

Investigation of Heavy and Unconventional Oil Upgrading Using High Density Water

By

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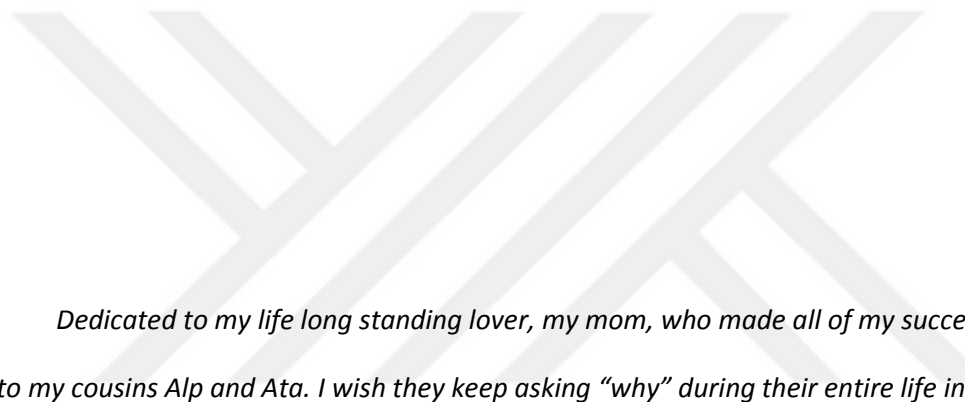
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*Dedicated to my life long standing lover, my mom, who made all of my success stories possible;
and to my cousins Alp and Ata. I wish they keep asking “why” during their entire life in order to progress.*

ABSTRACT

Upgrading of different types of bitumen, refinery side streams, heavy oils extracted from tar sand samples, and bitumen blended with microalgae *Chlorella vulgaris* was investigated in supercritical water (SCW) at 440 °C and 30 MPa in a home-made batch type bomb reactor. The effects of microalgae fraction in the feeds ranging from 0 (pure bitumen) to 100 wt. % (pure microalgae) and the effects of the water/feed ratio ranging from 2 to 10 were investigated. The effects of catalytic additives, reaction time and feed chemistry were studied. Five lumps kinetic model was derived. As a reference analysis, pyrolysis experiments in the absence of water were performed under the same reaction conditions. As for the results of microalgae upgrading, SCW was found to suppress the coke formation. 25 wt. % microalgae addition to bitumen increased VR conversion 20% with a considerable increase in gas content and diesel yield. Increasing microalgae fraction in the feed to 50 wt. % resulted in increased light liquid yields due to increasing conversion of VR and also led to undesired increases in coke and gas formation. Water/feed ratio of 10 led to increased gas yields with a lower VR conversion. As for the results of upgrading of varying heavy oil feeds, the tendency of coke suppression by SCW was found to be higher for tar sand feeds compared to bitumen samples. Low vacuum residue (VR) together with high amounts of lighter ends in the feed were shown to decrease the coke yields even if there are high amount of asphaltenes. Long reaction times resulted in similar yields and selectivities for different feeds. Use of iron containing red mud samples as an entrainer left hexagonal shaped column like deposits over the surface of the coke samples. The effect of sulfided forms of iron additives was shown to largely depend on reaction time. Tar sands were shown to be the optimum heavy oil resource for the upgrading studies performed in the presence of SCW for 40 minutes under the reaction conditions of this study.

ÖZET

Bu çalışmada 30 MPa basınç ve 440 °C sıcaklık altında, kapalı kap kesikli reaktörü içerisinde, süperkritik su (SKS) ortamında, dönüşüm reaksiyonları gerçekleştirilmiştir. Kullanılan reaksiyon şarjları şunlardır; rafinerilerden alınan farklı tip ve menşede bitümler, rafineri yan akımları, yerli katranlı kum (“tar sand” ya da diğer adı ile “oil sand”) örneklerinden ekstrakte edilmiş ağır yağlar ve *Chlorella vulgaris* olarak adlandırılan mikroalg tipinin bitüm ile olan fiziksel karışımları. Kullanılan şarj içerisindeki mikroalgin kütlece bulunma yüzdeleri %0 ‘dan (sadece mikroalg) %100’e (sadece bitüm) kadar çalışılmış, suyun toplam şarja olan etkisi ise su/şarj oranının 2’den 10’a çıkarılması ile tayin edilmiştir. Katalizör kullanımının, reaksiyon süresinin ve şarj kimyasının etkileri de çalışma kapsamına dahil edilmiştir. 5 alt gruptan oluşan kimetik model tasarımı gerçekleştirilmiştir. Gerçekleştirilen çalışmalardan elde edilen bulgulara referans olması sebebi ile, su eklenmeden, aynı deney şartlarında, piroliz reaksiyonları da gerçekleştirilmiştir. Mikroalg dönüşüm reaksiyonlarından elde edilen bulgular ile ilgili olarak, SKS’nin kok oluşumunu baskıladığı görülmüştür. Bitüm üzerine kütlece 25% mikroalg eklentisinin, vakum rezid (VR) dönüşümünü 20% arttırdığı, gaz ve dizel oluşumunda da ciddi artışlara sebep olduğu bulunmuştur. Mikroalg miktarının 50%’ye çıkarılmasının coke ve gaz oluşumlarında istenmeyen artışlara sebep verdiği, VR dönüşümü ve toplam sıvı ürün miktarını ise arttırdığı belirlenmiştir. Su/şarj oranının 10’a çıkarılması, artan bir gaz dönüşümü ve daha düşük VR dönüşümüne sebep vermiştir. Farklı ağır yağ tiplerinin dönüşüm reaksiyonlarının sonuçları ile ilgili olarak, SKS’nin ağır yağların dönüşümünde ortaya çıkan ve istenmeyen kok ürünlerinin oluşumunu baskılama kabiliyetinin bitüm ile yapılan çalışmalara göre, katranlı kum ile yapılan çalışmalarda daha yüksek olduğu görülmüştür. Şarj içinde, dönüşüm reaksiyonları öncesinde, kok oluşturma eğiliminin fazla olması beklenen asfaltenlerin miktarı yüksek de olsa, başlangıçtaki

düşük VR ve yüksek ince uçlu hidrokarbon ihtivasının, reaksiyon sonrasında daha düşük kok oluşumuna sebep olduğu görülmüştür. Başlangıçta şarj içindeki görece ince hidrokarbonların, mevcut ve reaksiyon esnasında oluşan asfalten yapılarının çözünürlüğünü arttırması ve polimerizasyon ve kondensasyon reaksiyonlarını önlemesinin kok oluşumunu azalttığı söylenebilir. Artan reaksiyon sürelerinin, farklı içerikteki şarjlarda benzer dönüşüm ve ürün dağılımı değerlerine sebep olduğu görülmüştür. Demir içeren kırmızı çamur örneklerinin katalizör olarak kullanıldığı çalışmalarda, kok örnekleri üzerinde, altıgen şeklinde kolon oluşumları gözlenmiştir. Demir içeren katalizörlerin sülfürlü bileşiklerinin etkilerinin ağırlıkla dönüşüm reaksiyonlarının süresine bağlı olduğu görülmüştür. Bu çalışmadaki deneysel şartlar altında, katranlı kum içinden çıkarılan ağır yağlar ile 40 dakikalık sürede yapılan çalışma en optimum olarak belirlenmiştir.

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Chapter 1

1. INTRODUCTION

The global energy consumption is rising rapidly with an estimated increase of 28% from 2015 to 2040, according to the U.S. Energy Information Administration's International Energy Outlook 2017 Report [1]. As for the breakdown analysis for this need, legislations and the state of the art technologies are shifting from heavy towards the light end fuels accompanied by a sharp decrease in the amount of available light crude oil resources [2]. Bitumen and heavy oil resources are estimated to be 5.6 trillion barrels whereas the amount of conventional crude oil reserves are 1 trillion barrels [3]. Although there is an increasing need on the demand side, the diversity of energy resources is still limited on the supply side. Fossil fuels for example are expected to make up about 77% of the energy mix by 2040 [1]. As for the cost of these conventional and light crude reservoirs, Brent crude oil prices, for example, have fluctuated in a wide range of 40 to 150 \$/barrel with sharp drops and escalations since 2008 [4]. Therefore, the continuity of this supply-demand relation is clearly open to debate and when combined with the volatile and unpredictable oil prices, energy policy makers & industry are forced to focus on both alternative energy conversion technologies and sustainable feedstocks for energy security.

Regarding the alternative energy resources, in addition to the heavy oils, the energy supplied from biobased resources is expected to increase and 27 % of transportation fuel could be provided by biofuels by 2050 [5]. Current regulations on greenhouse gas emissions require blending of fossil fuels with biofuels such as bioethanol or biodiesel produced from renewable sources such as sugar cane, corn and various vegetable oils [6]. However, using such edible feedstocks for biofuel production has raised a lot of concerns about food security and arable land

conservation [7]. Moreover, it has even been suggested that corn-based ethanol will increase greenhouse gas emissions due to converting forests and grassland into biofuel factories and thus eliminating positive contribution of these lands to carbon dioxide fixation [8]. Microalgae based biofuels, on the other hand, have potential to overcome these concerns. Microalgae which are unicellular, phototrophic microorganisms can be cultivated in saline and waste water, on non-arable land without competing with agricultural crops [9]. Therefore, it may be advantageous to blend biodiesel produced from oil extracted from microalgae or bioethanol produced by fermentation of microalgae with fossil fuels. An alternative would be to use microalgae directly as a refinery feedstock in the conventional refineries. Microalgae can be directly processed together with conventional hydrocarbon feedstocks in existing refineries resulting in fuels, a fraction of which is derived from biomass. Moreover, the components of microalgae such as proteins and carbohydrates can also be converted into useful fuels with improved yields [10]. However, direct utilization of microalgae feedstocks in the existing refinery operations is problematic due to high oxygen, nitrogen and sulfur content of microalgae. Undesired gum formation may occur due to high oxygen content of microalgae whereas high nitrogen and sulfur content of microalgae may lead to the deactivation of the catalyst in hydrocracking unit (HYCU) by exceeding the allowable nitrogen and sulfur limit in the feedstock of HYCU [11]. Therefore, innovative schemes are required for processing of microalgae in refineries.

In addition to the conventional but heavy oil resources and sustainable biobased resources, the utilization of the unconventional oil resources is of paramount importance as well. Oil sand, for example, is an unconventional oil resource and it corresponds to a significant proportion of the world's known oil reserves. Oil sand is also known as tar sand and is a mixture of heavy hydrocarbons, mainly bitumen, sand, clay and water. Their largest reservoirs are in Canada and

Venezuela. When combined, they have oil sand reserves that are estimated to be almost equal to the world's total reserves of conventional crude oil.

Therefore, alternative heavy/unconventional/ sustainable oil upgrading processes with low or no hydrogen consumption, improved heteroatom removal, increased conversion, suppressed coke formation, the capability of using different feeds with varying origins & properties together with the predictive models relating the properties of the required feedstocks to the desired products need to be developed.

There is no detailed study in the literature dedicated to the understanding of the effect of using different feeds with varying properties on the yield and selectivity of the upgrading reactions achieved in SCH_2O environment. Heavy oils such as bitumen are approximately composed of 10,000 molecules and they can be classified by several techniques where the most general one is the SARA fractionation (4 different sub-fractions of Saturate-Aromatics-Resins-Asphaltene). Not surprisingly, the reactivity of each sub-fraction of those heavy oils differs and they even have to be classified / lumped into further smaller groups for a better analysis by NMR, GC-MS, GC-Simdis (for TBP analysis) etc.

During the course of this Ph.D. study, the first literature review in its field, which was about the heavy oil upgrading studies achieved in SCH_2O environment, was published and given in Chapter 2 [12]. This chapter is organized into four sections. The current situation and corresponding demands in petroleum refining market with the main focus on the available feedstocks and projected demands of the refining products are discussed in the first section. A

summary of the studies in the literature on extraction, fractionation and reactions of hydrocarbons carried out in SCH_2O environment are given in the second section. The thermodynamics and kinetics of reactions of SCH_2O -hydrocarbon systems are discussed in the third section. The theoretical models for phase behavior and reaction mechanisms which are required to design such large scale processes are also provided. Finally, a discussion is given for prospective areas which need further investigation in order to be able to develop and successfully design and implement these processes.

Chapter 3 summarizes the methods for the characterization of the chemicals used in this study, the techniques developed for feed preparations, the details of the upgrading reactions, the procedures for product sampling and product analysis.

The results of the studies are given in Chapter 4 under two main topics. Firstly, the results of the reactions of the blends of microalgae and heavy oil upgrading are given in Section 4.1. This section is also a summary of the first published paper in its field that is about the blending microalgae and heavy oils for SCH_2O assisted upgrading reactions [13]. In this study, upgrading of mixtures of microalgae, *Chlorella vulgaris*, with bitumen in SCW was investigated at 440 °C and 30 MPa with water/feed ratios ranging from 2 to 10. Operating conditions were selected by considering optimum conditions for bitumen upgrading. Selected temperature was also close to optimum temperature (430 °C) determined for upgrading of algal oil with SCW with a product having lower oxygen, nitrogen and sulfur content as well as higher heating value[14]. Pyrolysis of pure bitumen and pure microalgae were also studied in the absence of supercritical water for comparison purposes. Morphological analysis of coke samples obtained after upgrading were

performed by SEM-EDX analysis to compare conventional and SCW upgrading in terms of type of coke formation.

Secondly, different heavy oils together with an unconventional oil resource, namely domestic tar sand samples from Turkey are upgraded and the corresponding results are given in Section 4.2. This study has focusses on three different objectives. The first objective of this study is to investigate the effects of different feed stocks on heavy oil upgrading in the presence of SCW. In addition to that, there are studies involving steam cracking of vacuum residue in the presence of red mud, which is a good indication that red mud has potential to be used as a catalyst for heavy oil upgrading purposes. Therefore, red mud should be a good catalyst for heavy oil upgrading in the presence of SCW. Consequently, the second objective of this study is to comparatively investigate the catalytic activity of various additives including red mud in the presence of SCW. Lastly, the third objective of this study is to develop a kinetic model based on the boiling point distribution of the products from different feed stocks.

Conclusions based on the findings of these studies are given in Chapter 5.

Chapter 2

2. LITERATURE REVIEW

2.1. INTRODUCTION

2.1.1. Current Situation and Demand in the Oil Refining Market

According to the International Energy Agency (EIA), approximately 8 trillion dollars will be spent by 2040 in order to develop new oil fields to meet the increasing energy demand in our world. This demand will partially be met by heavy oil and bitumen resources worldwide which are estimated to be approximately 6 trillion barrels [15]. However, this will create problems since there is a push to decrease heavy hydrocarbon usage with an increasing demand for light oils having low sulfur levels because of environmental concerns. As can be seen in Figure 1, fuel oil use is expected to exhibit a gradual decrease while diesel will obtain a higher share among the refining products market in the near future. Moreover, increasing sulfur levels and processing of sulfur-rich heavy oils brings serious problems on product quality and new challenges on processing conditions [16]. Therefore, developing solutions for the upgrading of heavy oil resources such as bitumen, tar sand, oil shale, residual oil and coal tar having high sulfur contents are becoming more important for the refineries to increase their profit, to meet the changing market demands and to fulfill the increasingly stringent environmental regulations.

State of the art technologies for heavy oil upgrading are based on improving the H/C ratio by either increasing the hydrogen amount or decreasing the carbon amount in the oil. Therefore, current upgrading technologies are classified into two groups as ‘hydrogen addition’ and ‘carbon rejection’ (See Table 1). Some more details for the commercially available upgrading technologies utilizing different catalyst types, various feedstock and processing conditions are given in Figure 2. The distillation process (atmospheric and / or vacuum distillation depending on

the feedstock and processing conditions) is the first step for the heavy oil upgrading. The bottom products from the distillation processes and in some cases their blends with the unprocessed heavy oil are subjected to further treatments by either adding hydrogen or removal of carbon to increase the H/C ratio and thereby to increase the fraction of lighter compounds. Moreover, the products obtained both from the distillation column and from other upgrading processes cannot be used directly for commercial purposes. The heavy trace metals and especially sulfur compounds in the crude oil tend to accumulate in the heavy bottom products which are the feedstock of upgrading processes. Therefore, secondary processes such as hydrotreating are needed to meet environmental regulations before delivering the products to the market. More details can be found in a comprehensive review published elsewhere [17].

Current technologies used for hydrogen addition and carbon rejection have their own drawbacks. For example, in hydroprocessing / hydroconversion technologies, the expensive catalysts can be easily deactivated by coke and metal depositions necessitating the use of expensive catalyst regeneration or renewal schemes. Moreover, hydroconversion processes consume huge amounts of hydrogen and hydrogen production units are one of the most costly operations of the refineries. As an alternative, catalytic hydrogen addition processes can be replaced by non-catalytic carbon rejection which would result in decreased liquid product yield together with a large amount of coke formation whose economic value is comparatively not as attractive as the lighter oils such as gasoline and diesel [16, 18, 19]. Therefore, alternative heavy oil upgrading processes with low or no hydrogen consumption, improved heteroatom removal, increased conversion (i.e. higher light liquid oil yield) and suppressed coke formations need to be developed. Utilization of supercritical

water (SCH_2O) in upgrading technologies may eliminate the need to use expensive catalysts or externally added vast amount of hydrogen.

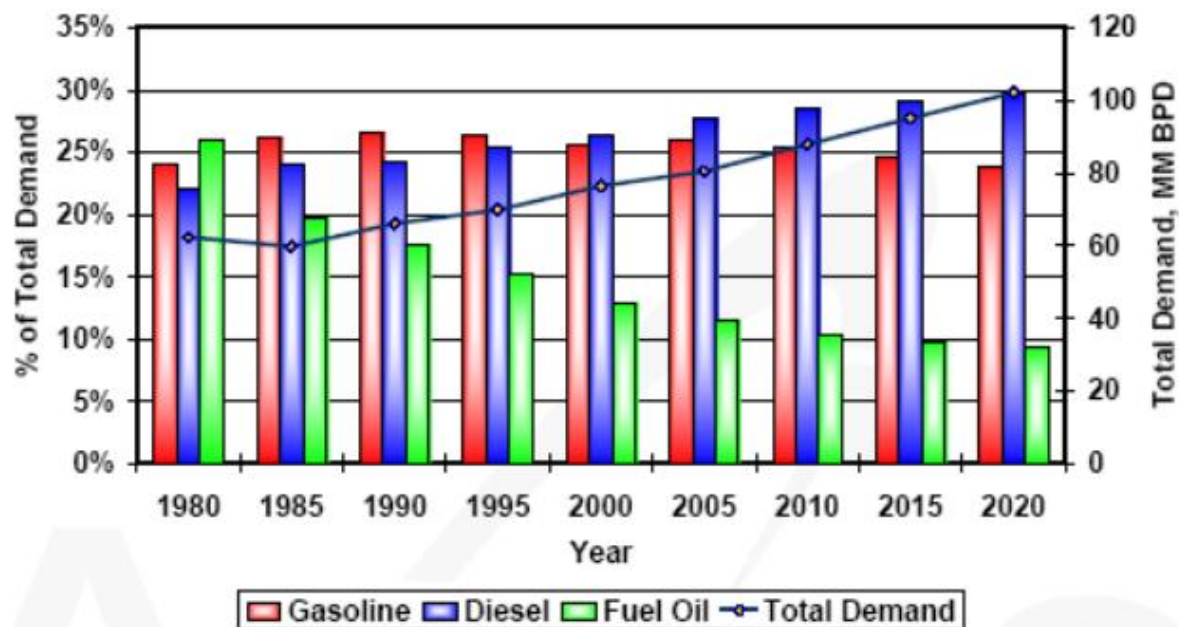


Figure 1: Global Market Demand for Refining Products, *taken from* [20].

Table 1: General Classification of Technologies for Upgrading of Heavy Petroleum Feeds, *taken from* [19]

	Carbon Rejection	Hydrogen Addition
Noncatalytic	Solvent deasphalting Coking Visbreaking	Hydrovisbreaking
Catalytic	Catalytic cracking of residue	Hydrotreating Hydrocracking

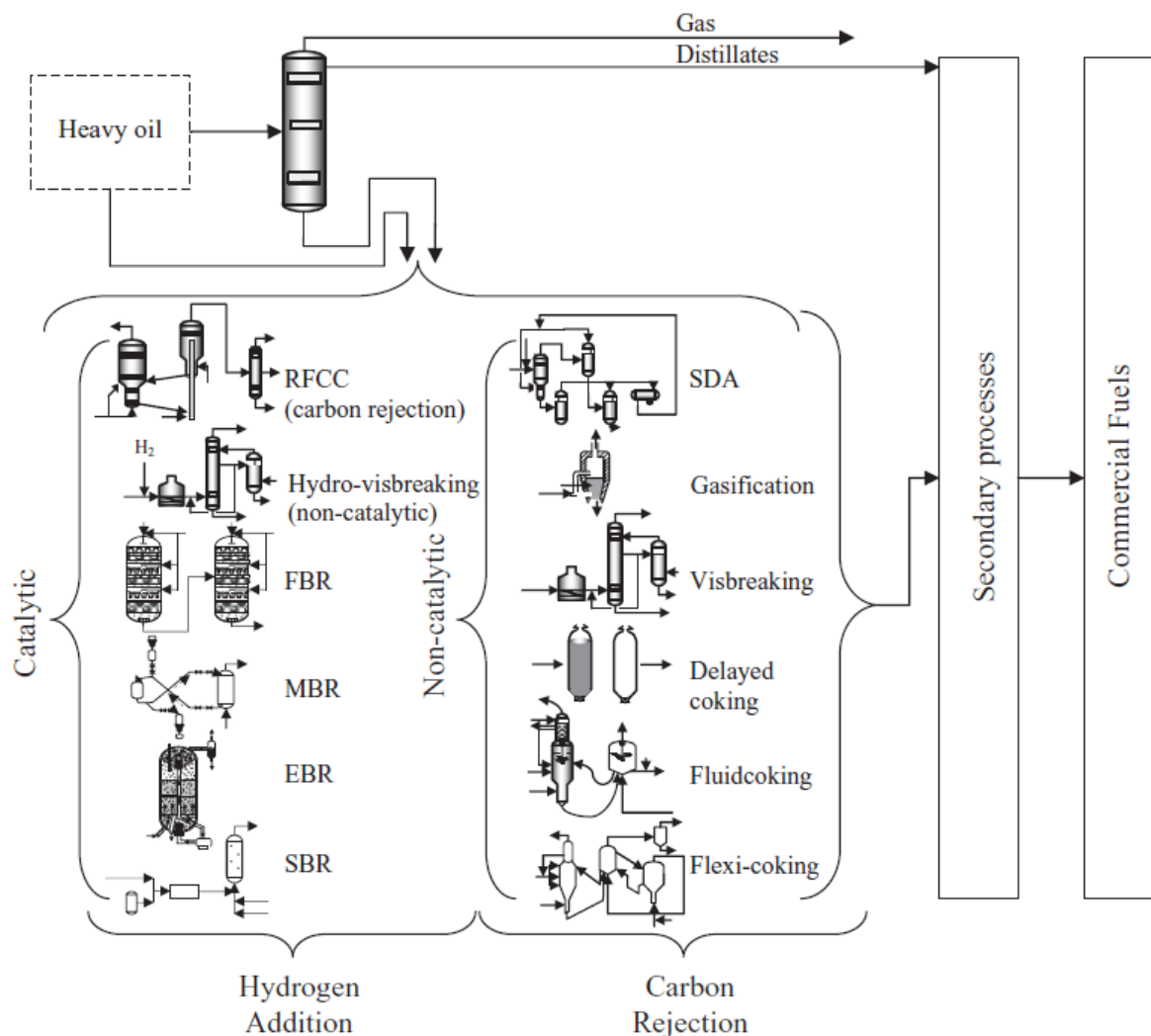


Figure 2: Process alternatives for upgrading of heavy oils, *taken from* [19]

2.1.2. SCF for Green Processes: An Alternative for Heavy Oil Upgrading

Due to a need to develop and implement green processes, new alternatives are emerging to replace the conventional, expensive and toxic chemicals in industry by environmental friendly solvents such as supercritical fluids (SCFs). When the temperature and the pressure of the fluid is above its critical values, it is called a SCF and critical properties of some selected fluids are listed in Table 2.

During the past few decades, SCFs have been under investigation for a wide variety of applications such as extraction of natural products, synthesis of nanostructured materials, as a solvent for a wide variety of chemical reactions [21-27]. SCFs are advantageous since:

1. They combine the properties of liquids and gases such as gas like viscosity and liquid like density. Typical ranges for the density, viscosity, and diffusivity of SCFs as compared to those of liquids and gases are given in Table 3.
2. They are capable of dissolving solutes like a liquid.
3. They exhibit almost no surface tension which can be beneficial for efficient removal from very small pores that are normally inaccessible by conventional techniques.
4. The reaction kinetics may be faster in SCFs.
5. Mass transfer can be faster in SCFs since the diffusivity of the compounds in SCFs is higher than in conventional solvents.
6. Their densities are sensitive to the changes in temperature and pressure which makes it possible to manipulate the solvent properties during processing. This may enable one to separate the products by changes in temperature and pressure.
7. Gases are soluble in SCFs which enables one to obtain high concentrations of gaseous species in the fluid phase which may lead to an increase in reaction rates involving gaseous reactants.

As a result of such favorable properties, SCFs have been investigated for upgrading heavy oils.

Among several types of SCFs, SCH_2O whose phase diagram is given in Figure 3 with $T_c=647.3$ K and $P_c=22.1\text{MPa}$ [28] is particularly attractive both as a reaction medium and as a reacting species (hydrogen donor). It can dissolve light hydrocarbons, aromatics and light gases [29-32].

High reactivity, increased light liquid oil yield, and coke suppression are other advantages of

heavy oil upgrading by SCH_2O [33-37]. These improvements can be attributed to some changes in the physicochemical properties of water when heated and pressurized above its critical temperature and pressure. For example, the ionic product of water (K_w), hydronium ion concentration $[\text{H}_3\text{O}^+]$ and the extent of hydrogen bonding change and SCH_2O becomes a non-polar solvent. Table 4 lists some of those properties of water under varying temperature and pressure ranges.

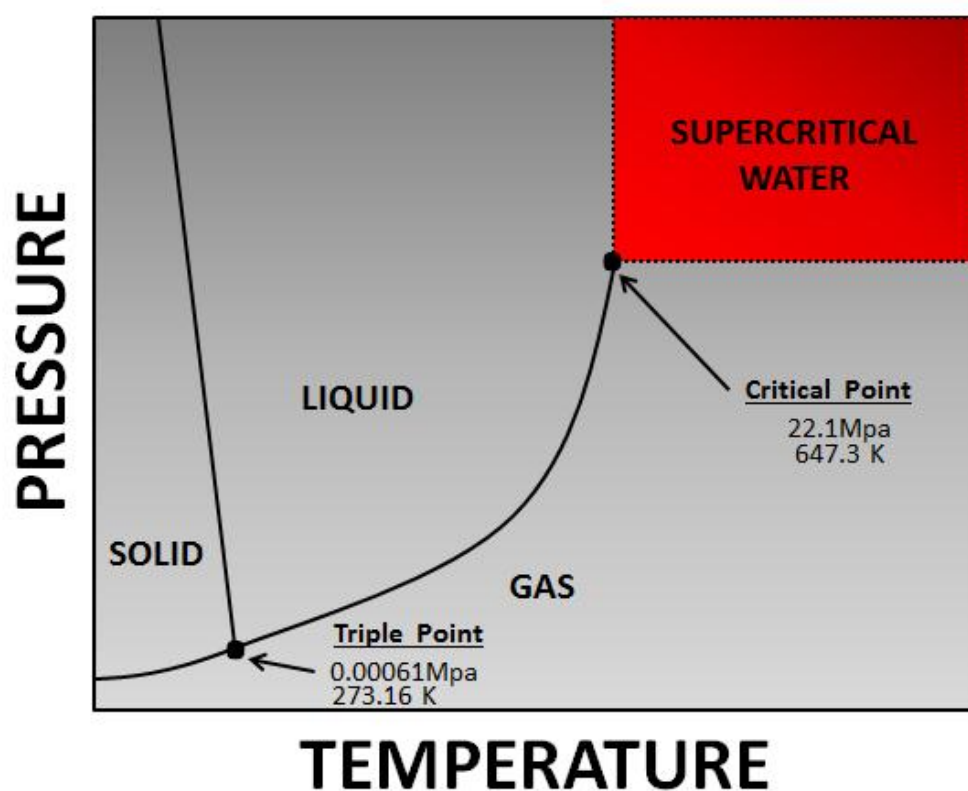


Figure 3: Phase diagram as a function of the pressure and temperature of water.

2.1.2.1. Pseudo Acidic Behaviour of Sub- and SCH₂O for Reactive Extraction

It was reported in the literature that although being neutral, sub- or SCH₂O behave like an acid or base catalyst depending on conditions which makes it advantageous to carry out several reactions in sub- and SCH₂O environment without using acid or base catalysts [22, 38-40]. Lu et al., for example, proposed that increased hydronium ion concentration makes subcritical water “a neutral” acid catalysts for the hydrolysis of nitroaromatic compounds in the absence of acid addition [41]. As shown in Figure 4, these can be attributed to the sharp changes in the ionic product of water (K_w) when water is approached to the supercritical region [42]. An increased K_w (i.e. decreased pK_w) value helps the concentration of both hydronium and hydroxide ions to increase as compared to the values at standard conditions which opens a possibility to carry out the acid/base-catalyzed reactions in SCH₂O environment.

