ph.D. has been a combination of support, guidance, and inspiration from numerous individuals, to whom I owe my deepest gratitude.

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RÉSUMÉ

La suppression des métaux et du soufre est une étape cruciale dans les processus d'amélioration des pétroles bruts, mais elle reste l'une des opérations les plus énergivores. Des méthodes traditionnelles telles que l'hydrodémétallisation (HDM) et l'hydrodésulfuration (HDS) ont été largement utilisées pour éliminer les métaux et les composés soufrés. Cependant, ces techniques sont associées à des coûts en capital importants, à des dépenses d'exploitation élevées et à une consommation excessive d'énergie. Dans le but d'électrifier les processus d'amélioration du pétrole brut et de réduire leur empreinte carbone et leurs impacts environnementaux, le chauffage par micro-ondes apparaît comme une technologie avancée offrant un potentiel prometteur pour une élimination efficace des métaux et du soufre dans le pétrole.

Cette thèse présente une étude complète sur l'élimination du nickel (Ni), du vanadium (V) et du soufre (S) du pétrole brut en utilisant l'acide bis(2-éthylhexyl) phosphorique (D2EHPA) et la technologie de chauffage par micro-ondes. La recherche englobe divers aspects, notamment la faisabilité de la commercialisation et de l'agrandissement à l'échelle, l'économie du procédé, la cinétique et le mécanisme de démétallisation, le mécanisme de désulfuration et les conditions de réaction optimisées. De plus, un nouveau liquide ionique à base de phosphonium appelé trihexyl tétradécyl phosphonium bis(2-éthylhexyl) phosphate [THTDP][D2EHP] est synthétisé et évalué pour la désulfuration extractive (EDS) des carburants liquides et du pétrole brut.

L'enquête commence par une analyse technico-économique pour évaluer les performances techniques et économiques de la technique à l'échelle industrielle pour traiter 50,000 barils par jour (BPD) de pétrole brut. Un schéma de processus industriel est développé et simulé dans Aspen Plus, démontrant la supériorité économique du processus développé par rapport aux techniques conventionnelles d'hydrotraitement. Les coûts en capital total estimés (CAPEX) et les coûts

d'exploitation annuels (OPEX) s'élèvent respectivement à 6.77 millions de dollars américains (MUSD) et 4.23 MUSD (équivalent à 0.24 \$/baril). De plus, une méthodologie efficace pour la séparation et la régénération du D2EHPA à l'aide d'acide sulfurique et de solutions d'hydroxyde de sodium est établie et validée par des analyses FTIR et ICP-OES. L'analyse de sensibilité met en évidence l'importance du développement d'un modèle cinétique précis pour les réactions de démétallisation et l'optimisation des principaux paramètres de procédé.

L'impact des principaux paramètres de procédé sur les efficacités d'élimination du Ni et du V sous irradiation par chauffage par micro-ondes est étudié de manière systématique. Les valeurs optimisées des paramètres de procédé sont déterminées, et les efficacités d'élimination du V et du Ni dans le pétrole brut iranien sont de 72% et 63% respectivement, à de faibles puissances de micro-ondes de 40 à 50 W. L'investigation FTIR révèle la formation de nouveaux liens azote-hydrogène (N-H) dans le pétrole traité, indiquant le remplacement des liens azote-métal (N-M) dans les porphyrines de Ni/V par le proton donné par le D2EHPA. Le modèle cinétique de l'élimination du Ni/V assistée par micro-ondes est étudié à des températures de 230 à 250 °C et dans des conditions optimisées, fournissant des informations sur la cinétique de réaction. Les réactions de démétallisation présentent une cinétique du premier ordre, avec des énergies d'activation estimées à 29.8 kJ/mol pour le Ni et 34.7 kJ/mol pour le V, ainsi que des facteurs pré-exponentiels de 16.5 min⁻¹ pour le Ni et 66.2 min⁻¹ pour le V.

La recherche se concentre également sur la désulfuration du pétrole brut et des carburants liquides en utilisant le D2EHPA, des solutions aqueuses de NaCl et le chauffage par micro-ondes. Des enquêtes expérimentales sont menées en utilisant différents échantillons de pétrole brut et des carburants de modèle synthétiques contenant des composés soufrés de thiophène. Les effets de la température de réaction, du temps de réaction et de la dose de D2EHPA sur l'efficacité de

suppression du soufre sont étudiés, et jusqu'à 36% et 64% de soufre sont éliminés respectivement du pétrole brut iranien et des carburants liquides à base de thiophène, sous 20 minutes de chauffage par micro-ondes à 65 °C. La formation d'un liquide ionique hydrosoluble entre le D2EHPA et le NaCl est observée à partir d'analyses FTIR et de conductivité électrique, suggérant l'extraction des composés de thiophène par interaction π - π .

Ensuite, un liquide ionique à base de phosphonium, [THTDP][D2EHP], est synthétisé et évalué pour la désulfuration extractive des pétroles bruts et des carburants de modèle. Les résultats démontrent son efficacité dans l'élimination des composés soufrés, en particulier le benzothiophène (BT) et le dibenzothiophène (DBT), à la fois dans les carburants de modèle et le pétrole brut iranien. Les résultats montrent des efficacités d'élimination du soufre allant jusqu'à 63% pour les carburants de modèle à base de DBT et 57% pour le pétrole brut iranien. Les conditions optimales d'extraction sont déterminées comme un rapport masse IL/carburant de 1:1, une température de 35 °C et une durée de 30 minutes. Des tests de caractérisation approfondis confirment les propriétés favorables du liquide ionique synthétisé, notamment une haute stabilité thermique, une faible viscosité et une bonne conductivité électrique, ce qui en fait une option prometteuse pour la désulfuration extractive des carburants liquides et des pétroles bruts réels.

Finalement, une évaluation techno-économique secondaire a été réalisée pour mettre à jour l'enquête initiale concernant la faisabilité de commercialiser la procédure proposée. L'étude a intégré les résultats de recherche sur les conditions de réaction optimisées et la cinétique de la réaction de démétaillisation afin de présenter une conception de processus industriel plus précise et une analyse économique. L'évaluation s'est concentrée sur une capacité de traitement de 50,000 barils par jour de flux (BPSD). Les résultats ont indiqué une augmentation significative à la fois des dépenses en capital (CAPEX) et des dépenses opérationnelles (OPEX), passant respectivement

de 6.77 millions de dollars à 42.1 millions de dollars et de 0.23 dollar par baril (bbl) à 1.31 USD/bbl. Cette augmentation était principalement due à la puissance micro-ondes plus élevée et à la taille plus grande du réacteur requises pour le processus. Malgré ces coûts élevés, le processus développé reste économiquement compétitif par rapport aux techniques conventionnelles de démétallisation et de désulfuration telles que HDM et HDS. Pour calculer la puissance micro-ondes nécessaire, les calculs économiques ont adopté une densité de puissance expérimentale de 0.65 kilowatt par kilogramme (kW/kg) pour le mélange de pétrole brut et de réactif. Cependant, une optimisation supplémentaire de la puissance micro-ondes requise et des conditions de mélange semble nécessaire pour améliorer les performances économiques du processus lors des opérations à grande échelle.

Dans l'ensemble, cette thèse contribue au développement de processus efficaces pour l'élimination du Ni, du V et du S du pétrole brut, tout en présentant un nouveau liquide ionique à base de phosphonium pour la désulfuration extractive. Les résultats améliorent notre compréhension de la cinétique des réactions, des mécanismes et de la faisabilité économique, ouvrant la voie à des approches durables et respectueuses de l'environnement dans l'industrie pétrochimique.

ABSTRACT

Metal and sulfur removal is a crucial step in the upgrading processes of crude oils, yet it remains one of the most energy-intensive operations. Traditional methods such as hydrodemetallization (HDM) and hydrodesulfurization (HDS) have been widely employed for eliminating metals and sulfur compounds. However, these techniques are associated with significant capital costs, operating expenses, and excessive energy consumption. In an effort to electrify crude oil upgrading processes and reduce their carbon footprint and environmental impacts, microwave heating emerges as an advanced technology offering promising potential for efficient metal and sulfur removal from crude oil.

This thesis presents a comprehensive study on the removal of nickel (Ni), vanadium (V), and sulfur (S) from crude petroleum oil using bis(2-ethylhexyl) phosphoric acid (D2EHPA) and microwave heating technology. The research encompasses various aspects, including commercialization and scale-up feasibility, process economics, demetallization kinetics and mechanism, desulfurization mechanism, and optimized reaction conditions. Additionally, a novel phosphonium-based ionic liquid (IL) called trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate [THTDP][D2EHP] is synthesized and evaluated for extractive desulfurization (EDS) of liquid fuels and crude oil.

The investigation begins with a techno-economic analysis to assess the technical and economic performance of the process at an industrial scale to treat 50,000 barrels per stream day (BPSD) of crude oil. An industrial process scheme is developed and simulated in Aspen Plus, demonstrating the economic superiority of the developed process compared to conventional hydrotreating techniques. The estimated total capital costs (CAPEX) and annual operating costs (OPEX) amounted to 6.77 MUSD and 4.23 MUSD (equivalent to 0.24 \$/bbl), respectively.

Furthermore, an effective methodology for the separation and regeneration of D2EHPA using sulfuric acid and sodium hydroxide solutions is established and validated through FTIR and ICP-OES analyses. Sensitivity analysis highlights the importance of developing a precise kinetic model for demetallization reactions and optimizing key process parameters.

The impact of primary process parameters on Ni and V removal efficiencies under microwave heating irradiation is systematically investigated. The optimized values for process parameters are determined, and the removal efficiencies of V and Ni from Iranian crude oil are found to be 72% and 63% at low microwave powers of 40–50 W, respectively. The FTIR investigation reveals the formation of new nitrogen-hydrogen (N-H) bonds in the treated oil, indicating the replacement of nitrogen-metal (N-M) bonds in Ni/V porphyrins by the donated proton from D2EHPA. The kinetic model for microwave-assisted Ni/V removal is investigated at 230–250 °C and optimized conditions, providing insight into the reaction kinetics. The demetallization reactions exhibited first-order kinetics, with estimated activation energies of 29.8 kJ/mol for Ni and 34.7 kJ/mol for V, along with pre-exponential factors of 16.5 min^{-1} for Ni and 66.2 min^{-1} for V.

The research also focuses on the desulfurization of crude oil and liquid fuels using D2EHPA, NaCl aqueous solutions, and microwave heating. Experimental investigations are conducted using different crude oil samples and synthetic model fuels containing thiophene sulfur compounds. The effects of reaction temperature, reaction time, and D2EHPA dosage on S-removal efficiency are studied, and up to 36% and 64% of sulfur is removed from Iranian crude oil and thiophene-based liquid fuels, respectively, under 20 minutes of microwave heating at 65 °C. The formation of a water-soluble ionic liquid between D2EHPA and NaCl is observed from FTIR and

electrical conductivity analyses, suggesting the extraction of thiophene compounds through π - π interactions.

Next, a phosphonium-based ionic liquid, [THTDP][D2EHP], is synthesized and evaluated for extractive desulfurization of crude oils and model fuels. The results demonstrate its effectiveness in removing sulfur compounds, particularly benzothiophene (BT) and dibenzothiophene (DBT), from both model fuels and Iranian crude oil. The findings show that sulfur removal efficiencies of up to 63% for DBT-based model fuels and 57% for Iranian crude oil are achieved. The optimal conditions for extraction are determined to be a 1:1 IL/fuel mass ratio, a temperature of 35 °C, and a duration of 30 minutes. Extensive characterization tests confirm the favorable properties of the synthesized ionic liquid, including high thermal stability, low viscosity, and good electrical conductivity, making it a promising option for extractive desulfurization of liquid fuels and real crude oils.

Finally, a secondary techno-economic evaluation is conducted to update the initial investigation regarding the feasibility of commercializing the proposed technique. The research findings on the optimized reaction conditions and demetallization reaction kinetics is incorporated to present a more accurate industrial process design and economic analysis. A treatment capacity of 50,000 barrels per stream day (BPSD) is assumed to conduct the economic analysis. The results indicates a significant rise in both capital expenditure (CAPEX) and operational expenditure (OPEX) costs, increasing from 6.77 million USD to 42.1 million USD and from 0.23 USD per barrel (bbl) to 1.31 USD/bbl, respectively. This increase is primarily attributed to the higher microwave power and larger reactor size required for the process. Despite these elevated costs, the developed process remains economically competitive compared to conventional demetallization and desulfurization techniques like HDM and HDS. To calculate the required microwave power,

the economic calculations adopt an experimental power density of 0.65 kilowatts per kilogram (kW/kg) for the crude oil and reagent mixture. However, further optimization of the required microwave power and mixing conditions seems necessary to enhance the economic performance of the process for large-scale operations.

Overall, this thesis contributes to the development of an efficient microwave-assisted process for the removal of Ni, V, and S from crude oil, while also presenting a novel phosphonium-based ionic liquid for extractive desulfurization. The findings enhance our understanding of the reaction kinetics, mechanisms, and economic feasibility, paving the way for sustainable and environmentally friendly electrified processing in the petrochemical industry.

TABLE OF CONTENTS

DEDICATION	iii
ACKNOWLEDGEMENTS	iv
RÉSUMÉ.....	vi
ABSTRACT	x
TABLE OF CONTENTS	xiv
LIST OF TABLES	xx
LIST OF FIGURES.....	xxii
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 LITERATURE REVIEW	5
2.1 Preface	5
2.2 Demetallization and Desulfurization Techniques.....	8
2.2.1 Physical Methods	8
2.2.1.1 Distillation.....	8
2.2.1.2 Solvent Extraction.....	8
2.2.1.3 Filtration.....	11
2.2.1.4 Adsorption.....	11
2.2.2 Chemical Methods.....	12
2.2.2.1 Thermal Cracking	12
2.2.2.2 Chemical Complexation.....	13
2.2.2.3 Hydrotreatment	13
2.2.2.4 Biodesulfurization (BDS)	15
2.3 Unconventional Heating Technologies	17
2.3.1 Induction Heating.....	17

2.3.2	Ultrasound	18
2.3.3	Plasma	20
2.3.4	Microwave Heating	21
2.3.4.1	Interaction of Materials with Microwave	22
2.3.4.2	Permittivity & Permeability	25
2.3.4.3	Microwave Heating as an Alternative to Conventional Heating	29
2.4	MW-assisted Upgrading of Crude Petroleum Oil	31
CHAPTER 3 OBJECTIVES AND THESIS STRUCTURE		42
3.1	Objectives	42
3.2	Thesis Structure	43
CHAPTER 4 ARTICLE 1 : PROCESS DEVELOPMENT AND TECHNO-ECONOMIC ANALYSIS OF MICROWAVE-ASSISTED DEMETALLIZATION AND DESULFURIZATION OF CRUDE PETROLEUM OIL.....		47
4.1	Abstract.....	47
4.2	Introduction	48
4.3	Methods	53
4.3.1	Process design	55
4.3.1.1	Microwave-assisted reactor	57
4.3.1.2	Washing & separation.....	58
4.3.1.3	DMDSA regeneration	60
4.3.2	Characterization techniques	61
4.3.2.1	FTIR.....	61
4.3.2.2	ICP-OES	62
4.3.3	Economic analysis.....	62
4.3.3.1	Total capital costs (CAPEX).....	63

4.3.3.2	Total annual operating costs (OPEX)	65
4.4	Results and discussion	65
4.4.1	Process installation configuration	65
4.4.2	Validation of washing and DMDSA regeneration methodologies.....	67
4.4.3	Capital and operating costs	69
4.4.3.1	Total capital costs (CAPEX).....	69
4.4.3.2	Total operating costs (OPEX).....	72
4.4.4	Sensitivity analysis of OPEX & CAPEX	74
4.5	Conclusion	79
CHAPTER 5 ARTICLE 2 : MICROWAVE-ASSISTED NICKEL AND VANADIUM REMOVAL FROM CRUDE PETROLEUM OIL USING BIS(2-ETHYLHEXYL) PHOSPHORIC ACID: A KINETIC STUDY		81
5.1	Abstract.....	81
5.2	Introduction	82
5.3	Materials and methods.....	85
5.3.1	Materials.....	85
5.3.2	Experimental setup.....	85
5.3.3	Experimental procedure	86
5.3.3.1	Reaction	86
5.3.3.2	Washing and separation	87
5.3.4	Characterization methods.....	87
5.3.5	Temperature measurement	88
5.4	Results and discussion	89
5.4.1	Effect of temperature.....	89
5.4.2	Effect of reaction time	90

5.4.3	Effect of D2EHPA dosage	91
5.4.4	Reaction mechanism	93
5.4.5	Reaction kinetics	97
5.5	Conclusion	107
5.6	Appendix Energy requirements	108
CHAPTER 6 ARTICLE 3 : MICROWAVE-ASSISTED SULFUR REMOVAL FROM CRUDE PETROLEUM OIL AND LIQUID FUELS BY BIS(2-ETHYLHEXYL) PHOSPHORIC ACID 110		
6.1	Abstract.....	110
6.2	Introduction	111
6.3	Materials and methods.....	114
6.3.1	Materials.....	114
6.3.2	Synthesis of model fuels	114
6.3.3	Experimental setup.....	115
6.3.4	Experimental procedure	115
6.3.4.1	MW-assisted IL synthesis and extractive desulfurization	115
6.3.4.2	Washing and separation	116
6.3.5	Characterization methods.....	116
6.3.6	Temperature measurement	117
6.4	Results and discussion	118
6.4.1	Ionic liquid synthesis and characterization	118
6.4.2	Effect of temperature.....	121
6.4.3	Effect of reaction time.....	123
6.4.4	Effect of D2EHPA dosage	124
6.4.5	Crude oil desulfurization.....	126
6.5	Conclusion	128

CHAPTER 7	ARTICLE 4 : EXTRACTIVE DESULFURIZATION OF CRUDE PETROLEUM OIL AND LIQUID FUELS USING TRIHEXYL TETRADECYL PHOSPHONIUM BIS(2-ETHYLHEXYL) PHOSPHATE IONIC LIQUID	129
7.1	Abstract.....	129
7.2	Introduction	130
7.3	Materials and methods.....	133
7.3.1	Materials.....	133
7.3.2	IL synthesis	133
7.3.3	Model fuel preparation	134
7.3.4	Extractive desulfurization	134
7.3.5	Characterization methods.....	135
7.4	Results and discussion.....	136
7.4.1	[THTDP][D2EHP] characterization and physical properties.....	136
7.4.1.1	FTIR analysis	136
7.4.1.2	Thermal stability (TGA analysis)	137
7.4.1.3	Viscosity analysis.....	138
7.4.1.4	Solubility analysis.....	139
7.4.1.5	Electrical conductivity analysis	140
7.4.2	Effect of reaction time.....	141
7.4.3	Effect of temperature.....	142
7.4.4	Effect of S-compound	144
7.4.5	Crude oil desulfurization.....	145
7.5	Conclusion.....	146
CHAPTER 8	UPDATED TECHNO-ECONOMIC ASSESSMENT	148
CHAPTER 9	GENERAL DISCUSSION	156

CHAPTER 10	CONCLUSION AND RECOMMENDATIONS	162
10.1	Conclusion	162
10.2	Recommendations	165
REFERENCES.....		167

LIST OF TABLES

Table 2.1 Pros and Cons of EDS methods ⁸	10
Table 2.2 Pros and Cons of adsorption methods ⁸	12
Table 2.3 Pros and Cons of HDS method ⁸	15
Table 2.4 Pros and Cons of BDS method ⁸	16
Table 2.5 Classification of plasmas by electron temperature.....	20
Table 2.6 Dielectric properties of some materials ^{1, 64}	27
Table 2.7 Microwave heating and conventional heating comparison (adapted from ⁸²)	30
Table 2.8 Penetration or skin depth of some metals (Adapted from ^{1, 64})	36
Table 4.1 Cost estimations for installing a new HDS unit by US EPA ⁸	49
Table 4.2 Dielectric properties of the processed materials	54
Table 4.3 CAPEX investment estimation	71
Table 4.4 Energy and utility consumption breakdown	74
Table 4.5 Impact of design parameters on OPEX & CAPEX costs.....	78
Table 5.1 Properties of Iranian crude oil	85
Table 5.2 Optimum values of the main process parameters	93
Table 5.3 Material balance of Ni & V in oil/aqueous phases for crude oil treated with 15 wt.% D2EHPA at 250 °C for 1h.....	96
Table 5.4 Determination coefficients for zero, first, and second order reaction kinetics	101
Table 5.5 Kinetic and Arrhenius parameters for Ni and V removal reactions.....	104
Table 5.6 Irradiated microwave power	109
Table 6.1 Properties of Iranian and Basra crude oils	114
Table 7.1 Properties of treated crude oils.....	134
Table 7.2 Properties of treated S compounds.....	144

Table 7.3 EDS efficiencies for Iranian and Basra crude oils treated with [THTDP][D2EHP] at 35 °C for 30 minutes.....	146
Table 8.1 Optimum values for primary process parameters	149
Table 8.2 Total CAPEX costs of the proposed process	152

LIST OF FIGURES

Figure 2.1 Examples of V & Ni porphyrins in crude oil (reprinted from reference ¹).....	7
Figure 2.2 Various classes of S-compounds in crude oil (reprinted from reference ²⁶).....	7
Figure 2.3 Schematic of an electromagnetic wave (reprinted from ⁶³)	22
Figure 2.4 The electromagnetic spectrum (image courtesy NASA)	22
Figure 2.5 Interaction of materials with electromagnetic waves	23
Figure 2.6 Polarization mechanisms in microwave heating (reprinted from ¹)	24
Figure 2.7 Crude oil elemental composition	33
Figure 2.8 Heating rate and penetration depth of various metals (Adapted from ⁶⁴).....	36
Figure 2.9 Suggested desulfurization and demetallization mechanism (reprinted from ²⁴)	40
Figure 4.1 Concentration (ppm) of (A) Vanadium, (B) Sulfur, (C) Nickel in raw and treated Iranian crude oil using conventional (CH) and microwave heating (MW). (Reported from ¹)	53
Figure 4.2 Flow diagram of the developed process (MUDMDSA: make-up DMDSA, MUWATER: make-up water diluted by NaOH, DEM: demulsifying agent, HA: DMDSA regeneration reagent (sulfuric acid), RECDMDSA: recycled DMDSA, RECWAT: recycled water, TROIL: treated oil,.....)	55
Figure 4.3 Process flow diagram of a typical crude distillation unit.....	56
Figure 4.4 Installation configuration of the proposed process (MW-DMDSU) in the crude distillation unit of a typical crude oil refinery	67
Figure 4.5 (A) Chemical structure of DMDSA (B) Absorbance FTIR of the mixture of DMDSA and Iranian crude oil before washing (blue line), after treatment with NaOH (black line), and raffinate process water (red line) after separation from crude mixture.	68
Figure 4.6 Phosphorous concentration of the raffinate process water before and after treatment with sulfuric acid measured by ICP-OES.....	69
Figure 4.7 Schematic of the simulated process (temperature [°C], flow rate [kg/h], OUT-REACT: reactor outlet stream, WASH-SOL: washing solution, AQ-RAFF: aqueous raffinate, OUT-	

MIX: mixer outlet stream, RECDMDSA: recycled DMDSA, TROIL: treated oil, EFFWATER: effluent water)	70
Figure 4.8 Share of major processing units in the total equipment costs.....	71
Figure 4.9 Cost fragments of the total annual OPEX costs.....	73
Figure 4.10 Impact of crucial parameters on total CAPEX costs	75
Figure 4.11 Impact of (A) mixture residence time and average bulk temperature increment (B) treatment capacity, DMDSA regeneration efficiency and consumption on annual OPEX costs	76
Figure 5.1 Impact of reaction temperature on V removal efficiency for crude oil treated with 5 wt.% D2EHPA for 10 minutes	90
Figure 5.2 Impact of reaction time on V removal efficiency for crude oil treated with 5 wt.% D2EHPA at 250 °C.....	91
Figure 5.3 Impact of D2EHPA concentration on V removal efficiency for crude oil treated for 1 h at 250 °C	92
Figure 5.4 Impact of D2EHPA concentration on Ni removal efficiency for crude oil treated for 1 h at 250 °C	92
Figure 5.5 Chemical structure of (a) Vanadium porphyrin (b) D2EHPA (reprinted from reference 1, 110).....	94
Figure 5.6 IR Absorbance (A) versus wavelength (cm-1) from FTIR analysis of blank crude oil (black) irradiated for 1h at 250 °C and treated oil with 15 wt.% D2EHPA at 250 °C for 10 minutes (red), 30 minutes (blue), and 1 h (purple).....	95
Figure 5.7 IR Absorbance (A) versus wavelength (cm-1) from the FTIR analysis of pure D2EHPA (orange), reacted D2EHPA (purple), and regenerated D2EHPA (blue)	97
Figure 5.8 TGA analysis of pure D2EHPA.....	99
Figure 5.9 Impact of reaction temperature on V removal efficiency for crude oil treated with 15 wt.% D2EHPA for 1h.....	101

Figure 5.10 $-\ln(1-X)$ versus reaction time of (a) V and (b) Ni removal for crude oil treated with 15 wt.% D2EHPA	102
Figure 5.11 Arrhenius plot of V and Ni removal for reactions at 230, 240, and 250 °C	103
Figure 5.12 Comparison of experimental and predicted data for (a) V and (b) Ni removal efficiency	105
Figure 6.1 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of the synthesized IL (red) and pure D2EHPA (black).....	120
Figure 6.2 Ionic liquid formation reaction scheme	120
Figure 6.3 Suggested mechanism for the extractive desulfurization of thiophene by the synthesized ionic liquid.....	120
Figure 6.4 The impact of reaction temperature on sulfur removal efficiency from model fuels irradiated for 20 minutes with 15 wt.% D2EHPA	123
Figure 6.5 The impact of reaction time on sulfur removal efficiency from model fuels irradiated at 65 °C minutes with 15 wt.% D2EHPA	124
Figure 6.6 The impact of the D2EHPA:fuel mass ratio on sulfur removal efficiency from model fuels irradiated at 65 °C for 20 minutes.....	126
Figure 6.7 S-concentration of the produced raffinate water, crude fuel, and treated fuel with 15 wt.% d2EHPA and irradiated at 65 °C for 20 minutes.....	126
Figure 6.8 S-removal efficiencies for real crude oil samples treated with 15 wt.% d2EHPA and irradiated at 65 °C for 20 minutes	127
Figure 7.1 Chemical structure of [THTDP][D2EHP] IL	133
Figure 7.2 [THTDP][D2EHP] synthesize reaction scheme	134
Figure 7.3 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of [THTDP][D2EHP] before (red) and after (blue) extractive desulfurization	137
Figure 7.4 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of pure D2EHPA.....	137
Figure 7.5 TGA results of [THTDP][D2EHP] IL	138
Figure 7.6 The effect of temperature on [THTDP][D2EHP] viscosity	139

Figure 7.7 The effect of temperature on [THTDP][D2EHP] electrical conductivity	141
Figure 7.8 Impact of time on EDS efficiency with [THTDP][D2EHP] at 35 °C.....	142
Figure 7.9 Impact of temperature on EDS efficiency with [THTDP][D2EHP] for 30 minutes .	143
Figure 7.10 EDS efficiencies for different S-compounds with [THTDP][D2EHP] at 35 °C for 30 minutes and 1:1 IL/fuel mass ratio.....	145
Figure 8.1 Updated process flow diagram	150
Figure 8.2 CAPEX costs breakdown.....	152
Figure 8.3 OPEX costs breakdown	153

CHAPTER 1 INTRODUCTION

Despite all efforts to replace fossil fuels by green and renewable energies to confront global warming and the tremendous release of greenhouse gases to the atmosphere, the current pace of energy transformation is not fast enough to achieve the goal of the Paris Agreement's Policy. To respect the Paris Agreement's policy, many countries have planned to reduce their projected energy-related carbon emissions by revising domestic emission regulations, which may lead to drop the projected global carbon emissions by 11% from 2015 to 2050. Current emission scenarios aim to reduce carbon dioxide release to the atmosphere from 1380 Gt to 1230 Gt, while new stricter policies plan to decrease the emissions even more to 34.8 Gt/year. However, an increase up to 3 °C in the global temperature is foreseen even with respecting the recently imposed scenarios that are far from the target of the Paris Agreement to limit the global temperature increase to 1.5 °C ¹.

The chemical and petrochemical industry relies on fossil fuels for over 50% of the total energy consumed, which creates a significant emissions concern. For instance, 26 chemical compounds in Europe account for more than 90% of the region's greenhouse gas emissions from the chemical sector, which comprise 150 million tons (Mt) or 0.6% of the world's total emissions. This includes energy used as feedstock. These chemical feedstocks will result in emissions of 200 Mt of CO₂ equivalents (Mt CO₂e) by 2050 if the industry maintains its current expanding trajectory ². The electrification of chemical processes is a key aspect of the energy transition movement, which seeks to reduce the carbon footprint of industries across the globe. As the world shifts away from traditional fossil fuels, the bulk of the renewable energy produced is in the form of electricity. As a result, the chemical industry, which historically relies heavily on fossil fuels for reactor heating, must reconfigure its processes to leverage electricity ³. Exploring various heating

technologies, which are not commonly utilized in the industry yet, may prove beneficial. These technologies have demonstrated improved energy efficiency and selectivity in multiple reactions at laboratory and pilot scales. They offer several advantages such as higher energy efficiency, reduced carbon footprint, and direct impact on the reaction's selectivity. This results in reducing waste streams and downstream purification processes, which are typically energy intensive ^{4,5}. The four unconventional heating mechanisms that have shown promise are microwave heating, induction heating, plasma, and ultrasound. By swiftly adopting these technologies in the industry, it could potentially replace a significant portion of the energy consumed by fossil fuels in chemical processes. As a result, it could positively impact their carbon footprint and environmental performance ³.

Upgrading processes for crude oil are essential in the petrochemical industry, but also among the most energy-intensive operations. These processes aim to eliminate hazardous components and impurities from crude oil. Metal and sulfur removal is one of the most widely used upgrading processes for crude oils, which is implemented in all refineries. The presence of metals—particularly nickel (Ni) and vanadium (V), and sulfur (S) in crude oil leads to significant technical challenges in the refinery processes, such as catalyst poisoning, ash formation, and corrosion. If not removed to a specific threshold from the final fuel products, these contaminants will release in the form of NO_x and SO_x emissions that can cause environmental problems and potential health risks for humans. The most widely applied technique for eliminating metals and sulfur compounds is hydrodemetallization (HDM) and Hydrodesulfurization (HDS), which eliminates metals and sulfur through reacting them with hydrogen at high temperatures and pressures, along with the use of costly catalysts ⁶. Achieving even lower metal and sulfur content through HDM/HDS would necessitate more severe conditions than presently used, leading to higher capital costs and operating

expenses including extreme energy consumption ^{7, 8}. Consequently, significant research is being conducted to identify green and less energy intensive methods for crude oil metal and sulfur removal.

As an attempt to electrify crude oil upgrading processes, microwave heating can be applied as an advanced technology for metal and sulfur removal from oil. Microwave heating (MWH) characteristics such as volumetric and selective heating make it a promising alternative for conventional heating (CH) in several fields such as food processing ⁹, chemical ¹⁰, and environmental engineering ¹¹. The utilization of MWH in upgrading petroleum crude oil processes is not well-investigated in the literature. Only a limited number of studies have explored the effects of MWH technology on the demetallization and desulfurization of crude oil ^{6, 12-15}. A novel technique for the joint removal of sulfur and metals from petroleum oil was introduced by Attia et al. in 2018 ¹. Bis(2-ethylhexyle) phosphoric acid (D2EHPA) was used as the reagent to remove metals and sulfur from crude oil under CH and MWH conditions. The remarkable advantages of microwave heating technology created a significant interest in investigating the feasibility of commercializing the proposed green process as an alternative to the conventional crude oil upgrading processes. The conventional crude upgrading methods are known to be costly, extremely energy-intensive, and they release significant amounts of carbon emissions. Despite the promising performance of the proposed technique by Attia et al. in laboratory scale, its potential for industrial scale adaptation was unknown. Therefore, in this study, we investigated the technical and economic feasibility of commercializing the proposed technique by performing a comprehensive techno-economic assessment. As crude oil demetallization and desulfurization under microwave irradiation undergoes a complex transformation, a comprehensive study focusing on the mechanism and kinetics of the reactions as well as optimization of the main process parameters

was carried out. With the appropriate understanding of the mechanism, the importance of the reaction kinetic will be highlighted as a possibility to optimize the process design and economics at large-scale operation. This work could set a basis for future studies towards commercialization of microwave-assisted demetallization and desulfurization of crude petroleum oils.

CHAPTER 2 LITERATURE REVIEW

2.1 Preface

Different types of metals can be found in crude oil, their presence and concentration depending on the extraction location. These metals can exist as inorganic salts, such as chlorides, or as organometallic compounds, mainly nickel and vanadium porphyrins. While metals are typically present in crude oil at low concentrations, ranging from 100 ppm to as high as 1000 ppm in some crude oils, nickel, iron, aluminum, calcium, vanadium, magnesium, and sodium are the most commonly occurring metals^{16,17}. Vanadium and nickel are present in crude oil in stable, oil-soluble compounds, including naphthenic acid and metalloporphyrin rings^{18,19}. Other metals are found as inorganic salts or in combination with naphthenic acid. The porphyrinic structure of the metals makes them hazardous, and extensive research has been conducted to gain a better understanding of their characteristics and structure²⁰. The removal of metals, particularly nickel and vanadium, which are in the form of stable metalloporphyrin compounds (illustrated in Figure 2.1), is a challenging process for several reasons. For instance, high concentrations of these metals exist in the organometallic form in crude oil. Additionally, metalloporphyrins are stable oil-soluble rings with decomposition temperatures greater than 350 °C, making removal processes costly and energy-intensive²¹.

The presence of metals in crude oil poses various technical and environmental issues. For example, vanadium in the form of vanadium oxide can cause irritation in the human body when reacting with mucus, while nickel carbonyl is a carcinogenic material that can lead to malignant neoplastic diseases. Furthermore, metals have detrimental impacts on refinery processes, such as catalyst deactivation and corrosion on contact surfaces. Calcium and magnesium chlorides, for instance, can produce highly corrosive HCl at temperatures above 170 °C¹. Heavy metals can plug

the pores of the catalysts, leading to fast catalyst deactivation and higher operational costs. Metal poisoning of the catalyst surface can also increase dehydrogenation reactions in cracking units, resulting in higher coke and dry gas production. Aside from technical challenges in refinery processes, high metal concentrations in final products like fuels pose health risks due to gaseous emissions and can affect engine performance. Metal contents in fuels can increase ash formation in the engine during combustion, causing corrosion in engine moving parts and reduced output power, therefore, extreme regulations have been recently imposed by regulatory agencies to limit the concentration of these metals in final fuel products to less than 0.1 ppm^{15, 22}.

After carbon and hydrogen, sulfur is the third most abundant element found in petroleum. In order to produce transportation fuels and petrochemical products that meet increasingly strict specifications, desulfurization of crude oil is a necessary step in the refining process. Thus, the removal of sulfur has become a crucial requirement for many refineries, with the sulfur content of crude oil affecting its price and processing cost. The average sulfur content in crude oil ranges from 0.1 to 15 wt.%, depending on the origin of the extraction site^{23, 24}. Sulfur compounds in crude oil exist in two forms: inorganic and organic. Inorganic sulfur, such as elemental sulfur, H₂S, and pyrite, can be present in dissolved or suspended form²⁵. Organic sulfur compounds, such as thiols, sulfides, and thiophenic compounds, are the primary source of sulfur in crude oil. Figure 2.2 illustrates some of the primary categories of organic sulfur compounds available in crude oils^{26, 27}.

High sulfur content in the crude has significant adverse effects on upgrading processes in refineries as well as hazardous influence on the environment. The combustion of sulfur compounds present in fuels produces SO_x compounds that are harmful to the environment and human health, causing respiratory problems and acid rain. Recent regulations limit the sulfur content of fuels to less than 1 ppm. Catalytic converters of vehicles are also negatively affected by these compounds

⁸. Moreover, the presence of sulfur in crude oil can negatively impact the performance of catalysts utilized in the refining processes. This is due to the tendency of sulfur to accumulate on the active sites of the catalysts, which can lead to reduced efficiency. As a result, the sulfur content in crude oil is a critical factor affecting both processing costs and the final cost of the end-product.

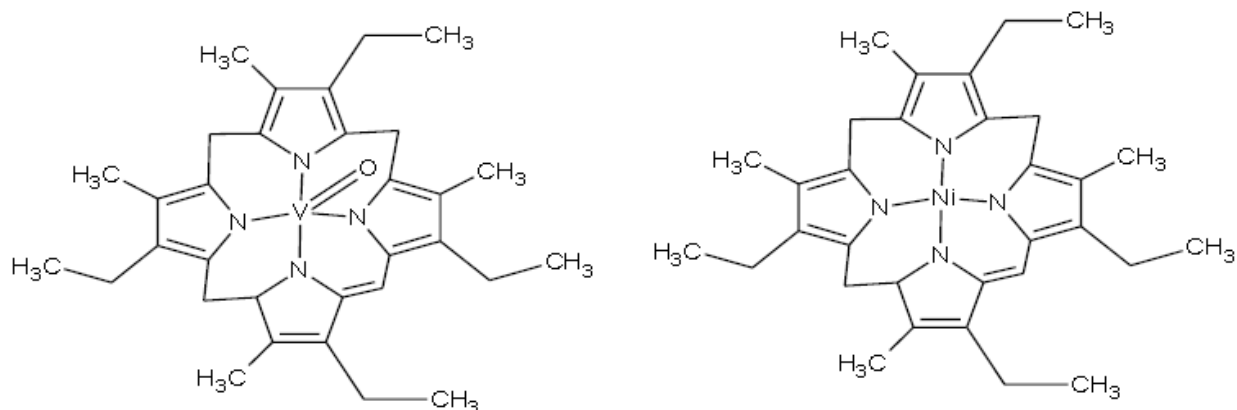


Figure 2.1 Examples of V & Ni porphyrins in crude oil (reprinted from reference ¹)

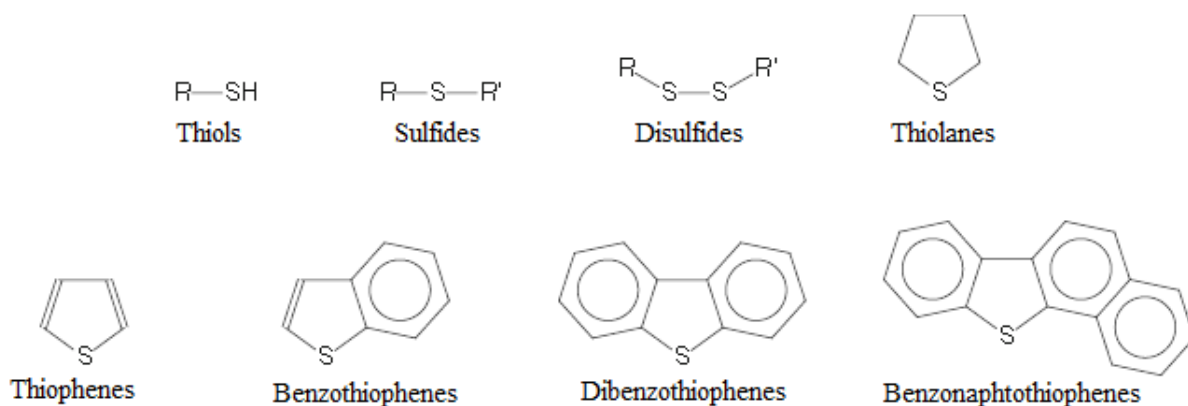


Figure 2.2 Various classes of S-compounds in crude oil (reprinted from reference ²⁶)

Numerous methods for removing metal and sulfur from crude oil have been developed since the mid-20th century. These methods can be classified into physical, chemical, and biological techniques. The following section provides an overview of the most used techniques. While most

of these techniques have proven to be effective in lab-scale experiments, only a few have been implemented on an industrial scale in petroleum refineries, primarily due to technical difficulties or economic feasibility issues.

2.2 Demetallization and Desulfurization Techniques

2.2.1 Physical Methods

2.2.1.1 Distillation

Petroleum crude oil is a complex mixture comprising various chemical compounds, mostly hydrocarbons, along with varying amounts of nitrogen, oxygen, sulfur, and metal compounds. Separating these compounds based on their boiling temperature or distillation has been a crucial technique employed in every petroleum oil refinery for a long time. The process involves heating the crude oil to the gas phase and then separating the oil fractions in a distillation column based on their boiling points. Subsequently, metalloporphyrins are extracted using a catalytic fixed bed reactor installed in hydrotreating units. However, distillation has several limitations that hinder its efficiency. For instance, distillation lacks selectivity to remove specific metals, and the removal efficiency is insufficient to extract all metalloporphyrin compounds in crude oil. Furthermore, since distillation eliminates the whole fraction that contains metals, the crude oil yield decreases, affecting downstream processes and overall production yield. Lastly, distillation transfers the metals to heavier fractions, which have recently gained attention for further processing and usage in various sectors ^{1, 17}.

2.2.1.2 Solvent Extraction

Solvent extraction, also known as liquid-liquid extraction, is a traditional method used to separate metal compounds by utilizing two immiscible phases, typically an organic and an aqueous phase. The separation is achieved by transferring the target compounds from one phase to another based on the difference in the chemical potential between the two phases. An example of this

technique is the extraction of uranium and rare earth metals from ores or uranium salts using acidic organic solvents. Similarly, solvent extraction can be employed to remove metalloporphyrin compounds from petroleum crude oil by utilizing appropriate solvents ^{17, 28}. The solvent properties play a vital role in this process since each solvent can remove a specific compound containing metals. Moreover, the required steps and process conditions may vary for each solvent, depending on the removal mechanism involved in the process.

Solvent extraction is typically conducted under mild temperature and pressure conditions, which is one of its primary advantages over other methods. However, the solubility of the solvent plays a significant role in determining the overall removal efficiency, solvent consumption and regeneration processes, and the yield of the treated oil. The solubility of the solvent is influenced by various factors, such as H-bonding forces, dipole-coupled forces, and dispersion forces. Ethylene carbonate, propylene carbonate, ethylene trithiocarbonate, and dimethylsulfoxide are among the favored solvents ¹⁷. However, there are significant challenges associated with this process, such as high solvent consumption per volume of the treated oil, low yield resulting from the removal of oil fractions containing metalloporphyrins, and limitations in application to oils with high bitumen content ^{1, 29}.

Extractive desulfurization (EDS), which utilizes solvents to remove sulfur compounds, has emerged as a promising alternative to conventional desulfurization techniques in petroleum refineries. Early solvents used for sulfur extraction included dimethyl sulfoxide (DMSO), dimethylformamide (DMF), pyrrolidones, and acetonitrile (AcN) ⁸. One major advantage of EDS over conventional techniques like hydrodesulfurization (HDS) is its lower cost due to milder processing conditions and the absence of hydrogen and catalysts ³⁰. Furthermore, EDS selectively extracts sulfur compounds without affecting other compounds, leaving their chemical structure

intact. Recovering the extracted sulfur compounds as raw materials is also possible. However, solvent selectivity is crucial as there are several hydrocarbons in crude oil with similar polarity to sulfur compounds. Poor selectivity will result in the removal of other fractions and a corresponding decrease in oil yield ^{30, 31}. Table 2.1 briefly summarizes the advantages and disadvantages of the EDS method. It should be noted that further research is needed to fully understand and optimize the EDS process.

Ionic liquids (ILs) have demonstrated significant potential as extractants in extractive desulfurization. ILs are composed of a mixture of ions, including anions and cations, that remain liquid at temperatures below 100 °C. These liquids are also known as room temperature molten salt, low-temperature molten salt, or ionic fluid. One of the advantages of using ILs as extractants is their high flexibility, which allows their properties to be tailored to specific applications. This is particularly advantageous in extractive desulfurization, where high selectivity for aromatic sulfur compounds is required ³². ILs have numerous applications, including catalysis ^{33, 34} and CO₂ capture ³⁵⁻³⁹, and their properties, such as low volatility, the ability to function as both oxidants and reductants, high thermal stability, and moisture tolerance, make them an attractive alternative to conventional organic solvents ^{8, 30, 40, 41}.

Table 2.1 Pros and Cons of EDS methods ⁸

Advantages	Disadvantages
Low pressure and temperature ⁴²	Risk of sulfur free compounds extraction ³⁰
Hydrogen free ^{31, 42}	Poor removal efficiency (<50%) ³⁰

Catalyst is not needed ³¹

No interaction with useful fuel oils ³¹

Reusability of the extracted sulfur ³¹

2.2.1.3 Filtration

In the past few years, membrane-based processes have emerged as a promising technology to decrease the viscosity, asphaltene content, and sulfur and metals content in heavy oils and residues. These methods usually involve the use of membranes to recover solvents from an initial extraction, phase separation, or dilution step ¹⁷. However, there are only a limited number of studies that have investigated the direct application of membranes for the removal of asphaltene, sulfur, and metals from heavy oil ^{17, 43}.

2.2.1.4 Adsorption

Adsorption is another method for desulfurization of crude oil, which involves the selective capture of sulfur compounds using adsorbents in a non-destructive and non-reactive process. To increase the interaction surface area, the adsorbent is placed on a porous and unreactive substrate. Zinc oxide, zeolites, alumina, aluminosilicates, and activated carbon are some of the common adsorbents used in adsorptive desulfurization. This method offers mild operating conditions and high removal efficiency. Several factors affect the effectiveness of adsorptive desulfurization, such

as the adsorption rate, the adsorption capacity of the adsorbent, regeneration potential, and selective adsorption ⁸. Table 2.2 summarizes the advantages and disadvantages of this technique.

Table 2.2 Pros and Cons of adsorption methods ⁸

Advantages	Disadvantages
Low temperature ^{42, 44}	Poor selectivity ⁴⁴
Hydrogen free ^{42, 44}	Requires large adsorbent beds or multiples ⁴⁴
No hydrogen sulfides production ⁴²	Few adsorbents available for refractory sulfur compounds ⁴⁴

2.2.2 Chemical Methods

2.2.2.1 Thermal Cracking

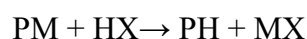
Thermal cracking, also known as visbreaking, is a commonly used method in petroleum refineries. The aim of this method is to reduce the concentration of metal content and kinematic viscosity of crude oil. In the visbreaking process, crude oil is heated in a furnace to convert large hydrocarbon molecules to light hydrocarbons, leading to a significant reduction in viscosity ⁴⁵. The reported maximum removal efficiencies for Ni, V, and S using visbreaking are 12%, 13%, and 5%, respectively. However, if aqueous ammonium solution is added to the oil, these efficiencies can increase up to 26%, 20%, and 14%, respectively, with the added benefit of reducing coke deposition from 0.61% to 0.27% ¹.

Despite being effective in reducing residual oil production in the distillation unit of refineries, visbreaking has several disadvantages. The low conversion efficiency and significant energy loss during the process are major concerns. There is also a risk of deposition of olefins and

asphaltene in the furnace, leading to the production of unwanted and toxic compounds such as tar and hardly recyclable products ⁴⁶.

2.2.2.2 Chemical Complexation

Acids have been utilized in petroleum refining processes for a considerable period of time to efficiently eliminate metals from crude oil. The primary reaction that takes place between the acid agent and the metal compounds in the crude oil can be demonstrated as:



This technique is not limited to removing metals from crude oil; it can also be utilized to eliminate other problematic compounds, such as nitrogen and sulfur, from the crude structure. Initially, this method was employed to refine animal and vegetable oils and upgrading crude oil with sulfuric acid is another well-known example of acid treatment ¹⁷. In 1908, Marcusson et al. studied the use of sulfuric acid to fractionate low boiling point naphtha and to precipitate asphaltenes ⁴⁷. However, using sulfuric acid carries the risk of sulfur dioxide formation during the demetallization process, which can initiate undesired side reactions with the unsaturated hydrocarbons present in the crude. This can result in a lower elimination rate in the demetallization process and increased complexity of the crude oil's chemical structure. Additionally, high acid consumption and low yield for the processed oil are among the other challenges associated with the use of sulfuric acid to remove metals from crude petroleum oil ¹.

2.2.2.3 Hydrotreatment

Hydrodemetallization (HDM) and hydrodesulfurization (HDS) are two conventional techniques that are commonly used to eliminate metals and sulfur from crude oil. Hydrogenation can also be employed to extract nitrogen and oxygen compounds present in crude oil. Ni, Mn, and Co based catalysts can be utilized to achieve high removal efficiency up to 90% in the

hydrodemetallization process ⁴⁷. The crucial factors affecting HDM include the nature and composition of the feedstock, catalyst characterization such as type, pore size, and contact surface, and residence time. Despite its high efficiency, HDM has several drawbacks, such as high operational costs due to severe process conditions, high hydrogen consumption, and rapid catalyst deactivation resulting from metal oxides precipitation on the catalyst's active sites ⁴⁸. The metal oxide-induced catalyst poisoning not only raises the operational cost but also increases the hydrogen requirement and reduces the treatment yield ^{1, 17}.

Raymond Fleck and Paul Nahin were the developers of the hydrodesulfurization technique in 1950 ⁴⁹. This method is used to convert sulfur compounds in crude oil to hydrogen sulfide gas by reacting the oil with hydrogen in the presence of catalysts in a trickle bed reactor under severe treatment conditions of 400 °C temperature and 130 bars pressure. The generated H₂S is then separated from the oil by the Claus process, which uses amines to wash H₂S. Increasing the severity of the process conditions can enhance sulfur removal efficiency, but it may also decrease the octane number of the final fuel product due to the saturation of the olefin products at high pressures and/or catalyst deactivation caused by increased coke formation at high temperatures. However, this method is not effective in removing all types of sulfur compounds in crude oil. Sterically hindered compounds such as 4,6-alkyl-substituted dibenzothiophene have a lower reaction rate due to the sulfur atoms shielding the catalyst surface ⁵⁰. Table 2.3 provides a summary of the advantages and disadvantages of HDS. To achieve 100% removal efficiency using HDS is theoretically possible according to thermodynamic equilibrium calculations ⁸, but economic considerations make it unfeasible ⁵¹. For instance, reducing the sulfur content to 50 ppm can cost four times more than reducing it to 200 ppm ⁵². Ibrahim et al ⁸ compared the installation of a new HDS unit to reduce sulfur content to 500 ppm and 15 ppm. They concluded that an HDS unit with a capital cost of 31-

42 million USD and a catalyst cost of 0.3-0.8 USD per barrel per stream day (BPSD) would be necessary to reduce the sulfur content of fuel blendstocks to 15 ppm.

Table 2.3 Pros and Cons of HDS method ⁸

Advantages	Disadvantages
Fully developed technology [37]	High temperature and pressure ^{16, 44}
Efficient in removing various sulfur compounds	High hydrogen consumption and cost
	Not effective on refractory sulfur compounds ³⁰

2.2.2.4 Biodesulfurization (BDS)

BDS, which stands for Bio desulfurization, is an alternative technique for desulfurizing fossil fuels including crude oil. This method involves the use of microorganisms that require sulfur to survive, which can eliminate sulfur compounds from the fuel. However, the microorganisms need to be isolated to consume the sulfur atoms found in proteins, amino acids, and microorganism enzyme cofactors ⁵³. There are different mechanisms proposed by researchers in the literature for BDS, which differ in terms of their attacking pathways. For example, the Kodama pathway involves the first attack on the carbon atom, whereas the 4S pathway initiates the first attack on the sulfur axis ³¹.

Recently BDS has emerged as a green technology. Researchers have conducted numerous studies to evaluate the efficacy of various bacterial species in the BDS process. *Pseudomonas*, *Rhodococcus* spp, *Brevibacterium*, *Gordona*, and *Arthrobacter* have demonstrated high desulfurization efficiency ⁸. BDS offers several benefits, including low capital and operational costs, significant reduction in greenhouse gas emissions, potential for producing high-value

byproducts, and high selectivity via enzyme customization. However, several drawbacks impede the large-scale implementation of BDS methods, such as low reaction rates and slow kinetics, high biomass consumption (around 250 wt. % biomass/sulfur), and restrictions on the process operating conditions due to the sensitivity of live microorganisms^{8, 44, 54}. On the other hand, the efficiency and rate of desulfurization are significantly affected by process conditions such as pH, temperature, and dissolved oxygen concentration. Additionally, some biochemical pathways utilized by microorganisms to eliminate sulfur can lead to a decrease in the desired hydrocarbons, thus reducing the final fuel energy content⁵⁵. The separation technology required to effectively distinguish the final treated oil from microbial biomass and the aqueous phase is not well-established and requires further research and enhancement⁵⁶. Table 2.4 provides a summary of the advantages and disadvantages of BDS.

With over 50% of energy consumption in the chemical and petrochemical industry stemming from fossil fuels, electrifying this sector would be a crucial stride towards meeting environmental targets set out to reduce greenhouse gas emissions using renewable and green energy sources. As a considerable portion of energy consumption is designated for heating purposes in petrochemical processes, innovative heating methods could play a transformative role in meeting the environmental goals. Among the unconventional heating mechanisms, induction, microwave, ultrasound, and plasma heating are the most frequently employed^{1, 3}.

Table 2.4 Pros and Cons of BDS method⁸

Advantages	Disadvantages
Low CAPEX and OPEX costs ^{54, 57, 58}	Low conversion rate ^{44, 54}

Production of byproducts with high value ⁴⁴

Difficulties in separation of microorganisms ⁵⁶

Mild pressure and temperature for removing refractory
sulfur compounds ^{54, 57, 59}

Shallow desulfurization ³⁰

Lower emissions ^{55, 57}

Sensitivity of microorganism ⁴⁴

The following section provides a brief overview of the fundamentals and primary applications of various heating mechanisms mentioned above, with a focus on the potential use of microwave heating in demetallization and desulfurization of crude oil.

2.3 Unconventional Heating Technologies

2.3.1 Induction Heating

Induction heating is a complex process that involves the interaction of various phenomena, including heat transfer, electromagnetism, and metallurgical effects. The method involves transferring heat to an electrically conductive object, such as metals, through electromagnetic conduction. However, due to the intricate nature of these phenomena, induction heating is not a linear process, and it can be affected by factors such as the intensity of the electromagnetic field, temperature, and the microstructure of the object. Faraday's law of induction is the basis of the induction heating mechanism, where the heat is generated in an object by eddy currents. According to Faraday's law, changing the magnetic flux can result in electromagnetic induction or electromotive force generation in an electric circuit ⁶⁰.

An example of induction heating can be explained through the generation of an alternating current in a coil by applying an alternating voltage, which leads to the formation of a dynamic magnetic field with the same frequency in the surrounding coil. When an electrically conducting object is positioned near the coil, the magnetic field induces eddy currents in the coil, causing the

current to flow in the opposite direction at the same frequency. The induced eddy currents generate heat in the object through joule heating, which is dependent on the object material's resistance. However, due to the effects of electromagnetic phenomena like skin effect, proximity effect, slot effect, ring effect, and edge effect, the induced current is not uniformly distributed in both the inductor and the object ¹. The following briefly describes the major effects: skin effect or penetration depth, which refers to the non-uniformity of induced current throughout the object's geometry, resulting in a decrease in current intensity from surface to center; proximity effect, which explains the interaction of the induced magnetic field and the conductor, leading to a redistribution of electrical current in the conductor and an increase in the AC resistance of the adjacent conductor; and slot effect, which represents the distribution of magnetic flux density in the space between the inductor and the conductor. Even though induction heating can suffer from the non-uniformity of induced current distribution due to the effects mentioned above, it is still capable of rapidly increasing the object temperature by several hundred degrees. While induction heating has been successfully applied on a laboratory scale, its industrial-scale implementation and commercialization require further research and development ³.

2.3.2 Ultrasound

Ultrasound refers to sound waves with frequencies higher than the upper limit of human hearing, typically ranging from 20 kHz up to several GHz, and it has various applications such as imaging, detection and ranging, acoustic microscopy, and power and processing. When high-power ultrasound waves pass through a medium, they can create cavitation bubbles that grow over cycles with the same frequency as the applied sound due to intermolecular attraction forces. However, the frequency of the ultrasound wave affects the key parameters such as bubble sizes, pressure, and generated heat. For example, at low frequencies near 20 kHz, the formed bubbles are relatively

large, causing strong shockwaves upon their collapse, which makes low-frequency ultrasound waves desirable for mixing and emulsification applications in chemical and medical industries. Conversely, high frequencies between 0.1 and 1 MHz are suitable for high-temperature applications such as sonochemical reactions, where the small-sized bubbles can cause a significant temperature increase in the medium upon their collapse. At frequencies higher than 1 MHz, the cavitation effect becomes less dominant, and ultrasound waves are commonly used in medical and imaging applications. Despite its various applications, the commercialization of ultrasound heating in industrial-scale applications is still under investigation ^{3, 61}.

The formation of bubbles in a medium under the influence of sound waves can lead to two effects - coalescence and rectified diffusion. Coalescence refers to the merging of two or more bubbles to form a larger bubble, while rectified diffusion occurs when individual bubbles grow cyclically under pressure higher than a specific threshold value. As bubbles grow, they may become large enough to move and leave the system due to the buoyancy force, resulting in degassing of the system. Unstable bubbles can also randomly collapse, and bubbles may dissolve in the medium if the pressure is below the threshold pressure for rectified diffusion ^{1, 3}.

There are two main theories in the literature to explain the effects of cavitation formation on chemical processes, namely the hot spot theory and the electrical theory. According to the hot spot theory, bubble cavitation generates spots with extremely high temperatures and pressures, exceeding 5000 K and 500 bars, respectively. On the other hand, the electrical theory explains the formation of an electrical charge on the surface of the bubble, which creates an electrical field gradient in the bubble, enabling bond breakage upon collapse. The size of the bubble grows until it reaches a resonance size, which depends on the applied sound wave frequency. At the resonance size, the bubble may experience either transient or stable cavitation. Transient cavitation occurs

when the bubbles become unstable and collapse after a few acoustic cycles, while stable cavitation occurs when the bubbles continue to oscillate repeatedly near the resonance size. In ultrasound-assisted chemical reactions, both transient and stable cavitation terms are utilized to assess the activity of the bubbles for efficient conversion and further process design and control ^{1, 3, 62}.

2.3.3 Plasma

Plasma is a state of matter that is commonly referred to as a gas consisting of ions, free electrons, excited and neutral particles, and photons. This mixture of gas is a robust conductor of electricity that is formed by exposing a neutral gas to a powerful electromagnetic field. When there is a balance of positive and electrical charges in the mixture, it is known as quasi-neutrality. Although the charges are not bonded together and the overall electrical charge of the mixture is almost zero, these charges are not considered free particles because they interact with each other through the present electric and magnetic fields ^{1, 3}. Plasmas are classified based on their electron temperature and density, as summarized in Table 2.5.

Table 2.5 Classification of plasmas by electron temperature

Category	Temperature (K)
Highly Tenuous	10^6
Ionosphere	10^3
Glow discharge	10^4
Fluorescent lamp	$2.5 * 10^4$
Thermonuclear fusion	10^6 - 10^8

Thermal plasma is generated when electrons are accelerated between two electrodes in a gas. However, this process occurs slowly at room temperature and an electrical breakdown is required to overcome the gas's natural electrical resistance. To induce electrical breakdown, multiple electrical charges are generated to increase the gas's electrical conductivity and establish a conducting path between the electrodes. Plasmas can be produced through various methods such as electrodeless RF discharges, microwave irradiation, shock waves, laser technology, particle beams, and high-temperature furnaces. Plasma finds applications in numerous industries such as aerospace, food packaging, coating, automotive, electronics, and others ^{1, 3}.

2.3.4 Microwave Heating

Electromagnetic radiation refers to a wave that travels at the speed of light, composed of alternating electric and magnetic fields that are perpendicular to each other and propagate in the direction of oscillation (see Figure 2.3). The frequency range of electromagnetic waves is broad, spanning from 300 MHz to 300 GHz, corresponding to wavelengths of 1m to 1mm. This broad frequency spectrum includes various types of waves, such as radio, microwaves, infrared, visible light, X-ray, and gamma-ray, as shown in Figure 2.4 ^{63, 64}. To avoid overlap, specific frequency and wavelength ranges are defined for each application. Microwave technology, developed significantly in the 20th century, has led to a multitude of applications in various fields such as power transmission, communication, radar detection, navigation, and heating. Particularly, microwave heating (MWH) has become an important aspect of numerous industries, especially in

the chemical sector. MWH is a promising and environmentally friendly alternative to conventional heating methods for the highly intensive chemical processes ¹.

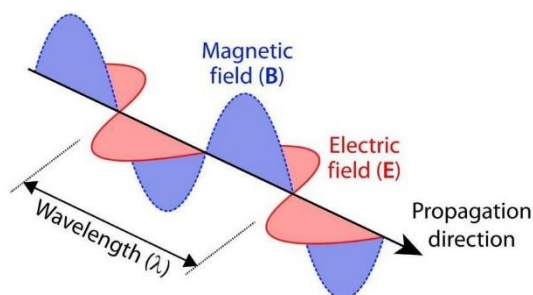


Figure 2.3 Schematic of an electromagnetic wave (reprinted from ⁶³)

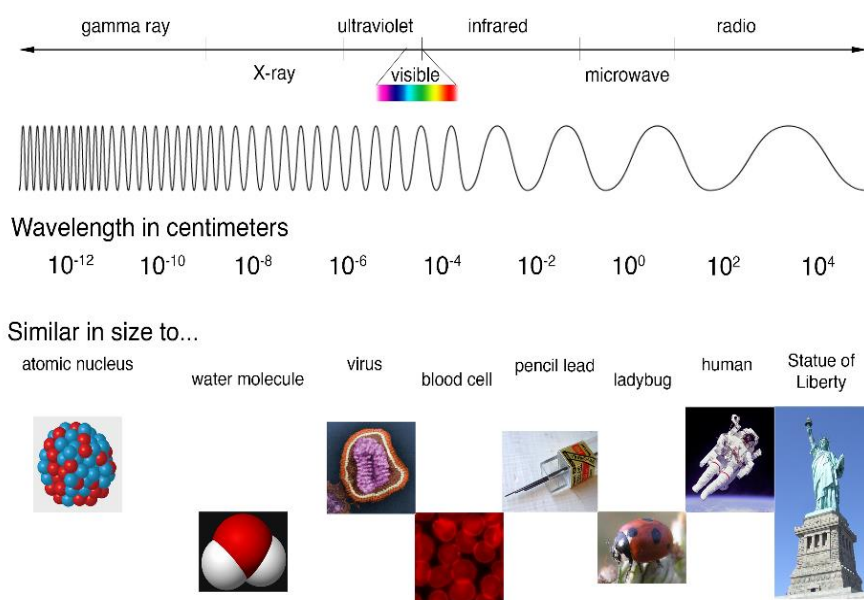


Figure 2.4 The electromagnetic spectrum (image courtesy NASA)

2.3.4.1 Interaction of Materials with Microwave

When materials are subjected to microwave irradiation, their behavior can be classified into three main categories, as shown in Figure 2.5. The first category includes absorbing materials, which have a high dielectric loss factor that allows them to efficiently transfer the energy of the absorbed microwave into heat. Examples of these materials include silicon carbide and carbon. The

second category includes transparent materials that allow electromagnetic waves to pass through them with minimal interaction. Examples of transparent materials include air and glass. The third category includes impermeable or opaque materials, which are perfect electrical conductors, such as metals. These materials reflect the incoming electromagnetic irradiation.

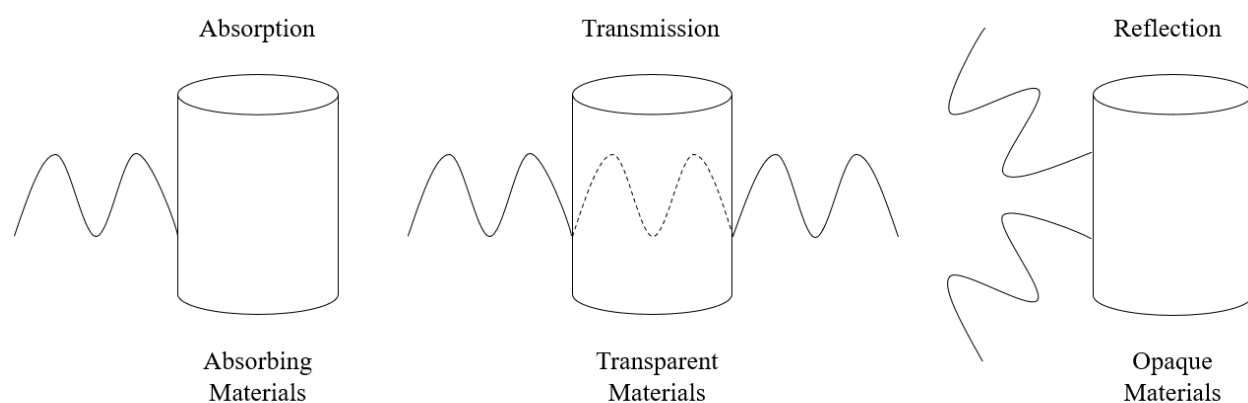


Figure 2.5 Interaction of materials with electromagnetic waves

There are several polarization mechanisms that explain the interaction between microwaves and materials, including electronic, atomic/ionic, interfacial, and orientation/dipolar polarization. Electronic polarization occurs when valence electrons are displaced around the nuclei, as depicted in Figure 2.6.a. Atomic or ionic polarization, shown in Figure 2.6.b, happens when positive and negative ions are dislocated from their equilibrium status due to electromagnetic field interaction. Figure 2.6.c demonstrates interfacial polarization or space charge, where separation of positively and negatively charged particles occurs as a result of an applied electromagnetic field. This separation leads to the formation of positive and negative space charges in the bulk of materials or in the interfaces of components in heterogeneous systems. Finally, orientation or dipolar polarization mechanism is illustrated in Figure 2.6.d, which explains that the permanent dipole moments of molecules synchronize and re-orientate themselves under an alternating electric field

The main mechanism involved in microwave heating is orientation or dipolar polarization. At equilibrium, permanent dipole moments of molecules are randomly oriented, resulting in a net dipole moment of zero. However, when an external electric field is present, molecules try to align themselves parallel to the external field, resulting in the formation of permanent dipoles. The frequency of the external field is too high for the agitated molecules to re-orient themselves quickly enough, resulting in a phase shift between the applied field and the re-oriented molecules. This causes the re-oriented molecules to collide randomly with each other, generating heat within the system. Microwave irradiation of materials can lead to these collisions and, consequently, heat generation ⁶⁵.

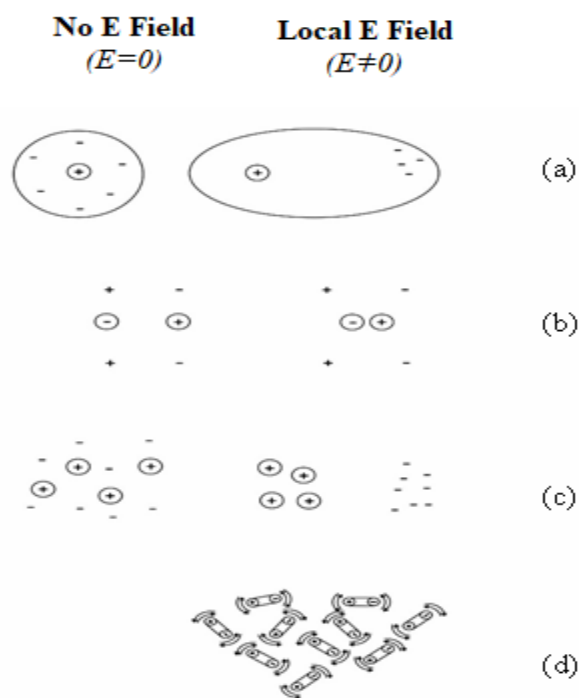


Figure 2.6 Polarization mechanisms in microwave heating (reprinted from ¹)

2.3.4.2 Permittivity & Permeability

To predict the heat generation potential resulting from the interaction between microwave irradiation and a material, two main parameters are defined: complex permittivity (ϵ) and complex permeability (μ). Microwave irradiation consists of alternating electric and magnetic field components, where complex permittivity describes the material's interaction with the applied electric field, and complex permeability represents its response to the magnetic field component. Complex permittivity reflects how well a material absorbs and stores electrical potential energy, while complex permeability describes the material's reaction to the magnetic field ¹. The following equations are used to define these parameters:

$$\epsilon = \epsilon' - j\epsilon'' \quad (2.1)$$

$$\mu = \mu' - j\mu'' \quad (2.2)$$

The two equations provided have real and imaginary parts. The first Equation, 2.1, consists of the real part, ϵ' , which is also known as the dielectric constant or permittivity. This represents how well the object can respond to the electric field of the microwave irradiation and to store the electrical energy. The imaginary part, ϵ'' , is called the dielectric loss factor, which measures the object's ability to dissipate the microwave energy as heat. The relative permittivity, which is the permittivity divided by the permittivity of free space, ϵ_0 (8.854×10^{-12} F/m), is also defined. To measure the phase shift between the applied alternating electric field and the reorientation of the dipole moments in the heated material, a parameter called the loss tangent ($\tan \delta$) is used. This is expressed in Equation 2.3 and is often used to describe how efficiently the object can convert absorbed microwave energy into heat.

$$\tan \delta = \epsilon'' / \epsilon' \quad (2.3)$$

Where δ is referring to the phase difference between the alternating electric field oscillation and the reorientation of the molecules of the object exposed to the microwave irradiation ⁶⁶.

The Equation 2.2, like Equation 2.1, has real and imaginary components. The real part, μ' , is known as magnetic permeability and indicates the capacity of the material to store magnetic energy. This value can be calculated by multiplying the free space permeability (μ_0), which is $4\pi \times 10^{-7}$ F/m, by the relative permeability (μ'_r). On the other hand, the imaginary part, μ'' , represents magnetic energy that can be converted to heat. Similarly, the magnetic loss tangent can be defined as the ratio between the imaginary and real parts of the complex permeability, as given by Equation 2.4 ^{1, 67}:

$$\tan \delta_{\mu} = \mu'' / \mu' \quad (2.4)$$

Microwave heating is mostly applicable to non-magnetic materials in the chemical industry. As a result, the energy transfer occurs through the interaction of these materials with the electric field component of the microwave irradiation. Therefore, it is essential to obtain accurate information about the processing material's ability to interact effectively with the electric field, especially when microwave heating is intended to be utilized. The dielectric properties of a material are dependent on both temperature and frequency. For instance, the dielectric constant of water decreases as both temperature and frequency increase. Various factors such as chemical state, purity, and manufacturing process can also affect the dielectric properties of a material. Thus, it is essential to gather a complete database of the dielectric properties of different materials at varying frequencies and temperatures. This will enhance the current knowledge and enable the efficient utilization of microwaves for material processing purposes ⁶⁴. Table 2.6 provides the dielectric constant, dielectric loss factor, and loss tangent values of common materials at certain frequencies

and temperatures. Table 2.6 clearly indicates that the interaction between materials and microwave irradiation varies, implying that not all materials are compatible with microwave heating.

Table 2.6 Dielectric properties of some materials ^{1, 64}

Material	ϵ'	ϵ''	$\tan \delta$	$T (^{\circ}\text{C})$	$f (\text{GHz})$
Air	1.0006	0	0	25	NA
Vacuum	1.00	0	0	25	NA
Distilled water	78	12	0.1538	25	2.45
Apple	57	12	0.2105	19	2.45
Potato	15.7	0.27	0.0172	25	2.45
Glass (Pyrex)	4.82	0.026	0.0054	25	3
Quartz	4	0.001	0.00025	20	2.45
Polyethylene	2.26	0.002	0.0009	NA	0.915
Methanol	32.6	21.48	0.6589	25	2.45
Ethanol	24.3	22.86	0.9407	25	2.45
Aluminum Oxide	9	0.0063	0.0007	25	NA
Zinc Oxide	3	3	1	25	NA

NA: Not Available

Two parameters, absorbed power and penetration depth, are defined to measure the quality of interaction between microwave irradiation and the material being exposed to it. Absorbed power

is the rate of energy absorbed by the material as heat or the amount of microwave energy lost and dissipated during interaction⁶⁶. As previously mentioned, the interaction of electromagnetic waves with an object involves interactions with both electric and magnetic field components. Hence, the total dissipated energy can be calculated by summing the energy dissipated from both components, as expressed in Equation 2.5.

$$P_{av} = \omega \epsilon_0 \epsilon''_{eff} E_{rms}^2 V + \omega \mu_0 \mu''_{eff} H_{rms}^2 V \quad (2.5)$$

where P_{av} : average absorbed power [W]; ω : angular frequency [s^{-1}], ϵ''_{eff} : effective dielectric loss factor; E_{rms} : electric field root mean square [V/m]; μ''_{eff} : effective magnetic loss factor [-]; H_{rms} : magnetic field root mean square [A/m]; and V : object volume [m^3].

In addition, the effective dielectric loss factor is the sum of conductive and polar losses expressed in Equation 2.6 as following:

$$\epsilon''_{eff} = \epsilon''_{polar} + \epsilon''_{cond} \quad (2.6)$$

In chemistry and chemical processes, most of the materials involved are non-magnetic, rendering the magnetic term of equation 2.5 insignificant. Consequently, the dissipated power mainly arises from the electric component interaction. To differentiate the electromagnetic wave interaction of materials in the absorbing category, the electric field penetration depth is used as a parameter. The penetration depth (d) is defined as the depth at which the intensity of the irradiations declines to $1/e$ or 36.8% of its value at the surface, as expressed in Equations 2.7 and 2.8. It is evident from Equation 2.8 that the frequency of the electromagnetic field has an inverse relationship with the penetration depth. Similarly, the power penetration depth is another parameter used to indicate the dissipated power, defined as $D_p = d/2$ based on the same concept^{1, 3, 64, 66}.

$$d = \frac{1}{\alpha} \quad (2.7)$$

Where α , attenuation factor, is defined as:

$$\alpha = 2\pi f \left(\frac{\mu_0 \mu' \varepsilon_0 \varepsilon'}{2} \right)^{\frac{1}{2}} \left[\{ 1 + (\tan \delta)^2 \}^{\frac{1}{2}} - 1 \right]^{1/2} \quad (2.8)$$

2.3.4.3 Microwave Heating as an Alternative to Conventional Heating

Microwave heating offers distinctive advantages over conventional heating, making it an appealing option for various industrial applications including food processing⁹, chemical^{3, 5, 10, 68}, and environmental engineering^{11, 69}. Unlike conventional heating, microwave heating is a volumetric heating mechanism that directly converts microwave energy into heat energy within the material's volume. This characteristic of microwave heating eliminates undesired temperature gradients within the subjected material. Furthermore, since electromagnetic wave interaction with materials is limited to their physical properties, such as dielectric properties, selective heating of targeted material becomes possible. This selective heating characteristic of MWH offers significant advantages over conventional heating, such as reduced energy consumption, improved production yield and efficiency, and avoidance of thermal hazards. Additionally, MWH has the potential to limit secondary reactions, promote the formation of new microstructures in products, activate reactions that are not possible with conventional heating, and establish new pathways and conditions for existing reactions⁷⁰⁻⁷⁶. Table 2.7 outlines some of the key characteristics of microwave heating in comparison to conventional heating.

Numerous studies in the literature have examined the impact of microwave heating (MWH) on the kinetics and conversion efficiency of chemical reactions. Shekara et al. found that chemical reactions achieved a higher conversion rate with MWH than with conventional heating⁷⁰. Monteiro et al. observed faster reaction rates and lower energy consumption when MWH was applied to

porous reactants ⁷¹. Other researchers, including Gude et al., Dogan et al., Nyutu et al., and Orozco et al., also confirmed that MWH can influence reaction rate and production yield ^{58, 77-80}. Zhang et al. noted improved kinetics, in terms of higher production yield and lower reaction time, with MWH ⁷². Budarin et al. found that MWH produced a purer oil with a higher concentration of aromatics ⁷⁴. Guiotoku et al. reported that MWH can enhance carbonization yield ⁸¹. Krzan et al. investigated the impact of MWH on catalyst loading and liquefaction and found improved catalyst performance with MWH ⁵⁸. Karthikeyan observed that MWH can lead to the production of different chemicals with higher extraction rates ⁷⁵.

To sum up, the effects of MWH on chemical reactions and processes are diverse, including reaction kinetics, production yield and quality, and energy requirements. However, the magnitude of these effects varies depending on the electromagnetic properties of the materials and processes involved.

Table 2.7 Microwave heating and conventional heating comparison (adapted from ⁸²)

Microwave Heating	Conventional Heating
Electromagnetic to thermal energy transformation	Thermal Energy transfer
Selective	Non-selective
Volumetric heating	Superficial heating (conduction/convection)
Local heating/hot spots	Homogeneous bulk heating
Precise & controlled heating	Less controllable
Instantaneous Heating	Time-consuming

2.4 MW-assisted Upgrading of Crude Petroleum Oil

The depletion of light and medium crude oil reserves has led to the necessity of developing new methods to process heavy crude oils. However, the presence of heteroatoms, metals, resins, and asphaltenes in heavy crude oil feedstocks creates several limitations in all stages of production, from extraction to transportation and processing^{16, 83}. Metals and sulfur, in particular, are present in high concentrations in heavy crude oils and can have detrimental impacts if not removed efficiently. These impacts can be divided into two categories: environmental and health issues, and technical issues in refinery processes. Heavy metals such as Ni & V, and sulfur in the final fuel products can result in the formation of SO_x and NO_x into the atmosphere, leading to the creation of acid rain and severe environmental damage. These impurities can also pose a risk to human health, causing high irritation and even malignant neoplastic diseases. In addition, they can cause several technical issues, including severe corrosion problems on the surfaces of process equipment and tubes, catalyst deactivation, and increased operational costs. Metals can also increase the risk of dehydrogenation and subsequent dry gas and coke formation in the cracking units of a petroleum refinery. If metals and sulfur are present in the final fuel product, ash can form during combustion reactions, resulting in deposits on the surfaces of burners and engines^{1, 8, 22}.

Crude oils have varying compositions depending on their sources, but they generally consist of a mixture of hydrocarbons with the addition of oxygen, nitrogen, and sulfur compounds⁸⁴. Metals, such as magnesium and sodium chlorides as inorganic salts or Ni and V in porphyrins as organometallic compounds, are present in varying concentrations ranging from trace amounts to over 1000 ppm. Some of the more prevalent metals found in crude oils include sodium (Na),

calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe), vanadium (V), and nickel (Ni) ^{1, 17}. The concentration of sulfur in crude oil ranges from 0.1 wt.% to 15 wt.% and is dependent on the oil's source ²³. It is present in various molecular forms, including mercaptans, sulfides, disulfides, and thiophenes. More detailed information on the chemical structure of crude oil is presented in Figure 2.7.

To develop effective processes for removing metals and sulfur from crude oil, it is necessary to gain a comprehensive understanding of the molecular structure of the compounds containing heavy metals and sulfur. Heavy metals are primarily found in oil-soluble naphthenic acid compounds or complex organometallic structures known as metalloporphyrin rings ^{18, 19}. The most problematic metals, V and Ni, are present in both porphyrin and non-porphyrin compounds, while other metals such as calcium, titanium, and magnesium can also be found in naphthenic acid compounds. To better understand the hazardous impact and separation challenges posed by porphyrins, several investigations have been conducted to elucidate their structure ²⁰. However, metalloporphyrin rings are difficult to remove due to their high thermal and chemical stability, requiring temperatures exceeding 350 °C for thermal decomposition ²¹. Figures 2.1 and 2.2 illustrate typical chemical structures of Ni and V porphyrins, as well as organic sulfur compounds present in crude oils.

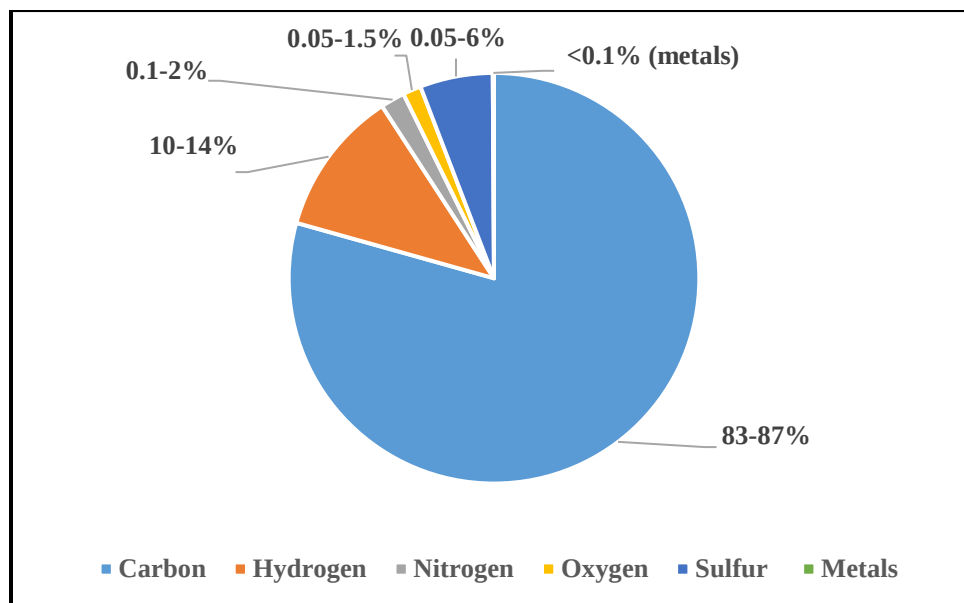


Figure 2.7 Crude oil elemental composition

The objective of the microwave-assisted demetallization process for heavy oil is to use microwave irradiation to provide the necessary energy to weaken metal bonds for removal. Although crude oil is a poor microwave receptor and converts only a small amount of microwave energy to heat, metals have a strong interaction with microwaves, and even small amounts can quickly reach high temperatures. This difference in dielectric properties between metals and crude oil leads to the formation of hot spots at the metal bonds, while the bulk temperature remains relatively stable. The high temperature at the metal bonds can weaken the metal-nitrogen bonds in the porphyrin ring, making metal extraction easier. Consequently, MWH can selectively remove metals from crude oil's chemical structure without adversely affecting the treated oil yield ^{1,3}.