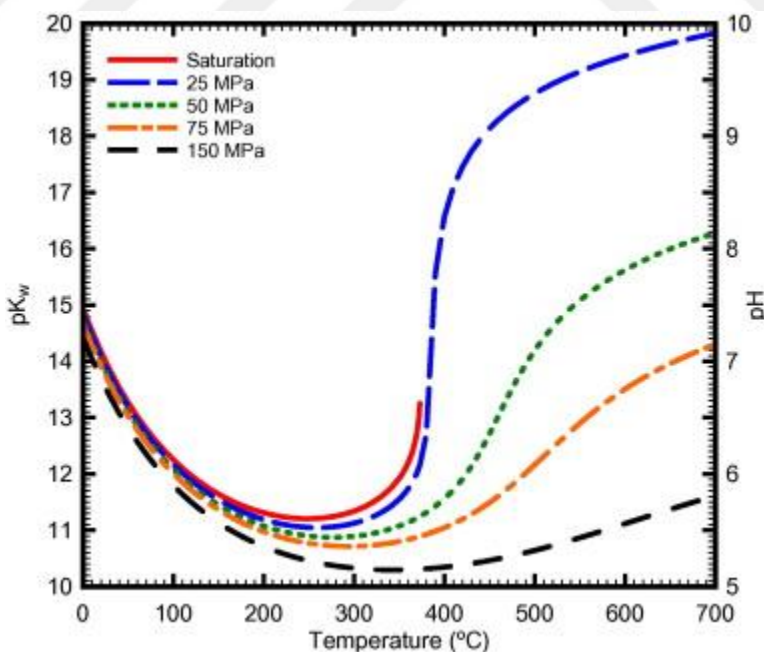


Figure 4: Ionic product and pH of neutral water, *taken from* [43, 44].

For instance, the K_w value is 10^{-11} at 573 K and 34,5 MPa as compared to the value of 10^{-14} at standard conditions which gives $[H_3O^+]$ value of 3×10^{-7} and a pH value of 6.52. The pH reaches 8 at the critical point [45].

Anikeev et al. [38] were able to demonstrate the effect of the density on the hydronium ion concentration and thus on the mechanism of the acid-catalyzed 2-propanol dehydration reaction at 666 K. They proved that the apparent rate constants are affected by the density via the high sensitivity of the $[H_3O^+]$ concentration to the solvent density.

2.1.2.2. Solvation Power of SCH₂O

Solubility in SCH₂O is another important property when the reactive extraction of hydrocarbons is of concern. Indeed, the solubility and thereby the extraction behavior of SCH₂O in heavy oil upgrading applications can be correlated with the dielectric constant (DC) and hansen solubility parameters (HSP). The DC is known to be the measure of the polarity. It decreases with increasing temperature at constant density which can be attributed to the disruption of the hydrogen bonding network of water [24]. The DC of water at 298 K and 0.1 MPa for instance is 78 while that of SCH₂O at 713 K ranges from 1.45 to 3.15 in the pressure range 20–35 MPa [46, 47]. Figure 5 illustrates the decrease in the DC with decreasing water density throughout the supercritical region. As a result, water changes gradually from a polar liquid to a non-polar fluid and becomes a good solvent for organic compounds such as hydrocarbons. This is illustrated in Figures 6 and 7. Figure 6 shows that the solubility of NaCl decreases drastically as the critical point of water is approached. Even though it is very soluble in liquid water at ambient conditions, the solubility of NaCl is around 0.1g/L at 25 MPa in SCH₂O. Figure 7, on the other hand,

illustrates that when hydrocarbons such as cyclohexane are contacted with water at high temperatures and pressures, phase boundaries start to disappear as the temperature approaches the critical temperature and above the critical temperature, cyclohexane and water mixture at this composition become miscible indicating the decreased polarity of SCH₂O [28].

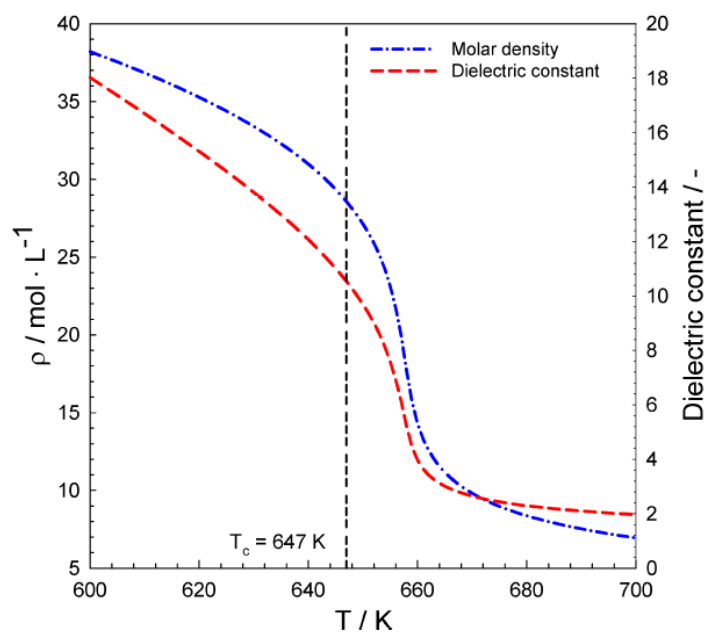


Figure 5: The dielectric constant of water at 25 MPa, *taken from* [48].

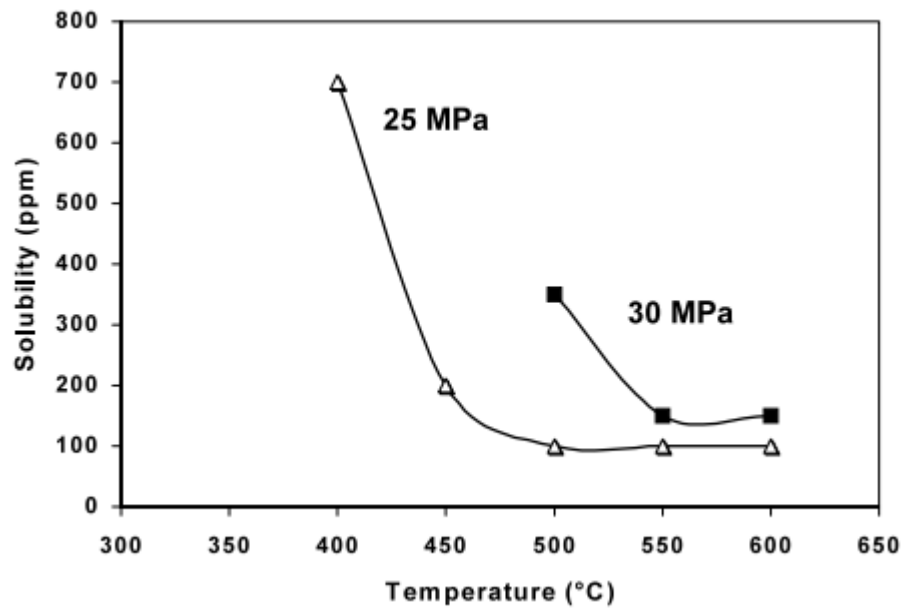


Figure 6: Solubility of NaCl in water with varying temperatures at different pressures, *taken from* [49]

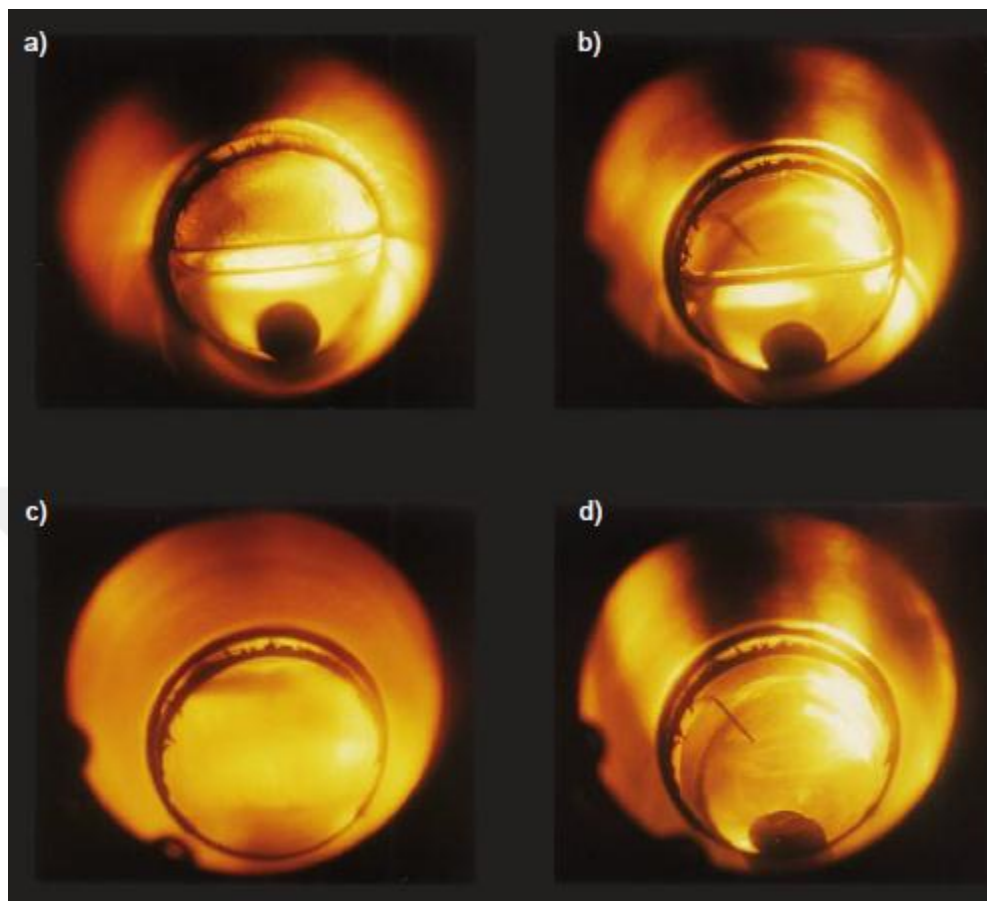


Figure 7: The disappearance of phase boundaries in the water/cyclohexane system (80/20 wt %): a) 298 K, b) 523 K, c) at the critical point, d) above the critical point *taken from* [28].

HSP which is the square root of the cohesive energy density ($\text{MPa}^{0.5}$) of a solvent can also be used to account for the solubility behaviour. HSP is composed of terms representing dispersive forces δ_D , polar interactions δ_p , and hydrogen bonding. It was reported that increasing HSP value caused by an increase in pressure do not favor high extraction yields in heavy oil upgrading [31, 50]. Morimoto et al. [46] conducted a comprehensive study and proposed a methodology to determine the optimum upgrading conditions of the complex systems based on HSP values.

Table 2: Critical Temperature and Pressure Values For Some Selected Fluids, *taken from* [21, 51]

Fluid	$T_c(K)$	$P_c(MPa)$
Ethylene	282.4	5.04
Xenon	289.7	5.84
Trifluoromethane	299.1	4.87
Carbon dioxide	304.2	7.37
Ethane	305.4	4.88
Nitrous oxide	309.6	7.24
Sulfur hexafluoride	318.7	3.76
Propane	369.8	4.25
1,1-Difluoroethane	386.6	4.50
Ammonia	405.6	11.3
Water	647.3	22.1
Tetralin	719.0	3.52

Table 3: Comparison of Typical SCF, Liquid, and Gas Properties, *taken from* [21]

	Liquid	SCF	Gas
Density (g/cm^3)	1	0.1-0.7	10^{-3}
Viscosity (Pa.s)	10^{-3}	$10^{-4} - 10^{-5}$	10^{-5}
Diffusivity (cm^2/s)	10^{-5}	10^{-3}	10^{-1}

Table 4: Properties of water under different conditions *taken from* [28]

Fluid	<u>Ordinary Water</u>	<u>Subcritical Water</u>	<u>Supercritical water</u>		Superheated Steam
Temperature $T(^{\circ}C)$	25	250	400	400	400
Pressure p (MPa)	0.1	5	25	50	0.1

Density ρ (g/cm ³)	0.997	0.80	0.17	0.58	0.0003
Dielectric constant ϵ	78.5	27.1	5.9	10.5	≈ 1
pK_w	14.0	11.2	19.4	11.9	/
Heat capacity c_p (kJ/kg.K)	4.22	4.86	13.0	6.8	2.1
Dynamic viscosity μ (mPa.s)	0.89	0.11	0.03	0.07	0.02
Heat conductivity λ (mW/m.K)	608	620	160	438	55

2.2. EXTRACTIONS, FRACTIONATION AND REACTIONS OF HYDROCARBONS IN SCH₂O ENVIRONMENT

2.2.1. Extraction and Fractionation of Hydrocarbons

Supercritical fluid extraction and fractionation (SFEF) can be used to extract desired or undesired components from various media followed by fractionation of the extract by changes in pressure and/or temperature. [52-55]. The state of the art process for deasphalting technology in the oil refining industry, for instance, is the Residuum Oil Supercritical Extraction (ROSE) process which is used to remove valuable deasphalted oil (DAO) out of several feedstocks such as atmospheric or vacuum residues by using light and paraffinic solvents such as propane. The ROSE process demonstrates that SCF based processes can be more economical and energy efficient than alternative processes [56, 57]. Over the years, there have been many studies to improve the ROSE process. For example, Zhao et al. studied supercritical fluid extraction and fractionation of heavy hydrocarbons with n-pentane [16]. In this study, n-pentane was chosen as the solvent since light parafins were previously shown to provide higher yields [58]. An asymmetric distribution of SARA components (saturates, aromatics, resins and asphaltenes) were observed among the separated fractions. Based on bulk analysis of the whole residue, average

structures were determined which were found to be quite biased towards the lighter fractions. This deviation limits the information obtained for the heavy components. A bitumen pitch was compared with residues obtained from benchmark crudes, heavy oils and bitumen from non-Athabasca sources. The comparison revealed that there was no significant difference regarding neither chemical ingredient nor the tendency to react with other hydrocarbons.

2.2.2. Reactive Extraction by SCH₂O

The processes which involve both extraction of the chemical species together with their reactions open possibilities to design new intensified process schemes and SCH₂O is a very good candidate for the reactive extraction of hydrocarbons. The solvent power of SCH₂O for example can be manipulated which enables one to optimize the processing conditions to perform the extractions selectively. The removal of desired cuts from various feedstocks such as oil sand, oil shale, asphalthene, vacuum residuum / bitumen / fuel oil and solid fuels have been studied by several authors before [31, 59-65]. In addition to the tunable solvation power, sub- or SCH₂O can also participate in reactions as an acid or base catalyst depending on the reaction conditions and be a medium for carrying out ionic or free-radical chemistry [21, 22, 66]. These promising properties of SCH₂O have led to a number of reactive extraction studies with different hydrocarbons resources as discussed in the following sections.

2.2.2.1. Bitumen and other heavy fractions

The term upgrading means converting the heavy and economically less valuable fossil and renewable feeds into light and more valuable fuels & chemicals and the heavy oils are those that

has a boiling point of higher than ~ 653 K. Bitumen, more specifically, has a boiling point above ~ 798 K. It comprises approximately 5% of the asphalt which is used to pave the highway roads and is usually obtained as the bottom product of the distillation (atmospheric & vacuum) processes in the refineries. It is composed of maltenes and asphaltenes. Maltenes are comprised of saturates, aromatics, and resins. The whole fraction is called as SARA. Depending on the processing conditions and the properties of the crude oil blends used in refining operations, the product obtained from the bottom of the vacuum residuum can be more like bitumen or a relatively lighter fraction such as fuel oil.

Vilcaez et al. [67] studied the behavior of the SCH_2O -bitumen mixtures up to 713 K and 29 MPa with a reduced mass ratio of 2.5:1 water to bitumen. They observed that nearly all of bitumen was solubilized in water phase, with the phase boundaries becoming almost disappearing at 713 K and 29 MPa. Moreover, the continuous increase in the intensity of the color implied that the fraction of bitumen in the water rich phase was increasing with increasing temperature. (See Figure 8).

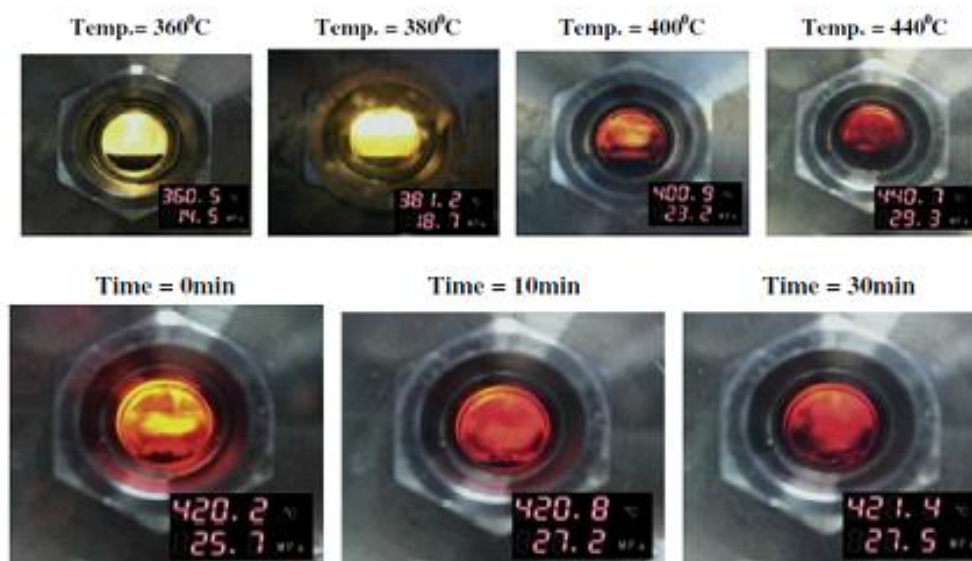


Figure 8: Phase behavior at mass ratio of 2.5:1 water to bitumen at different temperatures (top); Solubilization of bitumen in supercritical water at 693 and a mass ratio of 10:1 water:bitumen (bottom), *taken from [67]*

Morimoto et al. [46] studied the reactive extraction of asphaltene by SCH_2O at 673–723 K and 20–35 MPa and determined the optimum processing conditions. The optimum temperature was found to be 713 K. As for the optimum pressure, the extraction yield of AS reached its maxima at around 30 MPa and 713 K. Based on the findings, the extraction behavior was thought to be controlled mainly by the dielectric constant (DC) and Hansen solubility parameter (HSP) of the water and the optimum values providing the highest miscibility with AS were determined as $\text{DC} = 2.2$, $\delta_p = 6.4$, and $\delta_h = 9.7$. Actually, the temperature and pressure found by Morimoto et al. for asphaltene was also similar to the temperature and pressure observed by Vilcaez et al. [67] for bitumen. Along similar lines, Morimoto et al. estimated the DC and HSP of each run given in a study performed by Cheng et al. [68] on upgrading the vacuum residue at 653–693 K and water density of 100–200 kg/m^3 . The estimated parameters for the optimum upgrading conditions in Cheng's study (DC of 2.2, δ_p of 6.3, and δ_h of 9.9) were found to be quite close to values

determined in Morimoto's study ($DC = 2.2$, $\delta_p = 6.4$, and $\delta_h = 9.7$). These results imply that the optimal conditions for the extraction in AS-SCH₂O system can be applied to other heavy hydrocarbons. Since it is quite difficult to experimentally collect or statistically predict the optimal conditions for SCH₂O upgrading of heavy hydrocarbons because of complexity of the system, alternative technique developed in this study can be an easy solution for optimizing the processing conditions for other feedstocks.

Wahyudiono et al. [69] studied the liquefaction of bitumen by means of hydrothermal/solvothermal process without catalysts for the transformation of high-molecular-weight compounds into useful chemicals. In addition to bitumen, model compounds were also studied. SCH₂O at 673 K and elevated pressures were used in a batch reactor for hydrothermal process while solvothermal treatment was carried out using benzyl alcohol (BZA) ($T_c = 676.2$ K; $P_c = 4.6$ MPa) at its subcritical condition 523-573 K. The results of MALDI spectrum showed that hydrothermal process favored the formation of compounds with major peaks distributed among almost 400–500 amu while that of solvothermal process was around 300–400 amu. It was found that the yield increased with increasing reaction time for SCH₂O treatment. Higher rates of formation for bitumen-derived compounds were found when water density was increased at a constant temperature. The findings indicated that SCH₂O and subcritical BZA can be utilized as effective solvents for the degradative extractions of bitumen like components.

The processing conditions and the feedstock of the distillation processes in the refineries are altered depending on the market needs. This affects the properties of the products obtained from bottom of the vacuum distillation columns such as bitumen or comparatively lighter ones like fuel oil. Vacuum residuum upgrading has been studied by several authors. Cheng et al. [68] found that

optimum reaction conditions were 693 K, 0.15 g/cm³ for the water density, 2 g/g for the H₂O/oil ratio, and 1 h for the reaction time which gave light oil products with boiling point lower than 623 K and a yield of 83.3 wt % together with a low coke production of 3.64 wt %. Zhao et al. [63] had previously arrived at similar conclusions in a study on vacuum residuum upgrading by reactive extraction with SCH₂O with the optimum upgrading conditions determined to be 693 K and 25 MPa, with the reaction time of 1 h and the water/VR ratio of 0.7:1-2:1 resulting in a suppression in coke formation (a yield of 8.19 wt %) and a considerable decrease in asphaltene content with a 98.6 % increase in saturates. Morimoto et al., on the other hand, found no difference between the middle distillates of oil sand bitumen upgrading in SCH₂O and that in N₂ atmosphere suggesting that solvation effect and phase behaviors of each hydrocarbon-water systems system have to be carefully investigated to understand the reasons behind the above mentioned contradictory behaviour [37, 70].

In another study, petroleum asphaltenes were shown to undergo cracking in SCH₂O at 653 K and 22.9 MPa in a stirred autoclave reactor with a reaction time of 3 hours and a medium density of 0.33 g/cm³. 4.3% gas products and high solid fractions, coke, as much as 48.6 were detected. Approximately 30% of the remaining fraction of the products were close to the diesel fractions. Dealkylation of substituents in the aromatic fragments of molecules and the aromatizations were claimed to be the reactions that asphaltenes underwent during upgrading in SCH₂O [71].

2.2.2.2.Oil shale, hard coals, coal-tar

Oil shale is an organic-rich rock containing kerogen from which liquid hydrocarbons can be obtained. Canel and Missal [62] studied the sub- and SCH₂O extraction of oil shale. The non-isothermal technique employed by the authors enabled the determination of the kinetic parameters, conversion degree and yield in one single experiment. Activation energies and the

pre-exponential factors for the sub- and SCH₂O extractions were determined using a simple reaction kinetic model. Similar studies have also been performed on the sub- and SCH₂O extraction of hard coals, oil shales and liptobioliths in an autoclave type reactor [72]. The authors determined the yield and composition of conversion products between the reaction temperatures of 573K-673K. Benzene-solubles were classified as liquid products and their yield was found to be higher using extraction with sub- and SCH₂O as compared to the traditional semicoking. The effect of the addition of an entrainer such as a low-boiling hydrocarbon, CO₂ and chemically active reagents were also studied. It was found that extraction using water can lead to significant increase in extract yield when some portion of water is replaced by the same amount of hydrocarbon or CO₂. Yields of conversion products were found to be influenced by the experimental conditions and the origin of organic matter. It was also observed that there is a synergistic effect of the binary solvents on the yield of extract. The magnitude of the effect was found to depend not only on the structure of organic matter but also on processing conditions such as temperature, reaction time, type of the solvent, and the mass ratio of the entrainer. Large amounts of heteroatomic and high-polar compounds were detected in the extracts.

Han et al. [64] studied the upgrading of coal-tar samples by SCH₂O in a batch reactor in the pressure range 25 - 40 MPa, and the temperature range 673– 753 K. The reaction times were varied between 1 and 80 min. Product distributions were determined and it was found that the conversion of asphaltene to maltene was higher and to that of gas and char was suppressed in SCH₂O as compared to pyrolysis under N₂ atmosphere. Moreover, the percentage of the more valuable mixtures, i.e. lighter oil fractions, was higher when SCH₂O upgrading was used. Moreover, it was proposed that the main active component was the asphaltene being upgraded

into maltene, gas, and char. The rate of formation could be accelerated by an increase in temperature. The effects of pressure and time on coal tar pitch conversion, on the other hand, were found to be less.

2.2.2.3.Oil sand

Oil sand, also known as tar sand, is a mixture of heavy hydrocarbons, mainly bitumen, with sand, clay and water. The largest oil sand deposits are mainly accumulated in Canada and Venezuela. When combined, they have oil sand reserves that are estimated to be almost equal to the world's total reserves of conventional crude oil [73].

The SCH_2O extraction of oil sand is a promising technology due to its similar aspects to the techniques employed for the recovery of heavy hydrocarbon resources lying deep below the surface. For example, steam assisted gravity drainage (SAGD) is a method to separate the bitumen from sand using injected steam resulting in a product mixture of bitumen and water. Therefore, there may be a possibility for extracting and 'on-site' upgrading of the bitumen with water at high temperatures and pressures [31, 74].

Meng et al. [61] performed sub- and SCH_2O extraction of oil sand samples in a semi-continuous system to study the effect of temperature and pressure on extract yield, formation rate, and composition of the product. The extract yield was found to increase with increasing pressure and reached its maximum value of 81.1 wt % at 30 MPa. In contrast to pressure, the increase in temperature was found to decrease the extract yield perhaps due to a decrease in density with increasing temperature. The products obtained by fractionation of oil sand were oil, asphaltene, and preasphaltene. SARA analysis was further applied to the oil and it was found that with an increasing pressure formation rates of saturates and aromatics decreased, while that of resin

increased. As for the gaseous components, CO₂, CH₄, and H₂ were the main products but the gas yield was quite low.

There are also patents suggesting the possibility to combine bitumen extraction with bitumen upgrading [75]. Kamimura et al. [76] also suggested a similar configuration in which supercritical water was combined with SAGD system for on-site upgrading purposes at 700K using reaction times of 5-15 min, water loading of 20% (pressure=3.1MPa) and 0.1-1 M KOH. It was reported that upgraded oils had a viscosity of 10-20 mPa.s, sulfur content of less than 0.5 wt% and vanadium content of less than 10 wt.% and coke formation was highly suppressed. Similar to the other studies in the field, use of SCH₂O in this study also eliminated the necessity to use highly acidic and delicate catalysts and hydrogen.

2.2.2.4. Microalgae

There are numerous studies including production/upgrading of microalgae based biofuels by using SCW processing [77-80]. Hydrothermal gasification of microalgae at supercritical conditions results in production of a combustible gas mixture consisting of methane and hydrogen by successfully breaking the C-C bonds within microalgae [81]. Several authors [82, 83] reported that an increase in temperature resulted in higher gas yields. Effect of water/microalgae ratio on gas yield was also investigated and lower microalgae loading was found to increase gas yield [77]. For understanding the reaction mechanisms involved in upgrading of microalgae, decomposition of long chain saturated fatty acids which are present in microalgae was investigated in SCW environment at 400 °C and alkene production was observed [84]. Upgrading of algal bio-oil produced from hydrothermal liquefaction was also carried out in SCW at 400 °C in the presence of hydrogen with and without catalyst. Improved bio-oil quality

as well as coke and gas formation were reported [79]. The process is also attractive since it reduces the costs associated with the energy-intensive drying step. For hydrothermal gasification, slurries of microalgae can be used directly or after removal of some water. The studies in the literature indicate that operating conditions for hydrothermal gasification are 400-700 °C and 25-30 MPa which intersects with the conditions of bitumen upgrading in SCW [85]. In view of such information, it may be advantageous to blend microalgae into conventional heavy oil fractions of refinery such as bitumen. Prospective algae farms can be constructed next to refineries and microalgae can use CO₂ emission of refineries as the carbon source since it has been demonstrated that microalgae can utilize CO₂ from industrial exhaust gases containing 10-20 % CO₂ [86]. Using existing infrastructure of refineries as much as possible eliminates high capital investment of microalgae processing. Aqueous phase obtained after supercritical water processing is expected to include nutrients for microalgae cultivation such as ammonium, sodium, potassium which can be recycled to growth media bringing economic benefits [81]. Despite such advantages, to the best of our knowledge, there is no study investigating upgrading of bitumen blended with microalgae in SCW except the one we published [13].

Among a vast variety of microalgae species, fast growth rate of *Chlorella vulgaris* makes it a very promising candidate for biofuel production [87]. Moreover, commercial large scale cultivation of *Chlorella vulgaris* is performed in many countries in cost effective open ponds enabling high volume applications.

2.2.2.5. Effect of entrainers

Entrainers are the chemical additives which can be added into a SCF in order to improve the related physical and / or chemical properties such as the solubility of hydrocarbons in SCH_2O . The synergistic effects to improve the upgrading of bitumen were also studied by adding H_2 , and CO_2 into SCH_2O as entrainers. Sato et al. [88] studied the reactive extraction using a mixture of SCH_2O , H_2 and CO_2 in a semibatch reactor at temperatures from 633 K to 693 K and at 30 MPa. For the preparation of SCH_2O , CO_2 and H_2 mixture, a 10 wt. % aqueous solution of HCOOH was decomposed during preheating to produce CO_2 and H_2 . Coke formation was found to be pronounced above 673 K for SCH_2O and above 693 K for $\text{SCH}_2\text{O} + \text{H}_2 + \text{CO}_2$. The rate of coke formation (less than 4.3 wt %) was also lower for the mixture. The products for $\text{SCH}_2\text{O} + \text{H}_2 + \text{CO}_2$ treatment were shown to have a higher H/C ratio and composed of monomers and dimers. The decrease in the rate of formations of coke was attributed to the hydrogenation of asphaltene via reverse water-gas-shift reactions and to the more efficient removal of oil from the reactor in the case of a $\text{SCH}_2\text{O} + \text{H}_2 + \text{CO}_2$ mixture.

In another study on the upgrading of bitumen in SCH_2O , the effects of adding H_2 , CO , toluene, formic acid and tetralin to SCH_2O on reactive extraction of bitumen from 673 to 753K and at a water/oil ratio from 0 to 3 were investigated [31]. Higher conversions of asphaltene and lower coke yields were found in $\text{SCH}_2\text{O} + \text{HCOOH}$ as compared to reactive extraction by neat SCH_2O or pyrolysis. For comparison, bitumen upgrading was also performed in $\text{SCH}_2\text{O} + \text{H}_2$, $\text{SCH}_2\text{O} + \text{CO}$, toluene and tetralin. $\text{SCH}_2\text{O} + \text{HCOOH}$ mixture was found to promote coke suppression and asphaltene decomposition. The same trend was observed with increasing water/oil ratio in

$\text{SCH}_2\text{O} + \text{HCOOH}$. The order for the increase in the coke yield with reaction time was pyrolysis $> \text{SCH}_2\text{O} > \text{SCH}_2\text{O} + \text{HCOOH}$. The improvements in bitumen upgrading were attributed to the active species formed by formic acid in SCH_2O . The formation of the active hydrogen via WGS reaction is believed to suppress the formation of coke. An optimal reaction temperature of $\sim 450^\circ\text{C}$ was suggested similar to the previous studies.

2.2.2.6. Effect of Catalysts

D.S. Scott et al. [89] used activated carbon catalysts for the upgrading of bitumen in a bench-scale plug flow reactor in the presence of hydrogen gas and hydrogen rich solvents in a supercritical state and obtained promising results at pressures as low as 7 MPa and at temperatures 673-723 K. The liquid product conversion of 82-88 wt% and 6-8 wt% coke and pitch formations were found. There are also patented technologies combining the use of catalysts with SCH_2O for heavy oil upgrading in slurry-phase flow reactors [90, 91].

The use of catalysts have been shown to be beneficial for reservoir applications as well [92]. Catalytic emulsions consisting of Ni-W-Mo were used for catalytic upgrading of heavy oil and bitumen in a batch reactor at 3.45 MPa and temperatures ranging from 593 to 653 K. Large excess hydrogen was used to avoid the coke formation. The Monte Carlo simulation was used for estimation of the reaction parameters. This technique was combined with a batch reactor model which enabled the simulation of the results of a large number of upgrading experiments. Close agreement was obtained between the results of the simulations and experimental measurements. It was concluded that ultra-dispersed catalytic upgrading in a batch reactor provides residue conversion products with high yield.

Water-activated natural zeolites such as chabazites and clinoptilolites were shown to be quite active for the integrated extraction and low severity upgrading of oil sands bitumen [93]. Water added (~3 wt. % of feed) zeolites were used at 573 and 623 K and quite high liquid yields (up to 96%) with comparatively lower viscosity, boiling point distribution, and average molecular weight as compared to raw bitumen together with reduced concentrations of heteroatoms were obtained. It was suggested that the decreased viscosity of the products may lead to a reduction in pumping costs for transportation.

The use of iron based catalysts for heavy oil upgrading in SCW were also reported [94]. In one study, it was demonstrated that the use of silica supported Fe_2O_3 results in a decreased amount of coke formation down to 5.46 wt. % with a water:oil ratio of 80:3 and an oil:catalyst ratio of 3:1 at 450 °C for a reaction time of 60 minutes [95]. Catalytic performance of different nanoparticles, namely CeO_2 , Co_3O_4 , and MnO_2 , was investigated at 450 °C for 60 minutes with a water to oil ratio of 80/3 and catalyst to oil ratio of 1/5 [95]. The catalyst performance was evaluated based on the yield of maltene, coke, and asphaltene obtained from vacuum residue cracking. The best performance was obtained with CeO_2 , while non-catalytic cracking and SCW pyrolysis without any catalyst gave the poorest results. Performance of different transitional metal oxide nanocatalysts for upgrading of vacuum residue under SCW environment was investigated [96]. The experiments were carried out at a temperature of 450 °C for a reaction time of 60 min with water/oil ratio of 8/1 and catalyst/oil ratio of 1/5. The results revealed that NiO , CuO , ZnO , Co_2O_3 , and Cr_2O_3 , NiO gave the best performance in terms of maltene, asphaltene, and coke yield. Compared to non-catalytic cracking, coke yields decreased from 19.3% to 5.89%.

In addition to the metal oxide based catalysts, there were studies that investigated the catalytic performance of waste materials, such as red mud, a by-product of an aluminum industry,

for heavy oil upgrading. Performance of ZrO_2 -impregnated red mud catalysts for steam cracking of heavy oils was studied [97]. The results indicated that 3 wt% ZrO_2 impregnation resulted in the highest conversion and liquid yield under batch reaction conditions at 470 °C for a reaction time of two hours with superheated steam. In another study [98], the performance of ZrO_2 -impregnated macro- mesoporous red mud catalysts for cracking of vacuum residue (VR) in a steam atmosphere was investigated. The reactions were carried out under fixed-bed reaction conditions and the temperature was chosen as 500 °C. The results indicated that macroporous structure resulted in more access to active hydrogenation sites, as well as oxidative cracking, meaning greater catalytic activity.

The above- mentioned studies indicate that, the performance of heavy oil upgrading in presence of SCW can be improved by catalytic additives, such as metal oxides. In addition to that, there are studies that make use of waste materials, such as red mud, for heavy oil upgrading in the absence of SCW. These promising results indicate that waste materials can also be used as catalyst for heavy oil upgrading in presence of SCW.

2.2.2.7.SCWO

Among the several types of reactions that can be carried out in SCH_2O environment, supercritical water oxidation (SCWO) has also been under investigation because of its ability to destruct the organic compounds in industrial waste water streams [99, 100] into H_2O and CO_2 in single phase mixtures.

It was shown in several studies that partial oxidation of various organics such as methane [101, 102], propane [103], xylene [104] and polymers [105, 106] can be achieved in SCH_2O . In addition to that, partial oxidation of several hydrocarbons including bitumen in SCH_2O was also studied by several authors [29, 107-110]. A comparative study was conducted for the upgrading of asphalt by SCH_2O and SCH_2O partial oxidation at 613–673 K, 0–0.5 g/cm^3 water density under argon or air atmosphere [111]. The rates of desulfurization and asphaltene conversion were found to increase with increasing temperature under an argon atmosphere and at a water density of 0.5 g/cm^3 . Similar trends were observed for asphaltene conversion and the yield of CO_2 when water density was increased at a constant temperature of 673 K. The experiments conducted under an argon atmosphere at 673 K resulted in higher asphaltene conversion but lower desulfurization as compared to reactions in an air atmosphere. The partial oxidation of bitumen in SCH_2O was further studied by Sato et al. [29] in order to improve the understanding of the effects of the water density and air pressure on the reaction kinetics. The reaction conditions were 653 to 723 K, water/oil ratios ranging from 0 to 3, and initial air pressures up to 5.1 MPa. During the reaction, oxygen was almost totally consumed in the first 30 minutes and the contents of the reactor separated into a water rich phase and an oil rich phase (See Figure 9). The gaseous products were found to be CO, CO_2 and methane with a higher $\text{CO}/(\text{CO} + \text{CO}_2)$ ratio which is an indication of the degree of progress in partial oxidation. Moreover, coke formation was suppressed at low temperatures. $\text{CO}/(\text{CO} + \text{CO}_2)$ ratio reached its maximum at 653 K. When the water/oil ratio was increased from 0.5 to 3, a notable decrease in the total amount of gaseous products and a two-fold increase in $\text{CO}/(\text{CO} + \text{CO}_2)$ ratio was observed. In contrast, an increasing yield of CO and CO_2 with a decreased $\text{CO}/(\text{CO} + \text{CO}_2)$ ratio was observed with increasing initial air pressure. The observations imply the necessity of the high water/oil ratios in selective partial oxidation to produce CO. Moreover, it was figured out that the effect of the enhancement of

partial oxidation by SCH_2O dominates that of the CO oxidation by water and by water gas shift reaction.

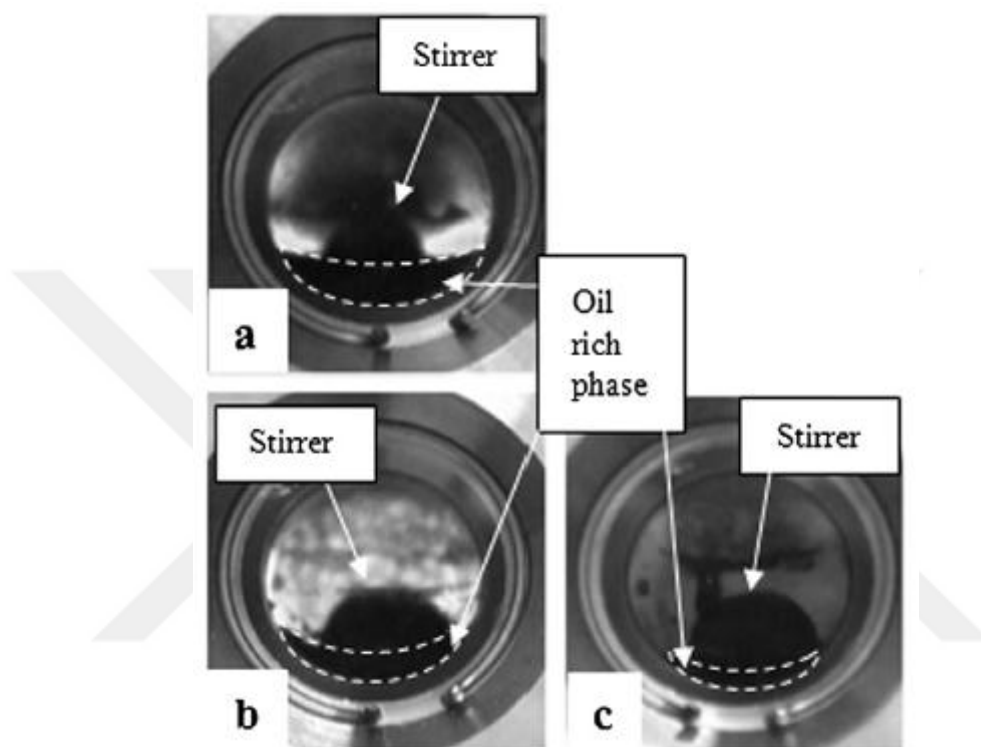


Figure 9: The observation of behaviour of bitumen-water-air system at 673 K and 2.1 MPa of initial air pressure (a: water/oil ratio=0, 5.3 MPa; b: water/oil ratio=1, 26.6 MPa; c: water/oil ratio=2, 29.3MPa [29].

2.2.2.8.Others

SCH_2O can also be used for gasification purposes. Pinkwart et al. [112] studied the influences of the four different commercial catalysts on n-decane conversion at low temperature in a continuously operated tubular reactor at 25 MPa and 823 K. It was shown that n-decane can be reacted under supercritical environment to form a hydrogen-rich gas. Approximately, 80% of n-decane was transformed into hydrogen and methane. Further experiments with diesel oil and the same commercial steam reforming catalysts at low temperatures gave similar results. Those

findings points out the supercritical reforming of hydrocarbons, heavy oil and biomass as a new route for the production of hydrogen at temperatures lower than that of state of the art industrial steam reforming technologies.

Reactive extraction of polyethylene (PE) and n-hexadecane (n-C₁₆) in SCH₂O were investigated [113] in a batch reactor operated at 673 to 723 K, a reaction time of 30 min, and up to a water density of 0.42 g/cm³. The reaction rate and the product distribution of the reactive extraction of n-C₁₆ in SCH₂O was similar to the runs carried out under 0.1 MPa argon (Ar) atmosphere. PE extraction, on the other hand, was found to be affected drastically by the SCH₂O environment such that higher yields of shorter chain hydrocarbons, higher 1-alkene/n-alkane ratio, and higher conversion was achieved as compared to the pyrolysis in argon atmosphere. Those variations can possibly be attributed to the phase behavior of the reaction mixture. Pyrolysis of PE takes places in a molten PE phase under Ar atmosphere. SCH₂O, on the other hand, is capable of dissolving some hydrocarbon products of PE decomposition which are further decomposed into smaller fragments. The reactions of these hydrocarbons in the supercritical phase should follow distinctly a different route than the one in a molten PE phase. As for the molten PE phase, PE extraction was thought to be influenced by the SCH₂O which was dissolved in PE phase up to some extent and improves its dilution.

2.2.2.9.Heteroatom Removal

In addition to the tunability of its solvation power, selective extraction and fractionation abilities and being an alternative reaction medium with several advantages, SCH₂O has also additional benefits such as the removal of the heteroatoms during the upgrading of hydrocarbon resources.

T. Sato et al. performed a study on bitumen upgrading in SCH_2O with and without oxygen at 613–673 K and 0–0.5 g/cm³ water density. The rate of desulfurization was found to be higher at 673 K under an air atmosphere as compared to that under an argon atmosphere and an increased desulfurization was observed for higher water densities [111]. Similar improvements were observed by Kawasaki et al. [114] in which sulfur, nitrogen and metals were removed by SCH_2O treatment. Zhao et al. obtained promising heteroatom removal results, too [63]. As compared to the feedstock, the reduction values of 53.9%, 83%, and 86% were found for sulfur, Ni and V contents, respectively under the processing conditions of 693 K, 25 MPa, 2:1(wt) ratio of water/vacuum residuum and a reaction time of 1 h. The N content on the other hand, did not show a sharp decrease and dropped only from 1.11 to 0.93 wt %. Yuan et al. [115] obtained even higher sulfur removal rates in catalytic desulfurization of a model sulfur-containing compound benzothiophene (BT) through partial oxidation in SCH_2O . The study was performed at 623–723 K and 30–40 MPa over sulfided $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ in a bomb reactor. At temperatures around 723 K, reduction of sulfides up to 67% was achieved.

There is no detailed explanation in the literature given for the mechanism of the heteroatom removal reactions during the course of the SCH_2O upgrading of heavy hydrocarbons. However, it is known that the hydrotreating reactions in historically known and commercially used petroleum refining operations are catalyzed by acidic supported metal catalysts with a considerable amount of hydrogen consumption resulting in gaseous by products such as H_2S . Therefore in situ generated hydrogen produced by the shift reactions or by the increased ionic product of water during the SCH_2O upgrading can potentially be involved in the heteroatom removal mechanisms to provide the necessary hydrogen for the related hydrotreating reactions. A rapid mass transfer in SCH_2O environment caused by the higher diffusivity of the compounds in SCH_2O as compared to

those in conventional solvents may also help and fasten the heteroatom removal reactions in the absence of catalysts. Zhao et al. [63] suggested a similar approach and claims that H^+ which is at high concentration in SCH_2O can attack CS bonds whose bond energy is the least as compared to those of CO, SH, CS. This approach, when combined with the proposed overall reaction formula, $RCH_2CH_2SCH_3 + 2H_2O \rightarrow RCH_3 + CO_2 + H_2 + H_2S + CH_4$, explains, up to some extent, the cleavage of the CS bond, formation of the gaseous H_2S and decreased amount of S in the liquid products.

The related analytical techniques for the measurement of the amount of the heteroatoms in products in the literature are generally based on the comparison of the amount in liquid products as opposed to that of feed. Thereby, the heteroatoms are not going to anywhere instead being transferred into gaseous H_2S and NH_3 . As for the heavier heteroatoms like V and Ni whose compositions are also said to be decreased upon SCH_2O treatment; since they are relatively higher as compared to S and N, it is not probable for them to be transferred into gaseous phase during the upgrading reactions. It can be suggested that after the reactions, when the remaining water phase is removed from the unconverted feed and products, the “so-called” decreased amount of V and Ni can probably be the one that is moved into the water in the form of water soluble intermediate chemicals or micelles containing Ni and / or V and being formed after SCH_2O treatment. Unlike to H_2S and NH_3 , the V and Ni containing species after in-situ hydrotreating process are not likely to be moved into the gaseous phase. More details for the removal of heavy metals from aqueous solutions by means of the supercritical fluids has been reported previously by Erkey [116].

The capability of SCH_2O in improving heteroatom removal during the upgrading of heavy hydrocarbons provides an opportunity to use the straight-run products without performing

hydrotreating processes to remove heteroatoms such as sulfur in the fuel (diesel, gasoline etc) before introducing them into the market which certainly provides a distinct economic benefit for refineries to cut down their operating costs as well as costs of expensive hydrotreating catalysts.

2.2.3. Corrosion by SCH₂O

Although supercritical water provides many advantages as a solvent for heavy oil upgrading, its corrosive nature [117] necessitates the use of special materials for construction of reactors and brings new processing challenges as well as additional costs which all affect the economics. Significant efforts are directed towards understanding the nature of corrosion and thus controlling the aggressive behavior of SCH₂O [118]. Studies carried out so far indicate that the process conditions need to be chosen very carefully so that the corrosion can be minimized up to a certain extent. As can be seen in Figure 10, generally, corrosion rates are low at densities below 200–300 kg/m³. At 573 K, a pressure of 10 MPa causes high corrosion rates, while at 773 K and at pressures higher than 50 MPa for high corrosion rates are observed. Increasing the pressure at constant temperature increases the rate of corrosion. The shift from no corrosion towards strong corrosion is only sharp at lower temperatures, although there is no clear dividing line at higher temperatures [117]. For example, SCH₂O is much less corrosive as compared to water under subcritical conditions. Hastelloy [33, 69], Inconel [119, 120], titanium alloy [29] type materials have been used in several studies under sub- and supercritical conditions. Among those, the stability of Inconel 625 having approximately 60 wt % nickel and 20 wt % chromium has been tested at temperatures of 603 to 683 K and pressures of 25 to 35 MPa in a corrosive environment of pure water, aqueous acetic acid and aqueous solutions containing oxygen [28]. The

temperature and pressure range of the study was based on the rapidness of the change of the physical properties of the aqueous media and the aqueous acetic acid is used to mimic the carboxylic acids produced during partial oxidation. The results indicate that Inconel 625 is stable in SCH₂O under acid and oxygenated environments. However, more commonly used materials such as stainless steel [67, 68] have also been used in the literature as a reactor material in sub- and SCH₂O environment with bitumen as a feedstock for both batch and flow systems at the operating conditions as high as 733 K and 30 MPa. Although the corrosion is a long-time process and those studies are not focused on the corrosive effect of the SCH₂O on the reactor material, no damage has been reported.

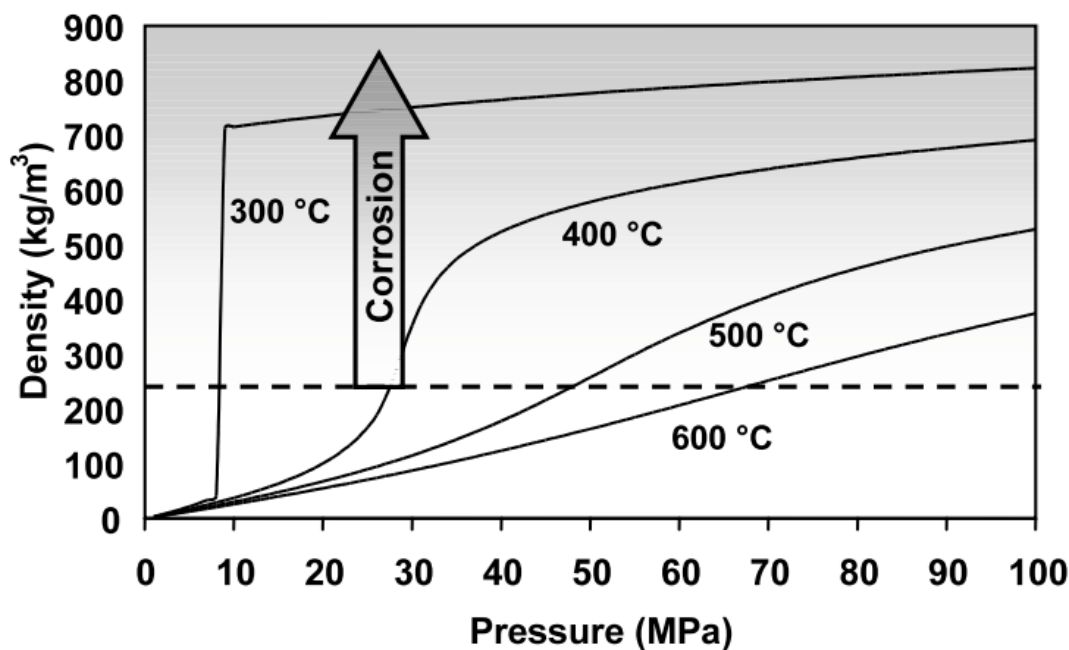


Figure 10: Density range of high corrosion at different temperatures. *taken from [49].*

2.3. THERMODYNAMICS, KINETICS AND PHASE EQUILIBRIA FOR HEAVY OIL UPGRADING BY SCH₂O

Thermodynamics, kinetics and phase equilibria for heavy oil-water mixtures need to be studied to understand the reaction mechanisms, to control the reaction rates, to predict rate of approach to equilibrium, to predict conversion and product distribution as a function of operating conditions, to design new processes or to improve existing ones, and to estimate the physical and chemical properties of hydrocarbon and water mixtures. Dielectric constant, hydrogen bonding, solubility constant, the tendency of SCH₂O to give its hydrogen/hydronium ion into the hydrocarbon upgrading reactions and gained acidic behavior are some of the properties of water affecting the phase equilibrium compositions [29, 30]. Some of these properties are explained in details in Section 2.1.2. “SCF for Green Processes: An Alternative for Heavy Oil Upgrading” and the rest will be discussed here in this section.

2.3.1. Transferring the Hydrogen of SCH₂O

It was proposed that CO formation is followed by water gas shift reaction giving hydrogen which then reacts with radicals and produces light liquid products during the hydrocarbon upgrading reactions [111, 121]. A similar route has been suggested for the partial oxidation of hydrocarbons where product CO undergoes water gas shift reactions and gives in-situ hydrogen [29, 107, 122]. Vilcaez et al. [67], recently studied the hydrothermal extractive upgrading of bitumen and found results that are in agreement with the literature indicating the possibility of the hydrogenation of heavy hydrocarbons for upgrading purposes by means of the transformation of in-situ generated hydrogen at near supercritical conditions. The in-situ hydrogen was shown to be more active as compared to molecular hydrogen when hydrogenation of heavy oil and heavy oil model

compounds via water gas shift reaction in sub- and supercritical water is of concern [29, 107, 122].

However, there are also some contradictory results in the literature stating that SCH₂O does not participate in the reactions, instead it behaves just as a solvent. Cheng et al. [68], for instance investigated VR upgrading by SCH₂O. CO was not detected, and infrared spectrum measurements revealed that hydrogen comes from the condensation reactions. Similar to Cheng's findings, the hydrogen donation by SCH₂O were not observed in other studies on pyrolysis of n-C₃₂H₆₆ [123], decomposition of tert-butyl benzene[124]; and polyethylene conversion reactions [113]. Yuan et al. carried out an MD study for the analysis of the solvation of hydrocarbons in sub and SCH₂O and reported that hydrogen coming from water takes part in the reactions by hydration of alkene instead of by H-abstraction from H₂O.[70]. Dutta et al. on the other hand used water doped with deuterium oxide (D₂O) to test hydrogen donation from steam to reacting bitumen molecules and suggested that steam is not a chemically inert compound during heavy hydrocarbon upgrading [125]. Similar findings have been reported elsewhere [32, 126, 127]. The studies carried out in slurry reactors to upgrade heavy oils by SCH₂O also suggested that hydrogen comes from water [90, 91].

2.3.2. Upgrading Mechanisms and Theoretical Studies

Based on the experimental findings [68], it is suggested that the enhancements in cracking achieved in SCH₂O as a reaction medium are due to two reasons given below:

- The solvent effect: Because of the adjustable solubility and transport properties of SCH₂O, the light liquid products upon the cracking of asphaltene can easily be

transferred (dissolution and diffusion) into the SCF phase which results in an increased reaction rate and higher liquid yield.

- The dispersion effect: Asphaltene, being one of the SARA components, has a quite large molecular structure making it only partially soluble in SCH_2O . Thus highly dispersed micro-emulsion formations are favored. Those emulsions suppress the coke formation and also provide more surface area which improves the mass transfer and increase liquid yield.

Although the reactivity of SCH_2O was not taken into consideration in Cheng's study, several studies on the effect of water on reaction mechanisms in heavy oil upgrading [67, 68, 125] suggested that water increased the concentrations of OH radicals. These radicals enhance the rate of reactions reducing the molecular weight of the products and increasing liquid yield. In addition to the mechanism based on OH radical formations, the more generally accepted reaction mechanism, on the other hand, relies on the hydrogenation with hydrogen from water. In details, CO formations are followed by the water gas shift reactions giving hydrogen. Produced hydrogen undergoes a reaction with the radicals and increasing the yield of products with lower molecular weights [67, 111, 121]

Efforts have also been dedicated to figure out the possible mechanisms of coke suppression. The generally accepted route for coke formation is through the cracking of asphaltene into aromatics and some smaller fragments of asphaltene which possess varying hydrogen accepting capabilities. Some portion of the cracked products accepts the required amount of in situ hydrogen provided by the water to turn into maltene. The remaining portion of the cracked products, on the other

hand, exhibits polymerization and condensation reactions resulting in asphaltene core and coke [71, 128, 129] Vilcaez et al. made further improvements to our understanding of the upgrading mechanisms and coke formations in continuous flow reactors where almost complete solubilization of heavy hydrocarbons in SCH_2O were achieved. It was shown in their study that the yield of bitumen upgrading can be increased and coke formation can be suppressed by means of the extraction of asphaltene core in order to overcome the mass transfer limitations which are reported to affect the bitumen upgrading and coke formation reactions if high degree of mixing is absent [67]. Thus, the coke suppression mechanism given in Figure 11 was proposed.

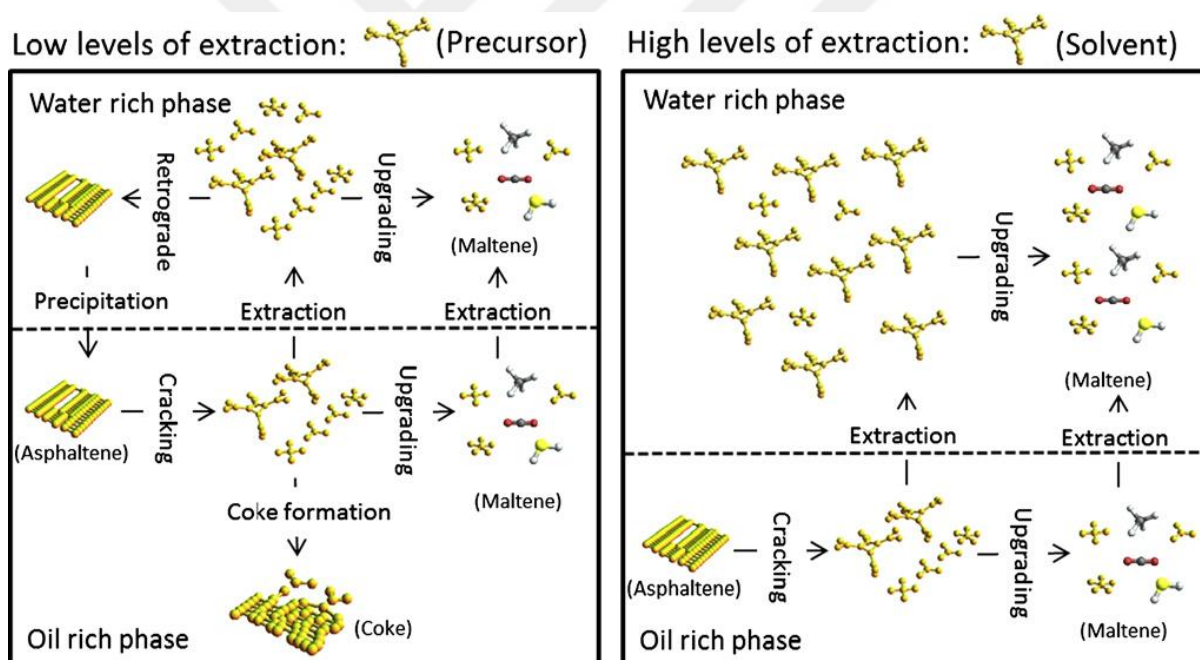


Figure 11: Schematic representation of the proposed mechanism of coke suppression [67].