It is widely acknowledged that metals, being conductors, are not easily heated using microwaves due to their limited penetration depths of just a few microns at the common microwave frequencies of 915 MHz and 2.45 GHz. Consequently, they tend to reflect most of the microwaves that are incident upon them. However, this arching phenomenon only applies to bulk metals. When

metals are present in the form of powders or small particles, they can absorb microwaves and be heated significantly. It has been long observed that the addition of small volume percentages of metallic particles, when effectively dispersed into a dielectric insulating material, which is generally known as artificial dielectrics, can result in enhanced microwave absorption ⁶⁴. In equation 2.9, the penetration depth (d) of a substance is expressed as a function of its electrical resistivity (ρ):

$$d = \sqrt{\frac{\rho}{\pi f \mu / \mu_0}} \quad (2.9)$$

Equation 2.9 clearly indicates that the penetration depth of applied microwaves decreases as the electrical resistivity of the exposed material decreases. In the case of an ideal conductor with zero electrical resistivity, the penetration depth of the electromagnetic wave should theoretically be zero, causing the target material to reflect the incoming wave entirely. However, conductors cannot entirely reflect microwaves due to two main reasons. Firstly, defects and impurities present in the molecular structure of the conductors result in limited electrical resistance, leading to a non-zero penetration depth of the electromagnetic waves. Secondly, according to Equation 2.10, the electrical resistivity of materials increases as the temperature rises. Hence, when the object undergoes microwave irradiation, the temperature elevation due to microwave heating increases the electrical resistivity of the target material. This leads to a higher penetration depth and consequently greater interaction between the object and microwaves during the irradiation process ^{1, 64}.

$$\rho = \rho_{amb}(1 + \alpha_R \Delta T) \quad (2.10)$$

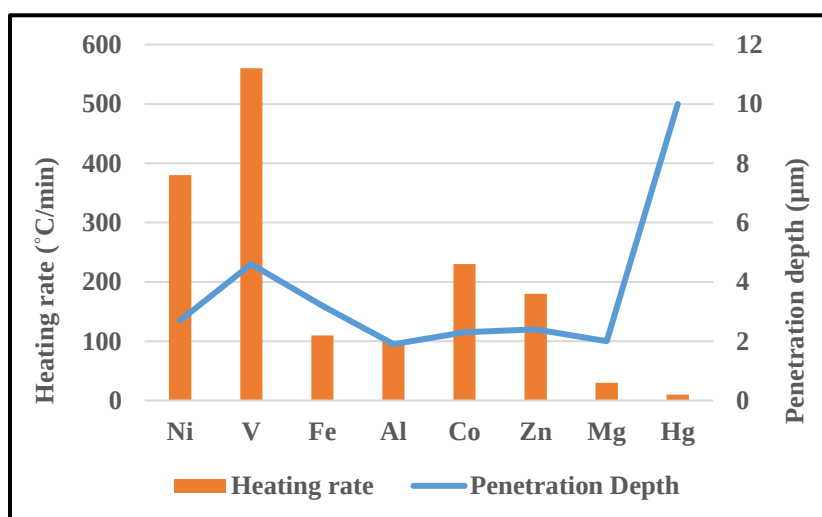
Where ρ_{amb} represents the electrical resistivity at the ambient temperature, α_R is the temperature dependent resistivity parameter, and ΔT is the temperature increment.

According to Table 2.8 and Figure 2.8, metals exhibit a penetration depth of only a few micrometers when exposed to microwaves. Therefore, the shape and geometry of the particles play a crucial role in microwave heating (MWH). Fine particles, such as powders, are expected to have a more efficient interaction with electromagnetic waves compared to sheet-like materials. When the penetration depth of the object is equal to or higher than its particle size, a more effective interaction can be achieved at a particular microwave frequency. Additionally, fine metal particles with a high surface-to-volume ratio tend to oxidize in the presence of oxygen, resulting in the formation of metal oxides on the surface of the particles. This fact increases the efficiency of the conversion of microwave energy into heat by increasing the penetration depth. Moreover, the shape irregularities in the particles of a target material can have a positive impact on the coupling between the microwaves and the object by affecting the induced electrical flux intensity and direction. Furthermore, the space between the particles, which is created by the shape of the particles, can enhance the penetration depth and the heating efficiency ^{1, 64}.

Different methods and processes have been established to refine crude oil and eliminate sulfur and metals. These techniques can be grouped into physical processes like distillation and solvent extraction, chemical methods such as chemical agent complexation, thermal and hydrogenation processes, and biological methods ¹⁷. These established technologies are well documented for removing elements like sulfur, Ni, and V from the crude oil structure. Nevertheless, the possible benefits of integrating microwave heating technology into these methods have not been fully explored.

Table 2.8 Penetration or skin depth of some metals (Adapted from ^{1, 64})

Metal	Penetration depth (μm)	f (GHz)
Nickel	2.7	2.45
Vanadium	4.6	2.45
Iron	3.2	2.45
Silver	1.3	2.45
Mercury	10	2.45
Zinc	6.4	2.45
Zirconium	6.7	2.45

Figure 2.8 Heating rate and penetration depth of various metals (Adapted from ⁶⁴)

Chemical agent complexation is a promising method among the aforementioned techniques, owing to its high efficiency and mild operating conditions. Acids such as sulfuric, nitric, and

phosphoric, as well as salts like boron trifluoride, group IA and IIA aqueous bases (carbonates and hydroxides), oxidative agents, and chlorine-based compounds (Cl_2 , SOCl_2 , FeCl_2 , SnCl_2 , ZnCl_2 , TiCl_4), are frequently used agents for eliminating metals from petroleum crude oil ¹⁵. Since both metals and these demetallization agents are polar compounds with strong interactions with electromagnetic fields, microwave heating can be employed in the demetallization process. Although crude oil itself is not a suitable microwave receptor, the metals present in its structure and the added demetallization agent exhibit high microwave absorption, resulting in local hot spots at the metal bonds. Therefore, by using microwave heating, it is feasible to heat only the local spots where the removal reaction between the metals and the demetallization agent occurs, while the temperature of the crude oil bulk remains largely unaffected ³.

The application of microwave heating for upgrading and treating petroleum crude oil has not been extensively studied in the literature, with only a limited number of studies investigating its effectiveness in demetallization and desulfurization of crude oils. One such study was conducted by Khan et al. in 2013, where they evaluated the impact of microwave heating on the sulfur removal efficiency of crude oil samples in a catalytic hydrodesulfurization process. They aimed to convert the sulfur content of heavy crude oil to hydrogen sulfides in the presence of microwave irradiation and hydrogen. Operating at a wide range of temperatures from 80 to 400 °C and pressures of 20 to 400 psi, it was observed that at 200 °C, the sulfur removal efficiency was approximately 20%, which increased by 2% with a rise in temperature. The optimal temperature range was determined to be between 200 and 250 °C. The study also examined the performance of various catalysts, including iron and palladium oxide diethanolamine ¹². In 2011, Wang et al. utilized cationic starches as a reagent to remove Ni and V from crude oil with the aid of microwave heating. They discovered that higher removal efficiency of metals can be achieved by using a starch with a higher

cationic substitution degree. They achieved removal efficiencies of up to 60% and 80% for Ni and V, respectively, when 200 mg/l of demetallization agent was mixed with the oil and exposed to 300 W of microwave irradiation for 5 minutes. On the other hand, Chamorro and his team developed a process that utilized microwave heating to simultaneously eliminate metals and sulfur compounds from carbonaceous samples. They employed a mixture of acids, including nitric, sulfuric, hydrochloric, and phosphoric acids as agents. The study reported removal efficiencies of 80% and 99% for Ni and V, respectively, when irradiation time ranged from 10 seconds to 1 hour at elevated pressures of up to 200 psi ⁸⁵. Shang et al. conducted a study in 2016 to explore the efficacy of microwave-assisted demetallization in removing Ni and V from Venezuela crude oil. Various functional group agents, such as diethyldithiocarbamate, carboxymethyl chitosan, chitosan, and methane sulfonic acid, were tested, with the latter showing the highest removal efficiency. The process involves the extraction of Ni and V from the porphyrin rings via the reaction between the vanadium oxide and the nickel cation and sulfonyl acid group, without damaging the ring structure and reducing the treatment yield. Since Ni and V are converted into water-soluble compounds, they can be eliminated by washing with water in desalting processes. The optimal process conditions were determined to be a microwave power of 600-800 W, a residence time of 3 minutes, and an agent dosage of 2 Wt.%. The highest removal efficiencies achieved were 83.3% for nickel and 84.7% for vanadium ¹⁵. Shang et al. conducted a study in 2019 to investigate the impact of microwave heating on the catalytic hydrodesulfurization of oil models containing thiophene. They observed that the use of microwave heating led to a 15% increase in sulfur removal efficiency compared to conventional heating. Microwave heating generated local hot spots in the catalyst, which consisted of Ni-Mo/Al₂O₃, thereby enhancing the reaction rate and boosting molecular collisions. However, the apparent activation energy was reduced due to the hindering effect of microwaves on minor adsorption mechanisms ⁸⁶.

Attia et al. developed a novel approach in 2018 to upgrade heavy petroleum oil by removing both sulfur and heavy metals like nickel and vanadium simultaneously. The technique employed Bis(2-ethylhexyle) phosphoric acid (D2EHPA), which acted as a proton donor to replace metal-nitrogen bonds in metalloporphyrin rings with hydrogen-nitrogen bonds, converting them to water-soluble metal salts of the reagent. By doing so, existing vanadium and nickel in organometallic compounds could be transformed to water-soluble compounds and efficiently separated through washing. D2EHPA might also form an ionic liquid with anions in the crude oil, such as chlorides, to extract sulfur compounds. The formed ionic liquid could then eliminate sulfur compounds through hydrogen bond formation or electrostatic force. Figure 4.4 and Figure 4.5 illustrate the proposed mechanism for removing heavy metals and sulfur, respectively ^{1, 24}.

Attia et al. conducted a study to evaluate the effectiveness of their developed process for simultaneous removal of heavy metals and sulfur from various types of crude oil under both conventional and microwave heating. They used Basra oil, heavy Iranian crude oil, light naphtha, and heavy aromatic naphtha and measured the removal efficiency of sulfur and different metals such as Ti, Na, Mg, Mn, Al, Ni, V, Cl, and Ca. The results showed that the process achieved removal efficiencies of 53%, 73%, and 32% for sulfur, Ni, and V, from heavy Iranian crude oil, respectively, under conventional heating. Additionally, they investigated the impact of microwave irradiation on the process performance using crude oil samples from Iran and Basra. The study revealed that microwave heating significantly improved the removal efficiency of most metals, as well as sulfur compounds, with reductions of up to 55%, 90%, and 99% for Ni, V, and sulfur, respectively. Increasing the residence time and microwave power led to higher removal efficiency, as more heat energy was absorbed by the target material, facilitating the removal mechanisms ^{1, 3,}

of emission-intensive crude oil upgrading processes. Despite the promising results reported by Attia et al, further investigations are necessary to elucidate the proposed method to remove metals and sulfur from crude oil using D2EHPA and microwave heating technology. First, an efficient methodology has to be developed to regenerate D2EHPA effectively given the complete miscibility of D2EHPA in organic solvents such as crude oil. Second, optimization of the main process parameters in respect to metal and sulfur removal efficiencies is inevitable. Third, the kinetic model of the demetallization reactions between Ni/V and D2EHPA under microwave heating has to be developed at the optimized process conditions as a significant step towards achieving the optimum process design. In addition, further investigations on the demetallization reactions and ionic liquid formation by D2EHPA have to be devoted to enhancing the understanding of the process. Last, despite several studies have attempted to remove sulfur from liquid fuels by a variety of ionic liquids (ILs), none of them have investigated the possibility of synthesizing D2EHPA-based ILs for extractive desulfurization of real crude oils as green alternative for conventional extractants. Therefore, this research is aimed to cover the above-mentioned gaps for the proposed process by Attia et al. to remove sulfur and Ni/V from crude petroleum oil by microwave heating technology, and the results are published or submitted for publication to peer-reviewed journals.

CHAPTER 3 OBJECTIVES AND THESIS STRUCTURE

3.1 Objectives

The main objective of this research is to develop an industrial process to eliminate heavy metals mainly Ni & V and sulfur from crude petroleum oil using bis(2-ethylhexyl) phosphoric acid (D2EHPA) and microwave heating technology. To accomplish the main objective of this work, the following steps are carried out:

- ❖ Perform a preliminary Techno-Economic Assessment by designing the industrial process scheme, main process equipment, and operating conditions of each processing unit.
- ❖ Provide the appropriate integration of the proposed process into typical crude oil refineries.
- ❖ Develop and validate an effective methodology for D2EHPA regeneration after reaction accomplishment.
- ❖ Investigate the economic performance of the proposed process operating at industrial-scale petroleum refineries compared to the conventional industrial techniques.
- ❖ Perform a sensitivity analysis of the main design parameters and their impact on the primary economic parameters such as total capital costs (CAPEX) and total annual operating costs (OPEX)
- ❖ Develop a kinetic model for microwave-assisted Ni/V removal reactions using D2EHPA
- ❖ Investigate the impact of primary process parameters such as reaction temperature, residence time, and D2EHPA dosage on Ni/V removal efficiencies and provide the optimized value of each parameter.
- ❖ Study the reaction mechanism between D2EHPA and Ni/V containing metalloporphyrin compounds as well as the chemical structure alteration of reacted D2EHPA.

- ❖ Introduce the kinetic model of Ni/V removal reactions and main kinetic parameters including reaction rates, activation energies, and pre-exponential factors.
- ❖ Investigate microwave-assisted sulfur removal from liquid fuels and crude oils using D2EHPA
- ❖ Systematic study of removing thiophene compounds from liquid model fuels and crude oils
- ❖ Explore the desulfurization mechanism by tracking the ionic liquid formation between D2EHPA and NaCl molecules under microwave irradiation.
- ❖ Study the impact of primary process parameters such as D2EHPA dosage, reaction temperature, and irradiation time on S-removal efficiency
- ❖ Develop a novel D2EHPA-based ionic liquid to remove sulfur from liquid fuels and crude oils by extractive desulfurization (EDS)
- ❖ Synthesize a new ionic liquid using D2EHPA to study the extractive removal of a variety of organic refractory sulfur compounds such as thiophene, benzothiophene, and dibenzothiophene from liquid model fuels
- ❖ Investigate the effectiveness of the synthesized ionic liquid to desulfurize real crude oils by EDS
- ❖ Conduct a conclusive techno-economic analysis by incorporating the obtained research findings on reaction kinetics and optimized process conditions

3.2 Thesis Structure

The scientific outcomes of this research are documented in four scientific articles which are covered and discussed in Chapters 4, 5, 6, and 7.

Chapter 4 is the first article, “Process Development and Techno-Economic Analysis of Microwave-Assisted Demetallization and Desulfurization of Crude Petroleum Oil” published in

Energy Reports journal, presenting the results of the preliminary techno-economic analysis of the developed process to remove metals and sulfur from crude oil using D2EHPA and microwave heating technology. In this study, an industrial process scheme was designed and a comprehensive discussion on the incorporation details of such a process into the real crude oil refineries was included. The commercialization feasibility of the process was investigated by estimating the total CAPEX & OPEX costs for treating 50,000 barrel per stream day (BPSD) crude oil and comparing the results were compared with the conventional hydrotreatment technologies. Additionally, a new methodology to recover and regenerate D2EHPA after the reaction with crude oil was developed and experimentally validated. Finally, a sensitivity analysis was carried out to study the impact of primary process parameters on the economic performance of the proposed process to elucidate the primary limitations toward the scale-up and exploitation of the proposed process in real industrial scope.

To address the research gap highlighted in the first article, in Chapter 5, as the second article, “Microwave-Assisted Nickel and Vanadium Removal from Crude Petroleum Oil Using Bis(2-ethylhexyl) Phosphoric Acid: A Kinetic Study” published in Industrial & Engineering Chemistry Research journal, the kinetics of Ni/V removal from crude oil under microwave irradiation was studied. In this paper, a systematic experimental investigation on the effect of primary process parameters such as reaction time, temperature, and D2EHPA:oil mass ratio on demetallization effectiveness was conducted and the optimized value of each parameter was reported. Given the optimized parameters, the kinetic of demetallization reactions was studied experimentally at 230-250 °C and the best fitting kinetic model for Ni and V reactions was introduced. Additionally, the reaction mechanisms were further studied by performing FTIR spectroscopy to track the changes in the chemical bonds present in the crude oil and reacted D2EHPA molecules caused by the

demetallization reaction. The primary kinetic parameters such as reaction rates, activation energies, and pre-exponential factors were reported for Ni/V removal reactions and the validity of the proposed kinetic model was examined by several experimental data. The data pertaining to the irradiated microwave power at different reaction temperatures and heating steps was also incorporated into the study.

Chapter 6 presents the third paper, “Microwave-Assisted sulfur removal from crude petroleum oil and liquid fuels by bis(2-ethylhexyl) phosphoric acid” submitted to Green Chemistry journal, is dedicated to study the removal of refractory organic sulfur compounds, such as Thiophene, from model liquid fuels and real crude oil samples through microwave-assisted ionic liquid synthesis. In this article, the formation of an ionic liquid between D2EHPA and NaCl aqueous solutions was explored under microwave heating that led to simultaneous extraction of thiophene S-compounds from liquid fuels and crude oils through π - π interaction. Sulfur removal effectiveness was studied at different D2EHPA dosage, irradiation time, and reaction temperature. Finally, the ionic liquid formation between D2EHPA and NaCl molecules was investigated by electrical conductivity and FTIR characterization analyses to explore the desulfurization mechanism.

In Chapter 7, as the fourth article titled as “Extractive desulfurization of crude petroleum oil and liquid fuels using trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate ionic liquid” submitted to Chemical Engineering Research and Design journal, a novel phosphonium-based ionic liquid was synthesized and its effectiveness to remove various refractory sulfur compounds such as thiophene, benzothiophene, and dibenzothiophene from crude oils and liquid fuels through extractive desulfurization was investigated. The characteristics of the synthesized ionic liquid was fully evaluated by FTIR, electrical conductivity, TGA, viscosity, and solubility analysis. The effect

of reaction time, temperature, and S-compound on the S-removal efficiency was investigated, and the results were reported.

According to the findings presented in Chapters 5 & 6 on the demetallization and desulfurization process, Chapter 8 presents an updated process design and economics for the proposed process. Accordingly, a new industrial process scheme is designed by adopting dedicated processing units with different operating conditions for metal and sulfur removal from crude oil at large capacity of 50,000 BPSD. The total OPEX and CAPEX costs of the updated process is then estimated and a conclusive discussion on the process scale-up limitations is provided.

Finally, in the last two chapters, Chapter 9 and Chapter 10, a general discussion of the findings presented in this research and the overall conclusions drawn from the results are provided.

CHAPTER 4 ARTICLE 1 : PROCESS DEVELOPMENT AND TECHNO-ECONOMIC ANALYSIS OF MICROWAVE-ASSISTED DEMETALLIZATION AND DESULFURIZATION OF CRUDE PETROLEUM OIL

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4.1 Abstract

Metals and sulfur, if not efficiently eliminated from crude petroleum oil during refining, may have severe detrimental impacts in refinery processes such as fluid catalytic cracking and hydrotreating units. Recently, the lab-scale microwave-assisted demetallization and desulfurization (MW-DMDS) of crude oil using Bis(2-ethylhexyle) phosphoric acid (D2EHPA) have shown several advantages such as high removal efficiency, being environmentally green, and lower energy requirements. This paper presents a comprehensive industrial process scheme for MW-DMDS by designing the required processing units. In addition, an effective methodology to regenerate D2EHPA using sulfuric acid and sodium hydroxide (NaOH) aqueous solutions was developed and experimentally validated. A Techno-economic investigation was carried out by adopting the ASPEN Plus process simulator to estimate the upscaling feasibility of the process to treat 50,000 barrels per stream day (BPSD) of crude oil. Total capital costs (CAPEX) and total annual operating costs (OPEX) were estimated at 6.77 MUSD and 4.23 MUSD (0.24 \$/bbl), respectively. The results indicated the economic superiority of the proposed process compared to the existing technologies, like hydrodemetallization (HDM) and hydrodesulfurization (HDS) due to the remarkably lower CAPEX and OPEX costs. Sensitivity analysis by changing the primary design parameters

demonstrated that the required microwave power and the corresponding purchase costs of the microwave generators have the highest share of the estimated CAPEX costs. Moreover, the annual operating costs seem to strongly depend on the DMDSA consumption and regeneration process effectiveness.

Keywords: techno-economic analysis, microwave heating, process design, demetallization, desulfurization, crude oil

4.2 Introduction

Crude oil upgrading processes are among the most energy-consuming operations in the petrochemical industry that are also very common and necessary. These processes are intended to remove hazardous components and contaminations such as metal and sulfur from crude oil. The presence of metals and sulfur causes severe technical difficulties in the refinery processes such as corrosion, catalyst poisoning and deactivation, and ash formation. Additionally, if not removed to a certain limit from the final fuel products, these contaminations lead to environmental disturbances and subsequent health issues in humans.

Various metals are present in crude oil and concentrations vary from trace (~100 ppm) to high (~1000 ppm) amounts depending on the extraction site origin. They can be present in the form of either inorganic salts such as chlorides or organometallic compounds, mostly nickel (Ni) and vanadium (V) porphyrins. Among the different metals, nickel, iron, aluminum, calcium, vanadium, cobalt (Co), magnesium and sodium are identified as the most abundant metals in crude oil ^{16, 17}. The sulfur content of crude oil varies from 0.1 wt.% to 15 wt.%, determined by its origin ²³, and exists in different molecular forms such as mercaptans, sulfides, disulfides, and thiophenes ²⁷. An extended discussion of the metals and sulfur content of crude oil and their detrimental impacts on the refinery processes can be found elsewhere ^{17-19, 87}.

Various methods for the demetallization and desulfurization of crude oil have been developed since the middle of the 20th century. They include physical methods like distillation or solvent extraction by deasphalting, and chemical techniques such as chemical complexation, hydrodemetallization (HDM) and hydrodesulfurization (HDS), visbreaking, and coking. However, the above methods are neither completely efficient nor without limitations and disadvantages. Despite the widespread exploitation of hydrotreating (HDM-HDS) methods in crude oil upgrading plants, high operating temperatures and pressures, high investment costs, fast catalyst deactivations, and extreme hydrogen consumption remain significant drawbacks of this technology. The United States Environmental Protection Agency (US EPA) has reported the capital cost of new hydrodesulfurization units to reduce sulfur content up to 500 ppm and 15 ppm as 16-21 MUSD and 31-42 MUSD respectively, on an inside battery limits (ISBL) basis, for the treatment capacity of 25,000 barrel per stream day (BPSD) ⁸. The US EPA cost estimations for a new HDS unit are given in Table 4.1.

Table 4.1 Cost estimations for installing a new HDS unit by US EPA ⁸

Item	500 ppm	15 ppm
CAPEX (USDM) (ISBL)	16-21	31-42
H ₂ Consumption (SCF/bbl)	147-738	240-1100
Electricity (kWh/bbl)	0.2-0.4	0.6-1.2
Catalyst (\$/BPSD)	0.1-0.3	0.3-0.8

As a novel technology, microwave-assisted metal and sulfur removal from crude oil could be an efficient alternative for the above-mentioned methods. The distinctive characteristics of microwave heating (MWH) make it a desirable alternative to conventional heating (CH) in various

sectors such as food ⁹, chemical ^{10, 68}, and environmental engineering ^{11, 69}. MWH is considered a volumetric heating technique where electromagnetic energy is directly converted to heat through the interaction of microwaves with polar molecules or ions within the volume of the target material ⁸⁸. This unique advantage could resolve many limitations of CH such as undesired temperature gradients within the target material ³. Given the interaction of electromagnetic waves with materials is limited to their electric and magnetic physical properties, e.g., dielectric properties, the selective heating of targeted materials becomes viable instead of heating the entire bulk of the object ¹⁵. Selectivity is a significant advantage of MWH over CH that may result in a huge reduction in energy consumption and operational costs, improvement in production yield and efficiency, and avoiding thermal hazards. Furthermore, the impacts of using MWH is not limited to the aforementioned thermal effects and could be extended to non-thermal effects such as intensified reaction rates, restricting secondary reactions, the possibility of new microstructure formation in the products, activating reactions that are not feasible with conventional heating, and establishing new pathways and conditions for existing conventional reactions ^{71, 89, 90}.

The application of MWH in petroleum crude oil upgrading processes is not well established in the literature and only a few studies have investigated the impact of MWH technology in demetallization and desulfurization of crude. In 2013, Khan and Al-Shafei investigated the effect of MWH on the efficiency of sulfur removal from crude oil samples in a catalytic hydrodesulfurization process. In this work, the impact of the catalyst, operating temperature and pressure, and microwave power were studied and a maximum of 22% of sulfur removal efficiency was reported ¹². In 2011, Wang et al. employed cationic starch reagents for Ni and V removal from crude oil using MWH. Removal efficiencies up to 60% and 80% were obtained for Ni and V, respectively, when 200 mg/l of the demetallization agent was mixed with the oil under 300 W of

microwave irradiation for 5 minutes⁸⁵. Chamorro and Romano developed a process to eliminate metals and sulfur compounds simultaneously from carbonaceous samples using MWH and a mixture of inorganic acids as the removal reagent. Removal efficiencies were reported as 80% and 99% for Ni and V when the irradiation time was in the range of 10 s to 1 h at an elevated temperature of up to 200 psi¹⁴. In 2016, Shang et al. investigated microwave-assisted demetallization of Venezuela crude to remove Ni and V. Various functional group agents were used, such as diethyldithiocarbamate, carboxymethyl chitosan, chitosan, and methane sulfonic acid, which showed the highest removal efficiency. The optimum process conditions were microwave power of 600 - 800 W, a residence time of 3 minutes, and an agent dosage of 2 wt.%. The highest obtained removal efficiencies were 83.3% for nickel and 84.7% for vanadium¹⁵.

In 2018, Attia et al. developed a new methodology for removing sulfur and heavy metals, such as Ni and vanadium, simultaneously from heavy petroleum oil⁹¹. They used Bis(2-ethylhexyle) phosphoric acid ((C₈H₁₇O)₂PO₂H) or D2EHPA as the demetallization desulfurization agent (DMDSA) to convert the target sulfur and metals in the crude from oil-soluble to water-soluble compounds that are extracted by washing in an aqueous phase. Attia et al. investigated the impact of both conventional and microwave heating on the process effectiveness. Under conventional heating, maximum removal efficiencies of 90%, 79%, and 53% were reported for V, Ni, and sulfur, respectively²⁴. In addition, they measured the performance of the developed process when MWH was applied. It was observed that MWH could boost the removal efficiency of almost all the target elements. The concentrations of V, Ni, and sulfur were reduced up to 90%, 50%, and 99%, respectively¹. A summary of the results is shown in Figure 4.1.

The promising results of the technique developed by Attia et al. coupled with the remarkable advantages of microwave heating technology created a significant interest in

investigating the feasibility of commercializing the proposed green process as an alternative to the existing conventional crude oil upgrading processes. The conventional methods are known to be costly, extremely energy-intensive, and they release significant amounts of carbon emissions. Although the microwave-assisted demetallization and desulfurization of crude oil has been reported for laboratory scale, its potential for industrial scale adaptation is still unknown. In fact, the industrial process design, required processing units, and details of incorporating such a process into crude refining processes have not yet been investigated. Additionally, without an effective DMDSA regeneration methodology, upscaling would not be economically feasible due to the high operating costs.

This study aims to develop an industrial process scheme for the proposed technique by Attia et al. by performing a comprehensive process design. The required equipment and the corresponding operating conditions of each processing unit, as well as the integration details of the proposed process into a typical crude refinery, are provided. Additionally, an effective methodology for DMDSA regeneration is developed and experimentally validated. The upscaling technical and economic feasibility of the developed process is investigated by performing a comprehensive techno-economic analysis at a large-scale crude treatment capacity. The results of such studies would guide the project direction for future research works and/or justify decisions for potential investors.

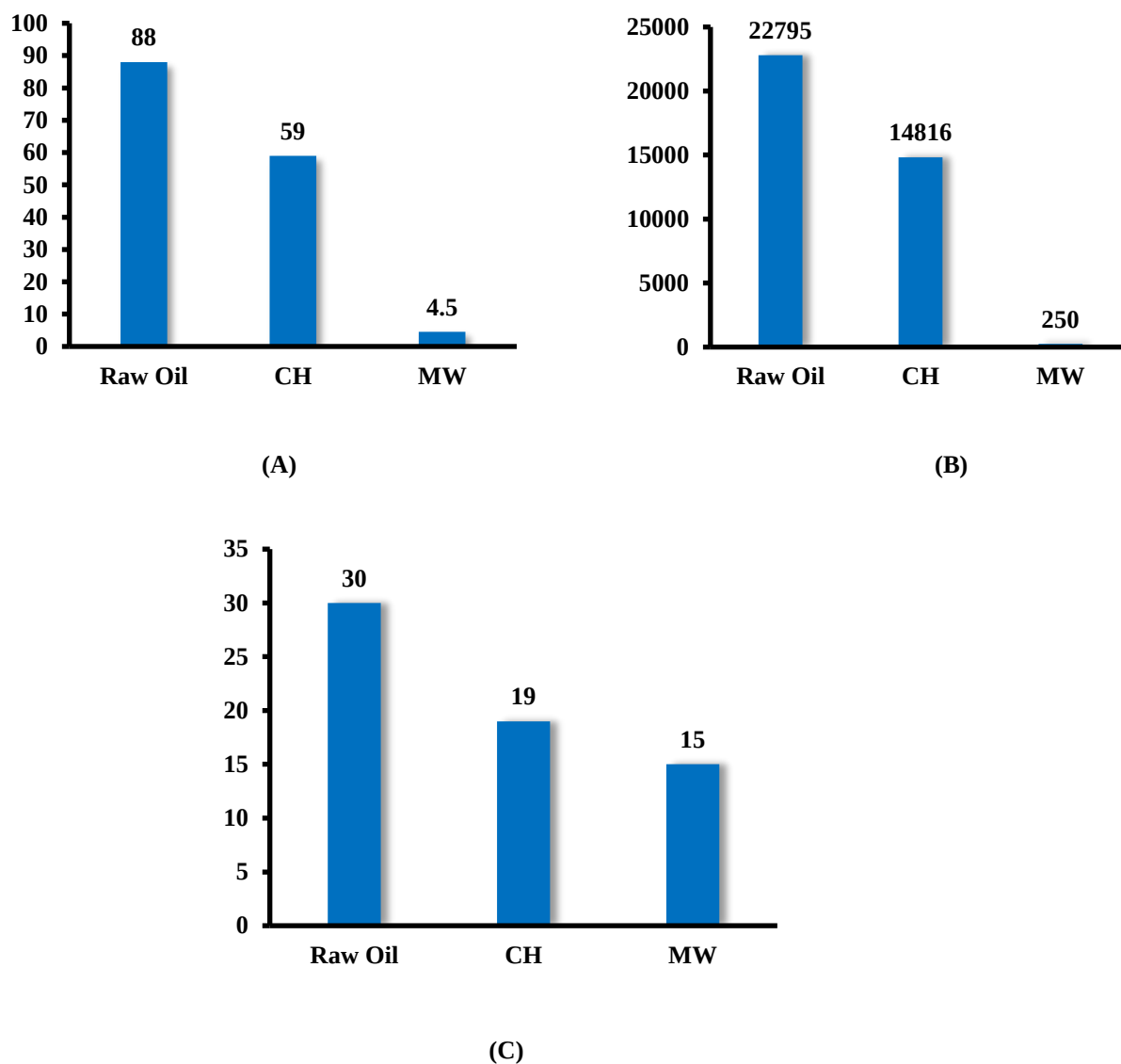


Figure 4.1 Concentration (ppm) of (A) Vanadium, (B) Sulfur, (C) Nickel in raw and treated Iranian crude oil using conventional (CH) and microwave heating (MW). (Reported from ¹)

4.3 Methods

The Iranian heavy crude oil sample adopted in this research was supplied directly by the refineries of TOTAL S.A in France and contains high concentrations of Ni, V, and sulfur. DMDSA and NaOH pellets were purchased from Sigma-Aldrich (Ontario, Canada) and sulfuric acid was received from Fisher chemicals (Ontario, Canada). The dielectric properties of the crude and

DMDSA were measured at the Electrical Department of Polytechnique Montreal, and the results are reported in Table 4.2. Although crude oil is a poor microwave receptor, DMDSA has a high interaction with electromagnetic waves and, therefore, is an efficient microwave to heat energy convertor.

Table 4.2 Dielectric properties of the processed materials

Material	ϵ'	ϵ''
DMDSA	77.2	10.6
Iranian crude oil	1.6	0.013

The proposed process was simulated at large-scale crude treatment capacities by leveraging the ASPEN Plus process simulator. The process flow diagrams, and all corresponding calculations were conducted using built-in tools and databases modified where required. The Aspen Process Economic Analyzer module was employed for investigating the economic performance of the developed process. The default annual operation time of 350 days per year was selected, while the remaining time (15 days per year) was considered for unit maintenance and regular engineering inspections.

In order to accomplish the principal goal of this study, the following steps were performed: (1) a process scheme was designed by determining the required processing units; (2) the process simulation was carried out in ASPEN PLUS to obtain the sizing data of the main processing units; (3) an effective regeneration methodology for DMDSA was developed and experimentally validated; (4) the total capital cost was estimated using the ASPEN Process Economic Analyzer and the literature; (5) the total annual operational cost of the process was calculated; and (6) a

The new process for the demetallization and desulfurization of petroleum crude oil using MWH consists of three major processing units including, a microwave-assisted reactor, washing, and reagent regeneration, as illustrated in Figure 4.2.

In all petroleum refineries, refining starts with the crude oil distillation unit (CDU) where the oil is separated into many fractions or cuts based on their boiling temperatures. These fractions are then introduced to converting units where processes, such as cracking and reforming, take place to change the chemical structure of the existing hydrocarbons in crude oil. Finally, various treatment and separation units following the conversion step are employed to remove undesirable elements and obtain the final quality of the products ⁹². In Figure 4.3. a typical crude oil distillation unit is shown. A comprehensive study on the processes involved in crude oil refineries was carried out to investigate where the new demetallization desulfurization unit (DMDSU) would be installed in a petroleum refinery.

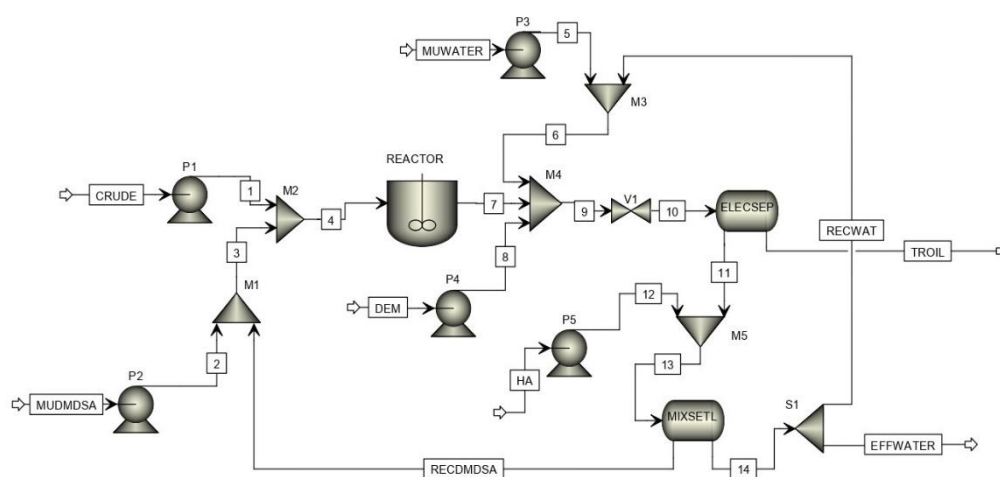


Figure 4.2 Flow diagram of the developed process (MUDMDSA: make-up DMDSA, MUWATER: make-up water diluted by NaOH, DEM: demulsifying agent, HA: DMDSA

regeneration reagent (sulfuric acid), RECDMDSA: recycled DMDSA, RECWAT: recycled water, TROIL: treated oil,

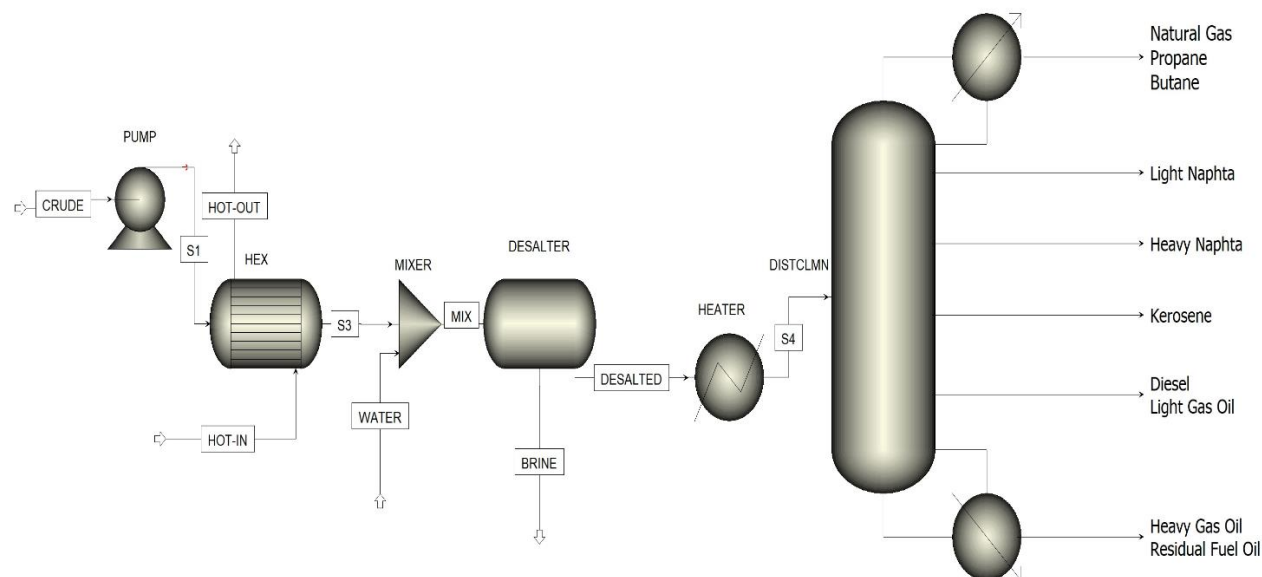


Figure 4.3 Process flow diagram of a typical crude distillation unit

As it can be noted from Figure 4.2, in the proposed process, a mixture of crude oil and DMDSA is introduced into the reactor, where the demetallization reaction and desulfurization mechanism take place under MWH for a certain amount of time. It is vital to note that the employed DMDSA has a high miscibility in crude oil, and therefore, no emulsification is required, which is one of the main advantages of this process compared to similar chemical complexation techniques for metal and sulfur removal of crude oil. During the reaction step, metal salts of the DMDSA are formed that are soluble in water and, therefore, can be removed by washing with water. Also, sulfur compounds are bonded to the formed ionic liquid by DMDSA and the existing anions in the crude through hydrogen and electrostatic bonds. The formed complex structure is highly polar and can be transferred into the aqueous phase and extracted from the crude. Therefore, washing with water

is necessary for final metals and sulfur extraction. Additional details on the metal and sulfur removal mechanism of this technique can be found elsewhere ²⁴.

4.3.1.1 Microwave-assisted reactor

The crude oil volume that is processed in the atmospheric distillation unit is typically considered as the petroleum refinery capacity, which varies from a few thousands up to 1.2 million barrels per day. However, the capacity of most refineries is in the range of 20 k-200 k barrels per stream day (BPSD). In this study, the designed process unit is assumed to be installed in a crude oil refinery with a capacity of 50,000 barrels per stream day. Based on the experimental data reported by Attia et al., DMDSA to oil volume ratio of 1-2 % and the mixture residence time of 5 minutes in the reactor were adopted ⁹¹. Herein, a stirred tank was selected as the appropriate reactor type for DMDSU, and its volume was calculated from Equation 4.1 expressed as:

$$V = F_{in} \cdot \tau_{res} \quad (4.1)$$

Where:

V : reactor volume (m³)

F_{in} : inlet flowrate (m³/h)

τ_{res} : residence time (h)

For 50,000 BPSD or 332 m³/h of the inlet crude oil and a residence time of 5 minutes, a cylindrical vessel (Stirred tank) with the liquid capacity of 28 m³ was selected with the design temperature and pressure of 80 °C and 1 bar respectively, based on the process requirements. The inlet flow rate for DMDSA of 3.3 m³/h was estimated based on the 1% DMDSA to oil volume ratio requirement.