The left hand side of Figure 11 is representing the low levels of asphaltene core extraction where the fraction of asphaltene core remaining in the oil rich phase enhances the polymerization reactions to form coke, or alternatively reacts with water and converted into maltene. The remaining fraction of the asphaltene core which is accumulated in the water rich phase accepts

hydrogen and turns into maltene but reverse reactions are also possible because of the high levels of light product concentrations. The high levels of asphaltene extraction, on the other hand, is sketched by the right-hand side of Figure 11 in which extremely low levels of asphaltene core remain in the oil rich phase suppress the coke formation. As for the water rich phase, the tendency of solubilization of asphaltene in water is increased because the high water concentration and coke formations are suppressed. According to the experimental results and the suggested coke formation mechanism, high levels of extraction decreases the rate of coke formation in the oil rich phase, and the solvent properties and increased solubility of asphaltene core in the water rich phase improves the upgrading of heavy oil. It can be concluded that asphaltene core can behave as coke precursor or as solvent for products derived from asphaltene cracking, depending on which phase that the asphaltene core presents, and depending on the concentration levels.

Other studies to determine the effect of temperature and pressure of SCH_2O on the kinetics of the reactions, such as the hydrolysis of ethyl acetate model reaction under the processing conditions of 23–30 MPa and 523–673 K were also conducted together with a derivation of a kinetic model representing the experimental data fairly well [119]. In one study by Yasar *et al.* [130], in the absence of SCW, pyrolysis experiments of Maya, Hondo, Ariabian heavy oils were carried out to determine the effect of reaction environment on reaction paths, kinetics, and mechanisms. The reaction temperatures were chosen as 400, 425, and 450 °C and reaction times ranged from 20 to 180 min. The reaction products were lumped as gas, maltenes, asphaltenes and coke. The results indicated that, at 400 and 425 °C, the asphaltenes reacted selectively to maltene, whereas at 450 °C, asphaltenes mainly reacted to coke. It was also found

that different feeds with varying chemical properties resulted in different kinetic parameters. In another study [131], the reaction kinetics for heavy oil upgrading in SCW and high pressure N_2 environment were measured and a first-order four-lump reaction kinetic model was developed. The reaction products were lumped as gas, maltenes, asphaltenes and coke. The results indicated that, as a result of significantly increased diffusion, the pyrolysis in the SCW phase is more sensitive to the changes in reaction temperature. In another study [132], crude oil was upgraded in presence of SCW to investigate the effects of reaction conditions on pyrolysis. A five-lumped kinetic model was used and the reaction products involved saturates, aromatics, resins, asphaltenes and coke. The results of this study revealed that coke is mainly produced from asphaltenes and increasing the surface area of asphaltenes, i.e. increasing the water density or water/oil ratio, resulted in an increase in the amount of light products and reduction in coke production. These models were developed based on sub fractions of heavy oil rather than the boiling point distribution of the products. Therefore, there is a need to develop a model based on boiling point distribution of products from different feed stocks, in order to estimate the amounts of products, such as gasoline and diesel, and make a better economic assessment.

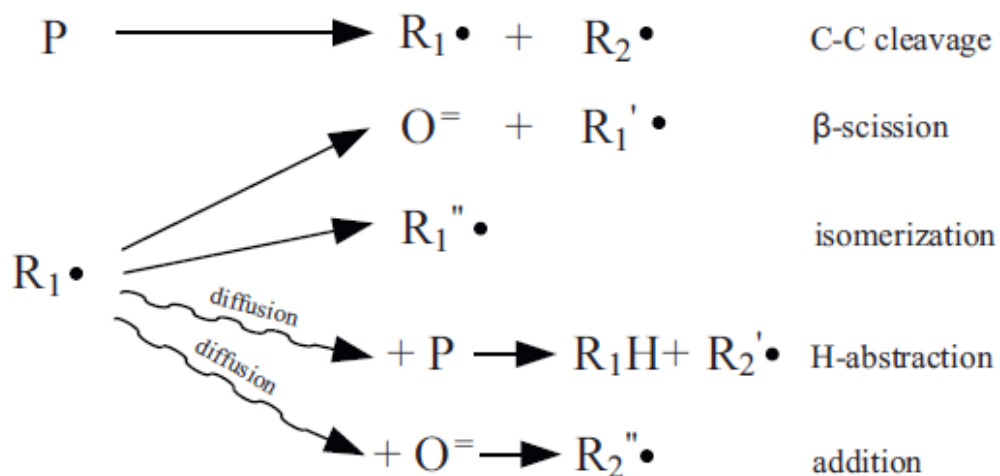


Figure 12: Elementary reactions involved in the thermal cracking of hydrocarbons *taken from* [70].

Thermal cracking of hydrocarbons is known to occur via free radicals involved elementary reactions which are given in Figure 12. C–C cleavage and β -scission are categorized as monomolecular reactions and sub- or SCH_2O is not expected to have a large influence on those reactions [70, 133-136]. The other elementary reactions given in Figure 12, on the other hand, can be affected by the sub- or SCH_2O environment. During isomerization, the first step is curling the main carbon chain of the radical. The second is the H-abstraction between the radical end and the curled main chain. For the rest of the elementary reactions which are H-abstraction and addition to olefin, they can be completed upon the formation of a transition state with other reactant indicating that they involve radical attack having a reaction barrier depending on the activity of the radical. As can be seen in Figure 12, the reaction mechanism for a radical is not set by only the reaction kinetics of the related elementary reaction, but also by the diffusion kinetics of the radical, thus it is possible for a hydrocarbon radical to involve in varying elementary reactions.

Application of theoretical tools such as MD for predicting the solvent properties and phase behavior is also possible. Yuan et al. studied the solvation of hydrocarbon radicals in sub- and SCH₂O with ab initio MD simulation [70]. Diffusivity and activity of radicals at temperatures ranging from 573 K to 673 K and at water densities ranging from 0.10 g/cm³ to 0.80 g/cm³ were also evaluated. The results implied that high water density approaching that of liquid phase and a thermodynamic state far away from the vapor–liquid equilibrium boundary and from the critical point promote the formation of solvent clusters around the radicals. The simulations showed that the hydrocarbon radical with the water cluster had a higher tendency to undergo monomolecular β -scission and isomerization rather than bimolecular H-abstractions and addition to olefin indicating an alteration in the cracking route of the hydrocarbons. The technique employed in this study was shown to be powerful in predicting the solvation structure of hydrocarbon radicals in sub- and SCH₂O.

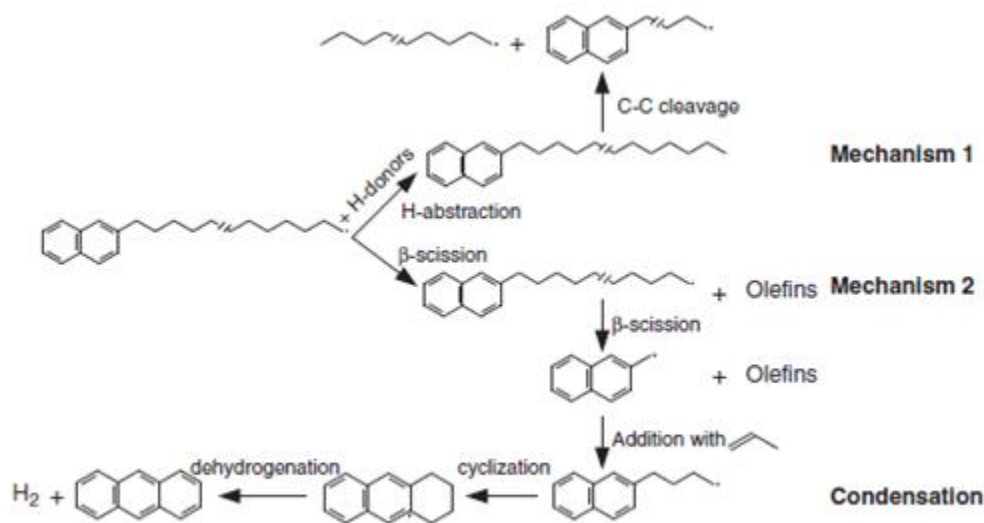


Figure 13: Key reactions involved in the upgrading of residual oil, *taken from* [137].

Similar results were obtained in a study conducted in a batch reactor at temperatures ranging from 653 to 713 K and at water densities of 0.05 to 0.20 g/cm³ [137]. It was found that thermal cracking via free radical mechanism (See Figure 13) dominates the upgrading of residual oil in sub- and SCH₂O with a very limited influence of ion mechanism based hydrolysis. A transition from a partially miscible two-phase structure to a pseudo single-phase structure was observed when the water density was increased. Figures 14 and 15 illustrate the estimated phase diagrams which are divided into three regions (immiscible two-phase region, partially miscible two-phase region and pseudo single-phase region) and show the effect of water/oil ratio on the reduction of the area of partially miscible two phase region. By using Aspen Engineering Suite 2006, the phase structure of residual oil in the presence of sub- and SCH₂O was also estimated and is given in Figure 16. Highly dispersed asphaltenes in the continuous water phase were detected together with a rapid diffusion of aromatic radicals from asphaltenes into the water phase which improves the liquid yield product and suppressed coke formations.

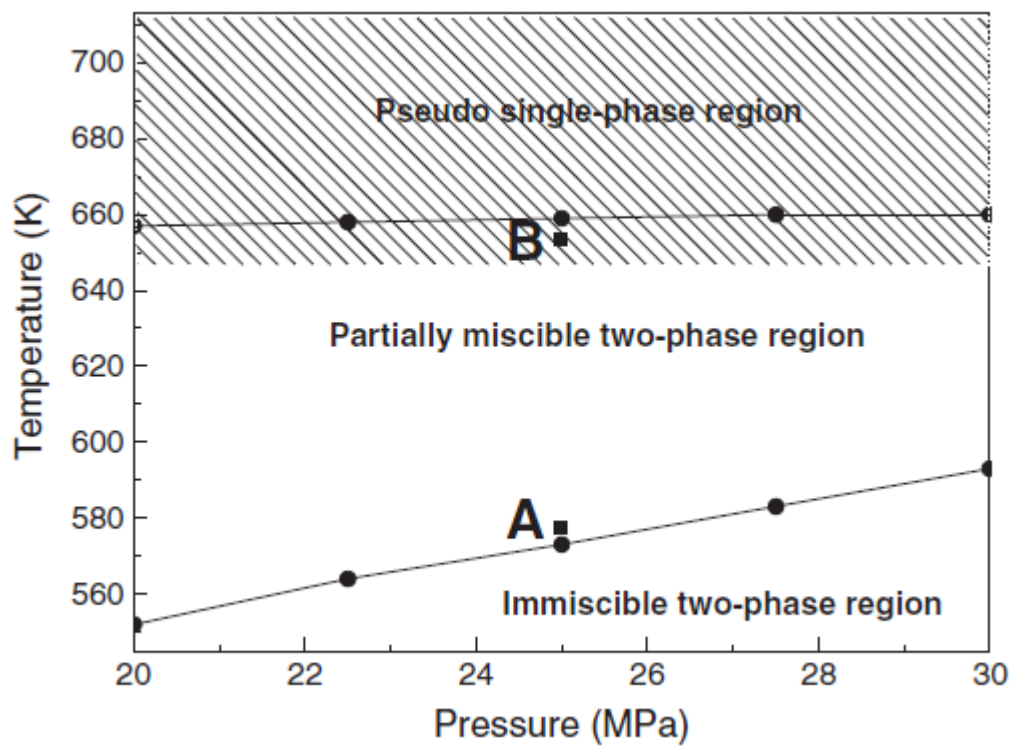


Figure 14: Phase structure of residual oil in the presence of sub- and SCH₂O; water:oil=1:4(wt); shadow region means the applicable temperature range for upgrading, *taken from* [137].

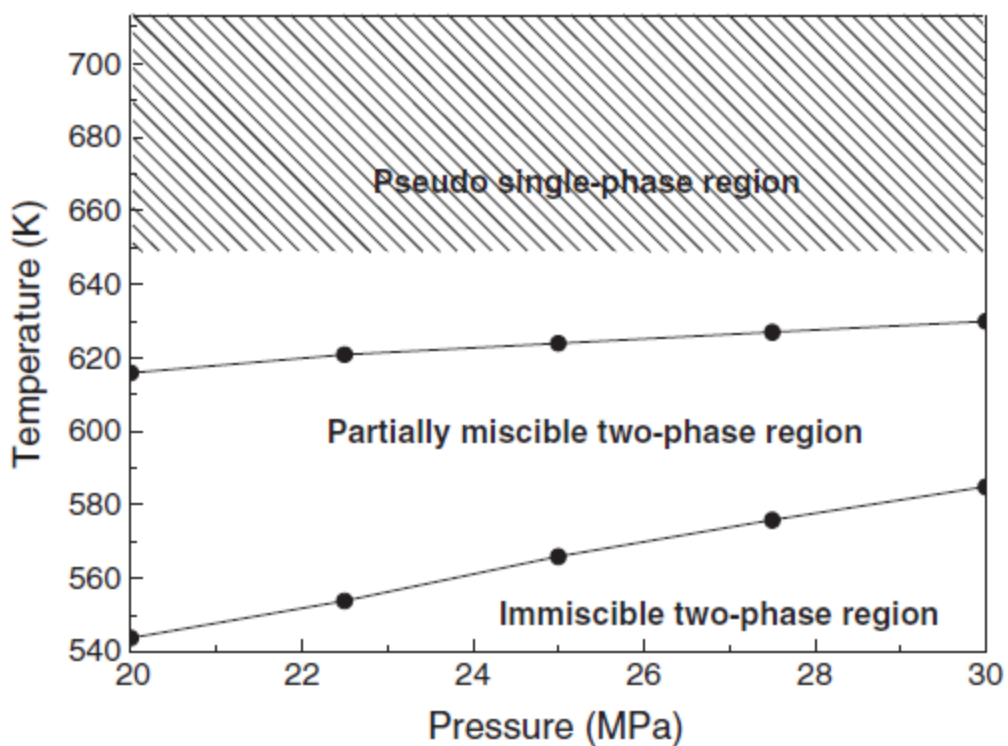


Figure 15: Phase structure of residual oil in the presence of sub- and SCH₂O; water:oil=1:2(wt); shadow region means the applicable temperature range for upgrading, *taken from* [137].

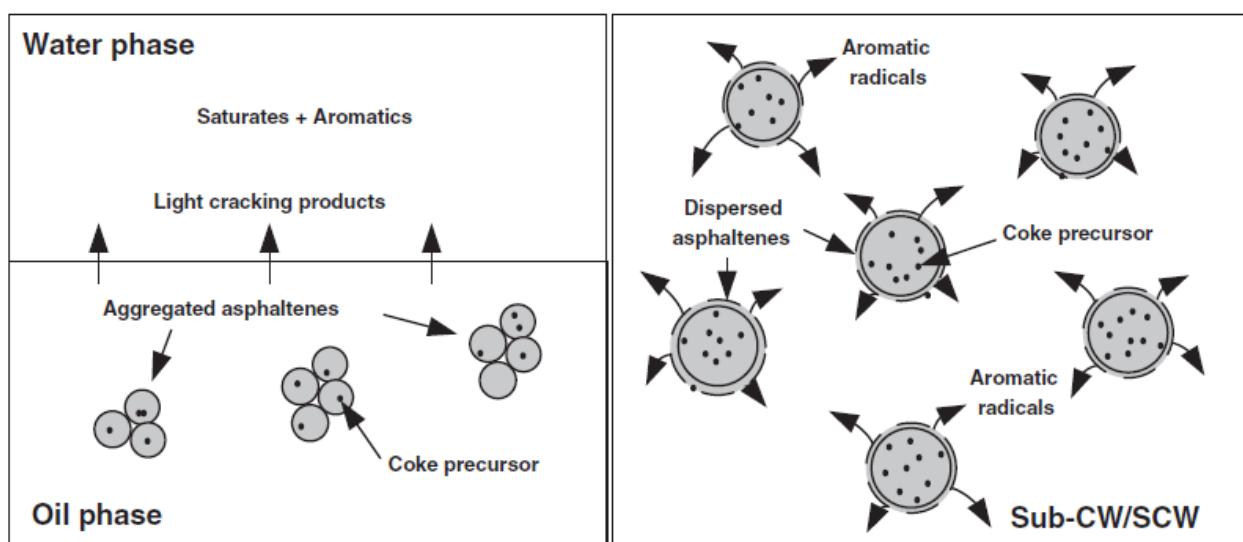


Figure 16: Phase structure of the upgrading system; left: partially miscible two-phase structure at low water densities, right: pseudo single-phase structure at high water densities [137].

2.3.2.1. Phase Behavior

Phase behavior of several hydrocarbon-water systems have also been studied in detail and the binary hydrocarbon-water systems were categorized as type II and III which are illustrated in Figure 17 below [138-141]. The mixtures of hydrocarbons with a critical temperature above the critical temperature of water follows the phase behavior in type II in which the critical points of water and hydrocarbon are connected with the vapour-liquid critical line. The type III, on the other hand, is representative of the mixtures with the critical temperature below that of water and (water + alkane) systems and it has a vapour-liquid critical line connecting the upper critical end point with the critical point of water or hydrocarbon. Brunner et al. [139], suggested that higher molecular weight hydrocarbons are not miscible even in high density water since phase diagram of hydrocarbon and water system is type III. Similar findings were reported by Stevenson et al. [142] who studied the system of dodecane-water and squalane-water (C_{30} hydrocarbon) mixtures and observed the liquid-liquid phase separation appearing under high pressures and at high water densities.

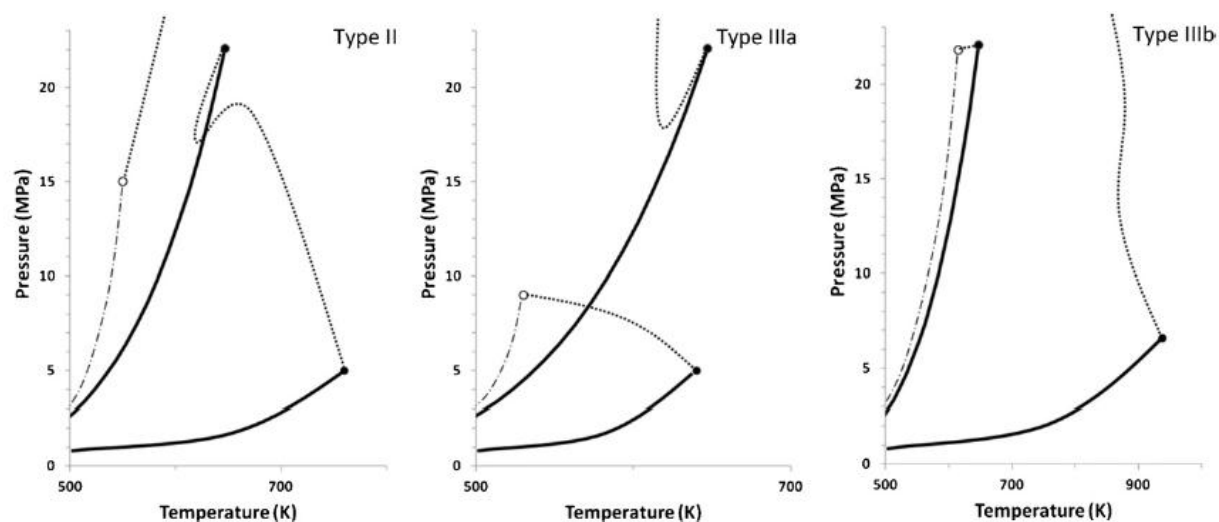


Figure 17: Schematic pressure-temperature projections for Type II, IIIa and IIIb phase behavior. Pure component vapor pressure curves (-), liquid-gas(LV) and liquid-liquid (LL) critical loci (.....), liquid-liquid vapor lines (—), pure component critical points (●) and critical end points (○) taken from [143].

Amani et al. recently published the results of a study on phase behavior of Athabasca bitumen + water mixtures (from, 9.2 to 96.6 wt% Athabasca bitumen) in the temperature range of 522.1–644.0 K and the pressure range of 4.2–35.7 MPa. Based on the observations in the study, the phase behavior of the mixtures was designated to be Type IIIb according to the van Konynenburg and Scott classification scheme [143].

M. Togo et al. [33] developed an experimental method for fast determination of the phase equilibria of hydrocarbon-water systems. The mixtures of water + p-xylene and water + decalin at temperatures from 573 to 623K in a flow type apparatus with microfluidic system were studied to measure the vapour - liquid and liquid - liquid equilibria. Slug flows in the micro tube for water + p-xylene system with p-xylene rich and water rich mixtures were observed. These slugs enhanced

the achievement of equilibrium by means of the high mass transfer rates between water and hydrocarbon phases by providing rapid mixing. The experimental data were also correlated by Peng–Robinson–Stryjek–Vera equation of state and correlations revealed that the systems of water + p-xylene and water + decalin have enclosed loops of liquid + liquid equilibria at 623 K.

2.3.2.2. Equation of States

The use of equations of state (EOSs) actually do provide a very powerful tool to simulate the reaction conditions, determine multicomponent phase behavior, predict thermodynamic product distributions and design upgrading processes. The most widely known EOS's are van der Waals together with some of its generalizations, namely Redlich and Kwong, Soave, and Peng Robinson. The way to handle these EOS's are reported in detail in the literature [144-147]. However, Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations are the most widely used EOS's for high pressure studies. After choosing the type of the EOS, the most suitable method should be determined for the calculation of the fugacities to describe the vapor- liquid equilibrium and the most generally accepted one for high pressure studies is the ϕ - ϕ thermodynamic approach where ϕ is the fugacity coefficient. The γ - ϕ approach, on the other hand, with γ being the activity coefficient, is not suitable for phase equilibrium studies of supercritical fluids. The reason behind this incompatibility is the fact that the γ - ϕ approach cannot simulate the variations in the critical region in a continuous manner because of treating each phase in different ways [56, 148].

I. Gracia et al. performed a study on modeling the phase behavior at supercritical conditions in order to derive a generalized algorithm for high pressure equilibrium calculations [149]. Commercial ASPEN-plus® software package together with the Peng–Robinson–Boston–Mathias

(PR-BM) and Redlich–Kwong–Soave (RKS) equations of state was utilized in order to process the available data in the literature for CO₂-oleic acid-triolin systems (OA: oleic acid; TO:) with OA mimicking low molecular weight compositions and TO representing the fatty content. The calculated values were found to be in good agreement with the published experimental data. Therefore, the derived algorithm can be used to make preliminary design analysis. V.I. Anikeev et al. also used Redlich–Kwong–Soave (RKS) EOS to investigate the effect of water density on rate and selectivity of 2-propanol dehydration in SCH₂O with the reaction products of propene and water at 0.24 and 0.58 g/cm³ water density, and the temperature range 654-686 K by using a model of activated complex and a model of acid-catalyzed reactions. The thermodynamic model (a model of activated complex) indicated that at constant temperature the activation volume depended strongly on pressure which did not agree with the experimental data which showed no pressure dependence for activation volume. Acid-catalyzed reaction mechanism on the other hand was shown to be valid to identify the mechanism of 2-propanol dehydration reaction in SCH₂O. The concentration of 2-propanol and H₃O⁺ ions increased the rate of reaction supporting the argument stating that the density of SCH₂O is a powerful tool to tune the rate and selectivity of chemical reactions [38].

The application of EOS's to determine the hydrocarbon – water phase behavior is also possible and their application to light hydrocarbons has been studied. F. Masoodiyeh et al. [150], for instance, recently modeled the PVT_x properties for several water/hydrocarbon systems such as water/methanol, water/ethanol, water/benzene, water/toluene, water/methane, water/n-butane, water/n-pentane, water/n-hexane, water/heptane, and water/octane in the temperature range 573-

698 K and the pressure range 7.0-276.0 MPa by using the equation of state-excess Gibbs energy (EoS/GEE) model and the cubic plus association (CPA) EOS. In the first model, the applied EOS was Peng-Robinson (PR) equation of state together with the combined mixing rules of Vidal-Michelsen (LCVM) and Wong-Sandler (WS) that were in conjunction with UNIQUAC activity coefficient model. The accuracy of both models were discussed by comparison with the experimental data. Comparatively, WS model gave better fits as compared to the others based on the calculated average absolute relative deviation (AARD) values to be 2.99, 11.11 and 5.14% for WS, LCVM, and CPA, respectively. However, predicting the conditions for heavy hydrocarbon systems is more difficult. In refineries, for instance, cubic equations of state (CEoS) employing distillation techniques together with an average density and molecular weight can be used to model the crude oil phase behavior. However, when the system of interest becomes heavy hydrocarbons with several solvents, the task gets more challenging [151-153]. This difficulty is caused by unavailability of the characterization data for the C_{30+} fractions comprising almost half of the heavy hydrocarbon. Therefore further modifications are required [154]. O.C. Díaz et al. studied the Peng–Robinson equation of state to model the phase behavior of bitumen and solvent mixtures by using the data for mixtures of bitumen, propane, and carbon dioxide [151]. The characterization of the bitumen was achieved by simulated distillation (SimDist) data that was extrapolated using six different approaches among which a Gaussian distribution of boiling points from the SimDist for the maltenes together with a Gamma distribution of the molecular weight of the asphaltene fraction were found to be the best ones. Lee–Kesler correlations gave a better fit to experimental data as compared to Twu property correlations. AARD values that are less than 6% were found for the predictions of the saturation pressures and liquid–liquid boundaries for pseudo-ternary mixtures of propane–CO₂–bitumen. The asphaltene precipitations on the other

hand were not successfully predicted with the developed model when bitumen was diluted in n-heptane.

Teoh et al. modeled the solubility of polycyclic aromatic hydrocarbons (PAHs) in subcritical water by using PR EOS with the classical mixing rules and good correlations were found for the water–anthracene and p-terphenyl–water binary systems [155]. Maciel et al. performed another study about separating the asphaltenes from lube oil through supercritical deasphalting technique. Extraction of the residue fractions from molecular distillations using supercritical propane or pentane as solvent was modeled with the Predictive Soave-Redlich-Kwong equation of state (PSRK) in which Holderbaum-Gemehling mixing rules that are capable of predicting the binary interactions at any pressure were preferred. Aspen plus simulator was used to derive the ternary phase diagrams that are given in Figure 18 which shows the increase of the area corresponding to the miscible region with increasing pressure. Pilot scale experimental studied were also conducted. The model employed was found to be a powerful technique for the determination of the phase equilibrium of ternary systems that are required for the preliminary design of the deasphalting extraction columns [56].

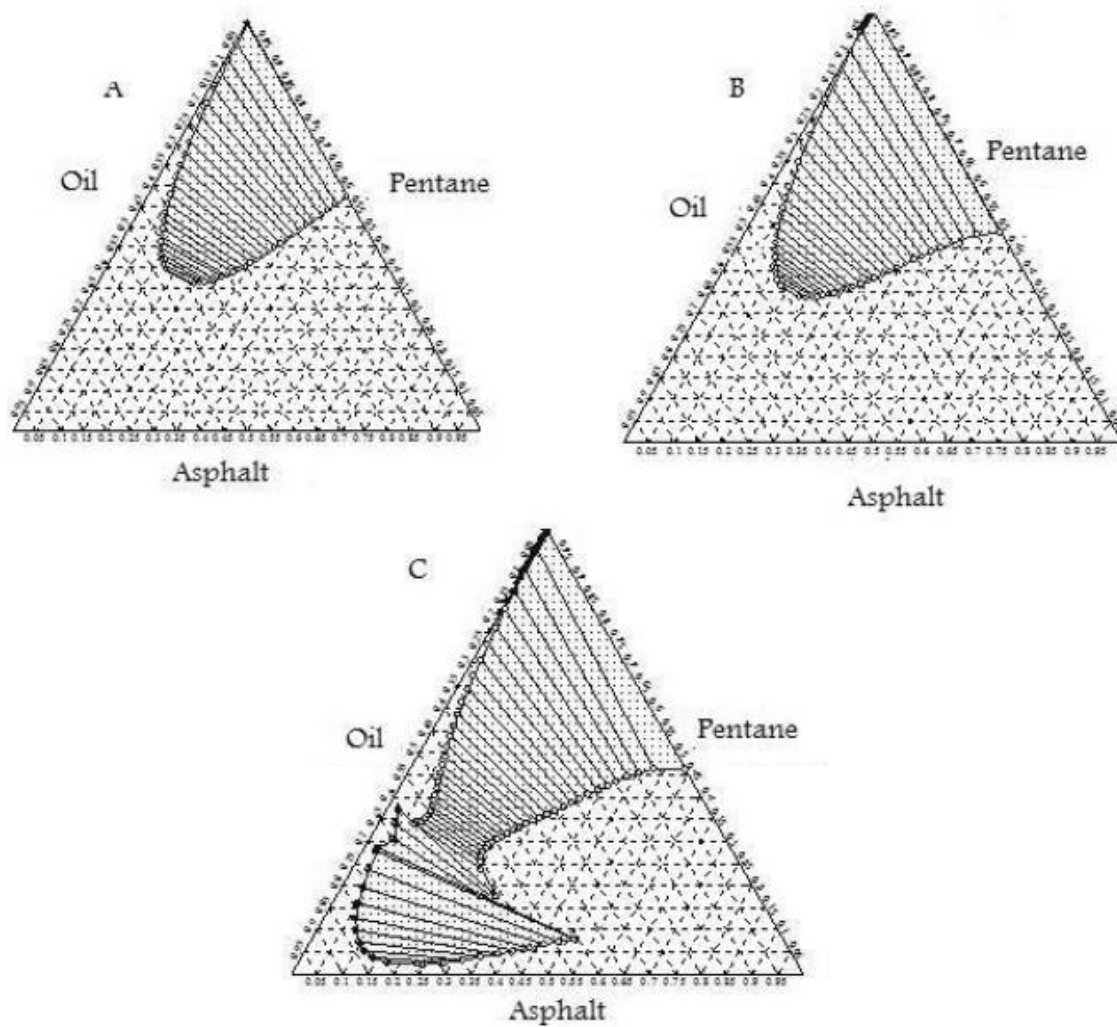


Figure 18: Ternary diagram of the asphalt-oil-pentane mixture at (A) 10 bar, (B) 33 bar and (C) 40 bar *taken from* [56].