For metal and sulfur removal by conventional heating, the oil and DMDSA mixture must be heated up to 250 °C to obtain the desired removal efficiency. On the other hand, in the microwave-assisted process, it was assumed that only metals were required to reach this temperature leading to a removal reaction initiation. Thus, by using the energy balance expressed in Equation 4.2, due to the low concentration of the Ni and V in the Iranian crude oil (100 ppm), the increase in the average bulk temperature of the treated oil in DMDSU was estimated to be as low as 0.1 °C:

$$(m. Cp)_{oil} \Delta T_{oil} = (m. Cp)_{metals} \Delta T_{metals} \quad (4.2)$$

Where m , C_p and ΔT are mass, heat capacity and temperature difference, respectively.

To supply the required thermal energy for the demetallization reaction, microwave generators were selected to create local hot spots at the metal bonds, based on the high interaction of metals with the electromagnetic waves, while the bulk temperature of crude was considered to have negligible variation. The energy required to heat metals (Ni and V) up to 250 °C is equivalent to the energy necessary for increasing the average bulk temperature of the crude up to 0.1 °C at complete mixing conditions. In this paper, a 2 °C increase in the crude average bulk temperature was considered to have a safe overestimation margin for the required microwave power.

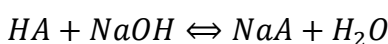
4.3.1.2 Washing & separation

The primary purpose of the washing step is to extract the metal and sulfur from crude oil that are transformed to water-soluble from oil-soluble compounds. Desalting is one of the initial processing units in refineries where crude oil salt content is decreased by washing with water in electrostatic separators. In this process, a mixture of crude and washing water enter the electrostatic separator where the coalescence of fine water droplets is carried out by applying an electric field throughout the vessel to separate the organic and aqueous phases when the desired desalting

efficiency is achieved. Since washing is necessary in the proposed process, an electrostatic separator was selected as the processing unit in the developed DMDSU.

In addition to separating the water-soluble metal and sulfur compounds, it is necessary to remove the unreacted DMDSA from crude oil for economic and reagent regeneration purposes. Given the DMDSA is completely miscible in crude oil, it is challenging to extract it after the dissolution takes place in the reaction step. Attia et al. proposed using ethanol for extracting the unreacted DMDSA from crude due to the high solubility of DMDSA in ethanol, reported as 100 mg/ml by the supplier (Sigma-Aldrich). Although ethanol is considered a highly polar molecule due to its hydroxyl group, and therefore, a suitable solvent for polar and ionic compounds, its ethyl group makes it a good solvent for non-polar substances such as hydrocarbons. Thus, using ethanol to eliminate the unreacted part of DMDSA from treated crude may result in the unwanted dissolution of other hydrocarbons in crude and the corresponding decrease in the total process yield.

To resolve this issue, a new method to extract the unreacted DMDSA was developed. DMDSA has a poor solubility in water due to the long hydrocarbon chain in its molecular structure. However, it is known that the sodium salt of DMDSA is somewhat soluble in water and accordingly, the partial saponification of DMDSA by NaOH is widely applied in metallurgical processes to improve the extraction efficiency of metals by enhancing the solubility of DMDSA in the aqueous phase⁹³. As a result, in the new method, NaOH is added to the washing water to extract the unreacted DMDSA by increasing its solubility through the following reaction:

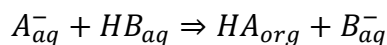


Where H is hydrogen atom and A stands for the anion of DMDSA molecule.

With the aim of assessing the validity of the proposed methodology, 2 vol% of DMDSA was mixed with 40 ml of Iranian crude oil for 20 minutes in a 250 ml quartz batch reactor using magnetic stirring of 800 rpm at 25 °C and atmospheric pressure. The mixture was then washed with 50 ml of 0.2 M NaOH aqueous solution for half an hour in the batch reactor with continuous stirring. Next, the mixture was centrifugated for 5 minutes at 4000 rpm for a complete separation of crude and process water. Samples from each phase were then sent for characterization by the FTIR technique.

4.3.1.3 DMDSA regeneration

In the proposed process, the DMDSA purchase cost plays a crucial role in the process operating costs. A comprehensive study on reagent consumption optimization and regeneration was therefore carried out to design a methodology and an appropriate processing unit for DMDSA regeneration. In the reaction step, DMDSA is converted to metal salts of its anion which are then transferred to the process water in the washing step. DMDSA could be regenerated by stripping its existing anions in the aqueous raffinate process water of the washing step with a strong proton donor agent such as sulfuric acid. The reaction occurs in the aqueous phase and the produced DMDSA appears as a second organic phase.



Where HA_{org} and HB_{aq} are DMDSA and an inorganic acid (e.g., sulfuric acid), respectively.

In order to investigate the effectiveness of the regeneration methodology, a stoichiometric amount of sulfuric acid was added to 200 ml of the process water containing 2 vol % of the anion part of DMDS in a 500 ml quartz batch reactor and the mixture was stirred continuously for 1-2 minutes using a magnetic stirrer at 800 rpm and ambient temperature and pressure. To efficiently separate the organic phase from the aqueous phase, centrifugation at 5000 rpm was carried out for

10 minutes and the aqueous part was sent for characterization by ICP-OES to analyze the Phosphorous concentration as the element representing DMDSA existence in the mixture.

In the liquid-liquid solvent extraction processes, mixer-settlers are commonly utilized where a phase separation follows the mass transfer between two different liquids to transfer the target compounds from one liquid phase to another. As the name suggests, the process consists of two stages: mixing of two immiscible liquids to promote mass transfer and the settler for separation by gravity. As a well-established technology, mixer-settlers are reliable, flexible, and efficient pieces of equipment even in processes where the extraction is problematic due to phase dispersion difficulty, high interfacial tension, and other mixing challenges ⁹⁴.

After the regeneration reaction, the recovered DMDSA appears as a second organic phase requiring the proper separation of organic and aqueous phases. Therefore, a mixer-settler was adopted as the processing unit for DMDSA regeneration. The mixer and the settler were modeled as a CSTR reactor and a decanter, respectively, in ASPEN PLUS to perform the technical and economic calculations of the designed unit.

4.3.2 Characterization techniques

4.3.2.1 FTIR

Fourier Transform Infrared Spectroscopy or FTIR is a fast, economical, and straightforward technique to detect chemical bonds and functional groups. In this study, a Perkin Elmer FTIR instrument was employed for sample characterization with scans in a wavelength range of 4000-600 cm^{-1} . The double chemical bond between phosphorous and oxygen atoms of the phosphate functional group of DMDSA was used to detect DMDSA presence in samples since this functional group does not exist in crude oil. In the FTIR technique, the P=O bond is detected as a stretching peak usually at the absorption range of 1100-1300 cm^{-1} ⁹⁵. In this study, different samples from the

mixture of DMDSA and crude oil, treated oil after washing with NaOH solution, and the effluent process water after the washing step were analyzed to detect P=O bonds and the corresponding DMDSA content.

4.3.2.2 ICP-OES

We used the Agilent 5110 ICP-OES instrument to analyze the phosphorous content of aqueous samples produced at the DMDSA regeneration step. Inductively Coupled Plasma Optical Emission spectroscopy or ICP-OES is a well-known method for the elemental analysis of organic and inorganic samples. In this technique, an argon plasma operating at 10000 kelvin provides the required heat to excite the atoms and ions of the elements. The excited atoms decay emission rays while returning to a lower energy state which could determine the type of element ⁹⁶. In this study, the final aqueous phase in the reaction step of the DMDSA regeneration method was analyzed after being diluted ten times (vol/vol) with nitric acid to determine the phosphorous content of the sample as an approach to measure the DMDSA concentration and the corresponding regeneration efficiency. The regeneration efficiency was calculated as:

$$\eta = \frac{C_{p,i} - C_{p,f}}{C_{p,i}} * 100 \quad (4.3)$$

Where $C_{p,i}$ and $C_{p,f}$ are the initial and final phosphorous concentrations in the treated aqueous phase at the regeneration step, respectively.

4.3.3 Economic analysis

A primary step to investigate the profitability and effectiveness of a new technology is to perform a preliminary economic analysis. This investigation determines how a new process is comparable with other existing solutions to decide whether to accept or decline the proposed technology. In this paper, economic estimations were carried out assuming 100 % microwave

energy to heat conversion efficiency, lab-scale experimental data¹ for the reaction step, and a crude refining capacity of 50 k BPSD operating for 350 days per year.

4.3.3.1 Total capital costs (CAPEX)

Total capital investment is defined as the total, one-time required expenses to put a project into operation including construction and equipment expenditures. The equipment cost of the developed process was estimated by adopting the Aspen Process Economic Analyzer for the main processing units such as the microwave-assisted reactor, washing unit, and regeneration unit. For each unit, the total cost is calculated by vendor cost data of material cost, shop labor cost, shop and office overhead cost, and profit. As explained in section 4.3.1.1, to estimate the required microwave power, an energy analysis has been carried out to calculate the required power to increase the oil and DMDSA mixture temperature for 2 °C in 5 minutes, the average residence time of the mixture in the reactor. The average cost of microwave generators is reported in the literature as 750-1250 US\$/kW varying by the employed microwave power and frequency as well as other design parameters⁹⁷. One of the main challenges in the scale-up of microwave-assisted processes is the low penetration depth of electromagnetic waves at large geometries. Penetration depth is defined as a depth at which 63% of the surface power density is attenuated, which depends on the physical properties of the subject material as well as the microwave frequency. Lower operating microwave frequencies would increase the penetration depth if the process chemistry and transformation regulations permit it and would therefore, benefit the scale-up of the microwave-assisted processes. For instance, microwaves with a 915 MHz frequency are assumed to have penetration depths three times higher than that of 2.45 GHz which is widely applied in lab-scale microwave reactors. In addition to a higher penetration depth, single 915 MHz magnetron-based microwave generators can provide up to 100 kW with a total efficiency of 82%, while 2.45 GHz can generate up to 30

kW with 55%-70% total efficiency⁹⁸. Therefore, in this study multiple magnetron-based 915 MHz microwave generators with a maximum power of 100 kW were selected from available microwave generators on the market and the corresponding cost of \$1000 US/kW was included in the total capital cost.

To estimate the total required capital cost of the proposed process, the Lang factor method was adopted, given it is a well-known method of cost estimation for refining and petrochemical industries. In this method, the fixed capital cost is calculated by multiplying the total purchase cost of the main equipment by the Lang factor parameter that is a function of the process characteristics⁹⁹. Equation 4.4 was used accordingly by assuming the Lang factor of 6.0 for liquid processing to calculate the total fixed capital costs of the designed process. The working capital cost was estimated as 20 % of the total fixed capital investment in Equation 4.5, and added to the total fixed capital cost to calculate the total required investment costs from Equation 4.6¹⁰⁰.

$$C_f = F_{Lang} \sum_{i=1}^n Cp_i \quad (4.4)$$

$$C_w = 0.2 * C_f \quad (4.5)$$

$$C_t = C_f + C_w \quad (4.6)$$

Where:

C_f : Fixed Capital cost of the process

Cp_i : Purchased cost for the major equipment units

C_w : Working capital cost

C_t ; Total required investment

n : Total number of main processing units

F_{Lang} : Lang factor

4.3.3.2 Total annual operating costs (OPEX)

The costs related to the operation of the proposed process are considered in this component of the economic evaluation. The most important operating expenditures could be listed as maintenance, insurance, electricity, reagent, overhead and operating labor costs. The maintenance, insurance and overhead costs were calculated as 3 %, 2 % and 2 % of the total capital cost, respectively ¹⁰¹. For DMDSA, washing water, and electricity, the unit costs of 750 USD/m³, 0.024 USD/m³, and 0.0405 USD/kWh were considered for commercial use, sequentially. To estimate the labor cost, three working shifts per day and the average yearly wage of 30 k USD per operator were considered. Three operators per shift was required based on the following equation ¹⁰².

$$N_{ops} = (6.29 + 0.23 N_{ps})^{0.5} \quad (4.7)$$

Where:

N_{ops} : number of operators per shift

N_{ps} : number of processing steps

4.4 Results and discussion

4.4.1 Process installation configuration

Among various methods for demetallization and desulfurization of crude oil, hydrodemetallization (HDM) and hydrodesulfurization (HDS) are well-established techniques that can theoretically achieve 100% removal efficiency based on thermodynamic equilibrium calculations ⁸. In a petroleum refinery, dedicated HDM-HDS units are installed in intermediate flow streams at that outlet the main distillation unit where the presence of metals and sulfur compounds may have detrimental impacts on the downstream processes or the final products.

This study proposes installing the developed process as the first processing unit of the oil refinery as illustrated in Figure 4.4. Installing the proposed DMDSU prior to the main distillation unit is advantageous for several reasons. For instance, adopting the existing electrostatic separators as the washing processing unit lowers the necessary modifications in downstream processes and the corresponding expenditures. In addition, installing DMDSU prior to the desalting unit could boost the mixture interaction with the microwave irradiation due to the presence of salts in the inlet crude stream. This leads to a lower microwave power requirement in DMDSU and therefore, higher energy savings. Lastly, the downstream metal and sulfur removal units would be redundant and would be eliminated leading to a significant reduction in energy consumption as well as process investment and operating expenses.

Upstream elimination of metals and sulfur to a high extent could mitigate several detrimental impacts of these compounds in the downstream processes while the chemical skeleton of oil is not degraded due to the selective removal of metal and sulfur compounds at low bulk temperatures. Despite other oil upgrading techniques such as HDM-HDS that suffer from reduced production yield due to severe operating conditions, selective heating of the target compounds in the proposed process prevents any reduction in the yield of treated oil and interference in its chemical structure. This occurs due to a significant difference in the dielectric and magnetic properties of the existing microwave receptor components in the crude and DMDSA mixture (e.g., metals, salts, DMDSA) and the crude oil itself, which is a poor microwave to heat converter. Therefore, local hot spots are expected to exist at the reaction sites while the bulk temperature of the crude oil is increased negligibly. Besides the selective removal of these impurities, based on the suggested demetallization mechanism by Attia. et al, the Metal-Nitrogen bonds of the existing porphyrin rings in the crude are replaced by N-H bonds through the demetallization reaction. In this reaction, the

donated hydrogen atoms from DMDSA are integrated into the metal-containing porphyrin rings without changing the chemical structure of the rings.²⁴ Thus, it can be concluded that installing the proposed DMDSU prior to the distillation tower unit would not have an adverse impact on the chemical network of the crude as well as the downstream processes in a crude oil refinery.

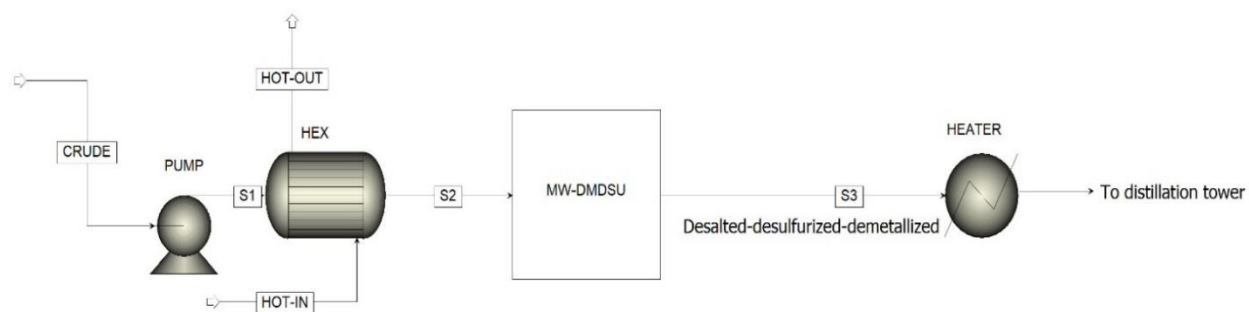


Figure 4.4 Installation configuration of the proposed process (MW-DMDSU) in the crude distillation unit of a typical crude oil refinery

4.4.2 Validation of washing and DMDSA regeneration methodologies

The effectiveness of the proposed technique to remove unreacted DMDSA from crude oil using NaOH solutions in the washing step was investigated. As can be noted from the chemical structure of DMDSA shown in Figure 4.5 (A), Phosphorous and its double bond with oxygen might be used to identify DMDSA in an organic mixture. The FTIR analysis results of the crude and DMDSA mixture before and after washing with a NaOH solution are illustrated in Figure 4.5 (B). As shown, the existing P=O peaks in the 1100-1300 cm^{-1} absorption range are eliminated from the primary oil and DMDSA mixture while new peaks in the same absorption range were appeared in the FITR spectrum of the separated effluent process water in the washing step. This confirms the transition of DMDSA molecules from crude to the raffinate aqueous phase in the proposed washing methodology.

In addition, the proposed process for DMDSA regeneration from the raffinate process water using sulfuric acid was evaluated. The results of ICP-OES characterization are shown in Figure 4.6. As can be noted, the concentration of Phosphorous in the initial raffinate process water has been significantly reduced through stripping by sulfuric acid. It can be concluded that DMDSA was successfully regenerated and separated as the organic phase that appeared after the regenerating reaction completion. The regeneration efficiency was estimated to be 99.8 % using Equation 4.3.

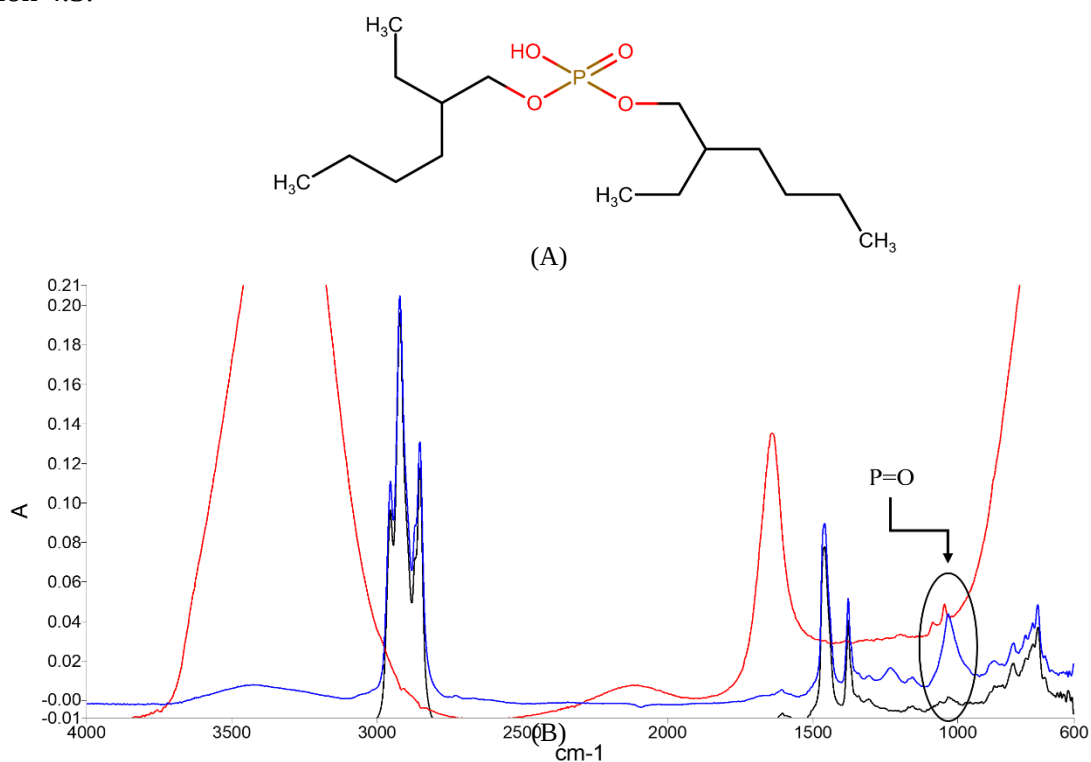


Figure 4.5 (A) Chemical structure of DMDSA (B) Absorbance FTIR of the mixture of DMDSA and Iranian crude oil before washing (blue line), after treatment with NaOH (black line), and raffinate process water (red line) after separation from crude mixture.

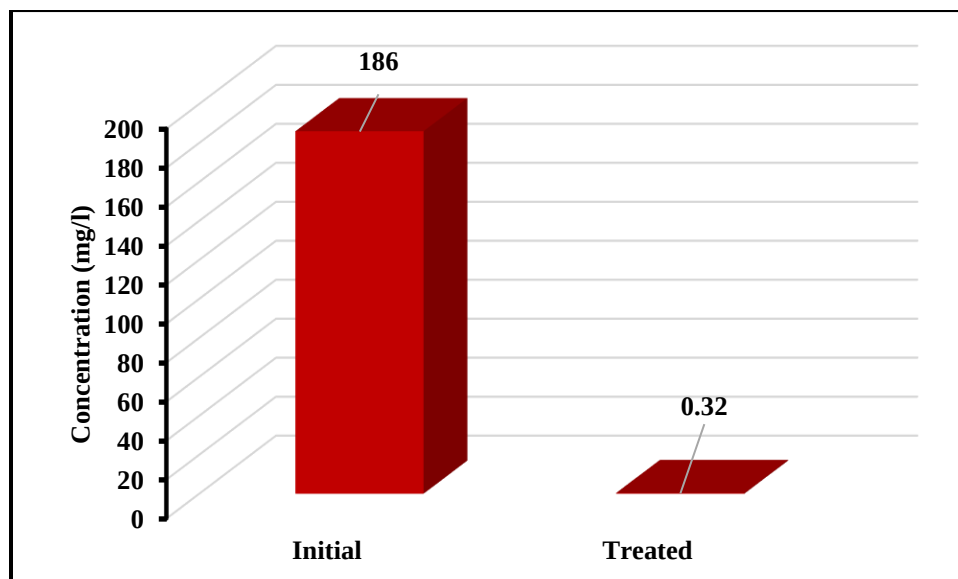


Figure 4.6 Phosphorous concentration of the raffinate process water before and after treatment with sulfuric acid measured by ICP-OES

4.4.3 Capital and operating costs

4.4.3.1 Total capital costs (CAPEX)

Design data and operating conditions of the major units were implemented in ASPEN. The microwave-assisted reactor was considered as a CSTR reactor while a decanter separator was chosen for the separation unit in both washing and regeneration steps. The mixer-settler unit was modeled as a CSTR reactor for the mixing step, followed by a decanter as the settler unit. The schematic of the simulated process in ASPEN and the corresponding results, including the process stream data, are shown in Figure 4.7. The sizing data of each unit was calculated in ASPEN based on the corresponding process conditions of each unit imposed by the total refining capacity of 50,000 bbl/day and the required process conditions. The required thermal power was estimated as 364.4 kW to obtain a 2 °C temperature increase for the mixture in the reactor in 5 minutes. To supply this power, four microwave generators with 100 kW capacity and the purchase cost of 100

k USD were required assuming a complete microwave to heat energy conversion. The cost data of the major equipment was estimated by the ASPEN Process Economic Analyzer based on the pricing data of the first quarter of 2018.

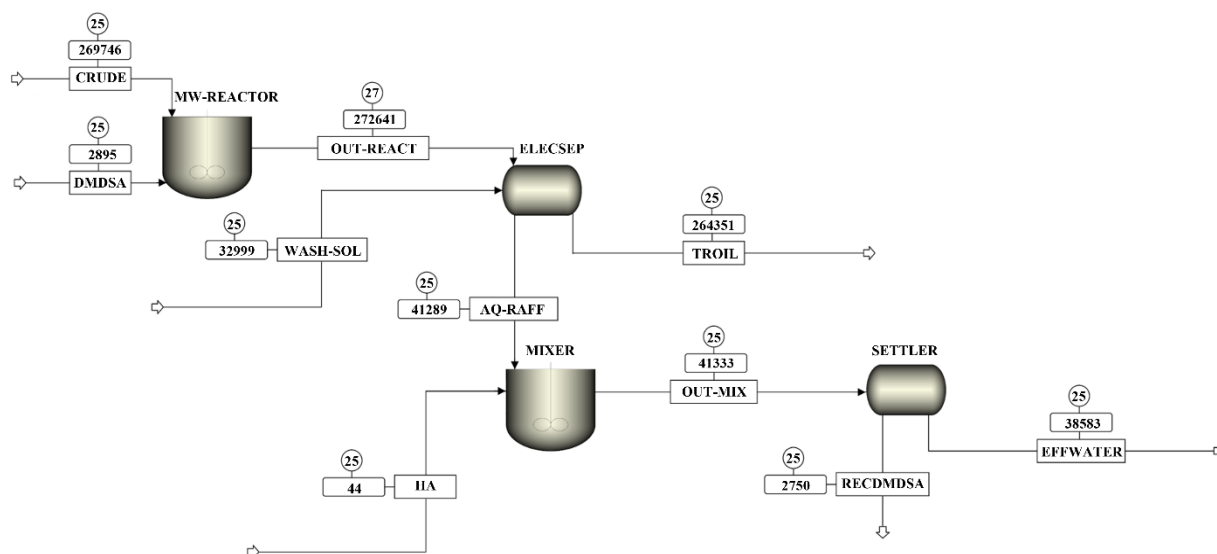


Figure 4.7 Schematic of the simulated process (temperature [$^{\circ}\text{C}$], flow rate [kg/h], OUT-REACT: reactor outlet stream, WASH-SOL: washing solution, AQ-RAFF: aqueous raffinate, OUT-MIX: mixer outlet stream, RECDMDSA: recycled DMDSA, TROIL: treated oil, EFFWATER: effluent water)

The total fixed capital investment of the proposed process was then estimated at 5.64 M USD from Equation 4.4 by selecting the Lang factor of 6.0 for fluid processing. By assuming the working capital cost as 20 % of the calculated fixed capital investment, the total required capital investment was estimated at 6.77 M USD from Equation 4.6. A summary of the CAPEX cost estimation is given in Table 4.3.

Table 4.3 CAPEX investment estimation

Item	Value	Unit
Major Equipment Total Cost	0.94	MUSD
Lang Factor, Fluid Processing	6.00	-
Fixed Capital Investment	5.64	MUSD
Working Capital	1.13	MUSD
Total Capital Investment	6.77	MUSD

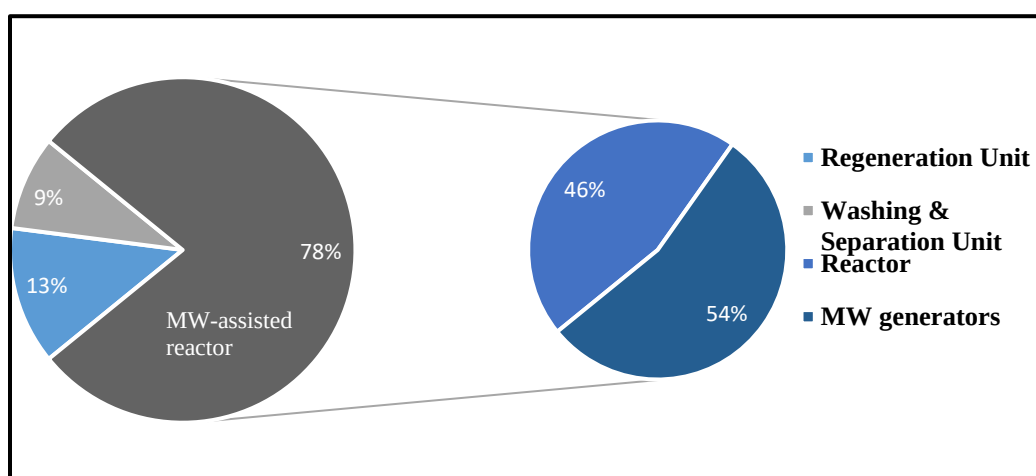


Figure 4.8 Share of major processing units in the total equipment costs

As illustrated in Figure 4.8, the microwave-assisted reactor accounts for more than 78 % of the total equipment cost as the main processing unit of the proposed process where more than 54 % of the unit cost is dedicated to purchasing the microwave generators. The critical role of the reactor design and sizing in the total estimated CAPEX costs underlines the necessity of optimizing the reaction kinetics to obtain the optimum mixture residence time in the reactor. On the other hand, it should be noted that the purchase cost of microwave generators does not increase linearly with the

power. For instance, the approximate price of 5 kW and 100 kW generators was reported at 15,000 and 125,000 USD in 2018 ³. Considering the low efficiency of magnetrons in electrical energy to microwave power conversion, optimizing the employed magnetron system could significantly increase the energy savings which will lead to reduced process costs ¹⁰³. In addition, the recent advancements of the semiconductor industry have led to introducing the revolutionary solid-state microwave generators. As a replacement to the classic magnetrons, the recent solid-state microwave generators have several advantages such as unlimited lifespan, full frequency control, uniform distribution of the electromagnetic field, and lower driving voltages (below 50 V). However, the low efficiency at high power levels and the cost related concerns have been reported as the main challenges towards the development of high-power solid-state generators. With the foreseen improvements of these issues, it is believed that the semiconductor technology rather than magnetrons will be the future in the generation of microwaves with lower costs and higher energy efficiencies ^{98, 104}. This will improve the feasibility of commercialization of the microwave-assisted processes by reducing both CAPEX and OPEX costs.

In comparison with the CAPEX costs of a new 25,000 BPSD HDS plant reported in Table 4.1 as 16-21 MUSD, the proposed process requires 60-70 % less investment costs for a double treatment capacity (50,000 BPSD). In addition, despite the proposed process, the estimated CAPEX costs in Table 4.1 do not account for the associated demetallization costs. Therefore, the developed process shows superior economic performance in terms of CAPEX costs compared to the existing HDM-HDS plants.

4.4.3.2 Total operating costs (OPEX)

The total annual operating cost for the proposed process was calculated considering major expenditures such as insurance, overhead, maintenance, labor cost, chemicals and reagents, and

utility costs. As a result, the total annual OPEX costs of the process were estimated at 4.23 M USD for the treatment capacity of 50,000 BPSD, equivalent to 0.24 \$/bbl. The share of each item in the reported OPEX costs is illustrated in Figure 4.9. As reflected in the figure, purchase costs of chemicals have the highest share of the estimated annual OPEX with more than 80 % or 3.23 M USD. The utility and labor costs are also significant expenses with 7.8 % and 4.98 % of the total yearly OPEX, respectively. Therefore, it can be easily inferred that the DMDSA consumption and regeneration efficiency are substantial parameters that critically impact the process economics.

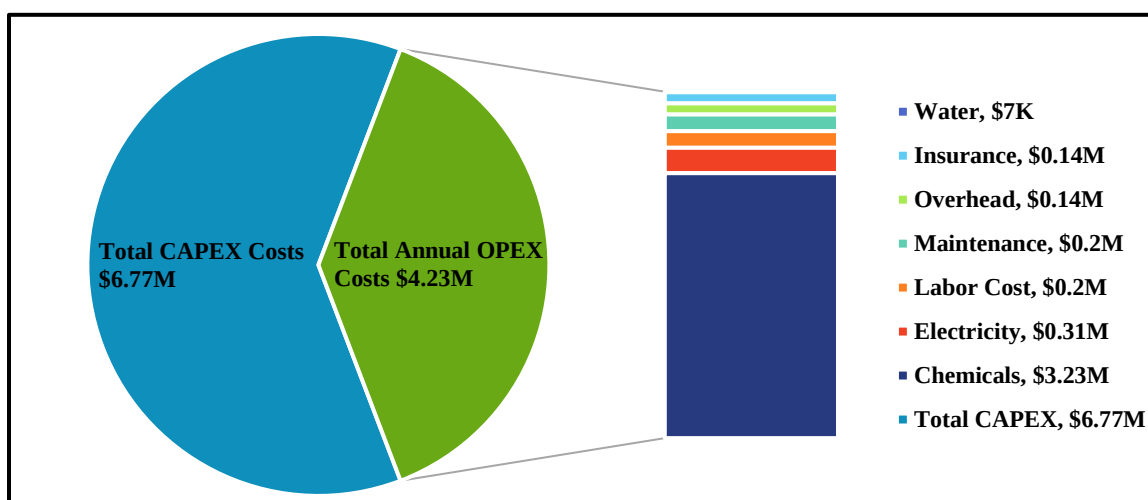


Figure 4.9 Cost fragments of the total annual OPEX costs

The breakdown of utility and chemical consumption is provided in Table 4.4. In fact, the per ton purchasing cost of DMDSA is about four times more expensive than sulfuric acid required for DMDSA regeneration. Thus, by optimizing the DMDSA regeneration to achieve higher regeneration efficiencies, it is possible to lower the operating cost further.

Table 4.4 Energy and utility consumption breakdown

Item	Value	Unit
Water	278880	m ³
DMDSA	1394.4	m ³
Sodium Hydroxide	3338.7	tons
Sulfuric Acid	4090	tons
Electricity	7652.2	MWh

Based on the data reported in Table 4.1, the hydrogen consumption of a new HDS plan to reduce the sulfur content of untreated diesel fuel blendstocks up to 500 ppm is 147-738 SCF/bbl. In 2019, the hydrogen production cost from fossil fuel feedstocks was estimated to be 1.48-2.27 \$/kg¹⁰⁵, which corresponds to 1.14-8.73 \$/bbl for hydrogen costs for the above-mentioned new HDS plant. Therefore, the OPEX costs of such a HDS plant could be estimated at 1.27-9.1 \$/bbl by adding the catalyst and electricity costs reported in table 1 which is significantly higher than the 0.24 \$/bbl estimated OPEX costs of the proposed process for the simultaneous removal of sulfur and metals from crude oil.

4.4.4 Sensitivity analysis of OPEX & CAPEX

In order to improve our understanding of how crucial design parameters affect total capital costs and the annual operating costs, a sensitivity analysis was carried. Accordingly, OPEX and CAPEX costs were recalculated for the selected range of treatment capacity (50-200 k BPSD), DMDSA:oil mixing ratio (0.5-5 %), DMDSA regeneration efficiency (50-100 %), the average bulk temperature increment (1-5 °C), and the residence time (2-10 minutes) of the mixture in the

microwave-assisted reactor. The results were reported as the percentage of increasing or decreasing CAPEX or OPEX costs compared to the base case-study with a treatment capacity of 50 k BPSD, 1% DMDSA:oil mixing ratio, 95% DMDSA regeneration efficiency, 5 minutes residence time and a 2 °C increase in the bulk temperature of the mixture in the reactor. The results are illustrated in Figures 4.10 and 4.11. In addition, the impact of changing each design parameter on OPEX & CAPEX costs while the value of the rest of variables was taken from the base case-study are listed in Table 4.5.

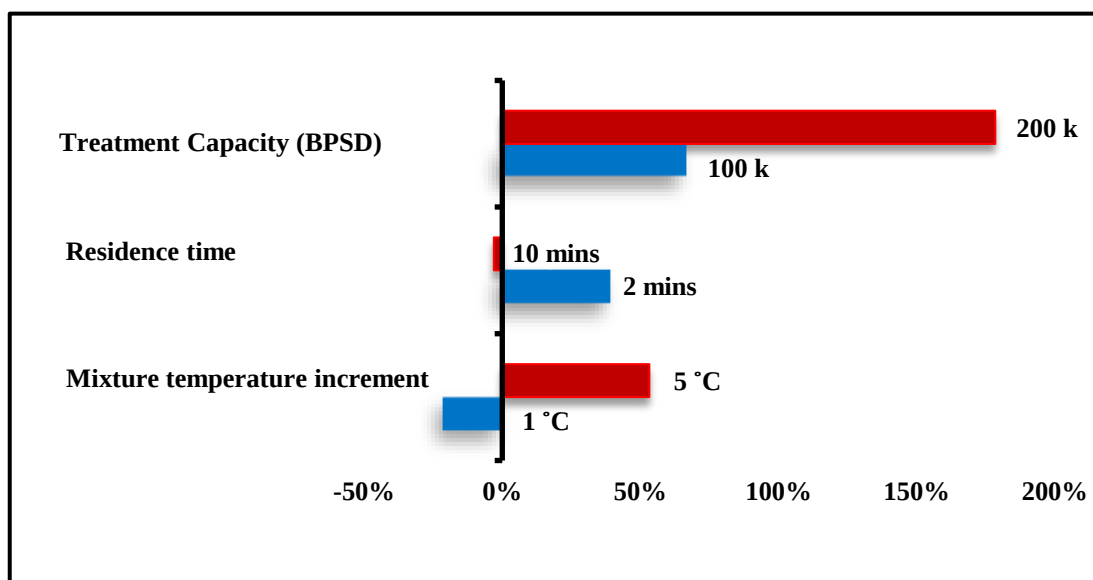
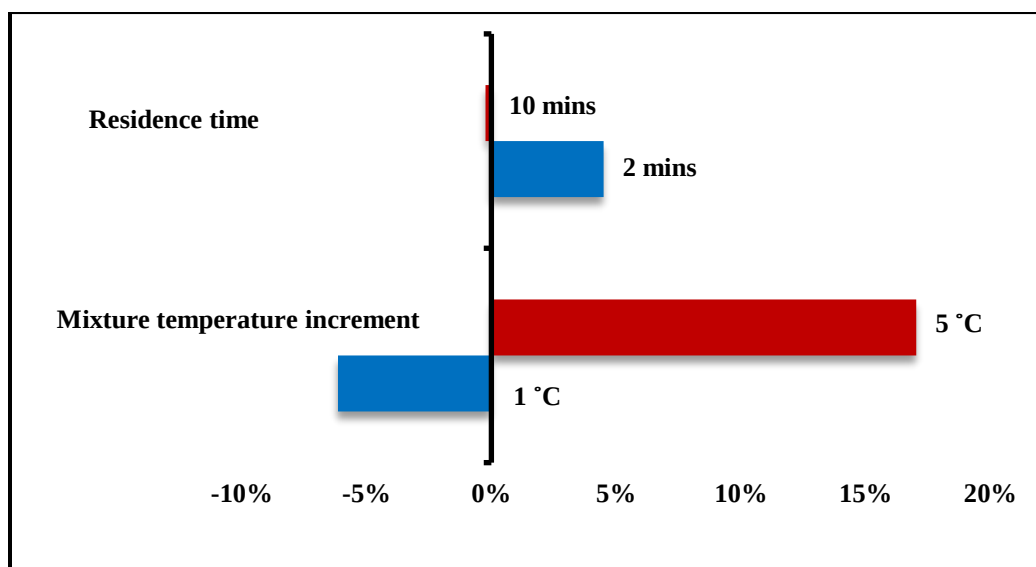
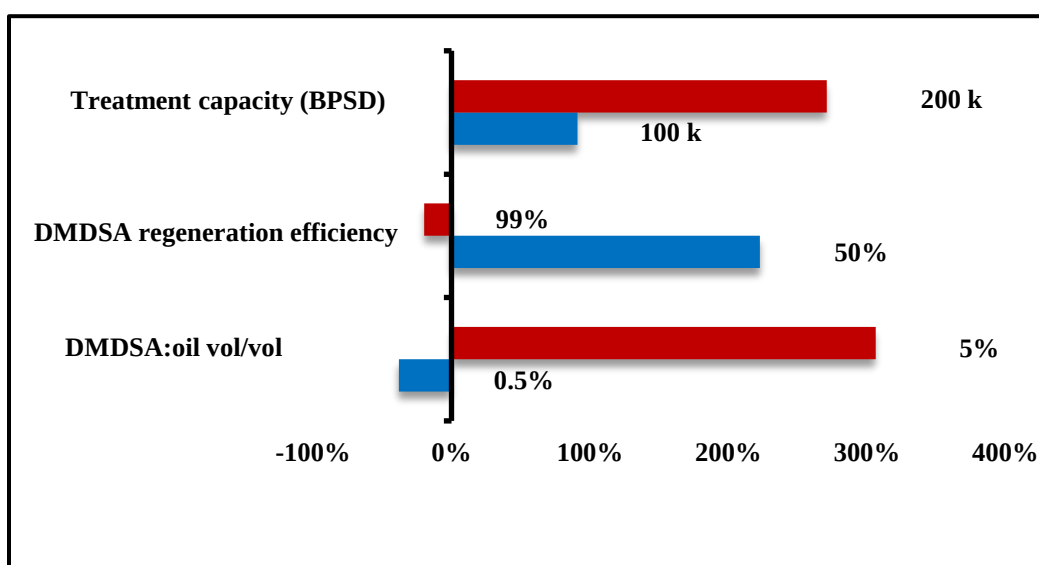


Figure 4.10 Impact of crucial parameters on total CAPEX costs



(A)



(B)

Figure 4.11 Impact of (A) mixture residence time and average bulk temperature increment (B) treatment capacity, DMDSA regeneration efficiency and consumption on annual OPEX costs

The results showed that the change in the treatment capacity has the highest impact on the total CAPEX costs. As can be noted from Figure 4.10 and Table 4.5, a rise in the treatment capacity

from 50,000 BPSD to 200,000 BPSD would result in a considerable increase in the CAPEX costs from 6.77 MUSD to 18.85 MUSD (about + 178 %), mainly due to the increase in the number of required microwave generators. For a same reason, a lower residence time and a higher temperature increment of the mixture in the reactor would lead to higher CAPEX costs. For instance, at a shorter residence time in the reactor, greater rates of heat energy should be supplied by the microwave generators to reach the desired outlet temperature. This requires a higher amount of microwave power and a subsequent larger number of microwave generators which will add to the CAPEX costs. As reflected in Table 4.5, 2 minutes residence time and a 5 °C increase in the average bulk temperature of the mixture in the reactor will increase the CAPEX costs from 6.77 MUSD to 9.42 (+ 39 %) and 10.37 MUSD (+ 53 %), respectively. It could be concluded that optimizing the power consumption and efficiency could highly affect the capital costs of the developed process.

Regarding the total annual operating costs, DMDSA consumption and its purchase cost have the highest share in the estimated OPEX costs. As indicated in Figure 4.11 (B) and Table 4.5, increasing the DMDSA to crude oil ratio in the reactor from 1 % to 5 % would raise the annual operating costs from 4.23 MUSD to 17.19 MUSD. Furthermore, a decrease in the regeneration efficiency from 95 % to 50 % will result in 231 % increase the total annual OPEX costs since more make-up DMDSA would be needed when the regeneration efficiency is lower. Although an increase in the treatment capacity from 50,000 to 200,000 BPSD would raise the total OPEX costs up to 271 %, the normalized operating costs per barrel of the treated crude oil remain almost constant with changes in the treatment capacity. Moreover, as shown in Figure 4.11 (A), variations of the other design parameters such as residence time and temperature increment of the mixture in the reactor, have minor effects on the estimated OPEX costs. Therefore, it can be concluded that lowering DMDSA purchase costs through effective regeneration and reduced consumption,

obtained from optimized mixing and kinetic parameters, will result in lower operating costs and a corresponding improvement in the process economic feasibility.

Table 4.5 Impact of design parameters on OPEX & CAPEX costs

Design parameter	Bulk temperature			Treatment capacity			Residence time			DMDSA:oil			DMDSA regeneration efficiency (%)		
	increase (°C)			(k BPSD)			(min)			vol/vol%					
	1	2	5	50	100	200	2	5	10	0.5	1	5	50	95	99
OPEX															
(MUSD/yr)	3.97	4.23	4.95	4.23	8.08	15.7	4.42	4.43	4.22	2.62	4.23	17.19	13.65	4.23	3.4
CAPEX															
(MUSD)	5.33	6.77	10.37	6.77	11.28	18.85	9.42	6.77	6.56	-	-	-	-	-	-

The data from this study reveals several advantages for adopting the proposed microwave-assisted process for metal and sulfur elimination from crude oil. In addition to the better economic performance, the proposed process is desirable for several reasons including mild operating conditions, a lower energy requirement due to selective microwave heating, simultaneous demetallization and desulfurization, and the lack of a need for a catalyst. Similarly, installing the new DMDSU prior to the distillation tower of a petroleum oil refinery mitigates the detrimental impacts of metals and sulfur in the downstream processes without altering the chemical structure of the crude or reducing the production yield. Ultimately, by applying microwave heating technology, which uses green electricity to generate the required heat instead of stationary fuel combustion, the proposed process would participate in decreasing carbon emissions of the petroleum refinery sector.

The results of the economic investigation showed the importance of a further optimization of the main process parameters to obtain a more accurate understanding of the process scale-up feasibility. Although the CAPEX costs of the proposed process were estimated to be much less than the similar techniques, the sensitivity analysis highlighted the necessity of developing a precise kinetic model of the sulfur and metal removal in future studies to minimize the required equipment investment cost. On the other hand, the annual operating costs seem to be the main limitation of the developed process commercialization if DMDSA is not optimally used and regenerated. Thus, further investigations in future research works should be devoted to optimizing DMDSA regeneration efficiency in the regeneration unit as well as the number of cycles that DMDSA can operate effectively without considerable chemical degradation.

4.5 Conclusion

A new process scheme for microwave-assisted demetallization and desulfurization of crude petroleum oil was designed through identifying the required processing units and their operating conditions as well as estimating sizing data by simulation in ASPEN Plus. Additionally, a methodology for the effective separation and regeneration of the demetallization desulfurization agent (DMDSA) using sodium hydroxide (NaOH) aqueous solutions and sulfuric acid was developed showing DMDSA regeneration efficiencies up to 99%. A comprehensive techno-economic analysis was performed to investigate the commercializing feasibility of the proposed process at industrial scale. The economic performance of the proposed process to treat 50,000 barrels per stream day (BPSD) of crude oil was investigated using the ASPEN Process Economic Analyzer that resulted in estimating total capital costs (CAPEX) and total annual operating costs (OPEX) at 6.77 MUSD and 4.23 MUSD (0.24 \$/bbl), respectively. The results show that the suggested process is economically superior to the common crude oil upgrading technologies such

as hydro-desulfurization (HDS) with the estimated CAPEX of 16-21 MUSD (25,000 BPSD) and OPEX of 1.27-9.1 \$/bbl. Other advantages, such as catalyst-free, ambient process conditions, and considerable energy savings through selective microwave heating are worth mentioning. The sensitivity analysis of the economic parameters by varying the main design parameters showed that the purchase cost of the microwave generators has the highest impact on the estimated CAPEX costs. On the other hand, the annual OPEX cost was found to be a strong function of the DMDSA consumption and regeneration effectiveness. In future studies, developing a precise kinetic model to optimize the primary process parameters such as the required microwave power, DMDSA to oil ratio, and the residence time would be indispensable to obtain the best economic performance of the proposed process.

CHAPTER 5 ARTICLE 2 : MICROWAVE-ASSISTED NICKEL AND VANADIUM REMOVAL FROM CRUDE PETROLEUM OIL USING BIS(2-ETHYLHEXYL) PHOSPHORIC ACID: A KINETIC STUDY

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5.1 Abstract

Among the various metals in crude oils, nickel (Ni) and vanadium (V) exist as oil-soluble organic compounds, making them extremely difficult to remove. The presence of these metals has been proven to have deleterious effects, such as catalyst poisoning and corrosion in crude refinery processes. This study aimed for Ni/V removal from Iranian crude oil using bis(2-ethylhexyl) phosphoric acid (D2EHPA) under microwave heating. The impact of primary process parameters, such as temperature, residence time, and D2EHPA dosage, on Ni and V removal efficiencies was studied. The demetallization reaction kinetics and mechanism were investigated at 230-250 °C and optimized conditions. The findings demonstrated that at low microwave powers of 40-50 W, Ni and V removal efficiencies could reach up to 63% and 72%, respectively, after a reaction time of 1 hour at 250 °C. The kinetics of demetallization reactions were found to be of first-order, and the activation energies and pre-exponential factors for Ni and V were estimated to be 29.8 and 34.7 kJ/mol, and 16.5 and 66.2 min⁻¹, respectively. A well-fitted kinetic model was proposed based on the coefficients of determination. The reaction between the metalloporphyrins in crude oil and

D2EHPA resulted in the substitution of Ni and V with protons provided by D2EHPA, leading to the formation of metal salts that are soluble in water. The formation of N-H bonds in the treated oil, as confirmed by the FTIR analysis results, indicated the occurrence of the demetallization reaction.

5.2 Introduction

As conventional light oil reserves around the world continue to decline, the significance of upgrading heavy crude oils is increasing ^{16, 83}. The concentration of impurities, such as metals, mainly nickel (Ni) and vanadium (V), sulfur, and nitrogen compounds, is much higher in heavy oils, making the upgrading of heavy oils more challenging and costly ¹⁷. Although crude oils contain only trace amounts of vanadium and nickel, these metals have various detrimental impacts in refineries, such as catalyst poisoning and catalyst deactivation in different processing units ^{18, 19, 87}. In addition, elevated levels of metals in the final fuel products can result in the emission of harmful pollutants, such as vanadium pentoxide, as well as corrosion and ash formation in power generation systems ¹⁰⁶. As the volume of heavy oils treated in refineries rapidly increases, the efficient removal of the aforementioned contaminants becomes more crucial than ever.

The conventional techniques for removing metals from crude oil are generally categorized as either physical, mainly involving deasphalting, or chemical processes, such as coking, visbreaking, and catalytic hydrodemetallization (HDM) ^{107, 108}. Although various studies have demonstrated the efficacy of these methods in literature, each technique has its drawbacks. For instance, deasphalting is unable to selectively eliminate metals from oil and instead removes the entire metal-containing asphaltene fraction, thereby decreasing the final product yield. The most extensively used technology, catalytic hydrodemetallization (HDM), can selectively remove Ni and V by converting them into sulfides via a catalytic reaction. However, this method has several disadvantages, such

as high operating temperatures and pressures (up to 400 °C and 130 bar), high hydrogen consumption, reduced catalyst lifespan, and significant energy requirements, which make it undesirable for upgrading heavy crude oils.^{17, 107}

The increasing environmental concerns have led to a growing interest in unconventional selective heating technologies such as induction, ultrasound, and microwave heating^{3, 60, 61}. Microwave-assisted demetallization has emerged as an advanced method for removing Ni and V from crude oils. The distinctive features of microwave heating, including selective, volumetric, fast, and controlled heating, make it a viable alternative heating technology in variety of fields, including chemical and petrochemical industries^{10, 11, 68}. The process of microwave heating differs from conventional heating in that it relies on the agitation of polar molecules when exposed to an alternating electric field, resulting in friction and heat production. Materials with higher polarity are generally more amenable to microwave treatment. Thus, microwave heating offers benefits such as selective and volumetric heating.^{3, 88, 90} The most common reagents used for crude oil demetallization are acids (e.g., sulfuric, nitric, phosphoric), salts, such as boron trifluoride, group IA and IIA aqueous bases (e.g., carbonates and hydroxides), oxidative agents, and chlorine-based compounds (e.g., Cl₂, SOCl₂, FeCl₂, SnCl₂, ZnCl₂, TiCl₄)^{15, 24}. Microwave heating is capable of selectively heating both metals and the aforementioned polar demetallization agents as they are strong microwave receptors.

A number of studies have been reported in the literature on microwave-assisted crude oil demetallization. Chomorro et al., for instance, achieved Ni and V removal efficiencies of 80% and 99%, respectively, using an acidic demetallization agent and 15 minutes of microwave heating¹⁴. A study conducted by Wen et al. investigated the demetallization of various crude oils using sodium dimethyldithiocarbamate and water with the assistance of microwave heating. The study achieved

removal efficiencies of 87% for V and 49% for Ni with microwave irradiation ranging from 100-800 W for 5-60 minutes ¹⁰⁹. Shang et al. applied demetallization agents with various functional groups to eliminate Ni and V from Venezuela's crude oil under microwave heating. In this method, Vanadium and nickel can be converted into water-soluble materials without disrupting metalloporphyrin ring structure, and subsequently removed through a washing. The most significant removal of Ni and V was achieved through the utilization of sulfonic acid as the demetallization agent, resulting in an 84% removal efficiency under microwave irradiation ranging from 600-800 W for 3 minutes ¹⁵.

The application of organic agents, such as cationic starches and Chitosan-based reagents, in microwave-assisted demetallization of crude oil has demonstrated high efficiency. ^{13, 85}. In 2020, Attia et al. developed a new technique to eliminate metals from different oils using bis(2-ethylhexyl) phosphoric acid (D2EHPA). The main mechanism involves D2EHPA serving as a proton donor and selectively eliminating Ni and V from the center of their porphyrin rings, while leaving the oil yield unchanged. Unlike most demetallization agents, D2EHPA can be mixed with oil without emulsification due to its high solubility in organic solvents, which is the primary advantage of this method. The removal efficiencies for Ni and V from Iranian crude oil were reported to be up to 73 % and 32 %, respectively, when treated with conventional heating for one hour ²⁴.

The feasibility of commercializing the proposed process by Attia was investigated through a techno-economic analysis presented by Solouki et al. in 2022 ¹¹⁰. The results demonstrated the necessity of optimizing the main process parameters and developing a precise kinetic model for the demetallization reaction under microwave irradiation. This study aims to explore the effects of using microwave heating in conjunction with D2EHPA as a demetallization agent to remove Ni

and V from crude oil. The effect of primary process parameters, such as temperature, residence time, and D2EHPA dosage, on metal removal efficiencies under microwave irradiation is studied, and the optimized values are determined. Furthermore, this study discusses the mechanism of Ni/V removal under microwave heating and develops a kinetic model for the demetallization reactions. It also presents the primary kinetic parameters, such as rate constants, activation energies, and pre-exponential factors of Ni and V removal reactions.

5.3 Materials and methods

5.3.1 Materials

Iranian crude oil supplied by TOTAL refineries in France was employed to conduct the experiments. All chemicals (D2EHPA, NaOH pellets) and solvents used in this study were purchased from Sigma-Aldrich (Ontario, Canada). The properties of Iranian crude oil are given in Table 5.1.

Table 5.1 Properties of Iranian crude oil

Density (kg/m ³)	Viscosity (cP)	Carbon residue						
(15 °C)	(10 °C)	(Wt.%)	API	S (ppm)	V (ppm)	Ni (ppm)	Na (ppm)	
881.2	18.4	6.88	28.9	24912	105	30	1.83	

5.3.2 Experimental setup

The experiments were conducted in an Anton Paar Monowave 400 synthesis microwave reactor. The reactor is equipped with a magnetron generating a maximum microwave power of 850 W, allowing for experiments to be conducted under operating conditions of up to 30 bar and 300 °C. During the reaction step, the crude oil and D2EHPA mixtures were placed into 30 ml

borosilicate glass vials containing a magnetic propeller for mixing. The vials were covered by caps made of polyether-ether-ketone (KEEP) and then placed inside the instrument. The samples were heated to the desired temperatures at continuous magnetic stirring and held for a specific amount of time. The temperature of the reaction vials was automatically measured and controlled by the instrument using an IR temperature sensor and a fiber-optic ruby thermometer immersed in the reaction mixture. By adopting a closed system configuration within the reactor, the pressure in the vials was automatically adjusted, thereby preventing any evaporation of the samples.

5.3.3 Experimental procedure

The process consisted of three main steps: (a) microwave-assisted removal of metals from crude oil through reactions with D2EHPA; (b) washing of the irradiated mixture with NaOH aqueous solutions to transfer the reacted metals to the washing solution; and (c) final separation of the resulting aqueous solution containing the removed metals and unreacted D2EHPA. The details of these steps are provided in the following subsections.

5.3.3.1 Reaction

Samples were prepared by mixing 20 ml of the Iranian oil with calculated weight percentages of D2EHPA using magnetic stirring for 30 minutes. Due to the miscibility of D2EHPA in organic compounds, such as crude oil, no emulsification was needed in this step. The mixture of crude oil and D2EHPA was then poured into a 30 ml borosilicate vial covered with a cap made of KEEP and placed in the microwave reactor (Monowave 400). The mixture was heated as fast as possible to the set temperature and was held at this temperature for a specific amount of time to accomplish the reaction. In previous studies, the optimal mixing condition for crude oil demetallization with D2EHPA under conventional heating was found to be stirring above 700 rpm

²⁴. To ensure a homogeneous thermal distribution throughout the reaction, continuous stirring at 800 rpm was applied in this study.

5.3.3.2 Washing and separation

A 50 wt.% NaOH aqueous solution was used to wash the treated oil and extract the reacted metals as well as the unreacted D2EHPA. The addition of NaOH to the washing water is crucial to remove the unreacted D2EHPA from the treated oil by promoting a saponification reaction between D2EHPA and NaOH, which enhances the solubility of D2EHPA in water ¹¹⁰. After the demetallization reaction, the mixture of oil and washing solution was heated conventionally up to 80 °C while being stirred constantly at 800 rpm using a magnetic hot plate stirrer for 20 minutes. Following this, the mixture was centrifuged at 4000 rpm for 10 minutes to separate the treated oil and the aqueous phase, which contained the metal-loaded D2EHPA (metal salts) and unreacted D2EHPA. In order to ensure complete removal of metals, the washing process was repeated three times with fresh washing solutions. Samples were taken from the finally washed oil for analysis to determine the concentrations of Ni and V.

5.3.4 Characterization methods

Fourier transform infrared spectroscopy (FTIR) analysis was carried out using Spectrum 65 FTIR instrument from PerkinElmer. For each sample, 32 FTIR spectra were recorded between 4000-600 cm⁻¹ with 4 cm⁻¹ resolution. A TGA 550 from TA Instruments was used to assess the thermal stability of D2EHPA at a scan rate of 10 °C/min between 25 and 800 °C under nitrogen flow. Neutron Activation Analysis (NAA) was used to quantify metal concentrations present in crude oil samples based on their nuclear characteristics. The samples were analyzed at Slowpoke analytical lab at Polytechnique Montreal (Quebec, Canada). In NAA, samples are placed in a

nuclear reactor where thermal neutrons convert stable isotopes of present elements to radioactive isotopes. The excited isotopes return to their stable state by decaying gamma-radiations, which are used to obtain a γ -ray spectrum and detect and quantify the elements ^{111, 112}.

5.3.5 Temperature measurement

Accurate temperature measurement is crucial in microwave-assisted processes. However, the presence of electromagnetic waves poses a challenge for temperature measurement, necessitating the use of appropriate measuring devices. There are two main categories of microwave temperature measurement methods: contact techniques, including thermocouples and thermal indicators, and non-contact techniques, such as optical and pyrometry methods. Shielded thermocouples are capable of measuring temperatures up to 2000 °C without the negative effects of direct exposure to the electromagnetic field inside a microwave cavity. Meanwhile, to minimize the risk of electromagnetic interference, fiber optic sensors are utilized in microwave systems for temperature measurement by analyzing changes in fluorescence characteristics. However, fiber optic sensors are limited to temperatures below 300 °C. Pyrometry is the most widely used non-contact technique for measuring temperature in the presence of electromagnetic irradiation. This method involves measuring the surface temperature of a heated target through the detection of thermal radiation in the near-infrared wavelength range ¹¹³. A comparison of temperature measurement techniques for microwave systems is provided elsewhere ^{114, 115}.

In this study, the sample bulk temperature was controlled and measured automatically by an incorporated IR temperature sensor within the instrument microwave cavity with a 0.1 °C precision. Considering the low interaction of Iranian crude oil with microwaves due to its poor dielectric and magnetic physical properties reported in our previous study ¹¹⁰, local heating of the target metals and D2EHPA is expected ¹¹⁰. Hence, it can be inferred that during the microwave-assisted

demetallization process, target metals should be at significantly higher temperatures than the average bulk temperature of the heated mixture.

5.4 Results and discussion

The study results are presented by analyzing the influence of process parameters on Ni/V conversion and by describing the demetallization reaction mechanism and kinetics. Firstly, the effect of reaction temperature, time, and D2EHPA concentration on Ni and V removal efficiencies are thoroughly discussed, and the optimal experimental conditions are reported. Secondly, the demetallization reaction mechanism and the kinetic models of V and Ni conversion are presented by utilizing the previously optimized process parameters. The metal removal efficiencies were determined using the following equation in the subsequent subsections:

$$\text{Metal removal (\%)} = \frac{C_{m,crude} - C_{m,treated}}{C_{m,crude}} \times 100 \quad (5.1)$$

Where $C_{m,crude}$ and $C_{m,treated}$ are the concentration of the corresponding metal (V or Ni), m, in the crude and treated oil, respectively.

5.4.1 Effect of temperature

The effect of reaction temperature on the V removal efficiency was studied within the temperature range of 80-250 °C, while maintaining the D2EHPA:oil mass ratio and reaction time at 5 wt.% and 10 minutes, respectively. At temperatures ranging from 80 to 200 °C, the vanadium removal efficiency was found to be below 11%. Nevertheless, as indicated in Figure 5.1, a sudden rise in V removal efficiency of up to 17% was observed at 250 °C. Consequently, it was concluded that V removal efficiency is low up to 200 °C, and hence all subsequent experiments were conducted at 250 °C.

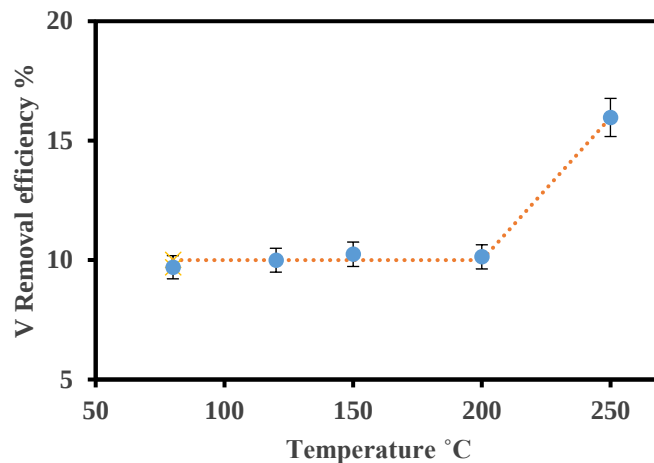


Figure 5.1 Impact of reaction temperature on V removal efficiency for crude oil treated with 5 wt.% D2EHPA for 10 minutes

5.4.2 Effect of reaction time

After observing the increase in V removal efficiency at 250 °C, subsequent experiments were conducted at this temperature using different reaction times ranging from 10 to 90 minutes and a D2EHPA concentration of 5 wt.%, as shown in Figure 5.2. The results indicate that the V removal efficiency gradually increases up to 45% at longer reaction times, with a peak observed at one hour. However, no further improvement in V removal efficiency was observed beyond one hour, as justified in section 5.4.5. Therefore, subsequent experiments were conducted with a one-hour irradiation time in the microwave reactor.

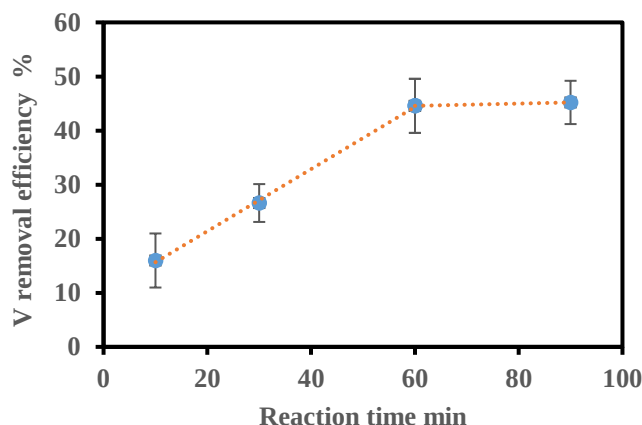


Figure 5.2 Impact of reaction time on V removal efficiency for crude oil treated with 5 wt.% D2EHPA at 250 °C

5.4.3 Effect of D2EHPA dosage

Experiments were conducted at different D2EHPA:oil ratios of 2, 10, 15, and 25 wt. % to study the effect of D2EHPA dosage, at the optimized reaction time of 1 hour and temperature of 250 °C. As illustrated in Figures 5.3 and 5.4, the removal efficiencies of V and Ni increase from 20 % to 72 % and 5 % to 63 %, respectively, when the D2EHPA concentration changes from 2 to 15 wt.%. No further boost in the metal removal efficiencies was observed when higher dosages of D2EHPA up to 25 wt.% were applied (a comprehensive discussion is provided later in section 5.4.5). Consequently, 15 wt.% was chosen as the optimum D2EHPA dosage in the investigated range. To ensure that the obtained results were not affected by factors other than D2EHPA, blank crude oil samples were also subjected to microwave irradiation at 250 °C for 1 hour. As shown by the results, there were no changes in Ni and V concentrations in the blank crude oil samples after treatment. This provides evidence that the removal of Ni and V is attributable to D2EHPA and the proposed demetallization mechanism, which will be further discussed in section 5.4.4.

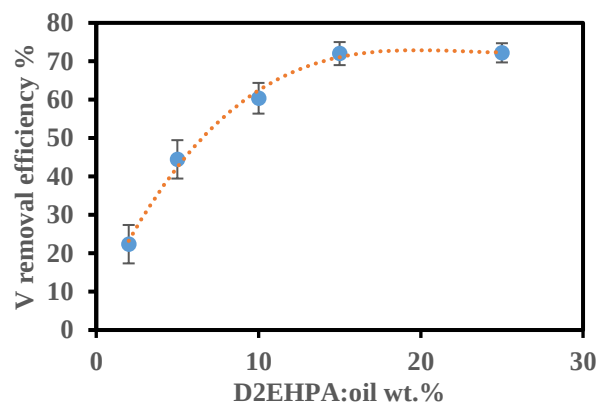


Figure 5.3 Impact of D2EHPA concentration on V removal efficiency for crude oil treated for 1 h at 250 °C

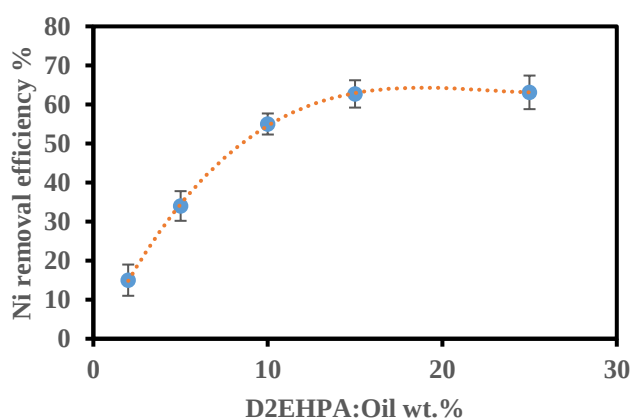


Figure 5.4 Impact of D2EHPA concentration on Ni removal efficiency for crude oil treated for 1 h at 250 °C

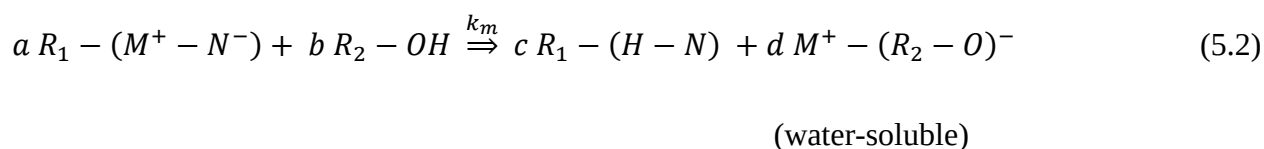
Table 5.2 provides a summary of the range investigated for each process parameter and the corresponding optimized value. These findings will be employed to explore the kinetics and mechanism of the microwave-assisted demetallization reaction.

Table 5.2 Optimum values of the main process parameters

Parameter	Temperature (°C)	Time (min)	D2EHPA Dosage (wt.%)
Investigated range	80-250	10-90	2-25
Optimum value	250	60	15

5.4.4 Reaction mechanism

According to Attia et al., demetallization reaction mechanism involves a proton exchange between the metalloporphyrin rings in the crude oil and D2EHPA molecules.^{1, 24} Figure 5.5 illustrates the chemical structures of a vanadium porphyrin and a D2EHPA molecule. During the demetallization reaction, the metal is released from the center of its porphyrin ring and is substituted by a proton from the reagent. As a result, the metal-nitrogen bonds in the metalloporphyrins present in the crude oil are replaced by nitrogen-hydrogen bonds, and the liberated metal ion combines with the dissociated reagent, which has lost its proton, to form a water-soluble metal salt. Further details regarding the mechanism of the demetallization reaction can be found elsewhere²⁴. Similar reaction mechanism is reported for microwave-assisted Ni and V removal from crude oil using different demetallization agents¹⁵. The demetallization reaction can be expressed as following:



Or:



Where $R_1 = (M^+ - N^-)$ or A and $R_2 = OH$ or B are the chemical formulas for metalloporphyrins and D2EHPA, respectively, and k_m represents the metal removal rate constant. The FTIR analysis results validated the formation of N-H bonds in the treated oil, which is attributed to the demetallization reaction. As depicted in Figure 5.6, N-H stretching bond peaks were observed at approximately 3380 and 1630 cm^{-1} in all treated oil samples, compared to the blank control sample of crude oil irradiated for 1 hour without D2EHPA addition. These peaks provide evidence of the successful conversion of N-M bonds in crude oil to new N-H bonds in the processed oil through the demetallization reaction with D2EHPA. However, further investigations in the future studies would be necessary to shed more light on the reaction mechanism. It is noteworthy that, for samples of equal weight, the intensity of the observed peaks was more pronounced in crude oil samples treated for longer reaction times (10 minutes, 30 minutes, and 1 hour), indicating a higher degree of metal conversion.

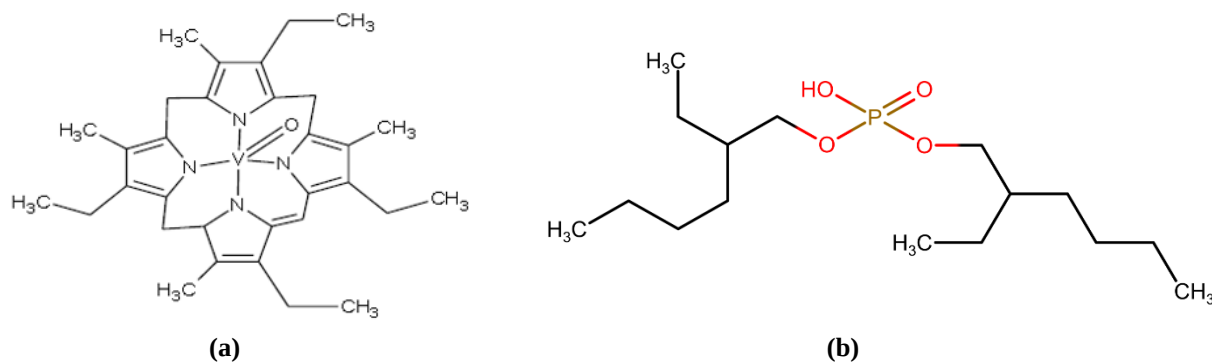


Figure 5.5 Chemical structure of (a) Vanadium porphyrin (b) D2EHPA (reprinted from reference ^{1, 110})

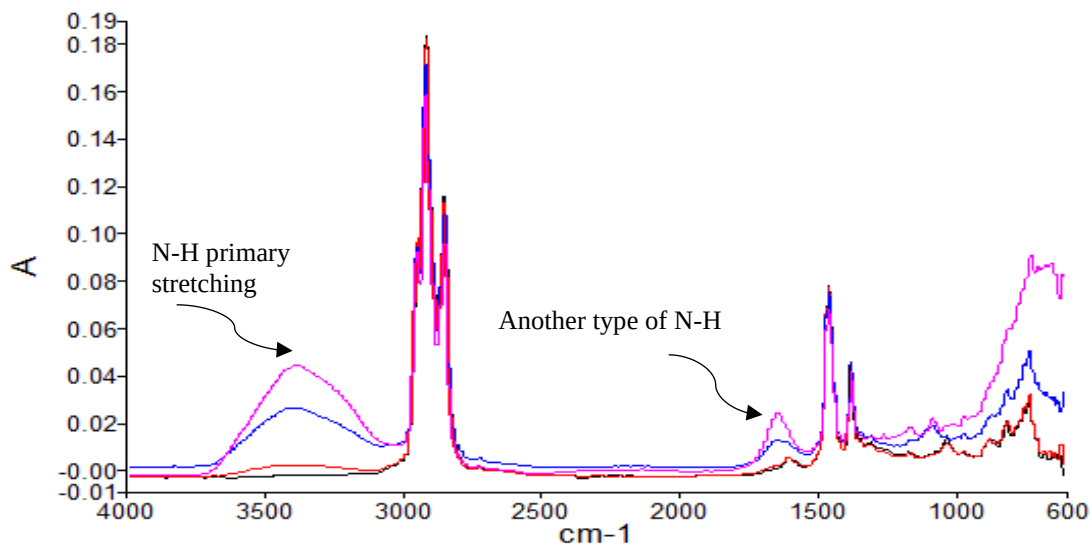


Figure 5.6 IR Absorbance (A) versus wavelength (cm-1) from FTIR analysis of blank crude oil (black) irradiated for 1h at 250 °C and treated oil with 15 wt.% D2EHPA at 250 °C for 10 minutes (red), 30 minutes (blue), and 1 h (purple)

To further validate the proposed mechanism for the demetallization reaction, the reacted D2EHPA was separated by distillation from the aqueous raffinate obtained during the washing step (Section 5.3.3.2) and subjected to FTIR spectroscopy analysis. Moreover, the raffinate phase was analyzed by NAA to determine its Ni and V concentrations, and the results are presented in Table 5.3. The discrepancies observed in the reported concentrations are suspected to be due to errors introduced during the washing process, either in the experimental procedures or during analysis. In the subsequent stage, the reacted D2EHPA was regenerated through stripping by stoichiometric sulfuric acid aqueous solutions, according to the standard procedure reported in the literature ¹¹⁰. The outcomes of the FTIR spectroscopy for reacted, regenerated, and pure D2EHPA are presented in Figure 5.7. Typically, the robust hydrogen bonds lead to the formation of D2EHPA dimers in a non-polar organic environment ⁹³. The peaks observed at 1015, 1680, and 2312 cm⁻¹ in the FTIR spectrum of both pure and regenerated D2EHPA are attributed to P-O, hydrogen bonds, and the

stretching vibration of O-H, respectively ^{116, 117}. As depicted in Figure 5.7, the FTIR spectrum of the reacted D2EHPA reveals the absence of O-H and hydrogen bond peaks, while the P-O bond shifts from 1015 to 1039 cm⁻¹ with a notable decrease in its intensity. These alterations might provide evidence for the replacement of the hydrogen atom with metals (M) in D2EHPA (O-H to O-M) through the demetallization reaction, which consequently results in the elimination of hydrogen bonds between the D2EHPA molecules.

Table 5.3 Material balance of Ni & V in oil/aqueous phases for crude oil treated with 15 wt.% D2EHPA at 250 °C for 1h

Material	Vanadium (ppm)	Nickel (ppm)
Treated oil	29.4	11.1
Aqueous raffinate	70.1	15.6
oil + raffinate	99.5	26.7
crude oil	105	30

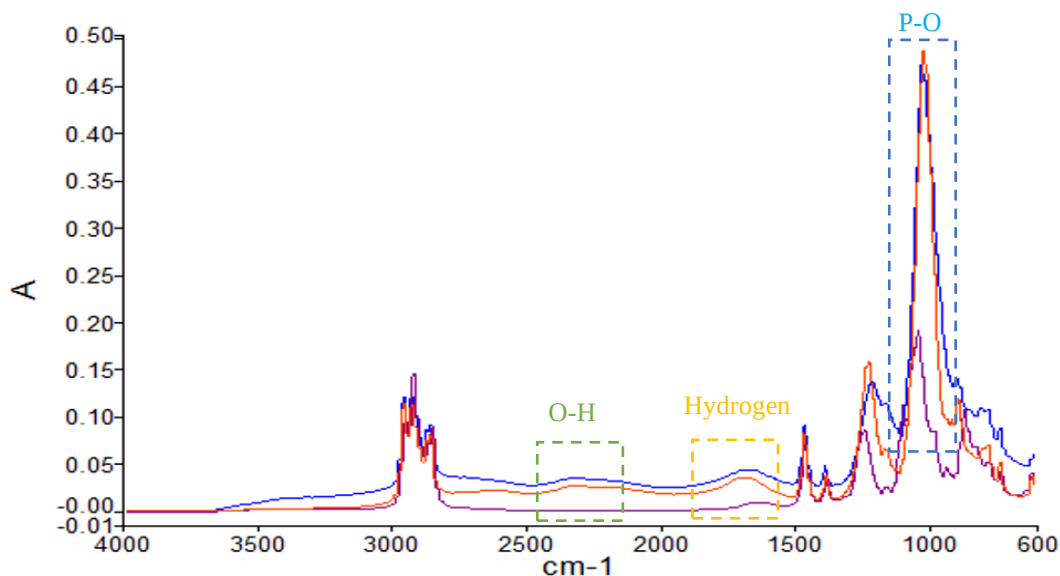


Figure 5.7 IR Absorbance (A) versus wavelength (cm-1) from the FTIR analysis of pure D2EHPA (orange), reacted D2EHPA (purple), and regenerated D2EHPA (blue)

5.4.5 Reaction kinetics

After adopting the previously optimized process parameters presented in Table 5.2, the focus shifted to investigating the kinetics of the demetallization reaction. The optimal experimental conditions were determined to be a D2EHPA:oil mass ratio of 15 wt.%, a one-hour reaction time, and a temperature of 250 °C. To determine the temperature range for investigating the reaction kinetics, the removal efficiency of metals was measured over a temperature range of 80 - 270 °C, below D2EHPA boiling temperature (295 °C) ²⁴, with an optimized D2EHPA dosage and reaction time. As shown in Figure 5.8, Thermogravimetric Analysis (TGA) of D2EHPA revealed that its decomposition initiates at temperatures around 280 °C, therefore, no experiments were conducted at temperatures above 270 °C. As depicted in Figure 5.9, no significant decrease in vanadium concentration was observed at reaction temperatures up to 220 °C. From 230 °C, an increase in the vanadium removal efficiency was observed, reaching its maximum value at 250 °C, with no further

change at higher temperatures up to 270 °C. It should be noted that metalloporphyrins possess high thermal stability, and the thermal degradation and liberation of most loaded metals typically begin above 350 °C ^{21, 118}. Even though crude oil is known to be a poor converter of microwave energy to heat, the interaction of metals and D2EHPA with electromagnetic waves makes efficient heating possible. As a result, it is expected that local heating and hot spots occur in the samples, leading to higher temperatures for the metals compared to the bulk temperature of the mixture ³. As a result, it is expected that the existing Ni and V porphyrins in the crude oil will reach much higher temperatures above 230 °C, where they will approach their degradation temperature and have sufficient thermal energy to react with D2EHPA molecules through the demetallization process.

To examine the effect of microwave heating on the demetallization effectiveness, experiments were also performed under conventional heating at optimized conditions. At 250 °C for 1 hour with 15 wt.% D2EHPA, the removal efficiencies of V and Ni were only 12% and 15%, respectively, which were significantly lower than those achieved by microwave heating at the same conditions (72% and 63%). These results indicate that local heating of metals might occurred during microwave heating, resulting in metals to be at much higher temperature than the average bulk temperature of the reaction mixture. As a result, higher removal efficiencies of the metals were obtained with microwave heating compared to conventional heating probably due to the thermal effects of the microwave heating ¹¹⁹. The variation in the demetallization efficiencies observed in this study under conventional heating, as compared to the study by Attia et al., may be attributed to the differences in the chemical composition of the crude oil samples used in the two studies. The crude oil matrix can comprise diverse metalloporphyrin compounds, which possess varying thermal stabilities, thereby affecting the efficiency of the demetallization process ¹²⁰. A

discussion on the necessary microwave power and energy considerations of the proposed demetallization method is provided in the appendix (section 5.6).