2.4. CONCLUSIONS and FUTURE CHALLENGES

SCH₂O among the available SCFs is a very promising candidate for use in heavy oil, unconventional oil or sustainable oil upgrading processes. Although there is a continuous debate on the detailed role of the water in upgrading of hydrocarbons by sub- and SCH₂O, it is widely studied and observed that water at high temperatures and pressures possesses tunable solvation and reactive properties that improves light liquid hydrocarbon yield, suppresses the coke formation, enhances the heteroatom removal, provides selectively extraction of products and may eliminate the need for hydrogen or catalysts. These enhancements should enable oil refineries to cut down their expenditures by developing SCH₂O based processes.

However, there is still a need for more detailed experimental work with model compounds in order to improve our understanding of the reaction mechanisms. Theoretical studies to express the complicated phase diagrams of water-hydrocarbon systems consisting of complex mixtures are necessary to develop combined reaction-separation schemes. Moreover, the predictive models providing the optimum upgrading processing conditions for varying feedstock compositions and optimizing the share of the required middle distillates and gasoline products based on the current market needs need to be developed. Some special catalysts that can both endure the severe SCH₂O environment and alter the reaction pathways need to be developed. Investigating the synergistic effects of the binary and ternary systems to improve the enhancements achieved by SCH₂O or to reduce the hydrogen consumptions are also other open research areas for further studies.

Chapter 3

3. EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

3.1. ORIGINS OF THE FEEDS

The bitumen feedstocks for this study were kindly provided by Turkish Petroleum Refineries Corporation (Tüpraş) and the tar sand from Arkim Energy Ltd. The samples were collected in a “straight-run” condition and not taken from ready to sell final bitumen tanks. Those different grades of bitumen (Izmit 50/70, Izmit 70/100, Batman 50/70) as well as the PDA bitumen that is the bottom product of a propene deasphalting (PDA) unit of a base oil complex were obtained by processing varying types of crude oils in different refineries. This enabled to have a versatile set of feedstocks with varying chemistry. Tar sand samples were subjected to crushing, grinding, sieving, and solvent extraction processes as explained below.

3.2. HEAVY OIL EXTRACTION BY A PILOT PLANT FROM TAR SAND SAMPLES

Tar sand lumps were obtained from a tar sand field and were between 10 cm - 20 cm. The tar sand samples were firstly crushed to 1-10 mm and then ground to less than 1 mm in a ball grinder at room temperature. Ground tar sand samples were dissolved in 50 v. % n-heptane and 50 v.% toluene mixture to obtain a solvent-diluted tar sand slurry. The solvent to tar sand ratio was approximately 5 in the extraction process. Both fresh solvent and recycled solvent from the evaporating process were used in the pilot plant. The solvent-diluted tar sand slurry was mixed at 70 °C for one hour and the solvent-diluted tar sand slurry was left to settle in the mixer. The upper phase was then pumped to a second mixer and filtered to obtain a solid depleted bitumen and bitumen-depleted sand. The solvent was recycled by evaporation and sent back to the mixer. The solid from the bottom of the mixers was sent into a screw dryer and dried at 100 °C. The

dried solid collected from the end of the drier comprised more than 95 wt. % of sand. The final solid depleted bitumen was composed of 95 wt. % bitumen and 5 wt. % sand. The final solid depleted bitumen was subjected to soxhlet extraction with toluene for 8 hours in the laboratory. The sand collected in the Soxhlet extraction thimbles and the toluene-bitumen solution was siphoned to the bottom of soxhlet flask. The toluene was separated from bitumen by using a rotary evaporator. The remaining bitumen-rich solvent solution in the flask was poured into a petri dish and dried in a vacuum oven at 40 °C for 4 hours. The 100 % neat bitumen was obtained and stored in a glass desiccator before using in the experiments.

3.3. FRACTIONATION OF COLLECTED HEAVY OILS

The SARA (Saturate-Aromatics-Resins-Asphaltenes) fraction of the bitumen like heavy oil feeds was determined, firstly, by removing the maltene (n-heptane soluble fraction, i.e. Saturate-Aromatic-Resin groups) from asphaltene (n-heptane insoluble fraction) by soxhlet extraction. To remove saturates from the maltene fraction, 5% maltene – heptane solution was prepared. A glass column of length of ~1 meter was filled with silica and washed with heptane. Then, 5% maltene – heptane solution was poured into the column and then additional pure heptane was poured on the column. After removal of yellow like saturate compounds, %50 heptane - % 50 toluene solution was added to the column to remove aromatics with a light brown color. Afterwards, to remove the resins having a dark color, the column was fed with a solution of % 50 methanol - %25 toluene - %25 petroleum ether. Each fraction was weighed after evaporation of the solvent to determine its SARA content.

Toluene, carbondisulfide (CS₂), NaNO₃, CaCl₂.2H₂O, MgSO₄.H₂O, K₂HPO₄, KH₂PO₄, NaCl, n-heptane, Fe₂O₃, and FeSO₄.7H₂O, FeSO₄.H₂O, H₃BO₃, EDTA, KOH, ZnSO₄.7H₂O,

MnCl₂·7H₂O, MoO₄Na₂·2H₂O, CuSO₄·5H₂O and CoCl₂ with high purity (> 99.8%) were purchased from Sigma-Aldrich. Zeolite based catalysts that are normally used for FCC (Fluid Catalytic Cracking) unit and the byproduct of an aluminum industry namely red mud were obtained from open market.

Microalgae *Chlorella vulgaris* was cultivated in a 27 litre flat panel type photobioreactor (PSI) available in our laboratory by using a slightly modified Bold's basal medium [156] with an aeration rate of 10 L/min (2% CO₂) and a light intensity of 480 μE. Cell and nitrate concentrations were determined by using spectrophotometer and measuring absorbance values at 680 and 220 nm, respectively, to monitor the growth of the cells. Cells were harvested at the early stationary phase by centrifugation. After sonication and drying, cells were ground by using liquid nitrogen prior to upgrading experiments.

Upgrading studies were carried out using ultra-distilled water. Home-made bomb reactors made from stainless steel tubes with an internal volume of 10 cm³ were used. The experiments were carried out at 440 °C and 30 MPa. The effects of varying water to feed (w/f) ratios ranging from 2 to 10 wt. % and microalgae to bitumen loadings with 25 and 50 wt. % were investigated where feed refers to the microalgae and bitumen mixture. For each run, the mass of empty reactor and its contents were measured as well as the closed and filled reactor before and after upgrading reactions. The contents of the reactor rapidly heated up to desired reaction temperature in less than 5 minutes. To stop the reaction, the reactor was removed from sand bath and immersed in a water bath at room temperature. During this 30 minutes long cooling period, the upgraded liquid products that are in liquid phase at room temperature condensed. Gas contents were determined by measuring the mass of the reactor before and after releasing the gas in the reactor by opening the top of the cylindrical bomb reactor slowly to atmosphere. Excess toluene was used to dissolve

the upgraded products in the reactor. Solubility analysis according to EN12592 was carried out for the determination of amount of solid by products, namely coke. Then, toluene was removed by rotary evaporator and the remaining products were dissolved in CS₂ for further true boiling point (TBP) analysis by High Temperature GC Simulated distillation (HT GC-SIMDIS), ANTEK-PAC, Custom Simdis-HT.

Thermal Gravimetric Analysis (TGA) analysis of microalgae was conducted by using TA Instruments TGA Q500. Temperature was increased with a ramp of 10 °C/min from 25 °C to 120 °C, kept constant at 120 °C for 2 hours and increased with a ramp of 5 °C/min to 400 °C. Elemental composition of samples was obtained by organic elemental analyser (Thermo Scientific Flash 2000).

The reference values regarding the classification of fuels according to their TBP values are presented in **Table 5**.

Table 5: TBP Distribution for Classification of Liquid Hydrocarbons.

			Kerosene	Light Diesel (L.Diesel)	Heavy Diesel (H.Diesel)	Light Vacuum Gas Oil (LVGO)	Heavy Vacuum Gas Oil (HVGO)	VR
Initial Boiling Point (°C)			150	250	300	350	390	549
Final Boiling Point (°C)			250	300	350	390	549	-

Morphological analysis of the cokes obtained after upgrading was performed by Zeiss Ultra Plus field emission scanning electron microscope. A secondary electron detector having accelerating voltage range of 5-15 kV and working distance range of 5.5-5.8 mm was used to get images. For EDX imaging, XFlash 5010 EDX detector was used.

Chapter 4

4. RESULTS AND DISCUSSION

This chapter is organized under 2 main sections, numerically 4.1. and 4.2. In the first one, the results of the upgrading studies performed by the blends of microalgae and heavy oil samples are given. In the second one, results of upgrading of different heavy oil feeds and samples of unconventional oils, such as tar sand are given. Findings of kinetic model derivation, effect of water loading and catalysts additions are also provided in the second section. The details are given below.

4.1. UPGRADING BLENDS OF MICROALGAE FEEDSTOCKS AND HEAVY OILS IN SUPERCRITICAL WATER

4.1.1. Feed Characterization

The properties of the bitumen sample are given in **Table 6**. It was found to be 50/70 penetration grade with a penetration value of 58. Compositions of bitumen's sub-components are given in **Table 7**. The SARA composition of the sample indicated that it was rich in aromatics with considerably high asphaltene content.

Table 6: Grading of heavy oil analysis according to EN 12591

Analysis	Standards	Units	Values
Penetration	TS EN 1426	0.1 mm	58.00
Softening Point	TS EN 1427	°C	48.2
Flash Point	TS EN ISO 2592	°C	326.00
Solubility	TS EN 12592	%	99.86
Short term aging (RT-FOT)	TS EN 12607-1	-	
Mass loss	-	%	0.18
Permanent Penetration	TS EN 1426	%	74.00
Softening Point	TS EN 1426	°C	52.4

Table 7: SARA composition of bitumen

Compounds	Composition
Saturates	26.2
Aromatics	41.9
Resins	18.9
Asphaltene	12.9

The elemental composition of the microalgae are presented in **Table 8**. H/C mole ratio of microalgae was found to be 1.69 which is higher than the one obtained for heavy oil sample suggesting that microalgae itself, together with SCW might provide hydrogen during upgrading reactions. Nitrogen content on the other hand was found to be more than 4 times of that of

bitumen. Thereby, it might be safer to use a low microalgae to bitumen ratio in order to reduce the possibility of poisoning catalysts in subsequent refining unit operations.

Table 8: Elemental Composition of Feeds

Element (% by weight)	Bitumen	Microalgae
Carbon	87.1	54.5
Hydrogen	10.5	7.7
Nitrogen	0.75	3.5
Sulphur	1.71	1.3

Based on the TGA analysis, water content of microalgae was found to be around 5% as shown in **Figure 19**.

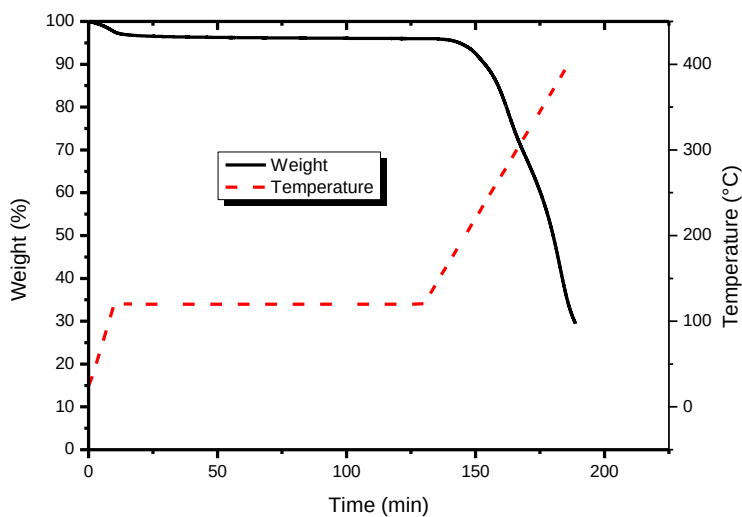


Figure 29: TGA Analyses of Microalgae.

4.1.2. Analysis of Upgraded Products

Table 9 shows the composition of the upgraded products consisting of coke, gas and liquid for various feeds and w/f ratios. Upgrading results of bitumen under SCW conditions with and without microalgae addition with a w/f ratio of 2 are presented in **Figure 20**.

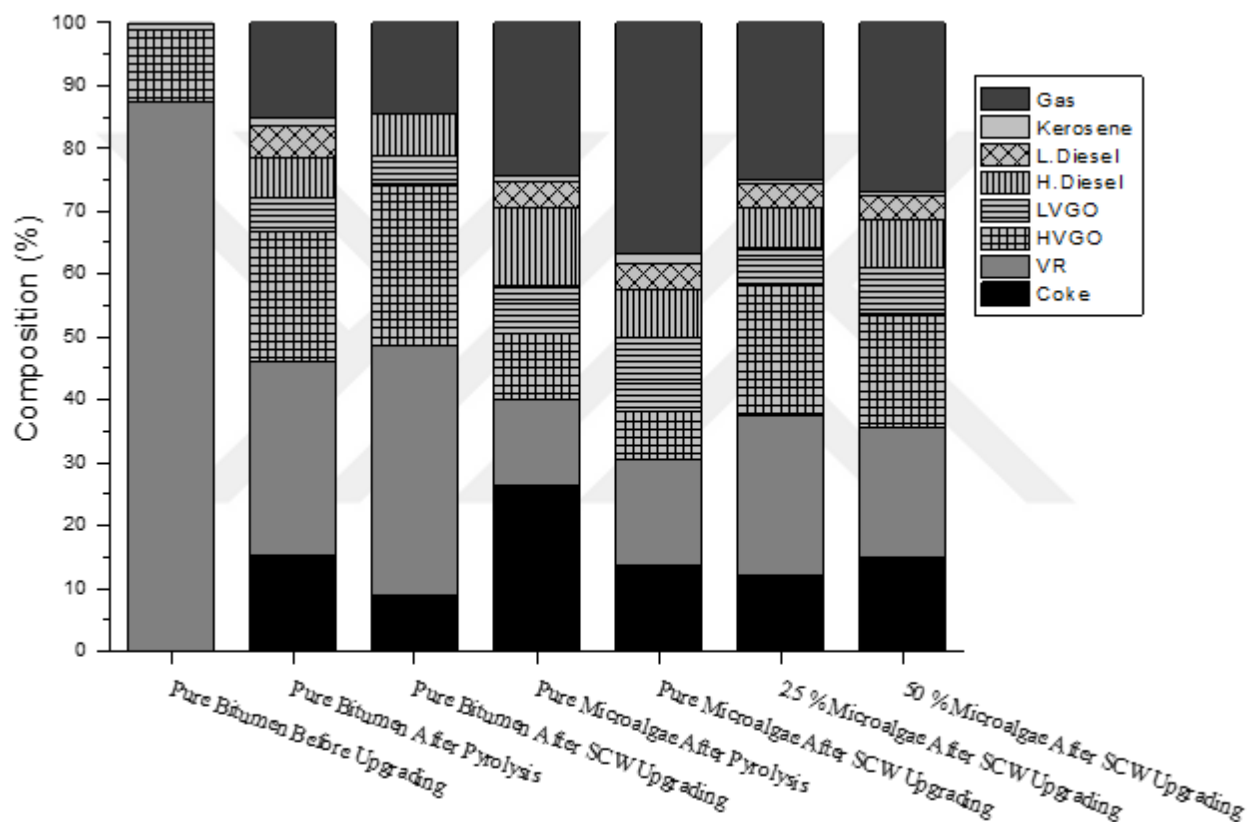


Figure 20: Composition of the products of upgrading reactions carried out in SCW environment at 440 °C, 1 hour, 30 MPa and w/f ratio of 2 and of pyrolysis of pure microalgae and pure bitumen

As shown in **Figure 20**, treatment of bitumen in SCW and its pyrolysis resulted in a significant decrease of VR fraction. The decrease was more significant for the pyrolyzed sample where VR fraction decreased to 30.6% from an initial value of 87.5%. The presence of SCW also

decreased the coke yield by nearly 40% from 15.4% down to 9% (**Figure 20**). This was also accompanied by a slight decrease in the amount of gas product which translates into a higher liquid yield by means of SCW upgrading. On the other hand, although low coke and high liquid yields are desirable for a more economical process, higher selectivity to lighter fractions such as kerosene and diesel among the liquid portion itself is desirable as well. However, as shown in **Figure 21** for a w/f ratio of 2, the liquid product in pyrolysis of bitumen contained higher fraction of light diesel and kerosene compared to the product obtained in the presence of SCW upgrading.

Table 9: Coke, gas and liquid's sub-component values for varying runs and for pure bitumen feed.

Sub-Component Analysis															
	Pure Bitumen Before Upgrading	Bitumen Pyrolysis		Bitumen SCW Upgrading w/f:2		Microalgae Pyrolysis		Microalgae SCW Upgrading w/f:2		25% Microalgae SCW Upgrading w/f:2		50% Microalgae SCW Upgrading w/f:2		25% Microalgae SCW Upgrading w/f:10	
Component (%)	Liquid	Liquid	Total	Liquid	Total	Liquid	Total	Liquid	Total	Liquid	Total	Liquid	Total	Liquid	Total
Gas	-	-	15.2	-	14.6	-	24.4	-	36.8	-	25.1	-	26.8	-	58.8
Coke	-	-	15.4	-	9	-	26.5	-	13.8	-	12	-	14.9	-	9.6
VR	87.50	44.1	30.6	51.7	39.5	27.6	13.6	33.4	16.6	40.4	25.4	35.6	20.7	47.6	15
HVGO	11.40	29.9	20.8	33.6	25.7	21.1	10.4	15.6	7.7	32.9	20.7	30.9	18	34	10.7
LVGO	1.10	7.7	5.3	6.1	4.7	15.3	7.5	24	11.9	9.5	6	12.6	7.4	8.1	2.6
H.Diesel	-	9.4	6.5	8.6	6.6	25.5	12.5	15.3	7.6	10.2	6.4	13.2	7.7	8.2	2.6
L.Diesel	-	7.3	5.1	-	-	8.6	4.3	8	4	6	3.8	6.3	3.7	2.1	0.7
Kerosene	-	1.6	1.1	-	-	1.9	0.9	3.7	1.6	1	0.6	1.4	0.8	-	-
Sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Pyrolysis of bitumen led to higher VR conversion than treatment in SCW. The gas and coke yields in SCW were also lower due to a lower VR conversion. SCW is believed to form layers between asphaltene sheets and thus prevent the coke precursors from agglomerating that would lead to the formation of coke by polymerization and condensation reactions. Thereby, SCW can retard the upgrading reaction so that coke precursors, instead of forming final solid by product of coke, form a maltene phase by the help of the SCW environment [67, 157-159].

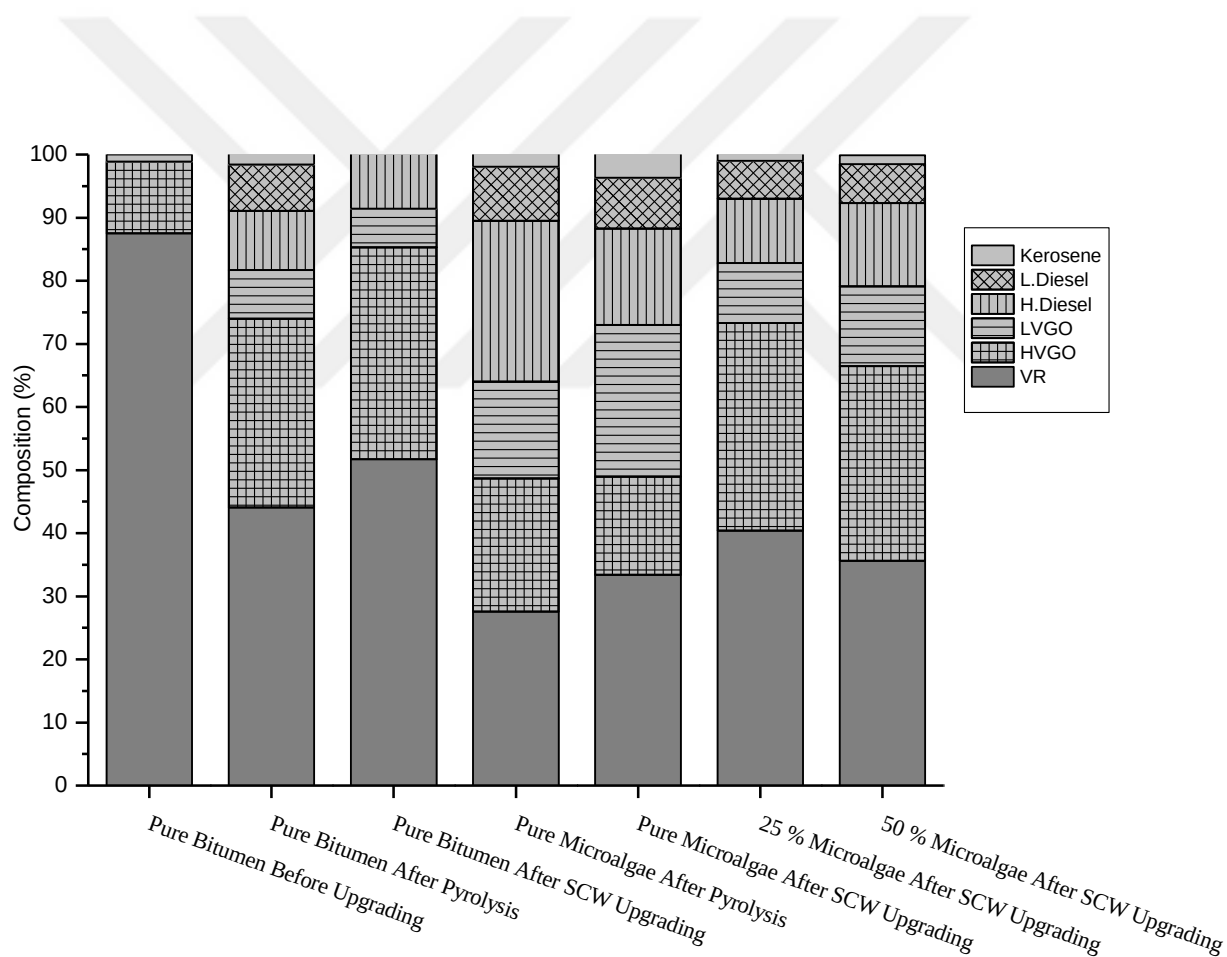


Figure 21: Composition of liquid fractions obtained by upgrading reactions carried out in SCW environment at 440 °C, 30 MPa, 1 hour, w/f ratio of 2 and by pyrolysis of pure microalgae and pure bitumen.

The feed which contained 25 wt. % microalgae was upgraded successfully in SCW resulting in a decreased VR content of liquid portion down to 40.4% (**Figure 21**) which was even lower than VR of the product obtained by pyrolysis of pure bitumen. Increased LVGO, diesel and kerosene yields were also observed with 25 wt. % microalgae addition to bitumen, as well. As can be seen in **Figures 20 and 21**, the feeds containing 50 and 100 wt. % microalgae had higher conversion of VR with the final VR fractions of 35.6 % and 33.4 % in liquid, respectively, together with highly improved diesel and kerosene yields. However, this was also accompanied by an increase in gas formation with gas fraction reaching values as high as 36.8%. Improvement in lighter fractions with microalgae addition can be explained by taking into consideration the chemical composition of microalgae. Although microalgae tends to yield more gas products in SCW, it can be seen in **Figure 20** that upgrading of pure microalgae in SCW yielded a product which was 50 % liquid. SCW can solubilize and hydrolyze algal oil, namely triglycerides into free fatty acids and glycerol and convert free fatty acids into corresponding alkanes which are diesel range hydrocarbons [10, 84]. Moreover, liquid range products can also be produced from protein and carbohydrates available in microalgae [10]. It has been shown that microalgae decomposition yields non-gaseous intermediate products during hydrothermal gasification, and these products are converted into gas or coke with different rates as reported by Guan et al.[77]. Moreover, increase in temperature during SCW upgrading of microalgae significantly increases gas yield [82]. Therefore, operating at relatively lower temperature for hydrothermal gasification decreased the rate of gasification or coke formation and improvements in liquid range products were obtained with microalgae addition into bitumen during SCW upgrading. Similar to the results of the experiments with pure bitumen, SCW treatment of pure microalgae resulted in coke yields significantly lower than coke yields obtained when pure microalgae was pyrolyzed. To investigate effect of water loading, feed containing 25 wt. % microalgae was selected since it

resulted in lower coke and gas yield. Moreover, lower blending ratios might be favorable when high cost of microalgae cultivation [160] and high nitrogen, oxygen and sulfur content of microalgae are considered. SCW upgrading results of feed containing 25 wt. % microalgae with w/f ratio of 2 and 10 are presented in **Figures 22 and 23**. Increase in w/f ratio resulted in decrease in coke formation due to retarding effect of SCW. However, gas formation was increased due to lower microalgae loading as expected[77].



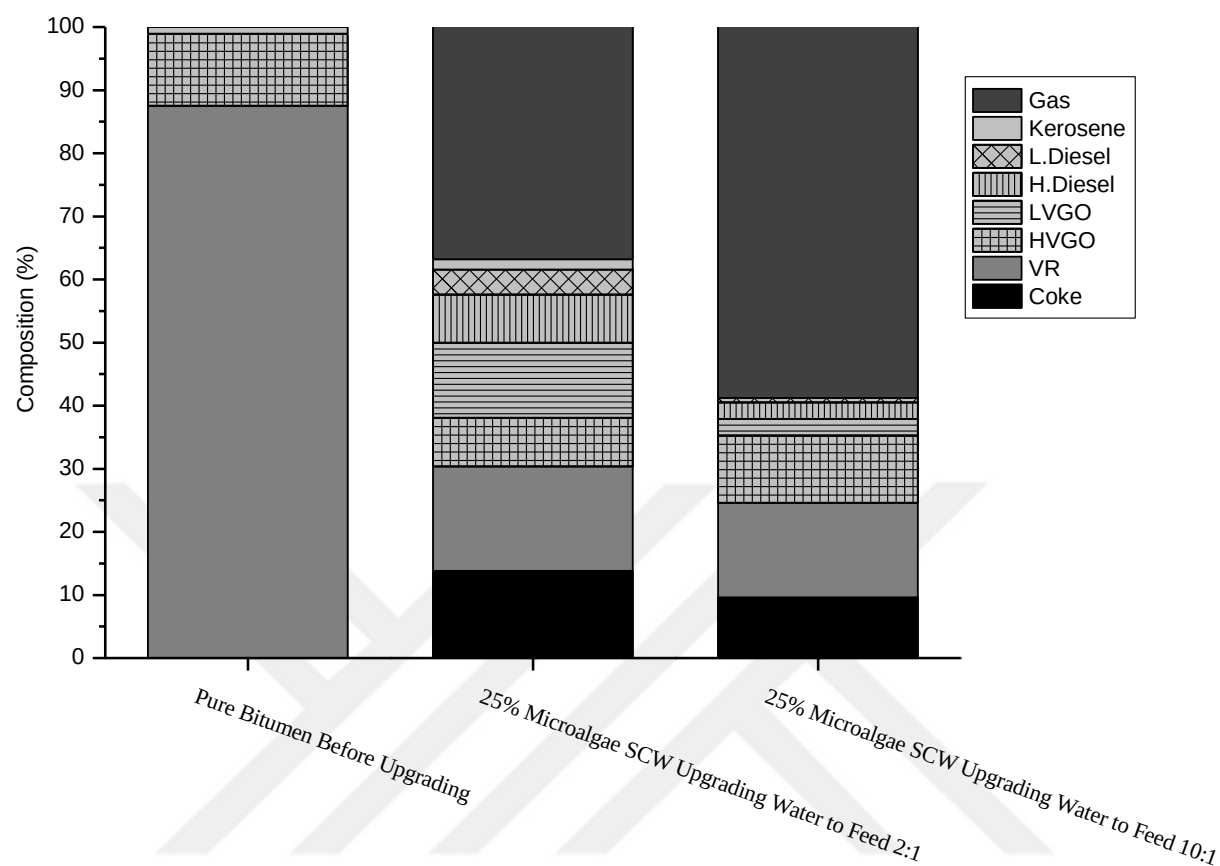


Figure 22: Composition of the products of upgrading reactions carried out in SCW environment at 440 °C, 1 hour, 30 MPa with a w/f ratio of 2 and 10 and by using the feed containing 25 wt. % microalgae.

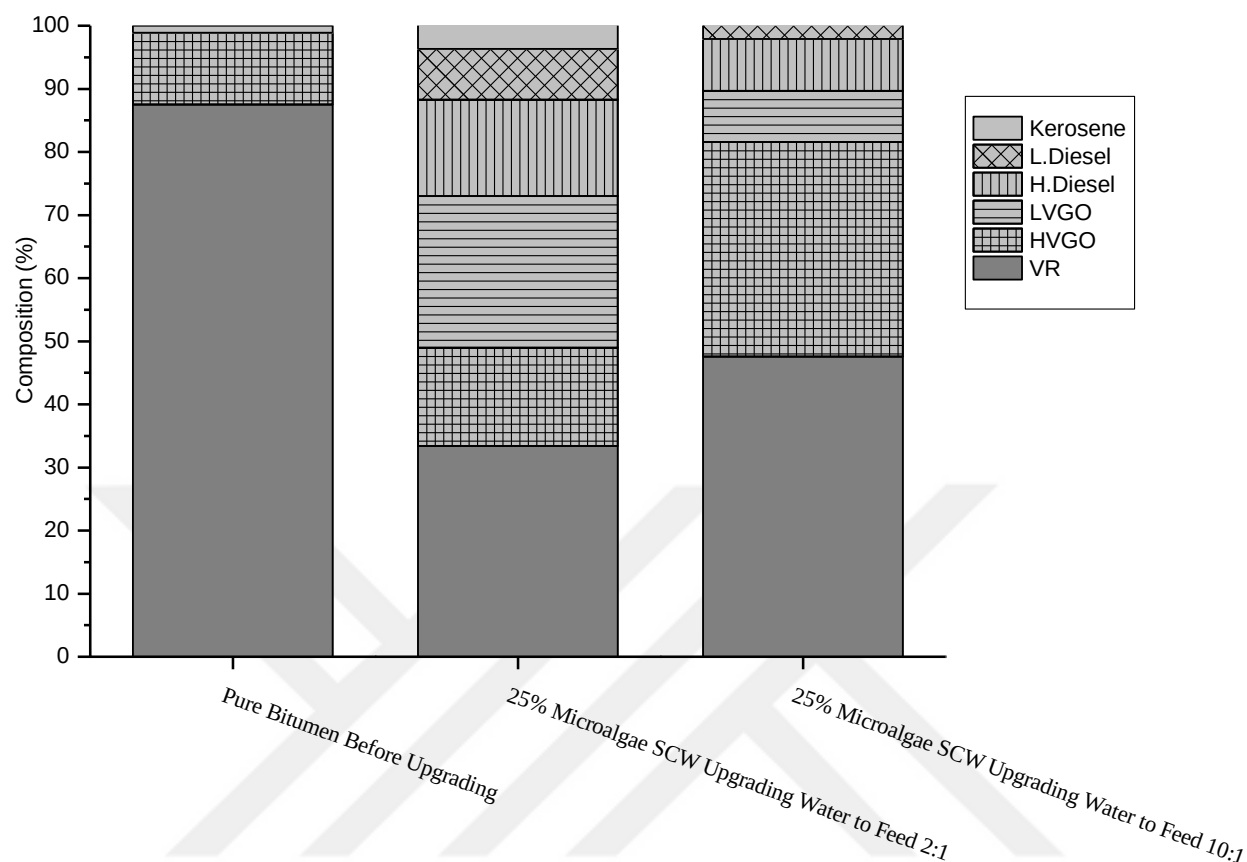
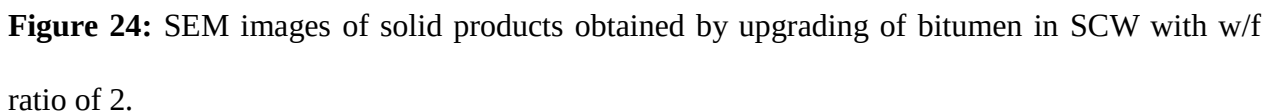


Figure 23: Composition of liquid fractions obtained by upgrading reactions carried out in SCW environment at 440 °C, 30 MPa, 1 hour, with a w/f ratio of 2 and 10 and by using the feed containing 25 wt. % microalgae.

Microalgae addition can improve VR conversion and light liquid yields to a great extent but the presence of SCW causes microalgae upgrading selectivity shift towards gas phase products at the operating conditions of this study. Since the scope of this study is to blend sustainable microalgae resources into oil refining operations, blends with a higher fraction of heavy oil than microalgae seems to be a more preferable application from an industrial point of view.

Delayed Coker Units (DCUs) where bitumen like heavy oil streams are heated in drums are commonly used for heavy oil upgrading and solid coke is a byproduct. Different types of coke are obtained depending on the feed chemistry and operating conditions. Shot, sponge or needle type cokes are the types which are generally observed. High asphaltene content usually results in shot type coke formations while the feeds that are rich in aromatics are preferable for the production of needle type cokes. In addition to SARA content, micro carbon residue (MCR) of the feed sample plays an important role on coke types. Asphaltene content should be below 50% of MCR to avoid shot type coke formations. Canadian type bitumens for example may have 25% asphaltene and 30% MCR suggesting shot type coke formations in DCU drums. We also investigated the type of coke formed in upgrading of bitumen-algae blends. For morphological analysis, SEM-EDX analysis of varying coke samples were also carried out and the results are given in **Figures 24-28**.



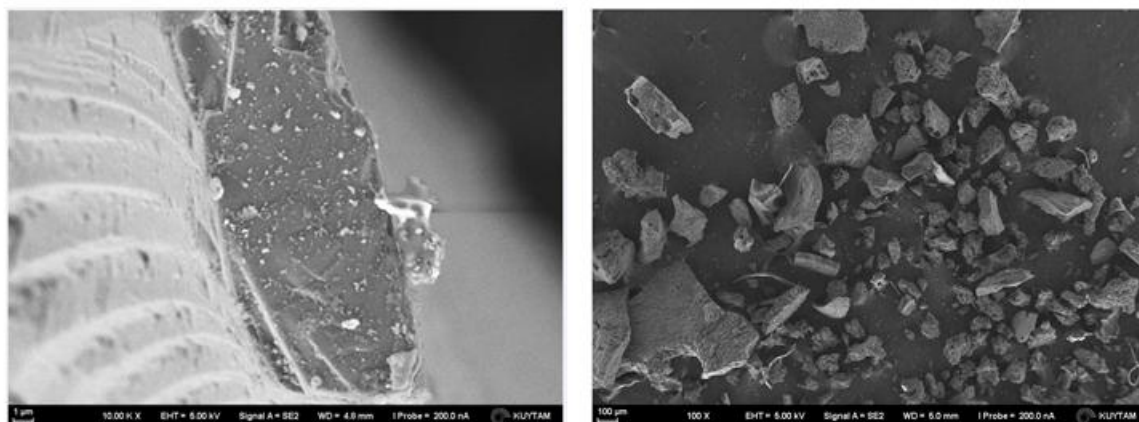


Figure 25: SEM images of solid products obtained by upgrading of microalgae in SCW with w/f ratio of 2.

Shot type coke formations were observed with almost no morphological alterations caused by changing the feed from pure bitumen (**Figure 24**) to pure microalgae (**Figure 25**) suggesting that aromatic content of algae is not high enough to alter the coke type from shot to sponge[161] . These findings are also supported by SEM analysis of coke samples obtained by upgrading of the feeds containing 25 to 100 wt. % microalgae in the presence of SCW with w/f ratio of 2. However, unlike other samples, some crystal like structures were detected on the coke surfaces for upgrading of the feed with 100 wt. % microalgae with a w/f ratio of 2 (**Figure 26**) and crater like hole formations were observed on the surface for a water loading of 10 times of the feed which contains 25 wt. % microalgae (**Figure 27**). Crystal deposits might be originating from the utilization of the ingredients in the growth media used for cultivation by microalgae which might be the reason for observation of this phenomena only at high microalgae loadings. The crater like holes form due to increasing water loadings which causes sharply increased gas yields. Thereby such a shift in the selectivity of the upgraded products towards lighter ends and

gases at a w/f ratio of 10 can easily cause those lighter ends to boil at the conditions of this study upon their formation during upgrading reactions and thereby form hole like structures in the coke samples.

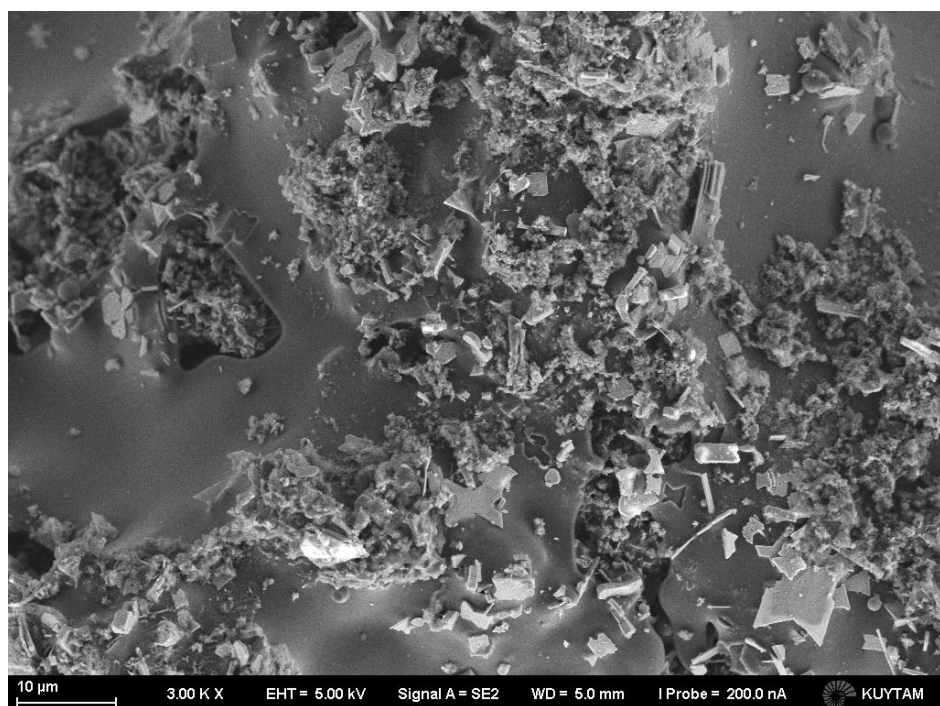
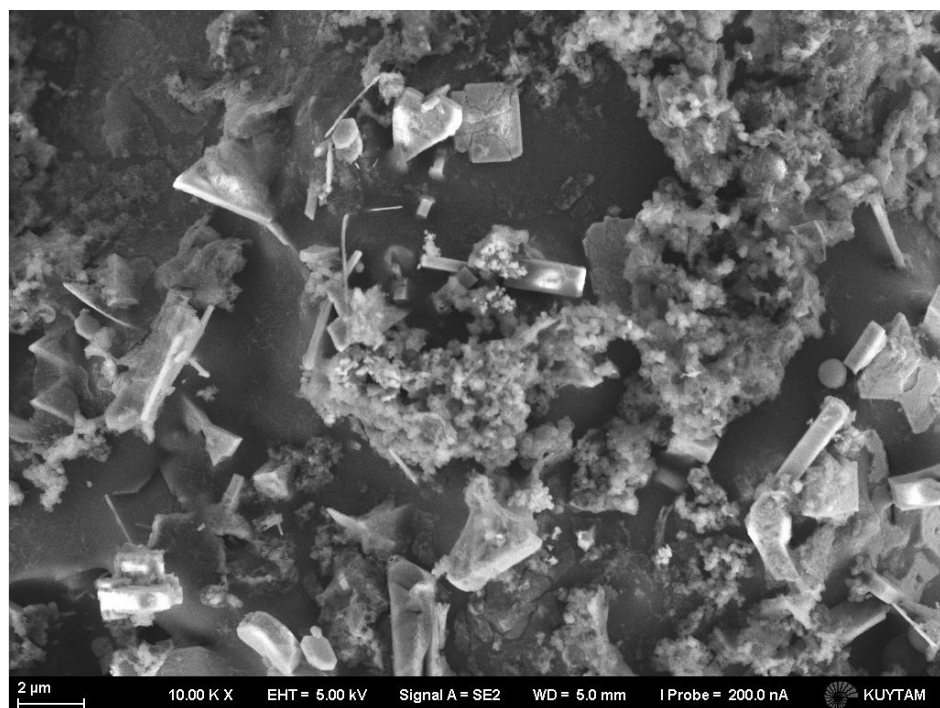


Figure 26: SEM images (top and bottom) of solid products obtained by the upgrading of the feed containing 100 wt. % microalgae with the addition of SCW with water/oil ratio of 2.

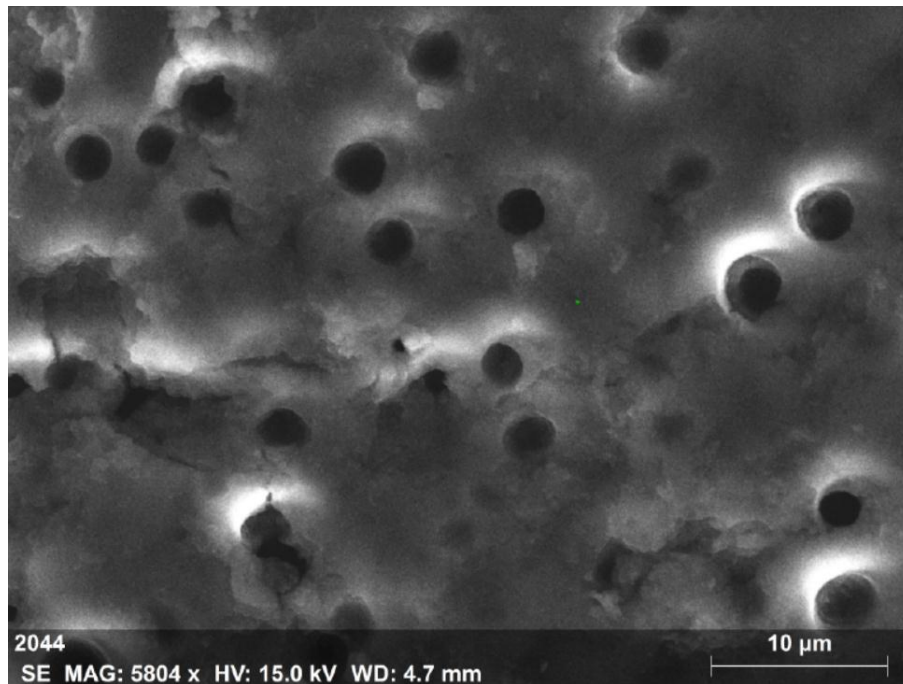


Figure 27: SEM image of solid products obtained by the upgrading of the feed containing 25 wt. % microalgae with the addition of SCW with water/oil ratio of 10.

Hexagonal structures of iron resembling a honeycomb structure were observed for the SCW upgrading of the feed containing 25 wt. % microalgae at a w/f ratio of 2 (**Figures 28 and 29**). Existence of iron might be explained by the presence FeSO_4 in the Bold's basal growth media used in cultivation of microalgae or by the presence of iron in bitumen. Crosses of red color in SEM images represent the point focused on during EDX analysis. Although there are some scattered electrons during EDX analysis reflected from the nearby accumulations that are in the proximity of the point of measurement, this comparative analysis given in **Figures 28 and 29**

suggests that hexagonal like formations are iron. Chaudhari et al. [162] presented similar findings for iron deposit growing via hexagonal shape column like structures in the aqueous media. Such structures may be playing a catalytic role in the upgrading reactions [163].



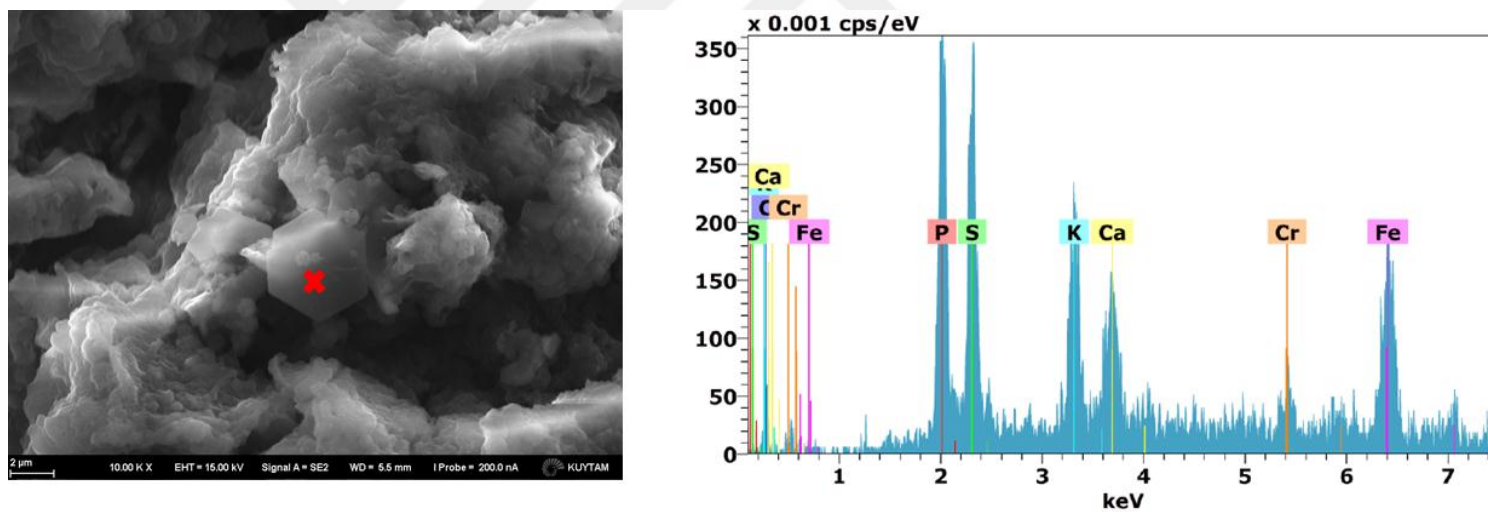


Figure 28: SEM images (left) together with the EDX analyses (right) of the point marked with a red cross for solid products obtained by the upgrading of the feed containing 25 wt. % microalgae with w/f ratio of 2.

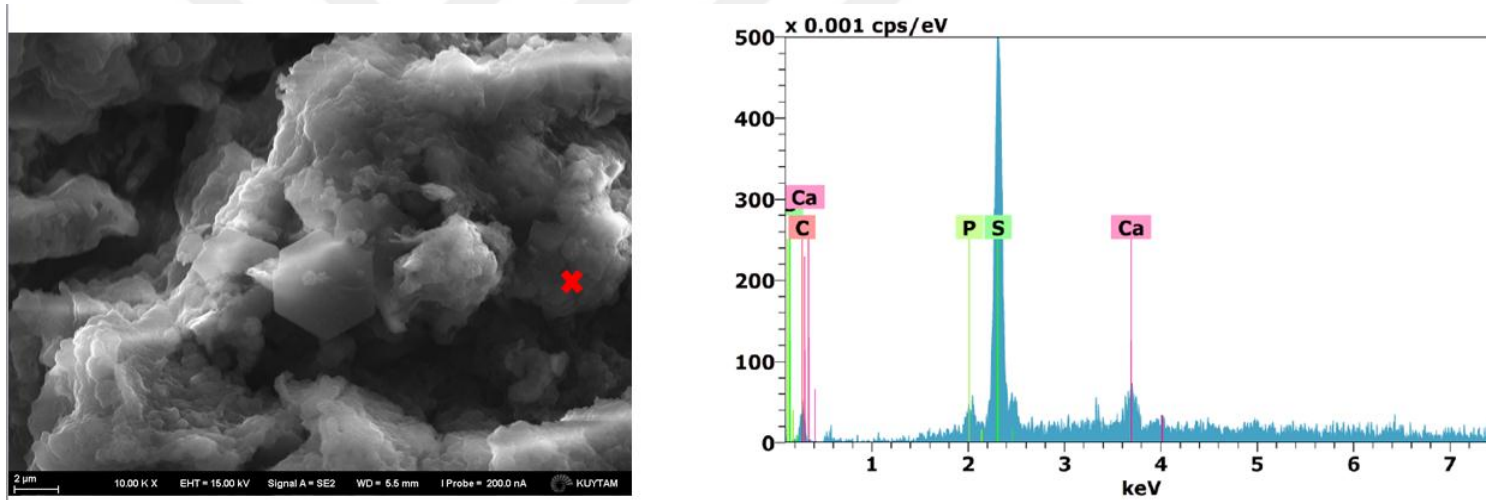


Figure 29: SEM images (left) together with the EDX analyses (right) of the point marked with a red cross for solid products obtained by the upgrading of the feed containing 25 wt. % microalgae with w/f ratio of 2

4.2. HEAVY AND UNCONVENTIONAL OIL UPGRADING IN SUPERCRITICAL WATER: EFFECT OF CATALYTIC ADDITIVES AND FEED CHEMISTRY ON KINETICS, YIELD AND SELECTIVITY

4.2.1. Feed Characterization

The properties of the heavy oil feedstock samples are given in **Figure 30** and **Table 10**. Classifications of the samples were done according to the boiling point distributions (See **Figure 30**), EN12591, weight % values of SARA sub-fractions and elemental analysis (See **Table 10**).

It was seen in **Figure 30** that not only the heaviest portion, VR content, but also the HVGO and diesel portions have different weight percentages in the feeds selected for this study. Some of the feeds on the other hand, such as PDA and Izmit 70/100 are found to have similar TBP distributions. This is of paramount importance to analyze the possible causes of different product distributions when feeds having similar TBP distribution are used for upgrading experiments.

Table 10 shows that all the feeds' solubility values were higher than 99% suggesting that the oil samples had almost no inorganic impurities that may affect the upgrading reactions. Ordinary bitumens' penetration values (the ones from Izmit and Batman) were found to be less than 50, higher than 50, and higher than 70. Since 50 & 70 are threshold values in the penetration grading system of bitumen, those samples enabled us to perform a study with a set of broad range of heavy oils falling in 3 different bitumen grading zones. Interestingly, close asphaltene contents were found for tar sand and bitumen samples although their VR content varied from each other

by 35%. Viscosity of tar sand bitumen was found to be the lowest that was in line with the low VR content and high amount of light ends found by TBP analysis in **Figure 30**.

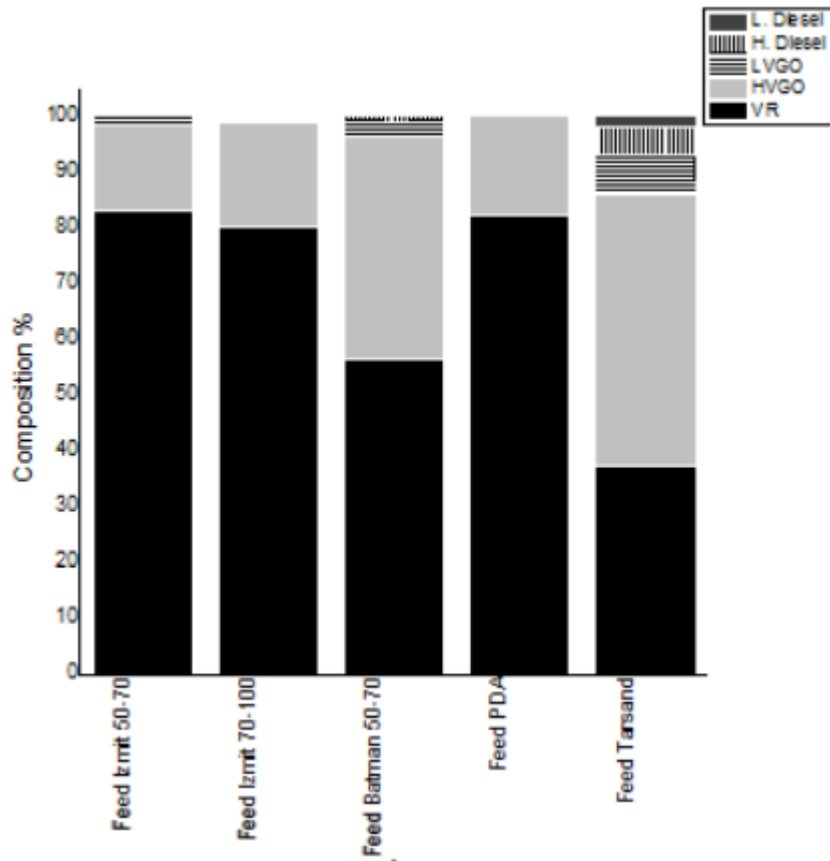


Figure 30: Composition of the feeds being used in this study.

Table 10: The Physical and Chemical Properties of The Heavy Oil Feedstock Samples.

Analysis	Standards	Unit	Izmit 50/70	Izmit 70/100	Batman 50/70	PDA	Tarsand
Penetration	TS EN 1426	0.1 mm	58	83	45	38	N/M
Softening Point	TS EN 1427	°C	48.2	46.2	56.6	N/M	N/M
Flash Point	TS EN ISO 2592	°C	326	328	302	N/M	N/M
Solubility	TS EN 12592	%	99.86	99.77	99.24	N/M	N/M
Short term aging (RT-FOT)	TS EN 12607-1	-	-	-	-	-	-
Mass Loss	-	%	0.18	0.25	0.78	N/M	N/M
Permanent Penetration	TS EN 1426	%	74	66	68	N/M	N/M
Softening Point	TS EN 1427	°C	52.4	51.2	65.4	N/M	N/M
Saturates		%	26.2	27.5	30.4	6.5	10.1
Aromatics		%	41.9	40.6	37.04	57.8	35.7
Resins		%	18.9	20	8.36	21.1	26.1
Asphaltenes		%	12.9	11.9	24.2	14.6	28.1
Carbon		%	87.1	87.6	85.5	84.3	80.6
Hydrogen		%	10.5	10.6	10.01	9.8	9.8
Nitrogen		%	0.67	0.67	0.75	0.83	0.91
Sulfur		%	1.71	1.12	3.73	4.4	5.9
Viscosity		cP	382.8	226.1	699.2	200	177.9

* "N/M" stands for "Not Measured".

4.2.2. Effect of Feed Chemistry

Upgrading results of various types of heavy and unconventional oil samples with and without SCW addition are given in **Figure 31**. For a better understanding of the reaction mechanisms, the composition of liquid portions separate from coke and gas are given in **Figure 32**. As shown in **Figure 31**, upgrading of oil samples resulted in high amount of coke formations, numerically higher than 20% for all the samples at the end of 2 hours of reaction time. As compared to pyrolyzed samples, use of SCW decreased the coke yields from 23,9% to 21,7% and from 27,98% to 21,3% for Izmit 50/70 and tar sand bitumen samples, respectively. These findings suggest that SCW suppresses coke formation during heavy oil upgrading which is consistent with previous findings in the literature [67, 157-159, 164].

Among other heavy oil feed samples treated in SCW, Batman 50/70 bitumen gave the highest amount of coke, 25,56%, which can be attributed to its high asphaltene content of 24,2%. However, tar sand bitumen has also high asphaltene content of 23,8% which is comparable with that of Batman 50/70 bitumen. Interestingly, upgrading of tar sand bitumen in SCW resulted in the least amount of coke formation of 21,3% which might be explained by the chemistry of tar sand bitumen. Among the various heavy oil feed samples used in this study, the tar sand bitumen had the least amount of VR (37,32%) while Izmit 50/70 bitumen had VR content as high as 83% as shown in **Figure 30**. VR is known to go through condensation and polymerization reactions which lead to formation of coke [165]. Moreover, the tar sand bitumen feed contained comparatively higher amounts of light ends such as VGO and diesel, as shown in **Figure 30**. Those lighter fractions, during SCW upgrading, may act as an entrainer for SCW for the dissolution of heavier fractions such as VR which then retards condensation and polymerization reactions of coke precursors and decreased the ultimate coke yield.

As can be seen in **Figure 31**, the VR content of 32,32% was obtained for upgrading of Izmit 50/70 under SCW while the VR content was 27,96% for the pyrolysis of the same feed in the absence of water supporting the idea of coke suppression by retarding the VR decomposition by means of SCW that is in line with our previous findings [164]. Among the upgraded products of the various feeds, highest amounts of light ends were obtained by the upgrading of tar sand bitumen both with and without SCW. This can be explained by the lower VR content, high amount of lighter ends and lower viscosity of tar sand while the viscosity of regular bitumen feed samples were in the range of 225- 700 cP. As compared to the upgrading of tar sand bitumen under SCW, pyrolysis produced higher coke as well as higher light ends such as heavy kerosene caused by further VR decomposition which occurred in the absence of SCW.