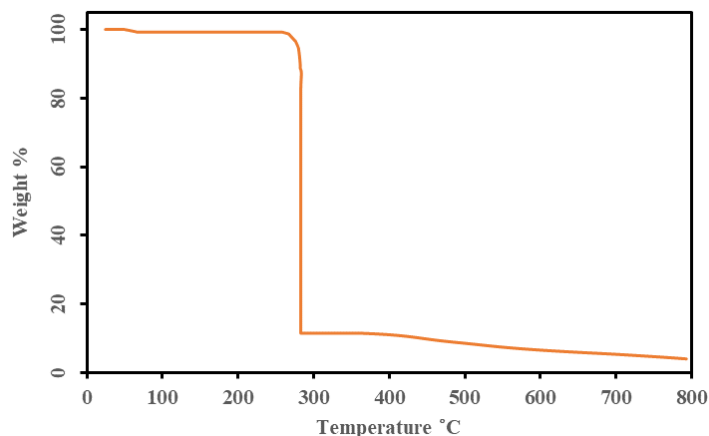


Figure 5.8 TGA analysis of pure D2EHPA

The kinetics of the reaction were studied in a temperature range of 230-250 °C. In order to determine the overall reaction order for removing Ni and V, several experiments were conducted with a constant 15 wt.% D2EHPA dosage at 230, 240, and 250 °C, with varying reaction times. According to the demetallization reaction expressed in Equation 5.3, the corresponding kinetic rate expression of this model was proposed as the following:

$$-r_m = k_m [m]^a [D2EHPA]^b \quad (5.4)$$

Where m and k_m correspond to metals and the reaction rate constant, respectively. Theoretical stoichiometric calculations were conducted to determine the required D2EHPA:oil ratio based on the proposed mechanism of the demetallization reaction by Attia et al., assuming a 1:4 molar ratio of porphyrins to D2EHPA molecules ²⁴. The findings suggested that a D2EHPA:oil ratio below 1 wt.% would suffice, given the low concentration of metals in the Iranian crude oil

(approximately 135 ppm). Due to the trace amounts of Ni and V present in the crude oil, as well as its high viscosity, the likelihood of contact between the metals and D2EHPA is quite low. However, as depicted in Figs. 3 and 4, increasing the D2EHPA dosage can improve the probability of contact between the reactants, thereby enhancing the removal efficiency¹⁵. Since a D2EHPA:oil ratio of 15 wt.% was used in the experiments, it can be assumed that the concentration of D2EHPA in the mixture remained constant during the demetallization reaction. Thus, [D2EHPA] in Equation 5.4 would be constant, and the equation can be re-expressed as:

$$-r_m = k_m [m]^a \cdot C = k'_m [m]^a \quad (5.5)$$

Where k'_m is the reaction rate at a constant D2EHPA concentration. The experimental data was analyzed by fitting it to Equation 5.5 using the Scipy.optimize module in Python to determine the best fitting reaction order based on the coefficient of determination, R^2 . Table 5.4 presents the R^2 values obtained for the experimental data fitted to zero, first, and second order reaction kinetics for Ni and V removal reactions. The data indicates that the first order reaction model has the highest R^2 values for both Ni and V removal reactions, indicating that the first order kinetic is the most suitable fitting reaction model. According to Equation 5.1, $X_{m,t}$, conversion of the corresponding metal m at the time t was calculated. The plot in Figure 5.10 illustrates $\ln(1-X_{m,t})$ versus reaction time, t, for Ni and V. The least square method was applied, and it was found that the y-intercept of the straight lines was nearly insignificant, which suggests first-order kinetics:

$$-\ln(1 - X_{m,t}) = k'_m t \quad (5.6)$$

Next, the slopes of the straight lines were calculated to determine the overall rate constant of the demetallization reaction at each reaction temperature. These reaction rate coefficients were then utilized to generate an Arrhenius plot, as shown in Figure 5.11, to determine the kinetic

parameters of the metal removal reaction. The activation energies for the reactions were 34,700 and 29,800 J/mol, respectively, and the pre-exponential factors were 66.2 and 16.5 min⁻¹, respectively. The temperature-dependent rate constants for the temperature range of 230-250 °C were expressed in the following equations:

$$k'_V(T) = 66.2 e^{-\frac{34700}{RT}} \quad (5.7)$$

$$k'_{Ni}(T) = 16.5 e^{-\frac{29800}{RT}} \quad (5.8)$$

Table 5.4 Determination coefficients for zero, first, and second order reaction kinetics

Metal/reaction order	R ²		
	Zero	1 st	2 nd
V	0.8577	0.989	0.908
Ni	0.8588	0.993	0.916

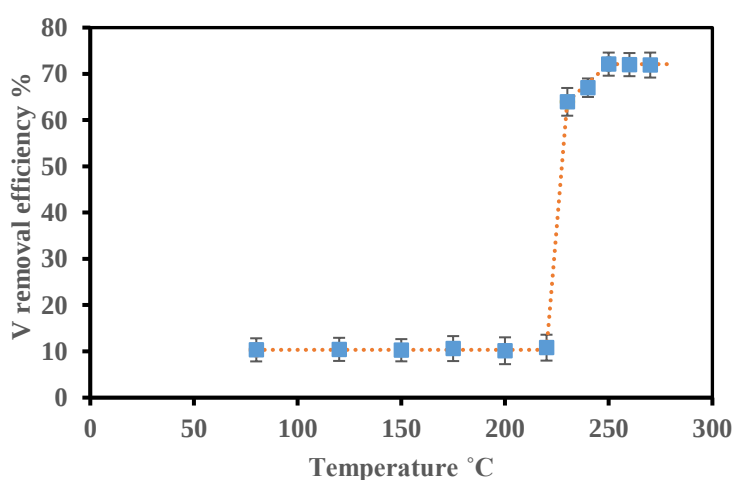
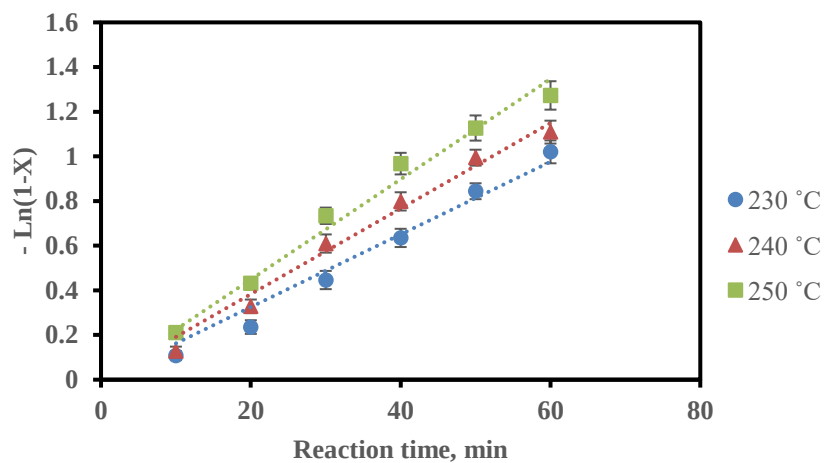
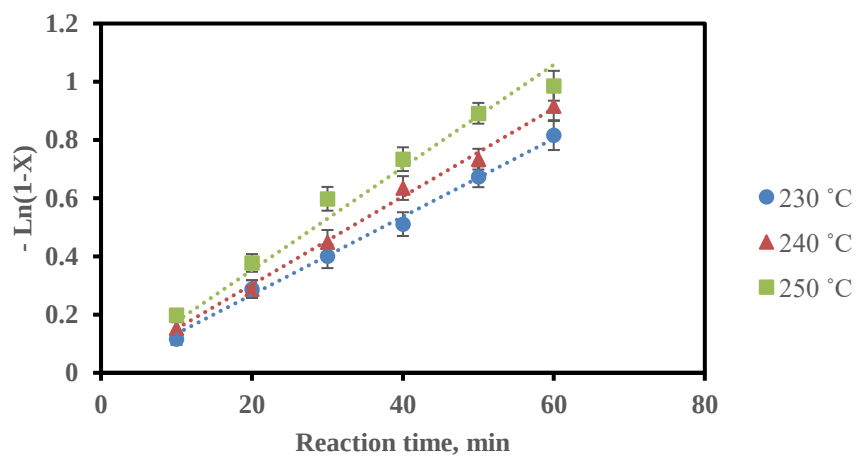


Figure 5.9 Impact of reaction temperature on V removal efficiency for crude oil treated with 15 wt.% D2EHPA for 1h



(a)



(b)

Figure 5.10 $-\ln(1-X)$ versus reaction time of (a) V and (b) Ni removal for crude oil treated with 15 wt.% D2EHPA

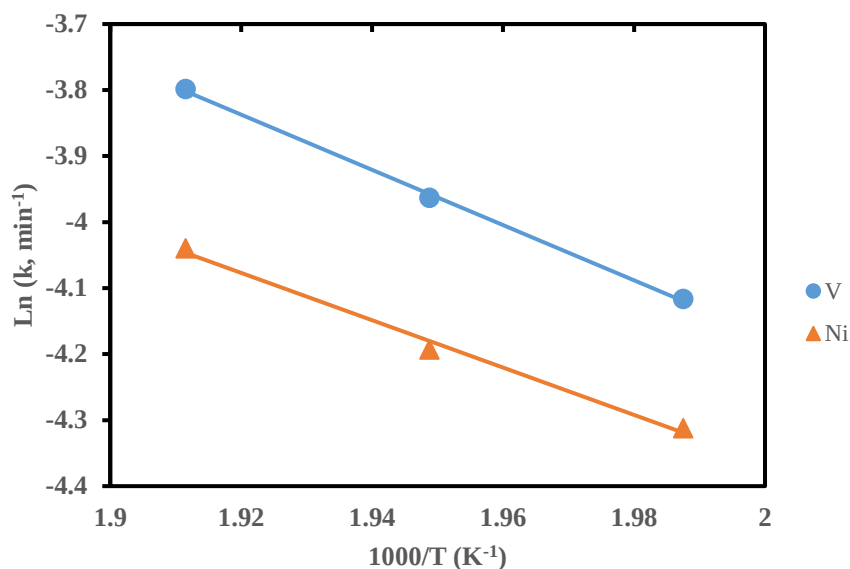
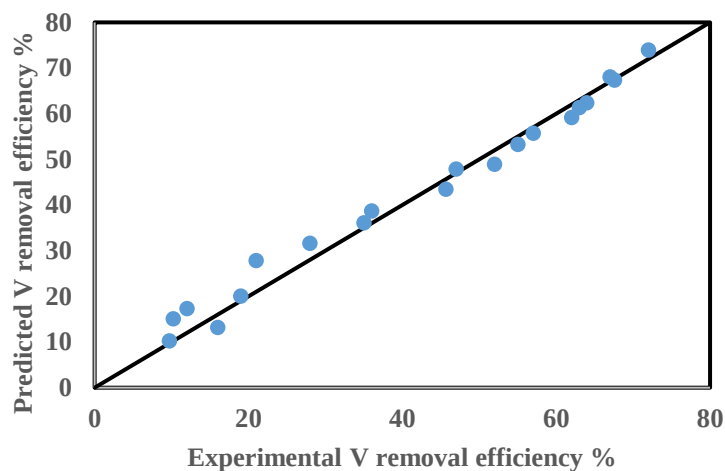


Figure 5.11 Arrhenius plot of V and Ni removal for reactions at 230, 240, and 250 °C

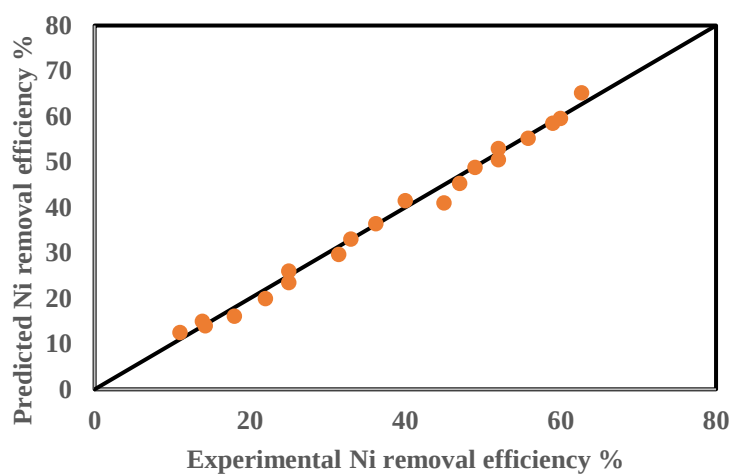
Table 5.5 presents the kinetic parameters obtained from the experimental data, including the rate coefficients and the Arrhenius parameters. To verify the accuracy of the proposed model, the experimental data of Ni and V removal efficiencies, which were not used for parameter adjustment, were compared to the corresponding predicted values calculated from the developed kinetic model using MATLAB. Figure 5.12 illustrates the comparison between the experimental and predicted data for V and Ni removal efficiencies obtained at different experimental conditions such as reaction temperature, time, and D2EHPA dosage. The determination coefficients, R^2 , were determined as 0.996 and 0.998 for V and Ni, respectively, indicating that the proposed kinetic model can effectively predict various experimental data.

Table 5.5 Kinetic and Arrhenius parameters for Ni and V removal reactions

Rate coefficients				
Temperature	Vanadium		Nickel	
	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
230	0.0163	0.993	0.0134	0.995
240	0.0192	0.996	0.0151	0.994
250	0.0224	0.997	0.0176	0.996
Arrhenius parameters				
	E _a , kJ/mol	A ₀ , min ⁻¹	R ²	
Vanadium	34.7	66.2	0.997	
Nickel	29.8	16.5	0.993	



(a)



(b)

Figure 5.12 Comparison of experimental and predicted data for (a) V and (b) Ni removal efficiency

The kinetic parameters estimated for the demetallization reactions indicate that the activation energy for Ni is lower than that for V. As illustrated in Figure 5.5, Ni and V atoms are bonded to the nitrogen atoms located in the center of their porphyrin rings. Since the Pauling

electronegativity of V (1.63) is lower than that of Ni (1.91), the corresponding V-N bonds are stronger than the Ni-N bonds due to the higher electronegativity difference between N (3.04) and the attached metal ¹²¹. Thus, liberating V from its porphyrin requires a higher thermal energy, which explains the higher activation energy estimated for V and its higher thermal stability relative to Ni porphyrins that have been reported elsewhere ^{21, 118}.

Although the Ni removal reaction was found to have a lower activation energy in the Arrhenius equation, its estimated pre-exponential factor was significantly lower than that of V. The pre-exponential factor in the Arrhenius equation represents the frequency of collisions between reactant molecules and the probability that these collisions result in reactions. It is well known that at higher concentrations of reactants, the probability of collisions between them increases, resulting in higher values of the pre-exponential factor and a faster reaction ¹²². Considering the lower concentration of Ni (approximately 30 ppm) in the Iranian crude oil used in this study compared to V (approximately 105 ppm), a lower pre-exponential factor for Ni in the Arrhenius equation than V is expected. This finding agrees with the estimated kinetic parameters reported in Table 5.5, which suggest that the V removal reaction occurs slightly faster than Ni despite its higher activation energy due to its much higher pre-exponential factor.

According to Figure 5.2, the V removal efficiency did not increase beyond 60 minutes, even with a D2EHPA dosage higher than stoichiometric (5 wt.%). Although the first-order kinetics model developed for the demetallization reaction predicts complete metal conversion, experimental data suggest a mass transfer limitation that prevents further metal conversion. Crude oil is a complex mixture that contains various fractions, including paraffins, aromatics, naphthalenes, and organometallics. The Nickel and Vanadium metalloporphyrins are concentrated in the asphaltene fraction, which has the highest density and viscosity ⁴⁷. During the demetallization reaction, the

primary mass transfer limitation is the diffusion of D2EHPA molecules to the metal-containing porphyrins, which have a low concentration (≈ 135 ppm). The diffusion coefficient of species into a medium decreases as the viscosity of the medium increases, suggesting a low diffusion coefficient of D2EHPA molecules into the viscous organometallic fraction of crude oil ¹²³. As the demetallization reaction progresses, the reduced concentration of unreacted metals in the crude oil will further lower the frequency of collisions between metals and D2EHPA molecules, leading to a plateau in Ni and V removal efficiencies.

The kinetic model developed in this study provides valuable insights for the process design of D2EHPA-assisted microwave demetallization of crude oil. The cost of the reagent plays a significant role in the total operating cost of the process, as emphasized in previous studies ¹¹⁰, and the stoichiometric calculations suggest that less D2EHPA is needed for effective crude oil demetallization. Therefore, future studies should investigate the use of advanced mixing methods, such as ultrasonication, to achieve effective demetallization with a reduced dosage of D2EHPA. It is also necessary to examine the impact of mass transfer on the kinetics of the demetallization reaction by developing a synthetic model fuel with a simpler chemical composition to optimize the reaction time. These investigations are crucial for process scale-up as they can significantly affect the design and economics of the process, with reactor sizing and reagent purchase costs having a substantial impact on estimated capital and operating costs.

5.5 Conclusion

The impact of primary process parameters on crude oil demetallization using bis(2-ethylhexyl) phosphoric acid (D2EHPA) under microwave heating was investigated. The optimum experiment conditions were 1h irradiation time, 250 °C, and a D2EHPA:oil mass ratio of 15 wt.%. Under the optimized conditions, maximum removal efficiencies were 72 % and 63 % for V and Ni,

respectively. The kinetics of the Ni and V removal reactions were investigated at the optimized D2EHPA:oil mixing ratio of 15 wt.%, and the kinetic parameters were estimated with the experiments at 230, 240, and 250 °C. A first-order kinetic model was consistent with the experimental Ni and V removal efficiency data based on the observed coefficient of determination. During the reaction between metalloporphyrins in crude oil and D2EHPA, Ni and V were replaced by protons given by D2EHPA and transformed into metal salts that are soluble in water. The formation of N-H bonds in the treated oil was confirmed by the results of the FTIR analysis, which is indicative of the occurrence of the demetallization reaction. By adopting the linear fitting for a first-order kinetic model to determine the Arrhenius parameters, the activation energies were 34.7 and 29.8 kJ/mol, and the pre-exponential constants were 66.2 and 16.5 min⁻¹ for V and Ni, respectively.

5.6 Appendix Energy requirements

The microwave power to heat the oil and D2EHPA mixture to various reaction temperatures is given in Table 5.6. The data for holding the mixture at the reaction temperature for the desired reaction time is also provided. The data in Table 5.6 show that the metal removal from crude oil with D2EHPA could be performed efficiently at low microwave powers. The high interaction of D2EHPA with microwaves resulted in requiring much lower powers compared to other similar techniques for microwave-assisted demetallization of crude oil reported elsewhere ^{14, 15, 109}.

Table 5.6 Irradiated microwave power

Temperature (°C)	Heating step			Holding Step		
	time (s)	P_{avg} (W)	P_{max} (W)	time (min)	P_{avg} (W)	P_{max} (W)
230	177	138	393	60	42	80
240	192	147	380	60	53	87
250	207	151	379	60	46	87

CHAPTER 6 ARTICLE 3 : MICROWAVE-ASSISTED SULFUR REMOVAL FROM CRUDE PETROLEUM OIL AND LIQUID FUELS BY BIS(2-ETHYLHEXYL) PHOSPHORIC ACID

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6.1 Abstract

As environmental concerns grow, there has been a surge in the development of alternative approaches to desulfurize petroleum crude oil and liquid fuels. This study focused on removing refractory thiophene compounds from crude petroleum oil and model fuels by employing bis(2-ethylhexyl) phosphoric acid (D2EHPA) and NaCl aqueous solutions under microwave heating. The impact of key process variables, including temperature, irradiation time, and D2EHPA dosage, on sulfur removal was examined. The desulfurization mechanism was explored by investigating the microwave-assisted ionic liquid formation reaction between D2EHPA and NaCl molecules through FTIR spectroscopy and electrical conductivity measurements. The results showed up to 36% and 64% sulfur removal from Iranian crude oil and thiophene-based liquid model fuels, respectively, after 20 minutes of microwave heating at 65 °C. This study presents significant insights into the innovative microwave-assisted synthesis of ionic liquids for extractive desulfurizing crude oil and liquid fuels.

6.2 Introduction

The presence of sulfur in crude oils and fossil fuels, like gasoline, diesel, and kerosene, presents a significant challenge for oil refineries. Crude oil contains various forms of sulfur, such as aliphatic (mercaptans, sulfides, and disulfides) and aromatic (thiophenes, benzothiophenes, and dibenzothiophenes) organosulfur compounds with a sulfur content ranging from 0.1 wt. % to 15 wt.%, depending on the oil source^{23, 124, 125}. The presence of sulfur in crude oil leads to increased corrosion during refining processes and hastens catalyst deactivation. When these sulfur compounds are combusted along with the final fuel products, they release SO_x compounds that can poison catalytic converters, cause respiratory issues, and contribute to acid rain^{44, 126}. As a result, regulatory agencies are implementing more and more rigorous standards for the maximum allowable level of sulfur in transportation fuels⁸. Hence, there is a significant research endeavor to explore alternative methods for the desulfurization of crude oils and liquid fuels.

Despite the development of numerous techniques for sulfur removal from crude oil and fuels, only a limited number have been implemented in industry due to various drawbacks and limitations. Currently, hydrogenation desulfurization (HDS) is the primary industrial process for converting organic sulfur in crude oil to hydrogen sulfide and corresponding hydrocarbons by employing metal catalysts^{44, 127}. However, the HDS method has several drawbacks, such as extremely high operating temperatures and pressures, high hydrogen and energy consumption, use of expensive catalysts, and reduction in the octane rating of gasoline^{6, 128}. Furthermore, it is even more challenging and costly to eliminate refractory sulfur compounds, such as thiophene (TS), benzothiophene (BT), dibenzothiophene (DBT), and their derivatives, through HDS due to their high stability and steric hindrance^{7, 30}. Therefore, developing alternative techniques, such as

adsorptive desulfurization (ADS)⁴⁴, extractive desulfurization (EDS)^{8,30}, microwave or ultrasound assisted desulfurization^{110,129}, and biodesulfurization (BDS)^{8,57}, have become a significant issue.

Recently, there has been a growing interest in the use of ionic liquids (ILs) as solvents for extractive desulfurization of crude oils and fuels. ILs are a type of salt that typically melts at or below 100 °C. They are typically composed of an organic cation and an organic or inorganic anion⁸. Ionic liquids are considered a potential substitute for conventional solvents in EDS owing to their numerous benefits, including but not limited to, low volatility, non-flammability, chemical and thermal stability, recyclability, and more¹³⁰. However, the application of ILs for fuel desulfurization on a large-scale is restricted due to several disadvantages, including high viscosity, complex and prolonged synthesis, and energy-intensive recycling^{131, 132}. Additionally, their effectiveness for sulfur removal from real fuels and crude oils has not been adequately investigated in the available literature.

The application of microwave heating in organic synthesis is gaining popularity due to its ability to significantly reduce synthesis time, improve yields, and minimize side reactions in comparison to traditional methods¹³³. Unique microwave heating characteristics, such as selective, volumetric, fast, and controlled heating, make it a viable alternative for unconventional heating in various fields, including chemical and petrochemical industries^{3, 10, 110, 114, 134}. The conversion of electromagnetic energy to heat energy in microwave-assisted processes is achieved through the agitation of polar molecules in the subjected material when exposed to an alternating electric field. Combining solvent-free organic synthesis with microwave heating can offer many advantages, including increased safety, improved reactivity and selectivity, cost savings, and energy and pollution reduction. Furthermore, nonthermal microwave effects can be achieved under microwave

heating, leading to significant enhancements in synthesis yield and time over conventional heating methods¹³⁵.

A novel method for the simultaneous demetallization and desulfurization of crude oil was developed by Attia et al. in 2020, using bis(2-ethylhexyl) phosphoric acid (D2EHPA)²⁴. The application of D2EHPA in the synthesis of ILs is reported in several studies^{136, 137}. Attia et al. suggested that D2EHPA can form an ionic liquid with the available salts in crude oil at continuous stirring under conventional heating. This leads to thiophene compound removal from crude oil through electrostatic forces and hydrogen bonding between the sulfur compounds and the formed ionic liquid. The maximum sulfur removal efficiency of 53% was reported for crude oil samples treated by conventional heating at 250 °C for 1 hour. However, further investigation is required to fully explore the synthesis and characteristics of a D2EHPA-based ionic liquid and its application in extractive desulfurization of crude oils. Additionally, the long reaction time and high reaction temperature associated with this method have certain disadvantages. For instance, the high reaction temperature could result in the undesired dissociation of the formed ionic liquid and the evaporation of light organosulfur compounds. Therefore, a systematic investigation is necessary to explore the effectiveness of the suggested process for removing refractory sulfur compounds from synthetic model fuels, which have simpler chemical matrices. The characteristics of microwave heating in enabling fast organic synthesis, and the selective heating of polar compounds, such as D2EHPA and NaCl solutions, created significant interest in exploring sulfur removal from model fuels and crude oils using microwave heating.

This paper focuses on the elimination of refractory sulfur compounds from synthetic liquid fuels and crude oils with D2EHPA and NaCl aqueous solutions under microwave heating. The effect of temperature, residence time, and D2EHPA dosage on S-removal efficiency was

investigated under microwave heating. The desulfurization mechanism was studied by investigating the ionic liquid formation between D2EHPA and NaCl molecules under microwave irradiation. The characteristics of the synthesized ionic liquid were studied by FTIR spectroscopy and electrical conductivity analysis. The current study positively provides valuable insight into the rapid microwave-assisted synthesis of water-soluble phosphonium-based ILs and their application in the simultaneous extractive desulfurization of liquid fuels and crude oils.

6.3 Materials and methods

6.3.1 Materials

Sodium chloride powders (NaCl), sodium hydroxide pellets (NaOH), bis(2-ethylhexyl) phosphoric acid (D2EHPA), and thiophene (TS) were purchased from Sigma-Aldrich (Ontario, Canada). Kerosene was purchased from Fisher Scientific (Ontario, Canada). TOTAL S.A. refineries in France provided Iranian and Basra crude oils used in this study.

6.3.2 Synthesis of model fuels

The model fuels used in this study contained 21000 ppm of S, which were prepared by dissolving calculated amounts of TS in 50 grams of kerosene. Table 1 presents the properties of the Iranian and Basra crude oils used in the experiments.

Table 6.1 Properties of Iranian and Basra crude oils

Oil	Density (kg/m ³)	Viscosity	Carbon residue	S-content	
	(15 °C)	(cP) (10 °C)	(Wt.%)	APA	(ppm)
Iran	881.2	18.4	6.8	28.9	24912
Basra	886.8	23.8	7.8	27.9	26350

6.3.3 Experimental setup

The Anton Paar Monowave 400 synthesis microwave reactor was utilized for conducting the experiments. This reactor can generate a maximum microwave power of 850 W and can operate at up to 30 bar and 300 °C. The reaction mixtures were placed into borosilicate glass vials of 30 ml capacity, fitted with a magnetic propeller for stirring, and covered with caps made of polyether-ether-ketone (PEEK). These vials were placed inside the microwave reactor, where the samples were heated to the desired temperature while being continuously stirred and held for a specific duration. The instrument automatically measured and controlled the temperature of the reaction vials using an IR temperature sensor and a fiber-optic ruby thermometer immersed in the reaction mixture. The closed system configuration of the reactor ensured preventing any evaporation of the samples.

6.3.4 Experimental procedure

The experiments involved three primary steps: first, ionic liquid (IL) formation through the reaction between D2EHPA and NaCl under microwave heating and the subsequent interaction between the IL and the S-compounds; second, washing the irradiated mixture to transfer the S-bonded IL and the unreacted D2EHPA to the washing solution; and finally, separating the resulting aqueous phase and treated fuel. Further information on these steps is provided in the following subsections.

6.3.4.1 MW-assisted IL synthesis and extractive desulfurization

The preparation of samples involved mixing 15 ml of model fuel with calculated weight percentages of D2EHPA using magnetic stirring for 30 minutes. No emulsification was required in this step due to the miscibility of D2EHPA in organic compounds, such as kerosene. Aqueous solutions were prepared by dissolving an excess amount of NaCl in 7.5 ml of deionized water. The

organic and aqueous mixtures were then combined in a 30 ml borosilicate vial and vigorously shaken for a few minutes to form a water in oil emulsion before being placed in the microwave reactor. The mixture was rapidly heated to the desired temperature and held there for a specific amount of time, with continuous stirring at 1000 rpm to achieve a homogenous thermal distribution within the mixture.

6.3.4.2 Washing and separation

The organic phase was separated after the completion of microwave irradiation and settling in a separatory funnel. To extract the S-bonded ionic liquid and unreacted D2EHPA from the separated organic phase, a 50 wt.% NaOH aqueous solution was used for washing. This step is essential to remove unreacted D2EHPA from the treated oil by facilitating a saponification reaction between D2EHPA and NaOH, which increases the solubility of D2EHPA in water. To achieve this, the extracted organic phase and added washing solution were heated conventionally to 50 °C in a 50 ml flat bottom quartz flask and continuously stirred at 800 rpm using a magnetic hot plate stirrer for 20 minutes. To prevent the evaporation of light compounds, a water-cooled condenser was fitted at the top and operated at -5 °C and ambient pressure. Afterward, the mixture was centrifuged at 4000 rpm for 10 minutes to separate the treated model fuel and the aqueous phase containing S-containing IL and unreacted D2EHPA. To ensure complete removal of the target organics from the treated fuel, the washing process was repeated thrice using fresh washing solutions. Samples were taken from the aqueous raffinate and the final treated model fuels for analysis to determine the concentrations of S.

6.3.5 Characterization methods

Neutron Activation Analysis (NAA) was conducted at the Slowpoke analytical lab at Polytechnique Montreal (Quebec, Canada) to measure the sulfur content of the model fuels before

and after treatment. NAA involves subjecting the samples to thermal neutrons in a nuclear reactor, and then quantifying the corresponding elements based on the gamma-ray spectrum produced by the excited isotopes. Fourier-transform infrared spectroscopy (FTIR) analysis was conducted on the synthesized ionic liquid using a Spectrum 65 FTIR instrument from PerkinElmer. The FTIR spectrum was recorded by taking 32 scans between 4000-600 cm^{-1} with 4 cm^{-1} resolution. The obtained results were analyzed to identify the chemical bonds and functional groups present in the synthesized ionic liquid. The electrical conductivity of the samples was determined at room temperature using a ZetaProbe Analyzer from Colloidal Dynamics.

6.3.6 Temperature measurement

An IR temperature sensor integrated within the microwave cavity was adopted to automatically control and measure the bulk temperature of the samples with a precision of 0.1 °C. Precise temperature measurement is crucial in microwave-assisted processes, but it can be challenging due to the presence of electromagnetic waves. Therefore, appropriate measuring devices are necessary. Two main categories of microwave temperature measurement methods include contact techniques, such as thermocouples and thermal indicators, and non-contact techniques, such as optical and pyrometry methods. Shielded thermocouples can measure temperatures up to 2000 °C without being adversely affected by direct exposure to the electromagnetic field within a microwave cavity. Meanwhile, fiber optic sensors are utilized in microwave systems to measure temperature by analyzing changes in fluorescence characteristics to minimize the risk of electromagnetic interference, but they are limited to temperatures below 300 °C. Pyrometry is the most commonly used non-contact technique for measuring temperature in the presence of electromagnetic radiation, which involves measuring the surface temperature of a heated object by detecting thermal radiation

in the near-infrared wavelength range. A comparison of temperature measurement techniques for microwave systems is provided in ¹¹³⁻¹¹⁵.

6.4 Results and discussion

6.4.1 Ionic liquid synthesis and characterization

The formation of an ionic liquid between D2EHPA and NaCl molecules was systematically investigated. Specifically, 5 g (0.015 mol) of D2EHPA was dissolved in 10 g of kerosene, and an aqueous solution containing 1200 mg of NaCl (0.03 mol) in 7 g of distilled water was added to the mixture. The resulting mixture was shaken vigorously for a few minutes, then poured into a 30 ml vial and placed in a microwave reactor. The mixture was heated rapidly to 65 °C and held at that temperature for 30 minutes with continuous stirring at 1000 rpm. After the irradiation was completed, the mixture was centrifuged at 4000 rpm for 10 minutes to separate the organic and aqueous phases. The organic phase was then washed three times with 50 wt.% distilled water, and the obtained raffinate water was added to the separated aqueous phase from the previous step. The resulting water-soluble ionic liquid was separated from the aqueous mixture by distillation, dried at 120 °C for 2 hours, and subjected to FTIR spectroscopy and electrical conductivity analyses.

Figure 6.1 presents the results of the FTIR spectroscopy analysis for the synthesized ionic liquid and pure D2EHPA. Normally, strong hydrogen bonds lead to the creation of D2EHPA dimers in a non-polar organic environment ⁹³. The peaks identified at 1018, 1224, 1686, and 2322 cm^{-1} in the FTIR spectrum of pure D2EHPA are linked to the stretching vibration of P-O, P=O, hydrogen bonds, and O-H, respectively ^{116, 117}. From Figure 6.1, it can be observed that all peaks except the one at 1224 cm^{-1} , which corresponds to P=O bonds, are also present in the FTIR spectrum of the resulting ionic liquid, indicating the preservation of the D2EHPA structure. However, the absence of the peak at 1224 cm^{-1} in the FTIR spectrum of the ionic liquid suggests

that P=O bonds are no longer present after the formation of the ionic liquid. Furthermore, two new peaks were detected at 1085 and 870 cm^{-1} , which correspond to stretching Na-O bonds in the ionic liquid ¹³⁸. Therefore, the results of the FTIR spectroscopy confirm the successful formation of the ionic liquid in accordance with the proposed reaction scheme, illustrated in Figure 6.2. The extractive desulfurization of aromatic organosulfur compounds with ionic liquids is based on a π - π interaction and CH- π interaction between the ionic liquid and S-containing molecules. It has also been suggested that the extraction of S-compounds are driven by hydrogen bonding between the IL cation and the S-compounds through the acidic proton ^{139, 140}. The suggested desulfurization mechanism is depicted in Figure 6.3. A strong interaction between thiophene derivatives and ionic liquids has been reported in the literature ¹⁴¹⁻¹⁴³.

The electrical conductivity of D2EHPA and the ionic liquid was also studied. D2EHPA is an organic compound that is not expected to significantly conduct electricity in its pure form. This is because it does not contain any charged species, such as ions or electrons, that are responsible for electrical conductivity. The electrical conductivity of D2EHPA was measured as 7 $\mu\text{S}/\text{cm}$ at 25 $^{\circ}\text{C}$, while the electrical conductivity of the synthesized IL was found to be 75 $\mu\text{S}/\text{cm}$ at room temperature showing a significant increase compared to that of pure D2EHPA. This shows the successful formation of IL between D2EHPA and NaCl molecules through the proposed microwave-assisted process.

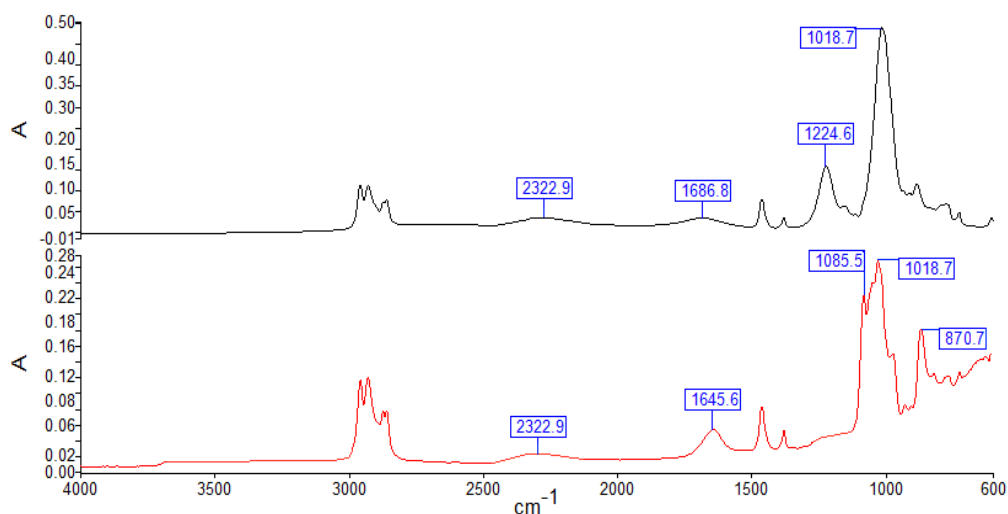


Figure 6.1 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of the synthesized IL (red) and pure D2EHPA (black)

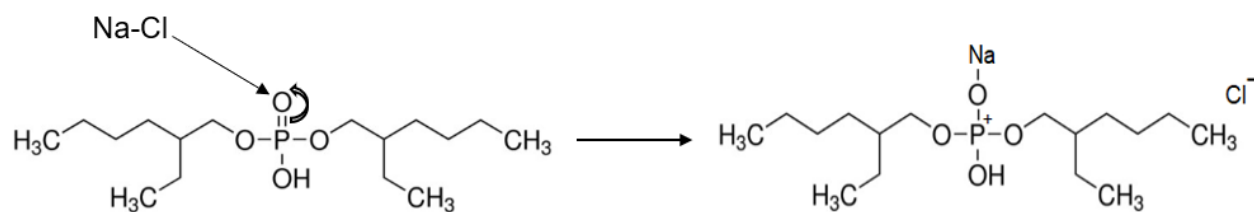


Figure 6.2 Ionic liquid formation reaction scheme

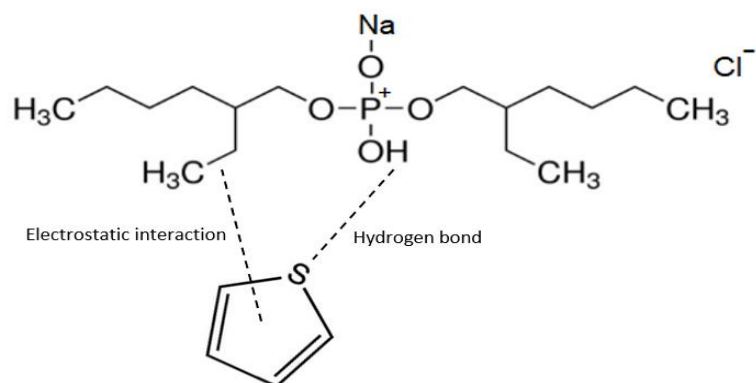


Figure 6.3 Suggested mechanism for the extractive desulfurization of thiophene by the synthesized ionic liquid

6.4.2 Effect of temperature

The impact of temperature on the sulfur removal efficiency from TS-containing model fuels was investigated over a temperature range of 25-80 °C below the thiophene boiling point (84 °C). All samples were heated by microwaves for 20 minutes at a D2EHPA:fuel mass ratio of 15 wt.%. Figure 6.4 illustrates that the S-removal efficiency increased as the temperature rose from 25 °C to 65 °C. In Section 6.4.1, it was explained that under microwave irradiation, D2EHPA can form a water-soluble ionic liquid with sodium chloride salts, through the reaction scheme depicted in Figure 6.2^{24, 144}. The process involves the formation of a two-phase (water in oil) emulsion by mixing a NaCl aqueous solution (dispersed phase) with the D2EHPA-containing model fuel as the continuous phase. For the ionic liquid synthesis reaction to occur, NaCl molecules need to diffuse into the organic phase and react with D2EHPA. To assess the impact of temperature on mass transfer during the formation of the ionic liquid, the concentration of Na and Cl elements in the final organic phase were measured for samples treated at different temperatures in the range of 35-65 °C. Accordingly, a mixture of a NaCl aqueous solution and the model fuel was prepared and subjected to microwave heating at various temperatures while continuously stirred at 1000 rpm. The concentrations of Na and Cl in the separated organic phase showed no significant changes. This led to the conclusion that in the investigated temperature range, mass transfer has a negligible effect on the ionic liquid formation reaction and the subsequent desulfurization mechanism, and the primary limiting step was identified as the reaction activation energy. As a result, the observed increase in S-removal efficiencies at temperatures up to 65 °C can be attributed to a higher conversion in the ionic liquid formation reaction with increasing temperature, producing more ionic liquid to further remove thiophenes from the fuel through the mechanism shown in Figure 6.3. Given the water solubility of the S-loaded IL, these compounds are separated from the treated fuel

in the washing step²⁴. As the temperature further rises, the stability of ILs tends to diminish, which may impact their ability to effectively bond with target S-compounds in EDS applications, particularly at higher temperatures¹⁴³. As a result, the rate of S-removal ceased to increase and even showed a decline at 75 °C and 80 °C indicating a potential further decrease at higher temperatures. The subsequent experiments were conducted at 65 °C as the optimum temperature for microwave-assisted TS removal from liquid model fuels.

The synthesis of ionic liquids using conventional heating methods often involves the need to maintain the reaction mixture at the desired temperature for long periods of time¹⁴⁵. It is important to note that polar compounds, like D2EHPA and NaCl, exhibit a significantly higher interaction with microwaves compared to crude oil or model fuels. This selective heating effect can result in these compounds reaching higher temperatures than the bulk of the mixture, enabling the synthesis of the ionic liquid at lower temperatures compared to conventional heating. Additionally, the formation of the ionic liquid during the process enhances the interaction between the reaction mixture and microwaves by increasing the polarity of the mixture. This leads to a reduced energy requirement for maintaining the mixture temperature at the desired reaction temperature under microwave heating. Hence, the adoption of the microwave heating technology effectively reduced both the time and energy requirements of the desulfurization process compared to that of conventional heating²⁴.

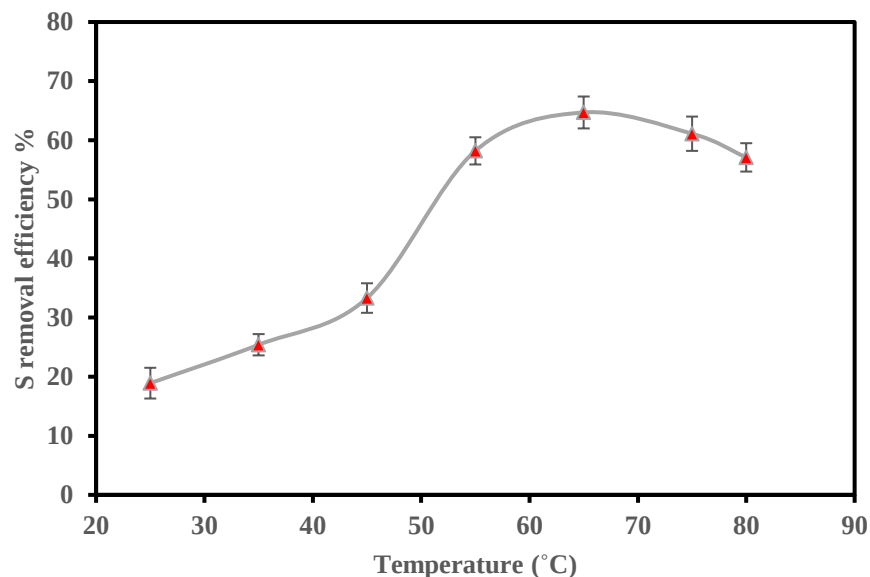


Figure 6.4 The impact of reaction temperature on sulfur removal efficiency from model fuels irradiated for 20 minutes with 15 wt.% D2EHPA

6.4.3 Effect of reaction time

To investigate the impact of reaction time on S-removal efficiency, experiments were carried out under microwave irradiation at 65 °C for 5, 10, 15, 20, and 30 minutes with a 15 wt.% D2EHPA:fuel mass ratio. The findings, shown in Figure 6.5, demonstrate that the concentration of S in the model fuel decreases as extraction time increases. At 5, 10, 15, and 20 minutes, the S removal efficiencies were 32.1%, 51.2%, 58.8%, and 64.7%, respectively. At 30 minutes, there was no longer any decrease in S-removal since equilibrium was already established. The ionic liquid formation is in its early stages during the initial phase of the reaction, resulting in a poor desulfurization efficiency at 5 minutes. After 10 minutes, however, there is a noticeable increase in S-removal efficiency, which is likely caused by the successful synthesis of the ionic liquid and its subsequent interaction with TS molecules in the model fuel. The desulfurization rate decreased as the reaction progressed beyond 10 minutes, and the S-removal efficiency no longer rose

noticeably due to the possible saturation of the synthesized IL with the high quantities of TS in the model fuel (21000 ppm). Thus, it was concluded that 20 minutes was sufficient for efficient sulfur removal.