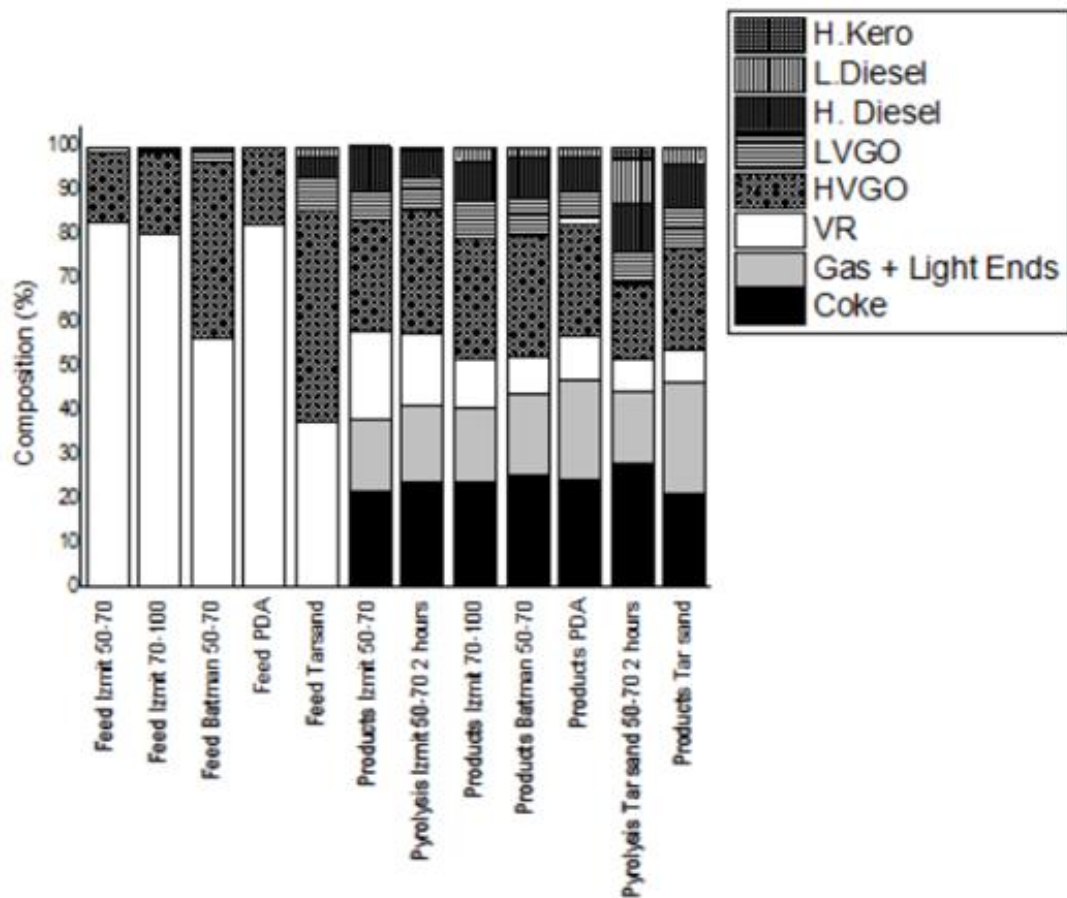


Figure 31: Composition of the products of upgrading reactions of various feeds carried out in SCW environment at 440 °C, 2 hour, 30 MPa and w/f ratio of 2 and of pyrolysis of tar sand and Izmit 50/70.

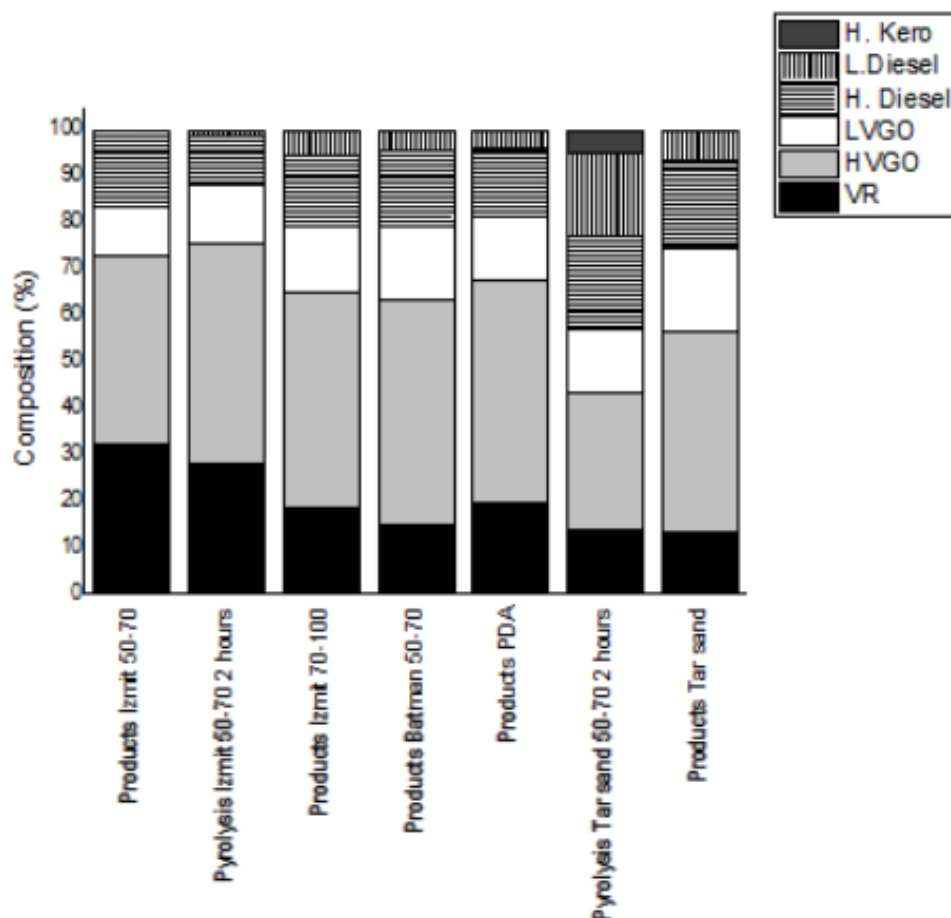


Figure 32: Composition of liquid fractions obtained by upgrading reactions of various feeds carried out in SCW environment at 440 °C, 2 hour, 30 MPa and w/f ratio of 2 and of pyrolysis of tar sand and Izmit 50/70.

4.2.3. Effect of Catalytic Additives

Upgrading results of Izmit 50/70 heavy oils with varying types of catalytic additives both in the presence and absence of SCW are given in **Figure 33**. The composition of liquid portions separate from coke and gas are given in **Figure 34**. As given in **Figure 33**, among the 2 hour upgrading reactions with catalytic additives, least amount of coke, 17,21 %, was obtained using FCC spent catalysts. Zeolite based FCC catalysts are usually known to have high acidity [166]

and high acidity favors cracking of C-C bonds during upgrading reactions [167]. Thereby decreased coke yield and improved diesel yields can be attributed to the strong acidity of the zeolite based spent catalyst. The sum of the gas and coke yields of the upgrading reactions carried out for 2 hours was lowest when red mud was used providing the highest liquid yield. In addition to an improved liquid yield, higher selectivities towards kerosene and light diesel formations were observed with red mud that can possibly be attributed to its high iron content. Iron is known to trigger hydrogenation and cracking reactions in slurry hydrocrackers therefore improved liquid yield and superior light end selectivity can be explained by iron compounds in red mud samples [168]. Based on the results obtained in runs containing red mud, pure Fe_2O_3 without any other additive was also used alone as a catalytic additive. A similar coke content and increased gas yields with decreased light end selectivity as compared to red mud was obtained. The results which are not better than those obtained by red mud can be explained by the synergistic effect of the other catalytically active metals existing in red mud such as Al, Si, Ti and Ca providing improved conversion and selectivity [169]

During the distillation of crude oil, sulfur like heteroatoms such as S, Ni, V, Fe existing in oil streams have a tendency to accumulate in the heavy bottom fractions providing a high content of sulfur in bitumen like heavy oils. Those sulfur accumulations may then poison the catalysts being used in SCW assisted heavy oil upgrading. Sulfur based supported metals on the other hand are known to be more resistant against sulfur poisoning as compared to the oxide forms of metals. Therefore, as a comparative reference to upgrading experiment carried out with Fe_2O_3 , FeSO_4 was also investigated. Interestingly, VR content was decreased and H. diesel formation was improved and the highest amount of coke formation, 23.56%, was observed among the upgrading reactions performed in SCW. This shows that there is no significant difference in conversion and

selectivity when sulfided forms of an iron based catalyst is used but an improved heavy diesel yield can be obtained. In an attempt to observe possible synergistic effects, FeSO_4 and FCC spent catalyst was used in equal amounts (2.5 % FeSO_4 + 2.5% FCC Spent). Improved heavy diesel yields were obtained but coke suppression ability was diminished and coke yield increased to 22,8% which was higher than the lowest value of 17,21% obtained by FCC spent alone.

In order to assess the effect of both reaction time and catalyst on yield and selectivity, upgrading of heavy oil sample was also carried out for 1 hour both in the presence and absence of SCW with FeSO_4 addition. In the presence of SCW, coke yield was decreased from 15 % to 9% while use of FeSO_4 together with SCW caused an undesired increase in coke yield up to 13,37%. However, use of FeSO_4 with SCW decreased VR content down to 28,26% from 51,68% obtained by SCW upgrading at 1 hour without any catalytic additive. Moreover, highly improved light end formation was observed when FeSO_4 and SCW were used together for 1 hour. Short reaction times seemed to favor light end formations while increased reaction times caused a shift from lighter ends towards heavier fractions. Results imply that both SCW and catalyst additions can suppress coke formations and right type of catalytic additives and proper reaction times can be optimized depending on the desired yield and selectivity.

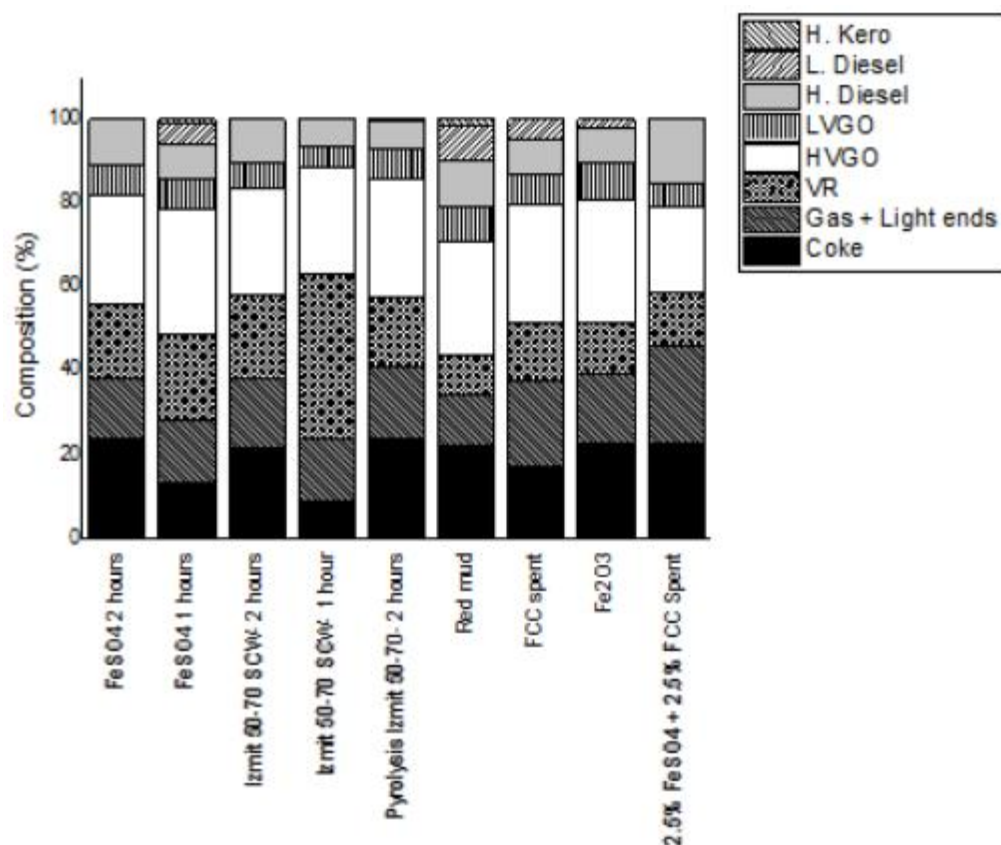


Figure 33: Composition of the products of upgrading reactions carried out in SCW environment by various catalytic additives at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of Izmit 50/70.

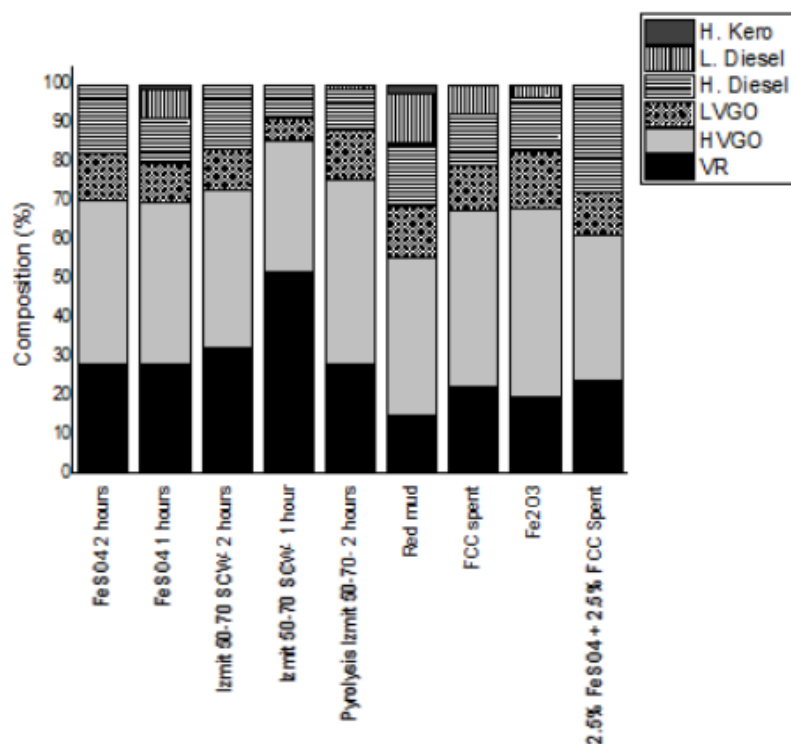


Figure 34: Composition of liquid fractions obtained by upgrading reactions carried out in SCW environment by various catalytic additives at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of Izmit 50/70.

4.2.4. Effect of Water Loading

The effect of water:oil ratios is studied and the results are given in **Figure 35-36**. Experiments are conducted at 1hour, 440C by using Izmit 50/70 bitumen where water loading is increased from 2 to 10 as compared to the weight of heavy oil. Coke yield has decreased by more than 20%. VR content decreased by 30% from 51,68% to 36,54%. Interestingly, if one keep increasing the water loading from 5 to 10, although HVGO, LVGO, and heavy diesel formations keeps increasing; coke yield starts to increase and L.diesel formation is diminished which indicates that increasing water loading may improve the liquid portion's selectivity but coke conversion values may also

be affected thereby depending on the desired product yields and selectivity, the operating conditions need to be optimized accordingly.

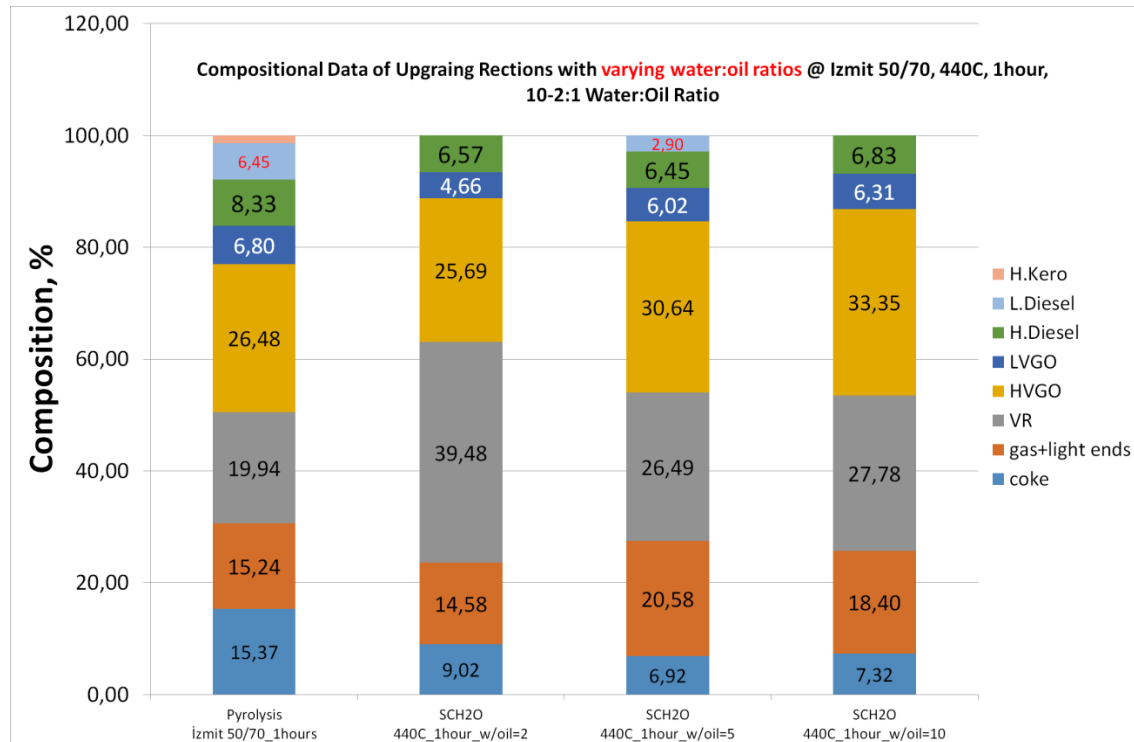


Figure 35: Compositional data of upgrading reactions' products with varying water/oil ratios are given in the figure including coke and gas+light ends.

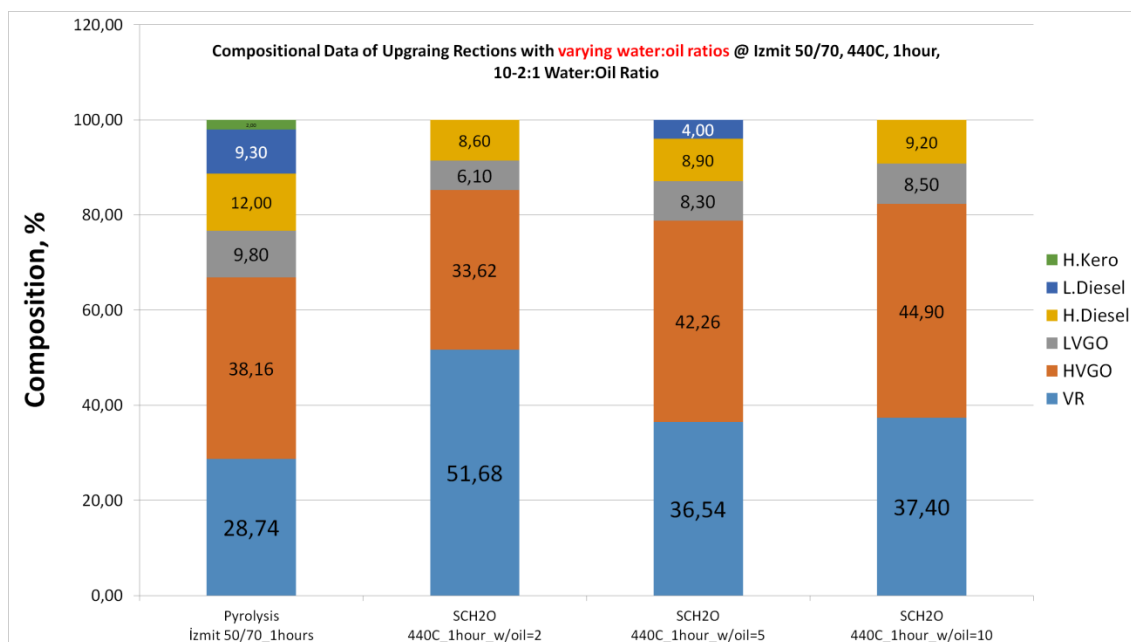


Figure 36: Compositional data of upgrading reactions' products with varying water/oil ratios are given in the figure (*only the liquid portion*).

4.2.5. Kinetic Analysis of Selected Feeds

Upgrading results of Izmit 50/70 with varying reaction times in the presence and absence of SCW are given in **Figure 37**. For a better understanding of the reaction mechanisms, composition of liquid portions separate from coke and gas are given in **Figure 38**. Similar analysis for tar sand bitumen was also performed and results are given at **Figures 39** and **40**.

As shown in **Figure 37**, at a reaction time of 40 min, VR content decreased down to 41,77% from 83% with highly suppressed coke formation of only 2,47%. Further increase in reaction time to 60 minutes caused an undesirable jump in coke content up to 9,02% together with increased gas yields. Indeed, as given in **Figure 38**, a close look to liquid fractions showed that increasing reactions times from 40 to 60 minutes, did not decrease VR content as expected, but instead slightly increased it from 47,3% to 51,68% suggesting the occurrence of favored back

condensation reactions from lighter fractions to heavier ones and finally to coke. This argument is also supported with decreased HVGO (from 39,7% to 33,63%) and increased coke yield (from 2,47% to 9,02%) trends.

Further reductions of VR content down to 26,77% were also observed with a longer reaction time of 90 minutes. When upgrading of Izmit 50/70 in the presence of SCW was extended to 2 hours, similar condensation reaction trends were observed compared to the results of a reaction time of 90 minutes. Coke content jumped from 16,7% to its highest value of 21,7 % together with a sharp decrease in HVGO content (from 46,92% to 40,58%) and an increase in VR content (from 26,77 to 32,32%). Such condensation reactions when coupled with polymerization reactions are the main causes of coke formation during the course of heavy oil upgrading. Light ends are converted to aromatic rings, asphaltenes, coke precursors and then finally to solid product of coke [130, 170, 171]

During heavy oil upgrading reactions, the ability of SCW addition to suppress coke formation for Izmit 50/70 bitumen was found to be more pronounced for a reaction time of 60 minutes (from 15,37% to 9,02%) as compared to a reaction time of 120 minutes (from 23,90% to 21,70%). The higher fractions in the liquid portion on the other hand were found to be less for the pyrolysis runs. VR content of 1 hour pyrolysis reaction for example was 28,74% whereas the upgrading reactions in the presence of SCW suppressed the cracking reactions of heavy oils and kept VR content at 51,68%. This is also associated with a suppressed coke yield from 15,37% to 9,02%.

As for the kinetic analysis of the upgrading of the tar sand bitumen, at 40 minutes, coke yield of 7,56% was obtained. This was almost three times higher than the coke yield obtained for

the upgrading of Izmit 50/70 under the same conditions. Such an increase at short reaction times might be explained by the high asphaltene content of tar sand bitumen. Similar to Izmit 50/70 kinetic analysis results, from 40 to 60 minutes, back condensation reactions caused VR content to increase from % 17,9 to % 27,82. For further reaction times, such condensation reactions caused the disappearance of heavy kerosene and the decrease of light diesel fractions. Unlike the upgrading results of Izmit 50/70, coke suppression effect of SCW is less pronounced at 60 min (from 19,89% to 17,64%) as compared to that of 120 min (from 27,98% to 21,30%). The maximum amount of gas formation was obtained by tar sand upgrading in SCW at 120 minutes which might be explained by high amount of light ends in tar sand feed favoring the shift towards gaseous phase products. The coke suppression ability of SCW at 120 minutes was found to be more pronounced for tar sand than Izmit 50/70.

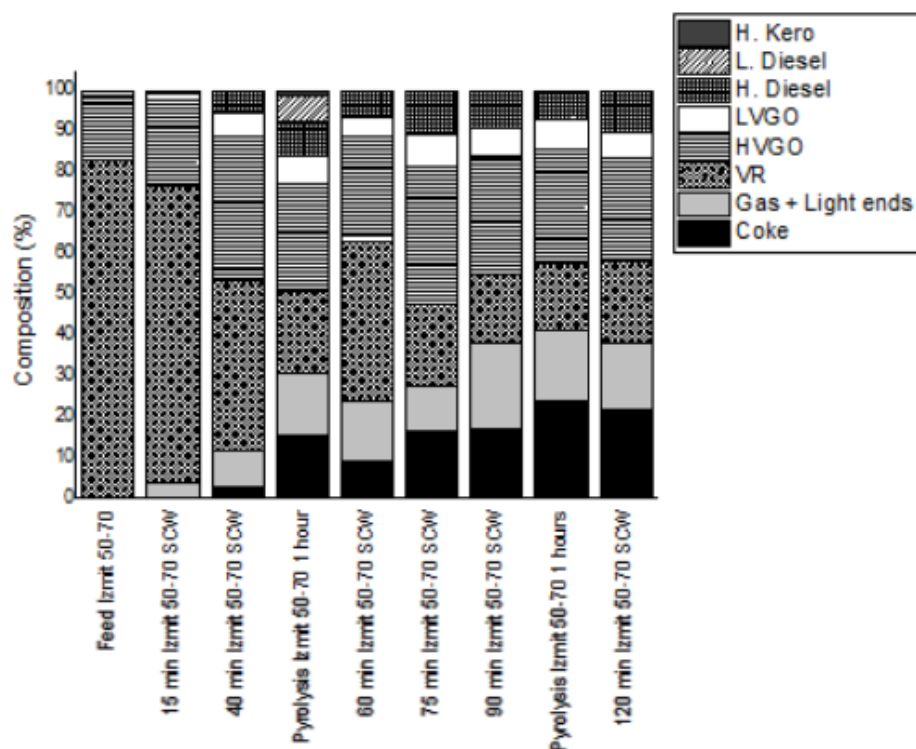


Figure 37: Composition of the products of upgrading reactions carried out in SCW environment by various reaction times at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of Izmit 50/70 for 1 hour and 2 hours of reaction times.

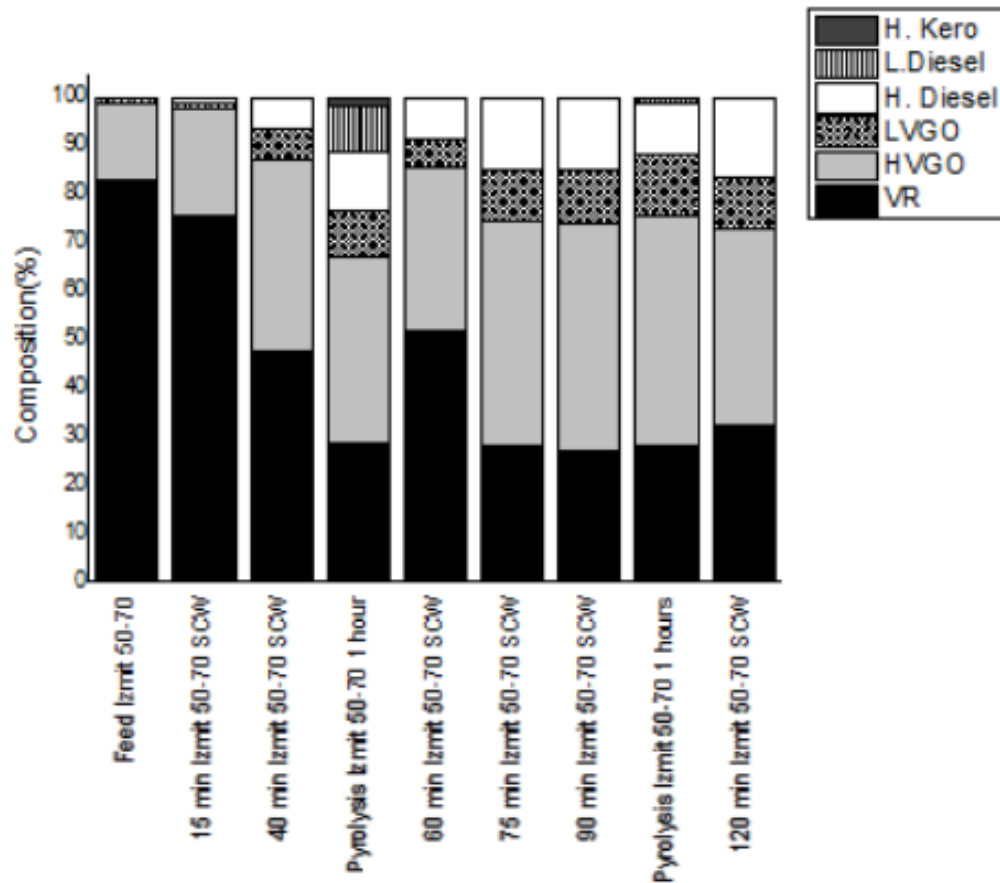


Figure 38: Composition of liquid fractions obtained by upgrading reactions carried out in SCW environment by various reaction times at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of Izmit 50/70 for 1 hour and 2 hours of reaction times.