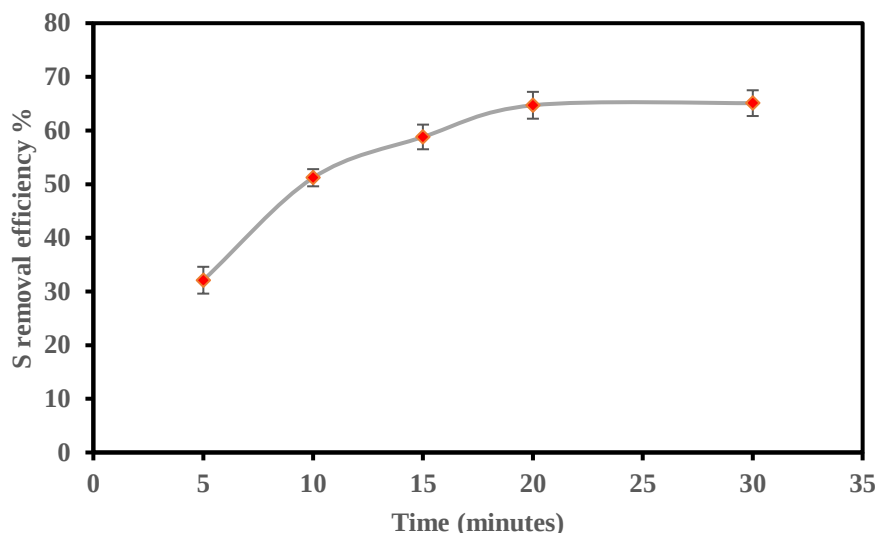


Figure 6.5 The impact of reaction time on sulfur removal efficiency from model fuels irradiated at 65 °C minutes with 15 wt.% D2EHPA

6.4.4 Effect of D2EHPA dosage

In order to investigate the effects of D2EHPA dosage on S-removal from model fuels, experiments were carried out at various D2EHPA:fuel mass ratios of 2, 5, 10, 15, and 30 wt.%. Samples were heated by microwaves up to 65 °C and held for 20 minutes to accomplish the reaction. As shown in Figure 6.6, when the D2EHPA:fuel mass ratio increases from 2 to 15 wt.%, the S-removal efficiencies rise from 15.3% to 64.7%. Given the constant NaCl/D2EHPA molar ratio provided for each experiment, it is anticipated that more ionic liquid will form throughout the reaction as the D2EHPA dose rises. As a result, the ultimate IL:fuel mass ratio would be greater, improving the desulfurization efficiency from the model fuel. However, further increasing the

D2EHPA dosage to 30 wt.% did not lead to greater S-removal efficiencies. The observed plateau in the desulfurization efficiency can be attributed to the diffusion limitation of NaCl molecules from the aqueous phase to the organic phase during the reaction. This diffusion limitation restricts the final concentration of NaCl in the organic phase to its equilibrium value, thereby limiting the extent of the ionic liquid formation reaction, even if there are sufficient D2EHPA molecules present in the organic phase. As a result, increasing the D2EHPA/fuel mass ratio will not lead to further improvements in desulfurization efficiency.

In addition, blank model fuel samples were treated by microwave heating at 65 °C for 20 minutes and washed three times with water to make sure the observed S-extraction was not the outcome of the heating or washing steps. Further blank experiments were also conducted under the same operating conditions by 15 wt.% of D2EHPA without adding NaCl solutions to the reaction mixture. There were no noticeable changes in the S concentration of the blank model fuel samples indicating that the observed results are only attributable to the interaction of synthesized D2EHPA/NaCl ionic liquid with S-compounds. To explore the efficient transfer of S-compounds from the fuel samples to the aqueous raffinate during the washing process, experiments were conducted under optimized conditions. The fuel and raffinate water samples were subsequently analyzed to determine their respective levels of sulfur content and the results are shown in Figure 6.7. The concentrations of sulfur in the crude fuel, treated fuel, and raffinate water were found to be 21000 ppm, 7560 ppm, and 13040 ppm, respectively. The hydrophobic nature of thiophene compounds led to the conclusion that the formed water-soluble ionic liquid effectively extracted the thiophene molecules and subsequently transferred them to the aqueous raffinate during the washing step.

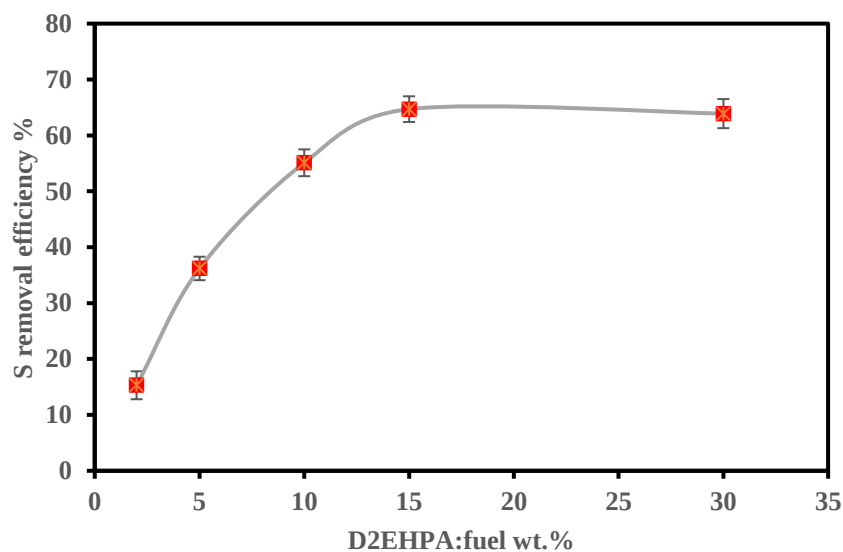


Figure 6.6 The impact of the D2EHPA:fuel mass ratio on sulfur removal efficiency from model fuels irradiated at 65 °C for 20 minutes

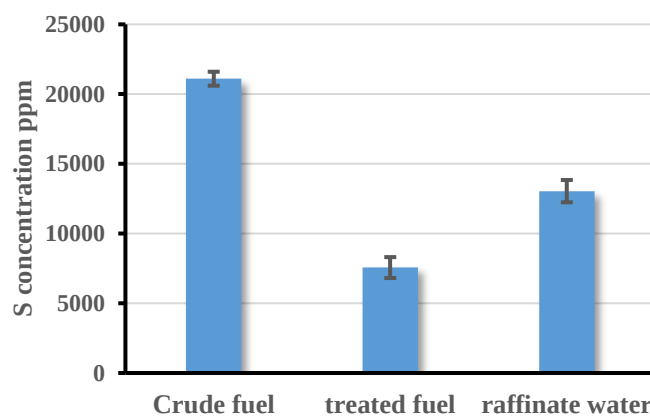


Figure 6.7 S-concentration of the produced raffinate water, crude fuel, and treated fuel with 15 wt.% d2EHPA and irradiated at 65 °C for 20 minutes

6.4.5 Crude oil desulfurization

It is more challenging to remove sulfur from crude oils because of their complex chemical matrix that contains several different sulfur compounds. In this study, crude oil samples from Iran

and Basra were treated with 15 wt.% D2EHPA and equimolar NaCl solutions under microwave heating at 65 °C for 20 minutes. The obtained S-removal efficiencies are illustrated in Figure 6.8. After the treatment, the initial sulfur contents of 24912 and 26350 ppm were reduced to 16043 ppm (35.6 % S-removal) and 18497 ppm (29.8 % S-removal), for Iranian and Basra crude oils, respectively. The findings indicate that the desulfurization effectiveness of the proposed process is lower for crude oils when compared to model fuels. Crude oils possess a considerably more complex chemical composition that includes various sulfur compounds and impurities, such as metals, nitrogen, and oxygen compounds, which can hinder the sulfur-extraction capacity of the proposed process. In addition, non-refractory compounds, such as thiols and sulfides, have shown low interaction with ionic liquids in the extractive desulfurization of crude oils and real fuels^{142, 145, 146}. Hence, the observed decrease in S-removal efficiency can be attributed to the proposed process' ability to solely eliminate the thiophene S-compounds present in the treated crude oil samples.

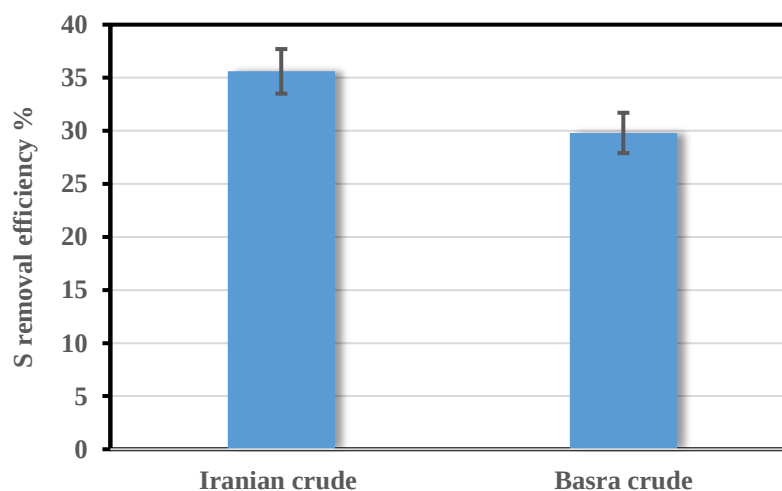


Figure 6.8 S-removal efficiencies for real crude oil samples treated with 15 wt.% d2EHPA and irradiated at 65 °C for 20 minutes

6.5 Conclusion

This study investigated the removal of thiophene (TS) organosulfur compounds from model fuels and real crude oils from Iran and Basra using D2EHPA and NaCl aqueous solutions under microwave irradiation. The effect of reaction temperature, residence time, and D2EHPA dosage on the S-removal efficiency of model fuels was examined, and the optimal values were determined. The results showed that up to 64% and 36% sulfur removal efficiencies were achieved from model fuels and Iranian crude oil, respectively, when treated with 15 wt.% D2EHPA under microwave irradiation at 65 °C for 20 minutes. The findings indicated the effective microwave-assisted desulfurization of model fuels at lower temperature and with a shorter reaction time compared to that of conventional heating. The successful formation of a water-soluble ionic liquid between D2EHPA and NaCl molecules during the irradiation time was confirmed through FTIR and electrical conductivity characterizations. The synthesized water-soluble ionic liquid was able to extract the S-compounds through a π - π interaction and was separated from treated fuels by washing with aqueous solutions.

CHAPTER 7 ARTICLE 4 : EXTRACTIVE DESULFURIZATION OF CRUDE PETROLEUM OIL AND LIQUID FUELS USING TRIHEXYL TETRADECYL PHOSPHONIUM BIS(2-ETHYLHEXYL) PHOSPHATE IONIC LIQUID

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7.1 Abstract

Increasing environmental concerns have led to the development of alternative methods for the desulfurization of petroleum crude oil and liquid fuels. Phosphonium-based ionic liquids (PILs) have recently demonstrated promising potential for effective extractive desulfurization (EDS). The present study focuses on the synthesis and application of trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate [THTDP][D2EHP] for EDS of synthetic model fuels and real crude oils. The molecular confirmation and thermal stability of [THTDP][D2EHP] were investigated using FTIR and TGA analyses. In addition, the conductivity, solubility, and viscosity of the synthesized ionic liquid (IL) were analyzed. The impact of reaction time, temperature, and sulfur compounds, such as thiophene, benozthiophen, and dibenzothiophene (DBT), on the desulfurization efficiency from synthetic fuels was also investigated. The results indicated up to 63 % and 57 % sulfur removal from DBT-based model fuels and Iranian crude oil, respectively. The optimum extraction conditions were found as 1:1 IL/fuel mass ratio, 35 °C, and 30 minutes. The findings of this study

provide valuable insights into the synthesis and utilization of PILs as promising solvents for extractive desulfurization of crude oil and liquid fuels.

7.2 Introduction

Today, oil refineries face a considerable challenge in the production of low-sulfur fuels, such as gasoline, diesel, and kerosene due to growing environmental concerns regarding the presence of organic sulfur compounds, namely sulfides, disulfides, and thiophenes in fuels ⁸. These compounds, upon combustion, result in the formation of sulfur oxides (SO_x), which are known as primary contributors to environmental issues, including acid rain and air pollution, as well as technical issues, such as catalyst poisoning in catalytic converters ³⁰. As a result, most countries are imposing increasingly stricter regulations on the permissible sulfur content in transportation fuels, creating a significant challenge for fuel desulfurization processes. In addition, with the rapid increase in the volume of heavy crude oils treated in refineries, the importance of efficient sulfur removal has become more critical than ever ²⁶. In response to these challenges, researchers have been investigating and developing new and efficient methods for removing sulfur from crude oils and fuels to comply with the regulations while still maintaining the desired fuel properties ¹⁴⁷.

The conventional method commonly used for desulfurization in crude oil refineries is hydrodesulfurization (HDS). This method involves a catalytic reaction with hydrogen at high temperatures and pressures, which converts the sulfur compounds into hydrogen sulfides ⁴⁴. Despite its effectiveness in removing aliphatic and non-aliphatic sulfur compounds, hydrodesulfurization (HDS) is found to be less efficient in eliminating aromatic refractory sulfur compounds, including thiophene (TS), benzothiophene (BT), and dibenzothiophene (DBT) and their derivatives. Furthermore, the HDS method is associated with several drawbacks, namely high consumption of hydrogen and energy, extreme operating conditions requiring temperatures up to

400 °C and pressures up to 130 bar, as well as a reduced gasoline octane grade. Additionally, the operating and investment costs for this method are considerably high^{8, 142, 147}. As a result, current research is actively investigating various alternative methods for fuel desulfurization, including biodesulfurization (BDS)^{8, 57}, microwave or ultrasound-assisted techniques¹¹⁰, adsorptive desulfurization (ADS)⁴⁴, oxidative desulfurization (ODS)¹²⁸, and extractive desulfurization (EDS) methods^{8, 30}. The extractive desulfurization (EDS) method is considered to be a promising technique for fuel desulfurization due to its several advantages, including low energy consumption, mild operating conditions, and the absence of a catalyst. However, the challenge lies in finding a reusable, eco-friendly extractant that can selectively remove sulfur compounds without contaminating the fuel. Although organic solvents are widely used in EDS, their volatility and toxicity can exacerbate environmental concerns.¹⁴⁸ Hence, there is a need to replace traditional solvents with new, safer, and more efficient extractants that promote the environmental sustainability of the fuel desulfurization process. Several studies have focused on identifying such novel green extractants for the EDS of liquid fuels^{30, 132}.

The potential of ionic liquids (ILs) as a replacement for conventional organic solvents has been demonstrated due to their desirable properties, such as low volatility, high thermal and chemical stability, moisture tolerance, and recyclability. ILs are composed of organic cations and inorganic or organic anions that have melting points below 100 °C, and their synthesis can be tailored to produce a broad range of characteristics by selecting specific cations and anions.^{8, 130} Various studies have investigated the use of ILs in the extractive desulfurization of fuels, with imidazolium-based, pyridinium-based, and Lewis and Brønsted acidic ionic liquids being the most used^{149, 150}. However, the exploitation of these ILs for large-scale fuel desulfurization is limited by drawbacks, such as high viscosity, high synthesis costs, and energy-intensive recycling.^{30, 131, 132} Hence, it is

essential to develop new ionic liquids with reduced synthesis costs, lower viscosity, and cost-effective recycling for EDS applications.

The availability of commercially produced phosphonium cations and their established chemistry has generated interest in the use of phosphonium-based ionic liquids (PILs) as a viable solvent for various applications^{142, 151-154}. Sun et al. have reported the synthesis and characterization of six PILs based on tetra-alkyl-phosphonium cation, and the application of these PILs to mitigate corrosion from magnesium alloys¹³⁶. The use of PILs as a solvent in EDS applications has several advantages over typical ILs, such as their ease of synthesis, lower synthesis costs, and higher chemical stability.^{145, 155} However, there have been limited studies exploring the performance of PILs in the EDS of liquid fuels^{143, 146, 151, 152, 156-158}. Furthermore, the efficacy of using PILs for extractive desulfurization of crude oils, which possess a more complex chemical composition compared to liquid fuels, like diesel and gasoline, remains unexplored.

In this study, a phosphonium-based ionic liquid called trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate [THTDP][D2EHP] was synthesized. For the first time, its efficiency in the extractive desulfurization of synthetic model fuels containing thiophene (TS), benzothiophene (BT), and dibenzothiophene (DBT) sulfur compounds, along with crude oils from Iran and Basra, was assessed. The chemical structure of the synthesized PIL is depicted in Figure 7.1. This study investigated the effects of primary process parameters, such as reaction time, temperature, and sulfur compound, on the efficiency of sulfur extraction. The findings of this research provide further insight into the synthesis and use of PILs as eco-friendly solvents for the extractive desulfurization of liquid fuels.

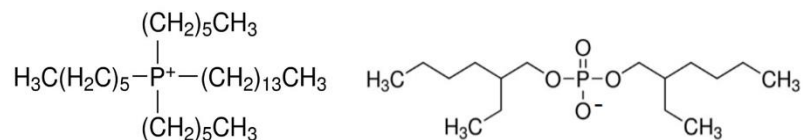


Figure 7.1 Chemical structure of [THTDP][D2EHP] IL

7.3 Materials and methods

7.3.1 Materials

[THTDP][D2EHP] ionic liquid was synthesized by adopting pure analytical grade chemicals. Sodium hydroxide pellets (NaOH), bis(2-ethylhexyl) phosphoric acid (D2EHPA), Trihexyl tetradecyl phosphonium bromide ([THTDP] Br), thiophene (TS), benzothiophene (BT) and dibenzothiophene (DBT) were purchased from Sigma-Aldrich (Ontario, Canada). Hexane and kerosene were purchased from Fisher Scientific (Ontario, Canada). Iranian and Basra crude oils were supplied by TOTAL S.A. refineries in France.

7.3.2 IL synthesis

The reaction path shown in Figure 7.2 was adopted to synthesize [THTDP][D2EHP]. The standard procedure to synthesize phosphonium-based ILs is given elsewhere^{136, 142}. In brief, 5.26 g (0.0163 mol) D2EHPA was mixed with 9.24 g (0.0163 mol) [THTDP] Br in 15 g hexane. An aqueous solution of 650 mg NaOH (0.0163 mol) in 18 g distilled water was then added dropwise into the reaction mixture and stirred for 4 h at 900 rpm and ambient conditions. The organic phase was then separated by centrifugation at 4000 rpm for 10 minutes and washed three times by 50 wt.% distilled water. Next, hexane was removed by distillation and the product was dried at 80 °C for 2h. The final synthesized IL yield was 96 %.

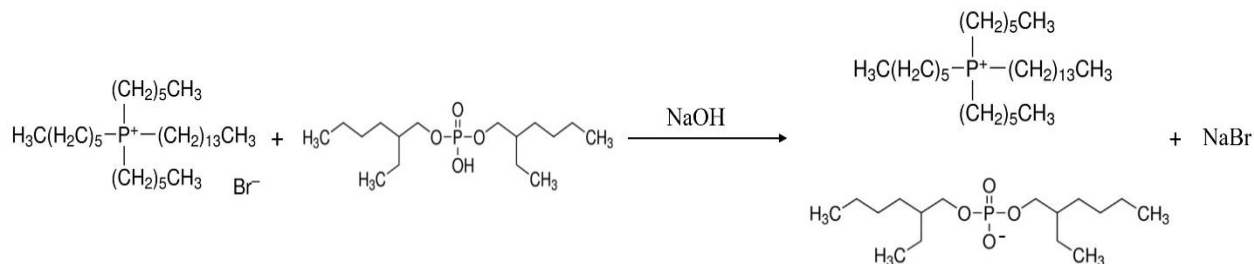


Figure 7.2 [THTDP][D2EHP] synthesis reaction scheme

7.3.3 Model fuel preparation

Model fuels containing 21000 ppm were prepared by dissolving calculated amounts of TS, BT, and DBT in 20 gr of kerosene. The properties of Iranian and Basra crude oils treated in this study are given in Table 7.1.

Table 7.1 Properties of treated crude oils

Oil	Density (kg/m ³)	Viscosity	Carbon residue	S-content	
	(15 °C)	(cP) (10 °C)	(Wt.%)	API	(ppm)
Iran	881.2	18.4	6.8	28.9	24912
Basra	886.8	23.8	7.8	27.9	26350

7.3.4 Extractive desulfurization

To conduct the EDS experiments, 10 gr of the fuel sample was mixed with various mass ratios of the prepared [THTDP][D2EHP] (fuel: IL 5:1, 3:1, and 1:1) in a 100 ml quartz flask. The mixture was stirred at 1000 rpm for 5 to 30 minutes at 35 °C on a magnetic hot-plate stirrer. After the reaction time passed, the fuel phase was separated by a separatory funnel and samples were sent for sulfur concentration analysis. The sulfur extraction efficiency was calculated as:

$$\text{Sulfur removal (\%)} = \frac{C_{s,i} - C_{s,f}}{C_{s,i}} \times 100 \quad (7.1)$$

Where $C_{s,i}$ and $C_{s,f}$ are the initial and final sulfur concentrations in the treated fuel samples.

7.3.5 Characterization methods

The purity and molecular structure of the synthesized [THTDP][D2EHP] were investigated by Fourier transform infrared spectroscopy (FTIR) analysis using a Spectrum 65 FTIR instrument from PerkinElmer recording 32 scans between 4000-600 cm^{-1} with 4 cm^{-1} resolution. The results were analyzed to detect the chemical bonds and the functional groups of the synthesized phosphonium IL. The thermal stability of the prepared IL was tested by a TGA 550 of TA Instruments, with the scan rate of 10 $^{\circ}\text{C}/\text{min}$ in the range of 25-800 $^{\circ}\text{C}$ under a nitrogen flow. Viscosity analysis was carried out using an MCR501 rheometer from Anton Paar in the temperature range of 25 to 80 $^{\circ}\text{C}$ with a rate of 0.05 $^{\circ}\text{C}/\text{s}$. To conduct the solubility analysis, a mixture of [THTDP][D2EHP] and different solvents were placed into a 100ml quartz flask and mixed by magnetic stirring for 20 minutes. Electrical conductivity was measured using the ZetaProbe Analyzer from Colloidal Dynamics at different temperatures between 25 to 70 $^{\circ}\text{C}$. The Neutron Activation Analysis (NAA) method was adopted to quantify the sulfur content of the fuels before and after extraction conducted at the Slowpoke analytical lab at Polytechnique in Montreal (Quebec, Canada). In this method, samples were irradiated with thermal neutrons in a nuclear reactor and the corresponding elements were quantified based on the γ -ray spectrum resulting from gamma radiations of the excited isotopes ¹¹².

7.4 Results and discussion

7.4.1 [THTDP][D2EHP] characterization and physical properties

7.4.1.1 FTIR analysis

The FTIR spectrums of [THTDP][D2EHP] before and after extraction are illustrated in Figure 7.3. The peaks at 2855-2960 cm^{-1} and 1462 cm^{-1} show the C-H stretching and bending functional groups, respectively. Two medium peaks at 811 cm^{-1} and 1376 cm^{-1} correspond to P-C and P-CH₂-R groups. Phosphate group bonds show strong peaks at 1239 cm^{-1} and 1057 cm^{-1} due to the existing P=O and P-O bonds, respectively, originated from D2EHPA molecules. The results of FTIR analysis confirms the successful synthetization of trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate. Similar FTIR spectrum was observed for [THTDP][D2EHP] after sulfur extraction showing no change in the measured wave lengths of the existing functional groups. D2EHPA molecules tend to form dimmers by forming hydrogen bonds in a non-polar organic medium⁹³. Figure 7.4 shows the FTIR spectrum of pure D2EHPA indicating broad peaks at 1687 cm^{-1} and 2325 cm^{-1} for hydrogen bonds and stretching vibration of O-H, respectively. As shown in Figure 7.3, these peaks are not detected in the FTIR spectrum of the prepared IL. Thus, it can be concluded that the phosphate group of D2EHPA has lost its proton confirming the suggested reaction path with NaOH for [THTDP][D2EHP] preparation.

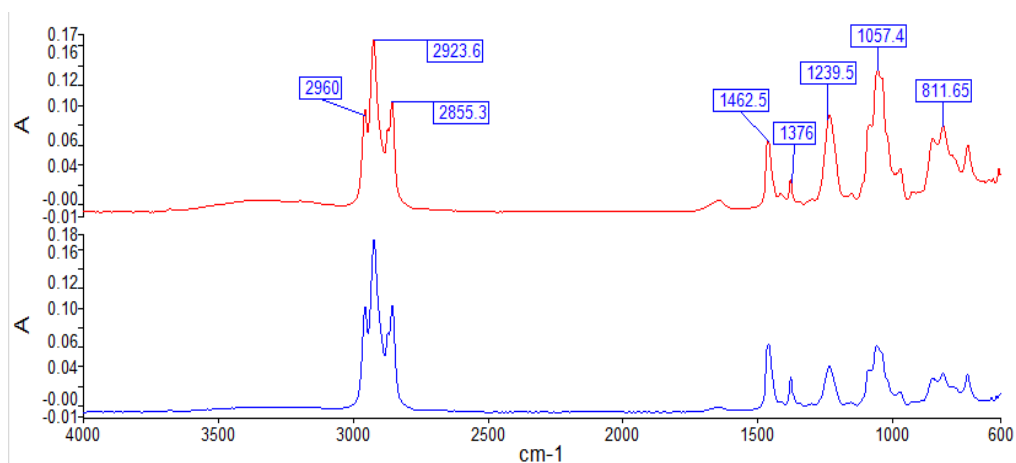


Figure 7.3 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of [THTDP][D2EHP] before (red) and after (blue) extractive desulfurization

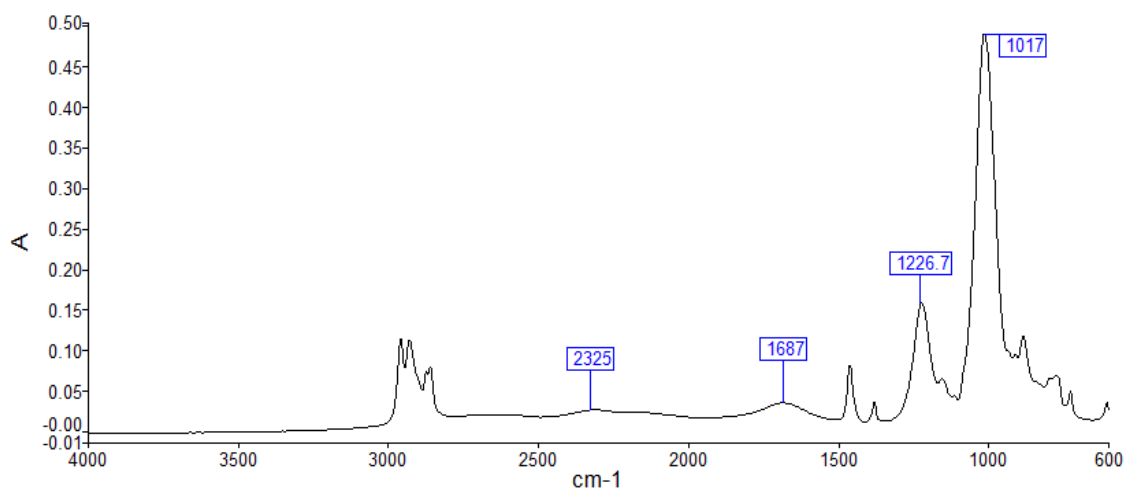


Figure 7.4 IR Absorbance (A) versus wavelength (cm^{-1}) from FTIR analysis of pure D2EHPA

7.4.1.2 Thermal stability (TGA analysis)

The results of TGA analysis for [THTDP][D2EHP] are illustrated in Figure 7.5. It can be noticed that the synthesized IL shows a good thermal stability, and no significant mass loss observed below 300 °C. As expected, the decomposition mechanism follows two primary

isothermal steps at 285 °C and 365 °C, with the total weight loss of 94 % combined, corresponding to evaporation of [THTDP]⁺ and [D2EHP]⁻ ions, respectively, confirming the purity of the synthesized IL.

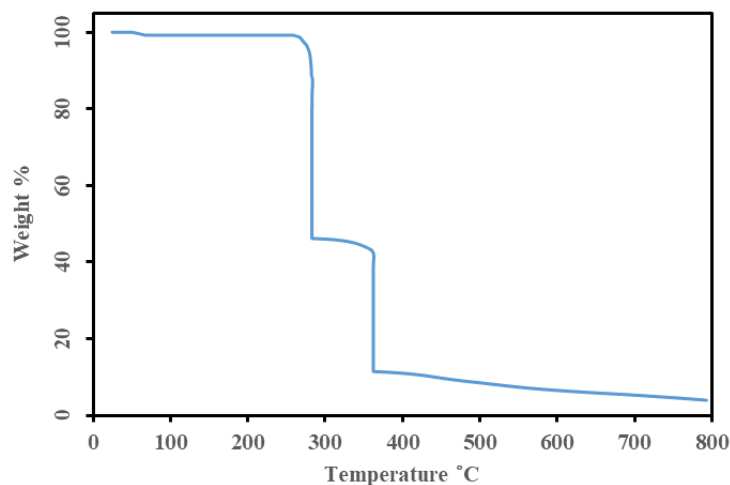


Figure 7.5 TGA results of [THTDP][D2EHP] IL

7.4.1.3 Viscosity analysis

Typically, ILs are highly viscous liquids, which their viscosity changes depending on their cation-anion pairing and can even be several orders of magnitude greater than that of water and commonly used organic solvents ¹⁵⁹. A primary drawback of using ionic liquids for EDS applications is their elevated viscosity, which is influenced by Van der Waals forces and hydrogen bonds. Nevertheless, this viscosity can be modulated to a tolerable level- such as 50–10000 cP- by selecting an appropriate pairing of cations and anions ¹⁶⁰. PILs have demonstrated substantially reduced viscosities compared to the commonly used ILs in EDS -such as imidazolium or pyridinium-based ILs- which can have viscosities ranging from several hundred mPa.s to thousands of mPa.s ¹³². Viscosity of [THTDP][D2EHP] was measured as 0.219 Pa.s at 25 °C using MCR501 Rheometer . The impact of temperature on the viscosity of [THTDP][D2EHP] is shown in Figure

7.6. As expected, the viscosity of [THTDP][D2EHP] varies inversely with respect to temperature indicating as temperature increases from 25 to 80 °C, the viscosity of trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate decreases from 0.219 to 0.027 Pa.s, respectively. These results indicate that [THTDP][D2EHP] possesses a considerably lower viscosity compared to the ILs commonly utilized in EDS. Low viscosity of [THTDP][D2EHP] is advantageous since high viscosity is a major challenge that impedes the successful implementation of ILs in industrial applications.

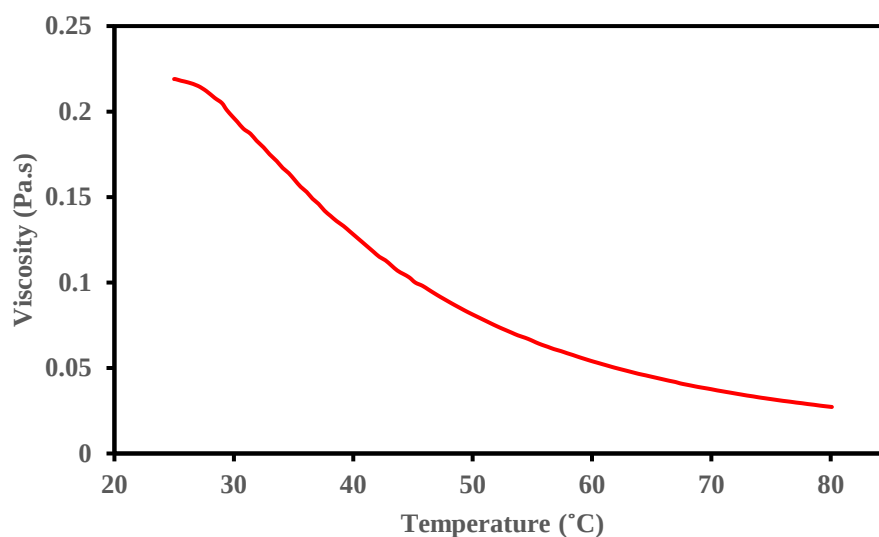


Figure 7.6 The effect of temperature on [THTDP][D2EHP] viscosity

7.4.1.4 Solubility analysis

In EDS, it is essential that the applied extractant or solvent has negligible mutual solubility with the target fuel medium to avoid fuel/extractant contamination and loss. Therefore, solubility is a primary factor to consider when synthesizing ILs for extraction purposes. PILs are reported as promising solvents for extracting organic compounds from aqueous media due to their extreme hydrophobicity behavior^{161, 162}. However, solubility of PILs in organic or aqueous medium could

be varied based on the type of the adopted anion⁸. [THTDP][D2EHP] solubility in six conventional solvents was studied. It was observed that [THTDP][D2EHP] has poor solubility in water, ethanol, and acetonitrile but it may be dissolved in conventional non-polar organic solvents such as hexane, benzene, and toluene. Experiments were conducted to measure the solubility of [THTDP][D2EHP] in the prepared model fuels. A mixture of [THTDP][D2EHP] and Kerosene with 1:1 mass ratio was prepared, and kerosene phase were analyzed with FTIR after separation. No phosphate peak was observed in the FTIR spectrum of the separated kerosene implying negligible solubility of [THTDP][D2EHP] in kerosene. In future studies, it is necessary to optimize the solubility of [THTDP][D2EHP] in petroleum-based liquid fuels.

7.4.1.5 Electrical conductivity analysis

The most significant factor affecting the electrical conductivity of ILs is the mobility of the ions, which is influenced by the diffusion coefficient of the ions, their charge density, and the viscosity of the ILs¹⁶³. Sun et al. have reported the electrical conductivity of a few phosphonium ILs as a function of temperature in the range of 20-70 °C¹³⁶. The results indicated lower conductivity (10^{-6} to 10^{-5} S cm⁻¹) of these ILs at room temperature compared to that (10^{-4} to 10^{-3} S cm⁻¹) of pyrrolidinium and quaternary ammonium amide based ILs. The electrical conductivity of [THTDP][D2EHP] was measured in the temperature range of 25 to 70 °C, and the results are shown in Figure 7.7. As can be seen, the electrical conductivity of [THTDP][D2EHP] changes directly with regard to temperature, showing that the electrical conductivity increases from 55 to 220 μ S/cm as temperature rises from 25 to 70 °C, respectively. The lower electrical conductivity of [THTDP][D2EHP] compared to the typical pyrrolidinium or ammonium amide based ILs could be due to its strong electron donating -OR group of D2EHPA¹³⁶. However, PILs are projected to provide significant benefits over traditional organic solvents¹⁶⁴.

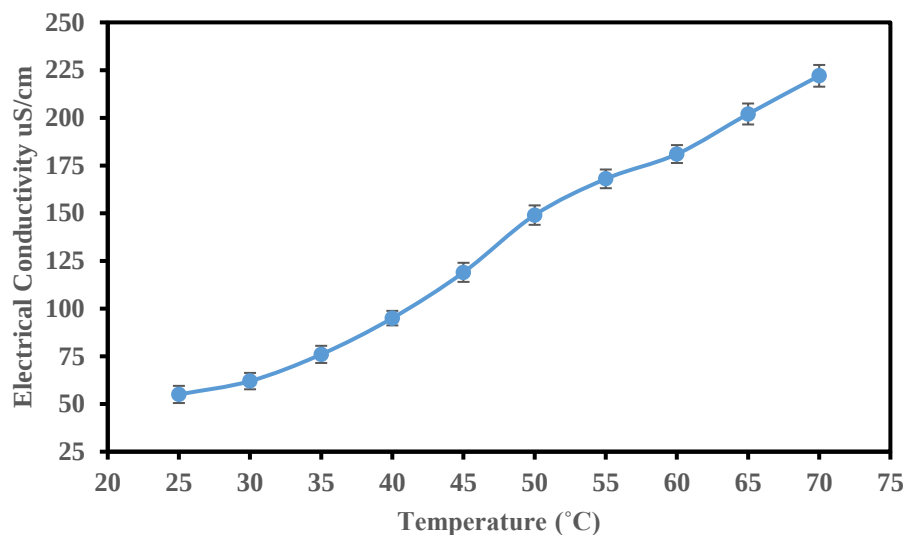


Figure 7.7 The effect of temperature on [THTDP][D2EHP] electrical conductivity

7.4.2 Effect of reaction time

In this study, the extraction of a model fuel consisting of DBT in kerosene was conducted using [THTDP][D2EHP] IL. The extractions were performed at 35 °C for 5, 15, 30, and 45 minutes with varying mass ratios of 5:1, 3:1, and 1:1 (model liquid fuel to IL). The results, depicted in Figure 7.8, show that the desulfurization process was rapid, with the concentration of S in the model fuel decreasing with an increase in extraction time. In 15 minutes, the S removal efficiencies were 37.6 %, 48.4 %, and 55.2 % for mass ratios of 5:1, 3:1, and 1:1, respectively. Furthermore, as the extraction time was extended to 30 minutes, desulfurization efficiencies increased continuously to 47.3 %, 57.8 %, and 63.7 % for mass ratios of 5:1, 3:1, and 1:1, respectively. At 30 minutes, no further reduction in S-removal was observed as equilibrium was reached, as reported elsewhere ¹⁴²,

145.

During the early stage of the extraction, the model fuel S-concentration was higher, which resulted in a high extraction rate and correspondingly high S-removal rate. As the reaction

continued, the extraction rate decreased, and the S-removal rate no longer increased significantly due to the possible saturation of [THTDP][D2EHP] with the high concentrations of DBT in the model fuel (21000 ppm). Figure 7.7 illustrates the findings, showing that [THTDP][D2EHP] required 30 minutes to establish an equilibrium with the model fuel. Therefore, the minimum time needed for effective sulfur extraction was determined to be 30 minutes.

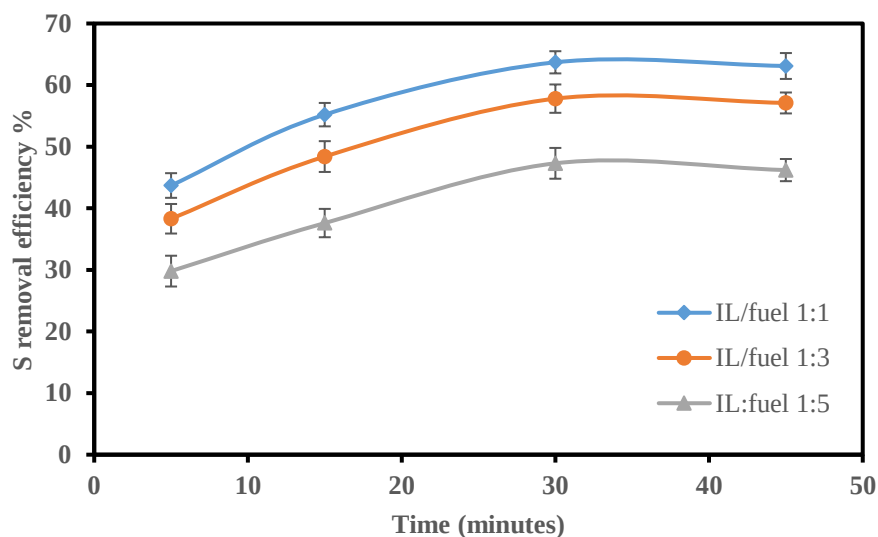


Figure 7.8 Impact of time on EDS efficiency with [THTDP][D2EHP] at 35 °C

7.4.3 Effect of temperature

The effectiveness of EDS is significantly influenced by the reaction temperature, as demonstrated in Figure 7.9, which illustrates the impact of temperature in the range of 25 - 65 °C on sulfur removal from DBT-containing model fuels. As depicted in the figure, the S-removal efficiency initially increased as the temperature increased from 25 °C to 35 °C, and then decreased. This may be attributed to the decrease in [THTDP][D2EHP] viscosity and the subsequent improvement in the mixing effectiveness of IL and model fuels with increasing temperature, which resulted in an increase in DBT removal efficiency. However, as the temperature exceeded 35 °C,

the desulfurization efficiency was not significantly enhanced. Consequently, the S-removal rate no longer increased and even declined to some extent. Similar temperature impact on EDS performance was observed with other ILs, as reported in the literature^{142, 145, 165-167}. As a result, the ability to perform sulfur extraction at room temperature is a positive development in terms of reducing energy consumption. The stability of ILs is known to decrease by increasing the temperature which can affect their effectiveness to bond with the target DBT molecules for EDS applications at higher temperatures¹⁴³. The best reaction temperature for removing DBT using [THTDP][D2EHP] was found to be 35 °C. At this temperature, the S-content of the model fuel decreased up to 47.3 %, 57.8 %, and 63.7 % with fuel to IL mass ratios of 5:1, 3:1, and 1:1 respectively, as shown in Figure 7.9. However, a drop in desulfurization efficiency was observed at 65 °C, with 35.9 %, 49.1 %, and 54.2 % S-removal achieved with mass ratios of 5:1, 3:1, and 1:1, respectively.

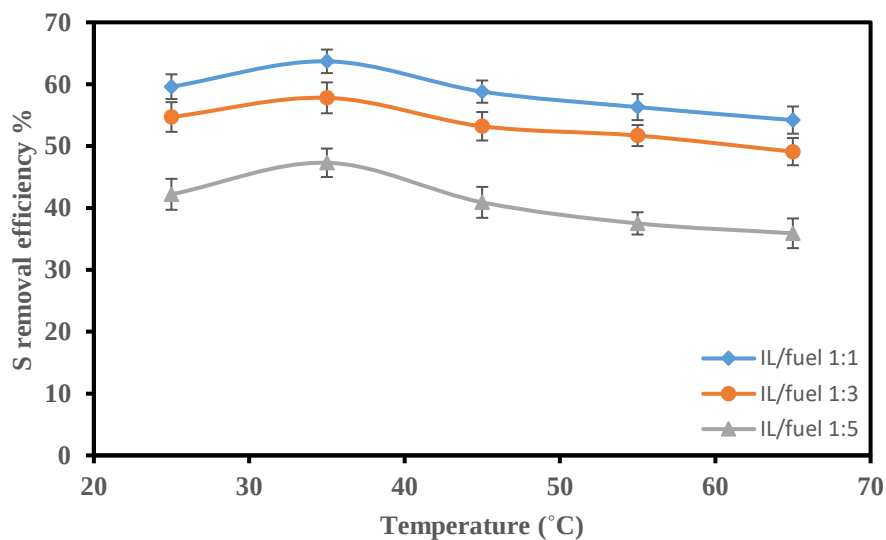


Figure 7.9 Impact of temperature on EDS efficiency with [THTDP][D2EHP] for 30 minutes

7.4.4 Effect of S-compound

Table 7.2 summarizes the molecular structures and properties of refractory sulfur compounds typically found in crude oils and liquid fuels. The S-removal efficiencies of three model fuels with different S-compounds treated with [THTDP][D2EHP] for 30 minutes at 35 °C and an IL to fuel mass ratio of 1:1 are depicted in Figure 7.10. The results show that [THTDP][D2EHP] is highly effective at extracting, TS, BT, and DBT. High interaction of PILs with thiophene derivatives is reported in the literature while low extraction efficiencies for thiols, sulfides, and related compounds were found ^{142, 145, 146}. In particular, the order of extraction efficiency for the S-compounds in [THTDP][D2EHP] is DBT > BT > TS, with removal efficiencies ranging from 56.1 % to 63.7 % within 30 minutes. This order can be explained by the relative aromatic π -electron density on the sulfur atoms. Compounds with higher aromatic electron density, such as DBT, have higher extraction efficiencies due to increased interaction with the IL.

Table 7.2 Properties of treated S compounds

Sulfur compound	Chemical formula	Boiling point °C	Molar weight g/mol	Density g/cm ³
TS	C ₄ H ₄ S	84	84.1	1.05
BT	C ₈ H ₆ S	221	134.1	1.15
DBT	C ₁₂ H ₆ S	332	184.3	1.25

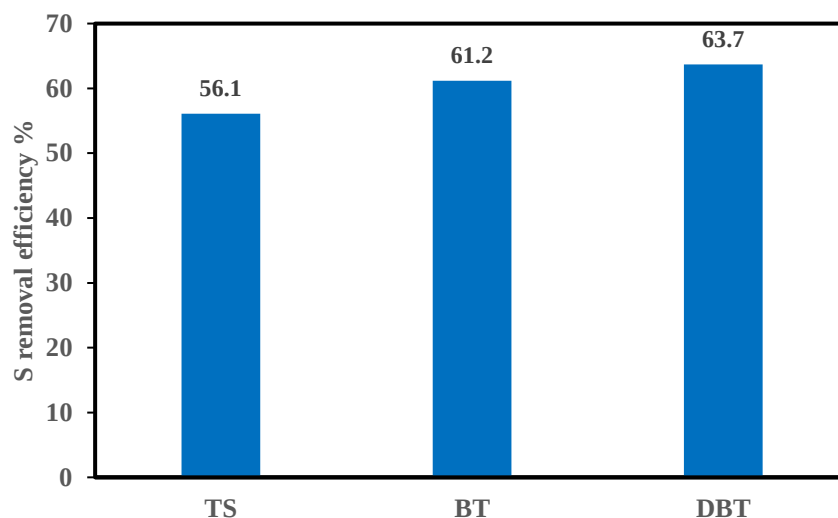


Figure 7.10 EDS efficiencies for different S-compounds with [THTDP][D2EHP] at 35 °C for 30 minutes and 1:1 IL/fuel mass ratio

7.4.5 Crude oil desulfurization

Extracting sulfur from crude oils is more challenging due to their complex composition of various sulfur compounds and other impurities such as metals, nitrogen, and oxygen compounds. PILs have shown promising results in extractive desulfurization of real fuels such as gasoline and diesel^{142, 145, 146}. In this study, trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate demonstrated high sulfur removal efficiency from Iranian and Basra crude oils in a single-stage extraction at 35 °C with IL to oil mass ratios of 1:1, 1:3, and 1:5, as presented in Table 7.3. [THTDP][D2EHP] showed a similar sulfur extraction ability for the both crude oil samples reducing the initial sulfur content of 24912 ppm to 10662 ppm (57.2 % S removal), 13278 ppm (46.7 % S-removal), and 15969 ppm (35.9 % S removal) with mass ratios of 1:1, 1:3, and 1:5 in single-stage extraction of Iranian oil, respectively. For Basra crude oil, the initial sulfur content of 26350 ppm was reduced to 10909 ppm (58.6 % S-removal), 13412 ppm (49.1 % S-removal), and 16232 ppm (38.4 % S-removal) with mass ratios of 1:1, 1:3, and 1:5 in single-stage extraction, respectively. The results

show an inferior desulfurization performance of [THTDP][D2EHP] for crude oils compared to the model fuels. This can be justified by considering that crude oils have significant more complex chemical structure containing various impurities and sulfur compounds which can decrease the sulfur-extraction ability of phosphonium ILs.

Table 7.3 EDS efficiencies for Iranian and Basra crude oils treated with [THTDP][D2EHP] at 35 °C for 30 minutes

Iranian crude oil			Basra crude oil		
IL/Oil	Final S-content	EDS efficiency	IL/Oil	Final S-content	EDS efficiency
(mass ratio)	(ppm)	(%)	(mass ratio)	(ppm)	(%)
1:1	10662	57.2	1:1	10909	58.6
1:3	13278	46.7	1:3	13412	49.1
1:5	15969	35.9	1:5	16232	38.4

7.5 Conclusion

The application of ionic liquids for the extractive desulfurization of fuels has shown promising results, particularly phosphonium ILs. In this study, trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate [THTDP][D2EHP] ionic liquid (IL) was synthesized, characterized, and adopted for the desulfurization of model fuels and real crude oil samples. The impact of operating conditions, such as temperature, IL:fuel mass ratio, and extraction time on extractive desulfurization effectiveness were investigated. [THTDP][D2EHP] showed a high extraction efficiency for model fuels containing refractory S-compounds, particularly thiophene derivatives, such as TS, BT, and DBT. However, their performance decreases when dealing with crude oil

samples from Iran and Basra, which have a much more complicated chemical structure and contain a variety of impurities, including metals, nitrogen and oxygen-containing compounds. The findings showed that the DBT-based model fuels and Iranian crude oil underwent the sulfur removal of as much as 63% and 57%, respectively. The most favorable extraction parameters were determined to be a 1:1 ratio of ionic liquid to fuel mass, a temperature of 35 °C, and a duration of 30 minutes. Further research is needed to optimize ILs for crude oil desulfurization and to investigate their potential environmental impact. The findings and outcomes of this study could offer valuable understanding and knowledge regarding the potential use of phosphonium ILs as a favorable solvent for extractive desulfurization of not only model liquid fuels but also real crude oils.

CHAPTER 8 UPDATED TECHNO-ECONOMIC ASSESSMENT

The preliminary techno-economic investigation of the proposed process for microwave-assisted demetallization and desulfurization of crude oil using D2EHPA is given in Chapter 4 of this thesis. The findings of this preliminary analysis highlighted the importance of developing a precise kinetic model for metal removal reactions as well as optimizing the primary process parameters for both demetallization and desulfurization processes, which are then presented in Chapters 5 & 6, respectively. In this Chapter, a second techno-economic assessment is carried out in accordance with the new findings reported in Chapters 5 & 6. This assessment aims to provide a more accurate analysis of the commercialization feasibility of such a process on a large industrial scale.

To achieve the main objective of this chapter, firstly, a new process scheme was developed by identifying the necessary processing units. According to the findings of Chapters 5 & 6, metal and sulfur removal from crude oil under microwave heating require different process conditions which will impose modifications in the preliminary process design presented in Chapter 4. Next, process simulation was conducted in ASPEN Plus to obtain sizing data for the main processing units according to the newly optimized process parameters. Additionally, the total capital costs (CAPEX) and the total annual operational costs (OPEX) were estimated by utilizing ASPEN Process Economic Analyzer and relevant process economic estimation methods.

According to the findings of Chapters 5 & 6, the optimized values of the primary process parameters for crude oil demetallization and desulfurization using the proposed process are reported in Table 8.1. As it can be noticed from the data reported in Table 8.1, different process conditions such as higher residence time and reaction temperature are required to remove metals compared to sulfur removal which can be carried out faster and under milder temperatures. As a

result, the preliminary process scheme would need to be modified to accommodate two separate microwave-assisted reactors for sulfur and metal removal from crude oil. The updated industrial process scheme of the proposed process is illustrated in Figure 8.1. As it can be noted, a mixture of crude oil and D2EHPA is introduced to the first reactor where the demetallization reaction take place under microwave heating. The treated mixture is then washed to extract the reacted metals that are converted to water-soluble compounds through the demetallization reactions. In the next step, the demetallized crude oil is mixed with an aqueous NaCl solution flowing through the second microwave-assisted reactor for sulfur removal through extractive desulfurization by ionic liquid formation mechanism. A second washing unit is installed after the second reactor in order to remove sulfur compounds and the unreacted D2EHPA molecules through saponification with NaOH aqueous solutions. Given the necessity for higher reaction temperatures in the demetallization process, it is advantageous to position the metal removal unit upstream. This is primarily due to the increased interaction of the crude oil, especially when it contains metals and other impurities like salts, with microwaves. By placing the metal removal unit in the upstream of the process, the crude oil can be more effectively heated with the electromagnetic waves, enhancing the energy efficiency of the demetallization process.

Table 8.1 Optimum values for primary process parameters

Process parameter	Demetallization	Desulfurization
Reaction Temperature (°C)	250	65
D2EHPA dosage (wt.%)	15	15
Reaction time (min)	60	20

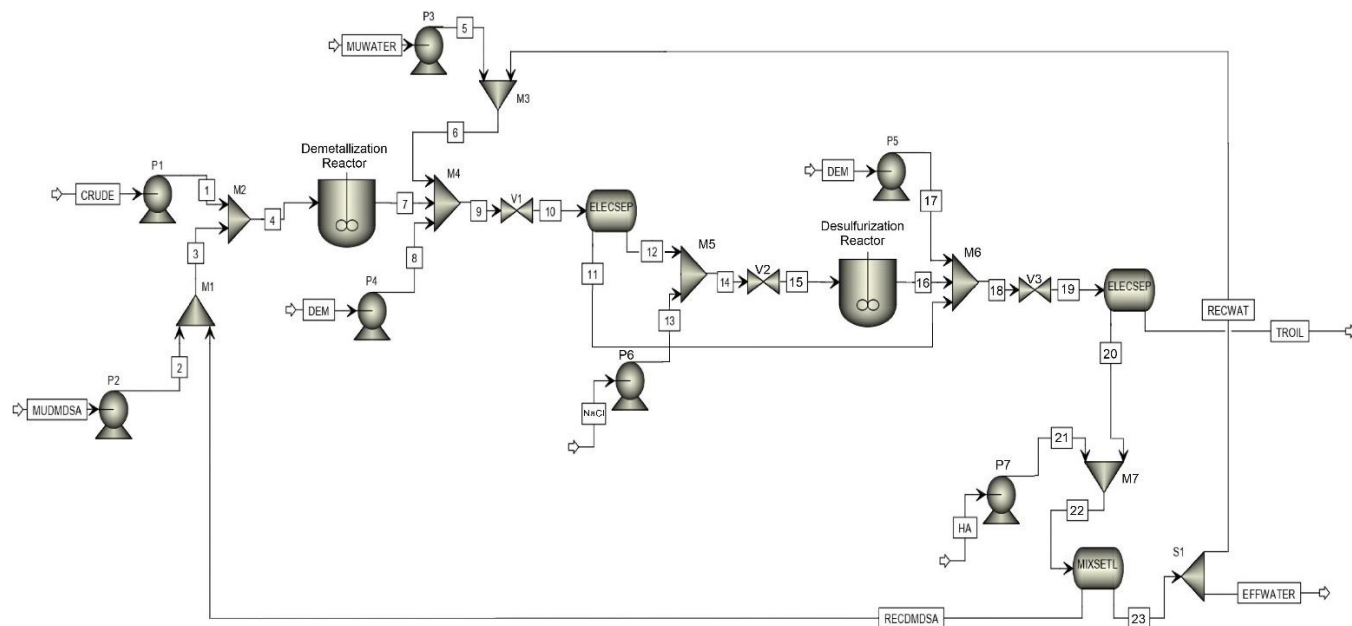


Figure 8.1 Updated process flow diagram

Next, economic estimations were conducted based on optimized process conditions obtained from the experiments. The assumptions for these estimations included a crude treatment capacity of 50,000 barrels per stream day (BPSD), operating for 350 days per year. It was assumed that the D2EHPA regeneration efficiency would be 95%, water:oil mass ratio of 10 % in washing steps, and the electric efficiency of microwave generators would be 40%, which was the same as in Chapter 4. To calculate the CAPEX (Capital Expenditure) costs, the installation costs of the primary processing equipment, such as reactors, electrostatic separators, and the mixer-settler, were estimated using Aspen Process Economic Analyze. The total fixed capital investment was then estimated by adopting the Lang Factor method, which assumes a factor of 6.0 for liquid processing, according to Equation 4.4.

In section 4.3.1.1, we initially implemented an energy balance to estimate the required microwave power to heat up the reaction mixture to 2 °C, assuming 100% conversion of microwave energy to heat. However, the results obtained in Chapters 5 and 6 indicated that the effective

removal of metals and sulfur from crude oil occurs at higher temperatures, specifically 250 °C and 65 °C, respectively. To obtain a more precise estimation of the required microwave power, we adopted the experimental data reported in section 5.6. Based on the experimental data, the average actual microwave power used to treat 30 grams of the reaction mixture was found to be 19.5 W, or 0.65 kW per kilogram of the mixture, for both the demetallization and desulfurization processes. Therefore, in the updated techno-economic assessment, we used a microwave power density of 0.65 kW per kilogram of treated oil to estimate the required microwave generators and their corresponding purchase costs. Considering a crude oil inflow rate of 50,000 barrels per day or 332 m³/hr, and a D2EHPA dosage of 15 wt.%, the required microwave power was estimated to be 18.45 MW. This would necessitate the installation of 184 units of magnetron-based microwave generators, each with a capacity of 100 kW and a cost of 100,000 USD. Furthermore, according to Equation 4.6, the updated CAPEX costs of the proposed process were estimated to be 42.1 million USD. Detailed information regarding the total capital costs of the developed process can be found in Table 8.2 and Figure 8.2.

The calculation of the overall annual operational expenses (OPEX) for the proposed process considered several primary costs. These costs include insurance, overhead, maintenance, labor costs, chemicals and reagents, and utility expenses. Based on these considerations, the estimated total annual operating costs for the process, with a treatment capacity of 50,000 barrels per stream day (BPSD), were found to be 23.02 million USD. This corresponds to approximately 1.31 USD per barrel (bbl) of crude oil treated. A breakdown of the proportion of each item in the reported operational expenditure costs is presented in Figure 8.3.

Table 8.2 Total CAPEX costs of the proposed process

Item	Value	Unit
Major Equipment Total Cost	3.3	MUSD
Lang Factor, Fluid Processing	6.0	-
Fixed Capital Investment	19.8	MUSD
Microwave Generators	18.4	MUSD
Working Capital	4.0	MUSD
Total Capital Investment	42.1	MUSD

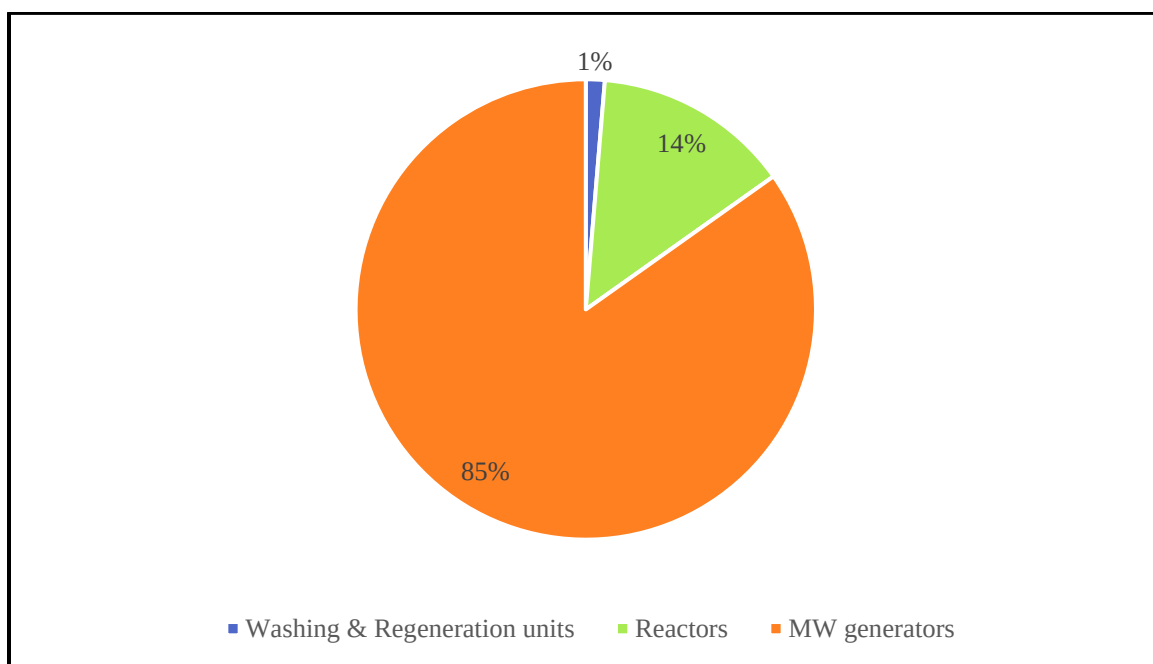


Figure 8.2 CAPEX costs breakdown

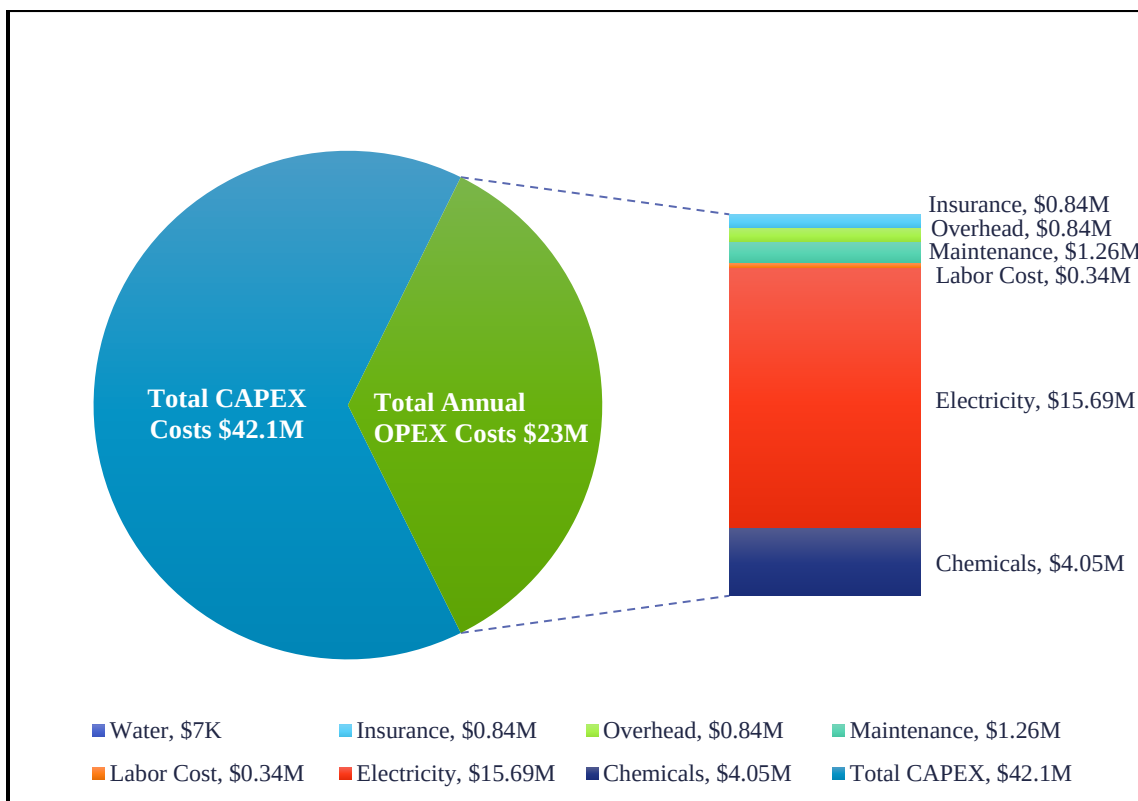


Figure 8.3 OPEX costs breakdown

The results of the updated economic analysis reveal a significant increase in both CAPEX and OPEX costs compared to the preliminary investigation reported in Chapter 4. The total CAPEX costs have risen from 6.77 million USD to 42.1 million USD, while the total annual OPEX costs have increased from 4.23 million USD per year (0.23 USD per barrel) to 23.02 million USD (1.31 USD per barrel). This increase in costs can primarily be attributed to the significant rise in the estimated microwave power requirement due to the new operating temperatures required for the demetallization and desulfurization reactors. In the preliminary investigation, a modest 2 °C increase in the bulk temperature of the mixture was considered. However, the optimized reaction temperatures for demetallization and desulfurization were found to be 250 °C and 65 °C, respectively. As depicted in Figures 8.2 and 8.3, the purchase cost of the microwave generators

and the annual electricity cost (based on electricity price in Quebec in 2021, 0.054 CAD/kWh) represent more than 85% and 68.2% of the total estimated CAPEX and OPEX costs, respectively. Additionally, the significant increase in the residence time of the reactor, from 5 minutes to 20 and 60 minutes, has necessitated larger reactor sizes and significantly increased the associated purchase costs. Nevertheless, despite these cost increases, the developed process remains economically competitive with the HDM-HDS technique. The HDS technique, with a treatment capacity of 50,000 BPSD, has been found to have CAPEX and OPEX costs ranging from 32-42 million USD and 1.27-9.1 USD per barrel, respectively, for desulfurization alone. Therefore, even with the higher costs, the developed process still offers economic viability when compared to the alternative technique.

The updated techno-economic analysis presented in this chapter highlights the significant impact of effective microwave heating on the economic performance of the developed process. However, further optimization of the required microwave power has the potential to substantially reduce both CAPEX and OPEX costs, thereby enhancing the overall economic viability of the process. To achieve this optimization, a combination of modeling and experimental investigations can be conducted. These studies would focus on determining the precise microwave power requirements for setups operating at larger oil treatment capacities than those adopted in the experiments of this work. By understanding the scaling effects and optimizing the microwave power accordingly, it would be possible to minimize the associated costs. Furthermore, improving the mass transfer efficiency in the demetallization process can also contribute to cost reduction. One approach is to explore enhanced mixing methods such as ultrasonication. By implementing ultrasonication or other similar techniques, the mass transfer rate can be improved, leading to a significant reduction in reagent consumption. This, in turn, would translate into lower OPEX costs.

By addressing these optimization opportunities, it is possible to further enhance the economic feasibility of the developed electrified process and establish it as a green alternative for crude oil upgrading.

CHAPTER 9 GENERAL DISCUSSION

The current hydrodesulfurization (HDS) and hydrodemetallization (HDM) techniques employed to eliminate metals and sulfur from crude oil contribute to the overall costs, complexity, and environmental impact. These processes are associated with high energy consumption and rely heavily on fossil fuels, leading to increased emissions. With the aim of electrifying these energy-intensive processes, some recent studies have attempted to introduce microwave-assisted chemical complexation with polar reagents ¹⁵. This new technique could benefit from several advantages of both microwave heating (i.e., selective/local, volumetric heating, energy saving) and chemical complexation (mild operating conditions). Recently, crude oil simultaneous demetallization and desulfurization with bis(2-ethylhexyl) phosphoric acid (D2EHPA) under microwave heating has been found as an efficient green technique ¹. However, to the best of our knowledge, no efforts have been devoted to investigating the potential and limitations of this method at large industrial scale. In addition, no research has investigated the demetallization reaction kinetics, D2EHPA regeneration methodology, desulfurization mechanism through ionic liquid formation, and optimized process conditions.

In this work, first, the commercialization feasibility of microwave-assisted sulfur and metal removal from crude oil with D2EHPA was studied by performing a comprehensive techno-economic analysis. The technical and economic performance of the designed process operating in a crude refinery with 50,000 barrel per stream day (BPSD) treatment capacity was explored for the first time. Total CAPEX and OPEX costs were estimated at 6.77 MUSD and 4.23 MUSD (0.24 \$/bbl), respectively, showing economic superiority of the proposed process compared to conventional HDS and HDM techniques. The results of sensitivity analysis of CAPEX & OPEX costs raised the importance of process parameter optimization and developing the kinetic model of

the demetallization reactions. However, in this study, the power requirement of the microwave generators was determined by conducting an energy balance analysis, assuming a complete conversion efficiency of microwave energy into heat. Since the purchase cost of microwave generators has a substantial impact on the capital expenditure (CAPEX) costs, the actual power requirement significantly influences the total CAPEX costs of the process. To mitigate this limitation, an overestimation factor was applied to estimate the required thermal energy, considering a metals temperature increase of 2 °C rather than the estimated 0.1 °C obtained from the energy balance calculations. For future studies, the required microwave power estimation could be improved by modeling and simulation. Additionally, given the significant share of D2EHPA cost in the estimated OPEX costs, an effective methodology to separate and regenerate D2EHPA through saponification with NaOH and stripping with sulfuric acid was developed and experimentally validated. In previous works, researchers have used ethanol to remove unreacted D2EHPA from the treated oil after the reaction step based on the high solubility of D2EHPA in ethanol ^{1, 24}. However, in this work, saponification through acid-base neutralization reaction with NaOH were applied for selective separation of D2EHPA from treated oils and to avoid the risk of unintentional removal of other crude fractions by ethanol and decreasing the oil yield.

Next, the removal of V (vanadium) and Ni (nickel) from Iranian crude oil using D2EHPA was studied under microwave heating. It was observed that the removal efficiencies of Ni and V were negligible at reaction temperatures below 230°C, reaction times below 10 minutes, and D2EHPA dosages less than 5 wt.%. Previous studies by other researchers have reported removal efficiencies of up to 95% for V and 50% for Ni under microwave irradiation at 1000W with 2 wt.% D2EHPA for 3 minutes ¹. In this study, using the optimized operating conditions of 15 wt.% D2EHPA, 1-hour irradiation at 50 W, and a temperature of 250 °C, removal efficiencies of up to 72% for V and

63% for Ni were observed. The disparity in the observed results could be attributed to variations in the microwave power utilized and the corresponding reaction temperature. Unlike other studies where the bulk temperature was not actively monitored during the reaction, this study employed precise temperature measurements using IR and fiber optic sensors. Consequently, it is possible that other studies achieved higher local temperatures of the metals by applying higher power, ranging from 1-3 kW, leading to faster removal of the metals ^{1, 15}. However, the systematic investigation conducted in this study establishes an accurate temperature range of 230-270 °C where the Ni/V removal reactions take place. Furthermore, the kinetics and mechanism of metal removal under microwave irradiation (40-50 W) were investigated under optimized conditions. The findings revealed that the Ni/V removal reactions adhere to a first-order kinetic model, and a proton exchange mechanism between D2EHPA and metalloporphyrins was identified. This mechanism aligns with the proposed mechanism reported in other studies ^{1, 15, 24}. Notably, to the best of our knowledge, no other studies have previously explored the kinetics of microwave-assisted demetallization of crude oil using D2EHPA or any other demetallization reagents. While stoichiometric calculations initially indicated that 1 wt.% D2EHPA would be adequate for successful removal of Ni and V, it was determined that the optimum dosage of D2EHPA was 15 wt.%. This finding suggests the presence of a mass transfer limitation within the mixture, which hinders the efficient interaction of reactants, leading to longer reaction times and lower conversion rates. Consequently, investigating the influence of mixing techniques such as ultrasonication and exploring different mixture matrices using a synthetic model fuel would be of great interest in future studies.

A comprehensive investigation of microwave-assisted desulfurization was carried out on model fuels containing thiophene and crude oil samples from Iran and Basra using D2EHPA and

NaCl aqueous solutions. The experimental setup involved microwave irradiation at 20 W for 20 minutes, with 15 wt.% D2EHPA at a temperature of 65 °C. The results demonstrated sulfur removal efficiencies of up to 64% for model fuels and 36% for Iranian crude oil. Comparatively, the sulfur removal efficiency observed in this study was lower than that reported in other works utilizing D2EHPA for crude oil desulfurization. Attia et al. achieved high sulfur removal efficiencies of up to 99% by applying 2 wt.% D2EHPA and microwave irradiation at 1000W for 3 minutes ¹. It is important to note that their study did not report the reaction mixture temperature. In contrast, this study employed precise temperature measurement and control using IR and fiber optic sensors. In their study, the sample mixture was subjected to temperatures much higher than 65 °C, which could potentially lead to the evaporation of thiophene compounds with boiling points around 84 °C. Additionally, there was a possibility of H₂S formation resulting from the thermal decomposition of organosulfur compounds in the oil due to the formation of hot spots ¹⁶⁸. Also, the sulfur concentration in the raffinate water obtained from the washing step was not reported. Furthermore, the previous study did not investigate the formation of an ionic liquid by D2EHPA during the microwave treatment. However, in this research, we specifically examined the formation of an ionic liquid between D2EHPA and NaCl molecules. This investigation was conducted for the first time, utilizing systematic blank experiments. The resulting ionic liquid was thoroughly characterized using FTIR and electrical conductivity measurements, suggesting the successful ionic liquid synthesis. Additionally, the sulfur content of the raffinate water was measured, providing confirmation of the effective transfer of thiophene compounds from the organic phase to the aqueous phase. These results indicated the extraction of thiophene molecules through π - π interactions with the ionic liquid. However, it is important to note that the observed results are

specific to thiophene compounds and may not be directly applicable to other sulfur compounds present in liquid fuels and crude oils.

The synthesis and application of a novel D2EHPA-based ionic liquid were also evaluated as an innovative and environmentally friendly solvent for extractive desulfurization of crude oils and liquid fuels. The newly synthesized ionic liquid demonstrated efficacy in removing refractory sulfur compounds, including thiophene, benzothiophene, and dibenzothiophene, from model fuels with a S-removal efficiency of up to 63% under optimized conditions. The performance of the ionic liquid was further investigated for extractive desulfurization of real crude oils obtained from Iran and Basra, showing removal efficiencies of up to 57% and 58%, respectively. While previous studies have explored the use of phosphonium-based ionic liquids (PILs) as potential solvents for extractive desulfurization of liquid fuels ^{145, 151, 152}, this study stands out as the first to synthesize a phosphonium-based ionic liquid using D2EHPA specifically for desulfurizing both real crude oils and liquid model fuels through ambient extraction conditions. In future investigations, it would be worthwhile to explore the recyclability and capacity of the synthesized ionic liquid for multi-stage sulfur extraction from diverse crude oils.

Finally, a second techno-economic assessment was carried out to update the preliminary investigation on the commercialization feasibility of the proposed process. The research findings on the optimized reaction conditions and demetallization reaction kinetics were adopted to present a more precise industrial process scheme and economic analysis of the proposed process operating at 50,000 BPSD treatment capacity. The results showed significant increase in CAPEX and OPEX costs from 4.77 MUSD to 42.1 MUSD and 0.23 \$/bbl to 1.31 \$/bbl, respectively, due to the significant increase in the required microwave power and reactor sizing. Despite the significant rise in the estimated CAPEX and OPEX costs, the developed process is still economically

competitive with the conventional demetallization and desulfurization techniques such as HDM and HDS. To estimate the required microwave power, the experimental power density of 0.65 kW per kg of the mixture of crude oil and reagent was adopted in the economic calculations. Further optimization on the required microwave power and mixing conditions seems inevitable to improve the economic performance of the process at large scale operations.

CHAPTER 10 CONCLUSION AND RECOMMENDATIONS

10.1 Conclusion

This work presents an industrial process to remove nickel (Ni), vanadium (V), and sulfur (S) from crude petroleum oil using bis(2-ethylhexyl) phosphoric acid (D2EHPA) and microwave heating technology. In this research, our understanding of commercialization & scale-up feasibility, process economics, demetallization kinetics & mechanism, desulfurization mechanism, and optimized reaction conditions are significantly improved. Additionally, a novel phosphonium-based ionic liquid (IL) was synthesized for extractive desulfurization (EDS) of liquid fuels and crude oil.

Firstly, a comprehensive techno-economic analysis was conducted to evaluate the technical and economic performance of this technique at large industrial scale, aiming to identify the primary challenges that require further investigation at lab scale to ensure a successful process scale-up. To achieve this, an industrial process scheme was developed to treat 50,000 barrel per stream day (BPSD) crude oil and simulated in Aspen Plus. Total capital costs (CAPEX) and annual operating costs (OPEX) were estimated to be 6.77 MUSD and 4.23 MUSD (0.24 \$/barrel), respectively, indicating the economic superiority of the developed process over conventional hydrotreating techniques. Furthermore, an effective methodology to separate and regenerate D2EHPA using sulfuric acid and sodium hydroxide (NaOH) solutions was developed and experimentally validated by FTIR & ICP-OES analyses. The sensitivity analysis of the process economics highlighted the significance of developing a precise kinetic model for demetallization reactions and optimizing key process parameters such as D2EHPA:oil mass ratio, reaction temperature, and residence time.

Secondly, a systematic investigation was conducted to evaluate the impact of primary process parameters on the removal efficiencies of Ni and V under microwave heating irradiation. It was

determined that the optimized values of the process parameters were 15 wt.% D2EHPA, a reaction time of 1 hour under microwave irradiation of 50W, and a reaction temperature of 250 °C. The concentration of metals in the raw oil, treated oil, and raffinate water was measured by neutron activation analysis (NAA), enabling the calculation of the removal efficiency for each metal. Under the optimized experimental conditions, V and Ni were removed up to 72% and 63% from Iranian crude oil, respectively. FTIR spectroscopy was utilized to investigate the mechanism of Ni/V removal reactions. The FTIR results revealed the formation of new nitrogen-hydrogen (N-H) bonds in the treated oil following the microwave-assisted reaction. This observation suggested that the existing nitrogen-metal (N-M) bonds in Ni/V porphyrins may have been replaced by the donated proton from D2EHPA, leading to the formation of new N-H bonds. The understanding of the reaction mechanism, along with the optimization of the reaction conditions, allowed the development of kinetic model for microwave-assisted Ni/V removal. Based on the experimental findings, it was observed that the Ni/V removal reactions occurred within a temperature range of 230 °C to 250 °C. The first-order kinetics was determined to be the best fitting model, and the primary kinetic parameters, including reaction rates, activation energies, and pre-exponential factors, were determined to further characterize the reaction kinetics.

Thirdly, the removal of sulfur (S) from crude oil and liquid fuels using D2EHPA, NaCl aqueous solutions, and microwave heating was investigated. The Experimental study included the use of two different crude oil samples from Iran and Basra, as well as synthetic model fuels containing thiophene sulfur compounds. The effects of reaction temperature, reaction time, and D2EHPA dosage on the S-removal efficiency from model fuels were examined. The results showed that under optimized conditions of 20 minutes of microwave irradiation at 65 °C, with 15 wt.% D2EHPA and 50 wt.% NaCl solution, S removal efficiencies of up to 64% and 36% were achieved

for model fuels and Iranian crude oil, respectively. The desulfurization mechanism was further investigated by performing blank experiments to explore an ionic liquid formation between D2EHPA and NaCl molecules during microwave irradiation. FTIR and electrical conductivity measurements suggested the successful formation of a water-soluble ionic liquid between D2EHPA and NaCl through microwave irradiation. This ionic liquid was found to facilitate the extraction of thiophene compounds from model fuels through π - π interaction. These findings contribute to the understanding of the desulfurization mechanism and demonstrate the potential of microwave-assisted extraction using D2EHPA and NaCl as a promising approach for sulfur removal in liquid fuels.

Next, a phosphonium-based ionic liquid named trihexyl tetradecyl phosphonium bis(2-ethylhexyl) phosphate [THTDP][D2EHP] was synthesized, and its effectiveness in extractive desulfurization of crude oils and model fuels containing thiophene (TS), benzothiophene (BT), and dibenzothiophene (DBT) compounds was evaluated. S-extraction from model fuels was conducted at various reaction time, reaction temperature, and IL:fuel mass ratios. Promising results were obtained, with up to 63% for DBT-based model fuels and 57% for Iranian crude oil. A comprehensive investigation of [THTDP][D2EHP] was carried out through various characterization tests including FTIR, TGA, electrical conductivity, viscosity, and solubility. The synthesized ionic liquid exhibited favorable properties such as high thermal stability, low viscosity, and good electrical conductivity, and demonstrated potential in extractive desulfurization of liquid fuels and more importantly, real crude oils.

Finally, a second techno-economic assessment was conducted to update the initial investigation regarding the feasibility of commercializing the proposed process. The assessment incorporated research findings on optimized reaction conditions and demetallization reaction

kinetics. These findings were used to present a more accurate industrial process design and economic analysis for the proposed process, considering a treatment capacity of 50,000 barrels per stream day (BPSD). The results indicated a significant increase in both capital expenditure (CAPEX) and operational expenditure (OPEX) costs. Specifically, the costs rose from 4.77 million USD to 42.1 million USD for CAPEX, and from 0.23 USD per barrel (bbl) to 1.31 USD/bbl for OPEX. This increase was primarily due to the higher microwave power and larger reactor size required for the process. Despite the substantial cost increase, the developed process remains economically competitive when compared to conventional demetallization and desulfurization techniques such as HDM and HDS. To estimate the necessary microwave power, the economic calculations utilized an experimental power density of 0.65 kilowatts per kilogram (kW/kg) for the crude oil and reagent mixture. However, further optimization of the microwave power and mixing conditions is essential to enhance the economic performance of the process on a larger scale.

10.2 Recommendations

In future studies, there is a room to address the following recommendations based on the findings of this work:

- ❖ Develop a more precise approach to estimate the required microwave power using modeling and experimental data. This would aid in better understanding the energy requirements and optimizing the process economics.
- ❖ Study the effect of chemical matrix and enhanced mixing methods such as ultrasonication to address the mass transfer limitation observed during the demetallization reaction
- ❖ It would be interesting to investigate the decomposition temperature of vanadium and nickel porphyrins to improve the thermal design of the process.

- ❖ Further investigation on demetallization and desulfurization mechanisms by other analytical techniques such as UV-vis and NMR spectroscopy would be complementary to this work. This would provide additional insights into the reaction pathways and help refine the understanding of the underlying mechanisms.
- ❖ Explore the recyclability, environmental impact, and cost-effectiveness of the novel synthesized ionic liquid developed in this study for extractive desulfurization of various crude oils at large-scale operations. This would provide valuable information regarding the practical application and feasibility of the synthesized ionic liquid on an industrial scale.

By addressing these recommendations, future studies can enhance the overall understanding, efficiency, and applicability of the proposed processes, leading to more sustainable and cost-effective approaches for microwave-assisted metal and sulfur removal processes in the petroleum industry.

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