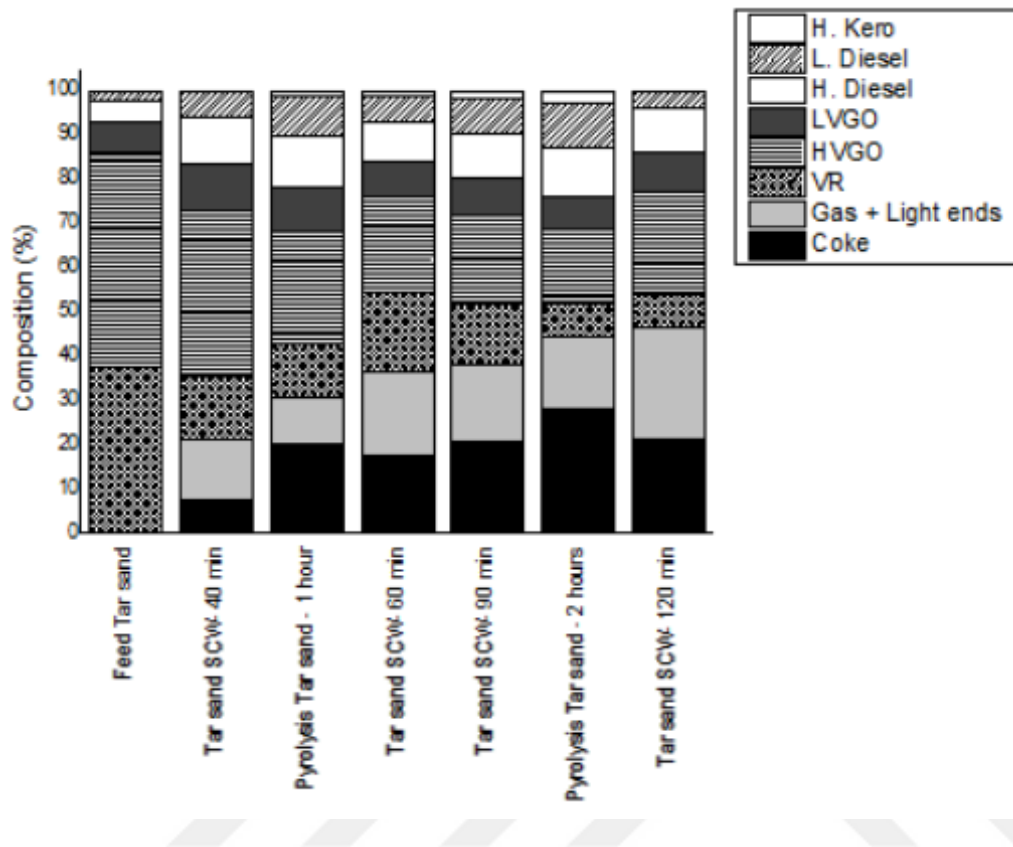


Figure 39: Composition of the products of upgrading reactions carried out in SCW environment by various reaction times at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of tar sand bitumen for 1 hour and 2 hours of reaction times.

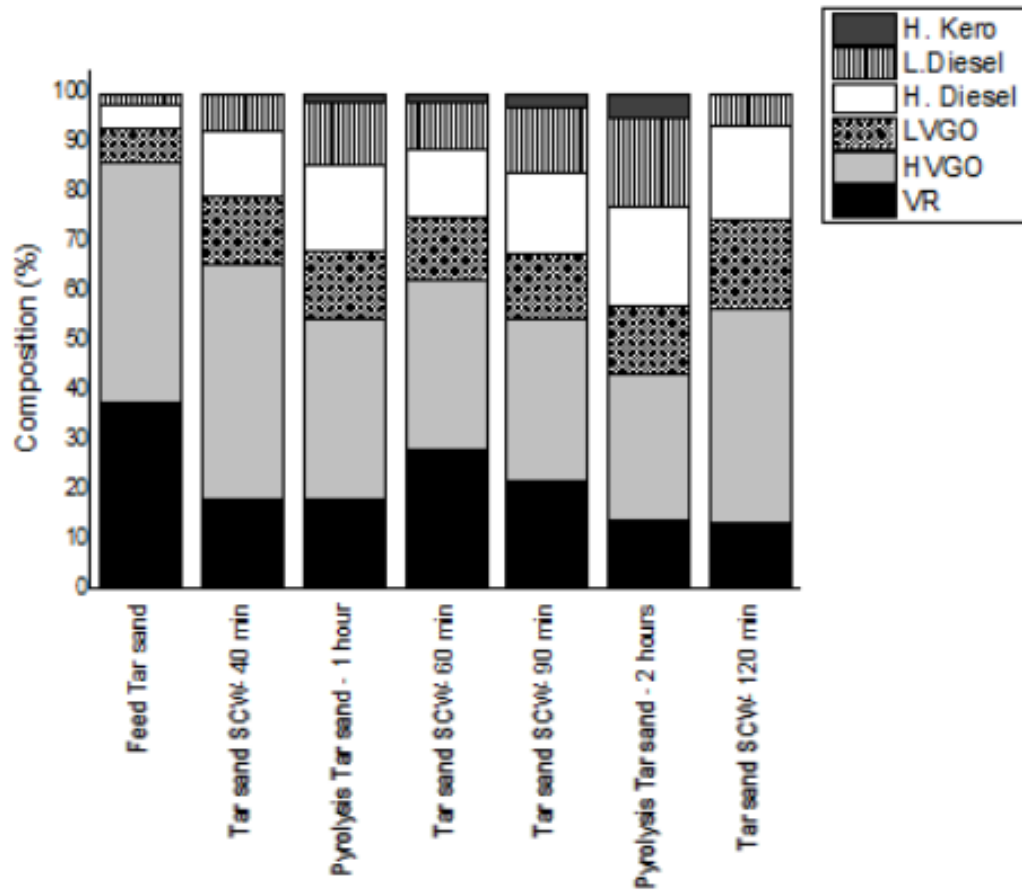


Figure 40: Composition of liquid fractions obtained by upgrading reactions carried out in SCW environment by various reaction times at 440 °C, 30 MPa and w/f ratio of 2 and of pyrolysis of tar sand bitumen for 1 hour and 2 hours of reaction times.

According to the recommendations in the literature for heavy oil upgrading studies both in the absence and presence of SCW [130, 170, 172], the composition data for Izmit 50/70 and tar sand upgrading by SCW were fitted to a reaction network consisting of 5 lumps as given in **Figure 41**. 1st order reaction was assumed. Set of ordinary differential equations (ODEs) governing the mass balance of the upgrading reaction in a batch reactor were solved by MATLAB. Regression by fmincon analysis was used to determine «k» values which are given at **Table 11**.

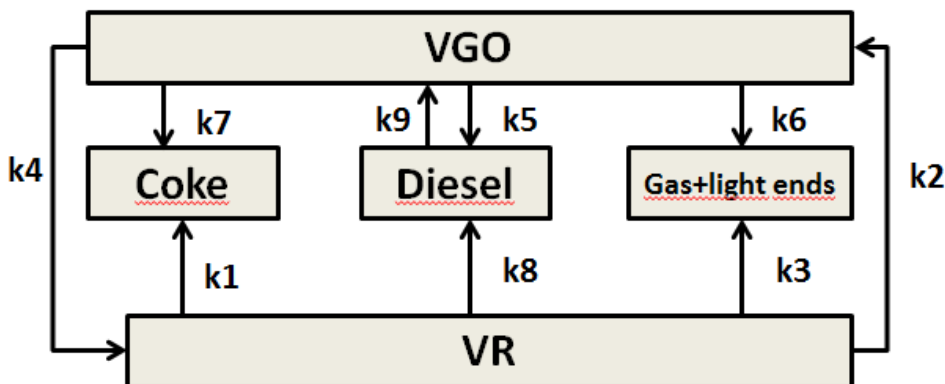


Figure 41: Assumed reaction network of heavy oil upgrading by SCW.

Table 11: k values of tar sand and Izmit 50/70 upgrading by SCW at 440 °C, w/f ratio of 2 at a reaction time of 2 hours in a 10 cc bomb reactor.

k values = [1/h]		
	Tarsand	Izmit 50/70
k1	0,003	0,0388
k2	0,9443	1,4693
k3	0,8345	0,2359
k4	0,4183	0,8292
k5	0,506	0,2518
k6	0,0145	0,0108
k7	0,2477	0,2609
k8	0,5083	0,059
k9	1,7044	0,8774

According to the calculated k values for Izmit 50/70 upgrading in SCW environment, the following conclusions were drawn. The value of k_2/k_4 which was higher than 1 indicated the tendency of asphaltene (VR) upgrading towards lighter compounds. Low k_1 value suggested that presence of SCW suppressed the coke formation and shifted the products towards lighter ones. k_5/k_9 value was less than 1 indicated that longer reaction times favored VGO formation. Low k_6 value suggested that no gas or light end formation occurred directly from malten (VGO) groups.

Moderate k_3 that was also higher than k_6 could be an indication of the fact that main source of gas and light ends was VR. This can be expected since when VR is cracked, short alkyl side chains of aromatic rings and hydrogens that are attached to carbon atoms are broken free resulting in an increased gas formation from VR. These conclusions are also in agreement with the findings of Yasar et al [130] and Tan et al [170] where upgrading of varying types of heavy oils in the absence and presence of SCW was studied, respectively.

Similar conclusions were drawn from the kinetic parameters obtained from runs with tar sand. The value of k_2/k_4 for tar sand was found to be more than that of Izmit 50/70. This indicates that the rate of VR decomposition to lighter compounds is higher for tar sand. The faster rates can be explained by the relatively lower viscosity and higher amount of light ends in the tar sand. Solvation power of SCW may become more pronounced for less viscous fluids. Moreover, cracking of light ends produces even lighter fractions as well as gaseous compounds which enables better dissolution of coke precursors in heavier fractions, accelerates upgrading towards light ends and hinders coke polymerization and condensation reactions towards bottom ends. The above inferences can also be supported by the relatively lower k_1 value of tar sand than Izmit 50/70.

4.2.6. Morphological Analysis of Solid Products

During the upgrading of heavy oil samples, a solid by product is produced known as coke. Mostly encountered coke types, their descriptions and the effects of processing conditions on the coke morphologies were explained in our previous study [164]. Morphological analysis of the cokes obtained by the use of various feeds and additives of this study were investigated by SEM-EDX measurements and the results are given in **Figures. 42-44**.

Table 12: XRF results for the red mud samples used during upgrading reactions

Metal oxide form	Corresponding %wt	Metal oxide form	Corresponding %wt
Fe ₂ O ₃	41.00	Cl	0.04
Al ₂ O ₃	21.90	MnO	0.03
SiO ₂	15.30	As ₂ O ₃	0.02
Na ₂ O	10.80	Sc ₂ O ₃	0.02
TiO ₂	5.77	PbO	0.02
CaO	3.57	Y ₂ O ₃	0.02
K ₂ O	0.45	Nb ₂ O ₅	0.01
SO ₃	0.38	Cr ₂ O ₃	0.10
MgO	0.29	NiO	0.08
ZrO ₂	0.16		

The SEM images of tar sand upgrading by SCW at 440 °C and 2 hours are given in **Figure 42**. Although tiny hole like structures are seen on the bottom left image, the main structure is not mature enough to be an example of a sponge like coke formation, thereby shot type cokes can said to be formed upon an upgrading of tar sand bitumen samples by SCW. Among the other feeds, the least amount of aromatics (35%) and the highest amount of asphaltenes (28%) were observed for tar sand bitumen feed. However, upgrading of other feeds

with relatively two-fold aromatic and half asphaltene content also gave similar results and shot type coke formations were observed for all the feeds analyzed.

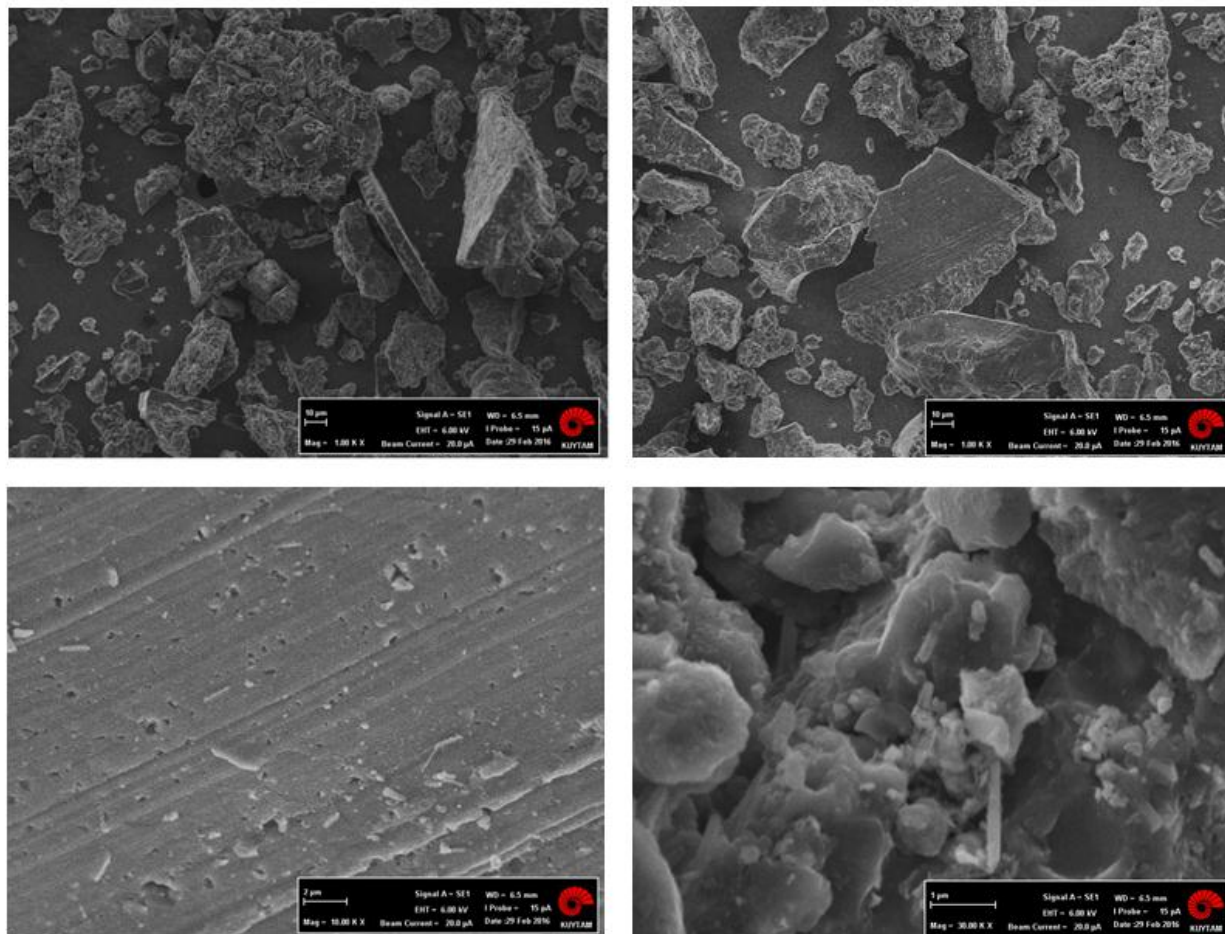


Figure 42: SEM images of solid products obtained by the upgrading of tar sand bitumen in SCW at 440 °C, 30 MPa and w/f ratio of 2.

As for the effects of additives, SEM images of solid coke products obtained by the upgrading of Izmit 50/70 in SCW with 5% by weight red mud addition at 440 °C, 30 MPa and w/f ratio of 2 resulted in multi-crystal deposits (**Figure 43**). Those hexagonal structures had a honeycomb shape and EDX measurement revealed that they were composed of iron accumulations (**Figure 44**).

Table 12 shows that red mud that was used in upgrading runs contained more than 40 % by weight of iron. It has been shown both in the literature and in our recent study [164] that when there are iron compounds in the reaction medium, SCW upgrading of hydrocarbon compounds can form coke supported hexagonal shaped iron columns. Since certain shapes of iron may have outstanding cracking activity, this is of paramount importance and highlighting the related mechanisms controlling the shape of iron deposits for a tunable catalytic function requires further research in subsequent studies [163].

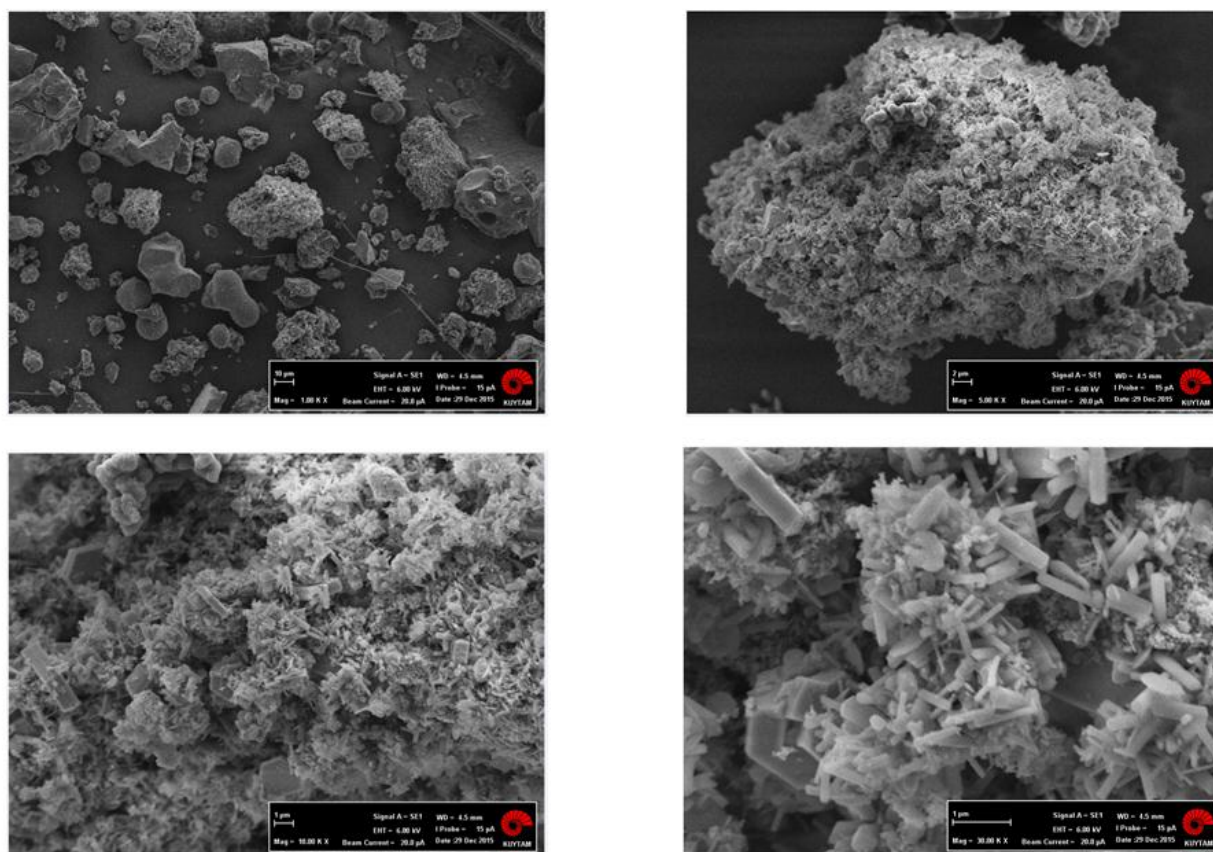


Figure 43: SEM images of solid products obtained by the upgrading of Izmit 50/70 bitumen with the addition of SCW+5% Red Mud 440 °C, 30 MPa and w/f ratio of 2.

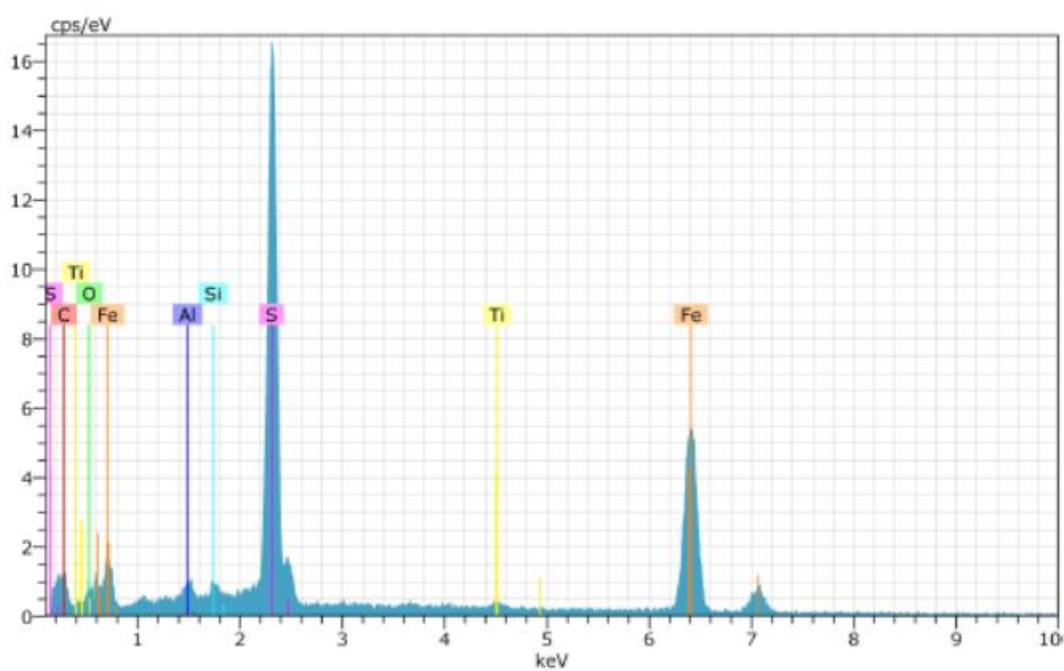
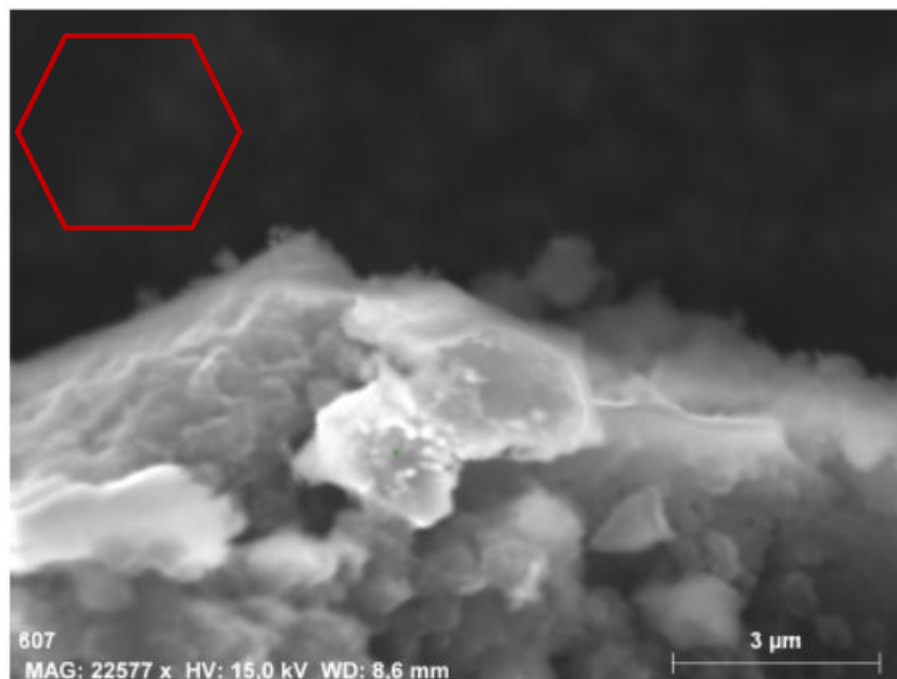


Figure 44: SEM (top) and corresponding EDX (bottom) images of solid products obtained by the upgrading of Izmit 50/70 bitumen with the addition of SCW+5% Red Mud 440 °C, 30 MPa and w/f ratio of 2.

4.2.7. Simple Economic Analysis

The cost of VR is assumed to be the price for bitumen as published online (on 22/12/2017) by TUPRAS which is the only operating oil refinery in Turkey. It is important to note that if it is going to be the refinery that makes this heavy oil upgrading by SCH_2O investment, then bitumen will not be bought from outside based on this price; instead it will most probably be produced within the same refinery with a considerably much lower cost. It might be assumed to be the 75% of the bitumen selling price for such an alternative economic analysis.

The cost of tar sand is assumed to be around ~15\$/ barrel-oil that is equal to ~100\$/ton-oil. Other assumptions to get a barrel of heavy oil from tar sand extract are 3\$/ton of cost of extract for the surface mining activity; ~15% by weight of oil content for each ton of tar sand extract; and around 10\$ for shipment, crushing, grindings and solvent extraction. Knowing the fact that the economic feasibility criteria of tar sand extraction in Canada in practice is around the crude oil price level of higher than 30\$/barrel, this 100\$/ton can said to be a reasonable assumption.

The cost of water for industrial uses is assumed to be 2\$/ton based on the data published by municipality authorities of Istanbul, Turkey.

The prices for kerosene, diesel, VGO like components are not taken directly from market since they include taxes, instead possible refinery output selling prices were assumed.

Cost of heating water to SCW conditions of this study was assumed to be around 1.5MJ/kg.

Cost of heating for 1 MJ was assumed to be around 1 cents. Thereby around 15 \$ is needed for each ton of water to be heated to the reaction conditions of this study in the absence of heat

integration. Normally, in the state of the art industrial processes, the products can be used to heat up the input streams for a more feasible study.

The economic value of the feed being upgraded is simply compared with the value of collected products and some of the results are tabulated in **Table 13**. Since the cost of tar sand is quite low as compared to that of bitumens, the results of the feasibility study suggest that tar sand is the optimum feedstock for upgrading reactions by SCW. More to consider is definitely the heat integration so that heat content of upgraded products can be used to heat up the initial feed streams. Additionally, it should be noted that the products such as HVGO are not necessarily to be sold for a given price, instead, conventional refineries can further process them in hydrocracker units to end up with even lighter and more valuable products (mainly diesel) which would increase the economic feasibility of SCH_2O based conversion processes' investments. Lastly, remaining VR in the products can be recycled for further upgrading to increase the overall efficiency of the study that might provide different feasibility analysis at the end.

Table 13: Cost of subcomponents of feed and prospective market values for obtained products for upgrading of tarsand & Izmit 50/70 under 440 °C for 40 minutes, 1hour and 2 hours with w/f ratio of 5&2 and in the absence and presence of red mud & FeSO₄ as a catalyst.

Subcomponents	Unit Cost or Price (US \$)/ton	Amounts (ton)							
		Input Stream (Tarsand Bitumen)	Input Stream (Izmit 50/70)	Out (W/O: 5, Izmit 50/70, 440C, 1hour)	Out (W/O: 2, Izmit 50/70, 440C, 2hour)	Out (Red mud, W/O: 2, Izmit 50/70, 440C, 2hour)	Out FeSO ₄ , W/O: 2, Izmit 50/70, 440C, 1hour	Out (W/O: 2, Izmit 50/70, 440C, 40 minutes)	Out (W/O: 2, TARSAND, 440C, 40 minutes)
Water	2		5						
Entering VR as feed	380		0.85	0					
Gas	600		0	0.2058	0.1652	0.1175	0.151	0.0923	0.1364
Heavy Kerosone	590		0			0.0165	0.0079		
Light Diesel	600		0	0.029		0.0837	0.0536		0.0599
Heavy Diesel	600		0	0.0645	0.1019	0.1075	0.0837	0.0556	0.1032
LVGO	400		0	0.0602	0.0655	0.0857	0.0715	0.0592	0.1072
HVGO	400		0.15	0.3064	0.2507	0.2697	0.2964	0.3506	0.3767
Remaining VR in the product stream	380		0	0.2649	0.1997	0.0963	0.2021	0.4177	0.1411
Coke	70		0	0.0692	0.217	0.2231	0.1337	0.0247	0.0756
Estimated Cost or Price for in and out streams (\$/ton)		100	393	431.73	377.816	389.326	410.958	413.115	432.17

Chapter 5

5. CONCLUSIONS

Upgrading of mixtures of microalgae and bitumen in SCW were investigated. For bitumen and microalgae, SCW environment led to lower coke yields accompanied by a decreased VR conversion and lower liquid yield compared to pyrolysis in the absence of water. Microalgae addition during SCW upgrading of bitumen improved VR conversion as well as light liquid selectivity. Increase in microalgae ratio in the feed increased gas formation significantly due to operating temperature favoring microalgae gasification. SEM and EDX analysis of coke obtained after SCW upgrading indicated that it was shot type. Tar sand bitumen and various types of heavy oils were also upgraded in absence and presence of SCW. SCW environment was shown to be more effective for tar sand bitumens to decrease the coke yield compared to pyrolysis. The rates of VR decomposition towards lighter compounds was found to be higher for tar sand due to the chemistry of the feed. Various types of additives were investigated and runs were carried out at different reaction times. Long reaction times were found to favor a shift from diesel range products to VGO. Tar sand upgrading for a period of 40 minutes in SCW was found to be the most optimum case. Shot type coke formations with hexagonal shaped columns of iron deposits over coke samples were found by SEM and EDX analysis when red mud was used as an additive.

The preliminary results obtained in this study show that blending microalgae with bitumen and upgrading the mixture in SCW is a promising technology for production of fuels with a certain renewable fraction directly in refineries. Catalytic SCW upgrading of bitumen and

microalgae mixture with hydrogen addition may provide higher liquid yields and will be investigated in future studies. Processing conditions such as water loading, reaction time, use of catalysts and types of feed stocks were found to have huge effect on both selectivity and yield of oil upgrading by SCW. Optimum conditions need to be determined based on the needs of the local market and availability of the raw materials. Therefore feasibility result may vary from one part of the world to another one. In general, findings of simple preliminary economic analysis suggest that use of tar sand with short reaction times is the optimum case and further improvements can be achieved if unconverted VR in the output streams will be recycled for a higher conversion and heat integration study will be performed for a more feasible investment. Lastly, most of the oil samples of this study fall in a class of penetration grade bitumens that are suitable for road pavement purposes. Therefore, their use for direct heavy oil upgrading with or without microalgae blends will compete with their use for paving industry. This should be comparatively analyzed in future scale-up studies as part of feasibility analysis.

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