

Investigations on Hydrodesulfurization Reactions using Slurry Catalysts and Supercritical Water

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Abstract

Depletion of easily accessed and light crude oil sources is shifting future crude oil supply to less attractive heavier oil fractions. Vacuum residue, as the heaviest fraction found in crude oil and the bottom product of the vacuum distillation column in a refinery, has therefore been gaining more and more attention in the past years. It is mostly used as heavy fuel oil in the shipping sector on open seas. Globalization and rising demand of international transportation of goods has led to a strong increase of heavy fuel oil consumption. Sulfur, present in vacuum residue to high extent, forms environmentally hazardous sulfur oxides (SO_2 and SO_3) when being burnt in the ships engines. In order to counteract rising sulfur oxide emissions, the International Maritime Organization has released a number of restrictions of which the last reduces the maximum allowed sulfur content in fuel for ships on open seas from 3.5% to 0.5%. These new sulfur regulations have come into force on January 1st 2020 and have led to increasing prices for fuels that comply with the sulfur regulations. On the other hand, high sulfur fuels exceeding the sulfur cap of 0.5% are declining in price, also affecting refineries margins when selling high sulfur vacuum residue. Developing a solution for removing sulfur directly from vacuum residue therefore bears large economic potential. Existing hydrodesulfurization technologies severely suffer from catalyst deactivation, coking and plugging as a result of high asphaltenes, heavy metals, and Conradson Carbon present in the viscous vacuum residue. Slurry phase hydrodesulfurization presents potentials for overcoming some of these downsides by using unsupported, highly dispersed catalysts and additives. In this work, process conditions, catalysts, and additives were tested and evaluated with respect to their activity in enhancing desulfurization of high sulfur vacuum residue. Experiments were conducted in a 2 l semi-batch slurry reactor that had the possibility of collecting oil and residue fractions separately. At low temperature, long residence time, and high H_2 partial pressure, undesired conversion reactions could be minimized while desulfurization reactions could be maximized. Screening of active substances that influence the reactions, revealed a catalyst and an additive that showed very different effects on conversion and desulfurization reactions than the majority of the tested catalysts. Supercritical water, as very cheap additive, supported solely conversion reactions yielding large amounts of oil, while leaving a high sulfur residue behind. Investigations on sulfur containing model compounds underlined the absence of desulfurization reactions with supercritical water. The novel catalyst showed a strong hydrogenation activity thus destabilizing the sulfur bonds and enabling desulfurization of the high sulfur vacuum residue. Desulfurization of above 90% was achieved while at 400 °C and 310 bar undesired conversion reactions could be kept below 30%. Both mechanistic pathways behind supercritical water hydroconversion and hydrodesulfurization with the novel catalyst were inves-

tigated intensively and laid basis for an economic assessment of both hydrotreating routes. On basis of a 50,000 barrels per day vacuum residue upgrading plant, the two cases were calculated. Catalyst cost displayed a large penalty on the economic performance in case of the hydrodesulfurization with the novel catalyst. High sulfur content of the remaining residue in case of the supercritical water process presented the downside of the investigated hydroconversion path. The potential of utilizing the novel catalyst in direct hydrodesulfurization of vacuum residue for the production of Very Low Sulfur Fuel Oil is given though at the current state of research, catalyst cost make the process economically unfeasible. The long term price trends for heavy fuel oils as well as future research on improvement of the novel catalyst will show the potential for commercial applications.

Zusammenfassung

Die Erschöpfung leicht zugänglicher und leichter Rohölquellen verlagert die künftige Rohölversorgung auf weniger attraktive schwerere Ölfraktionen. Die Aufbereitung von Vakuumrückstand, als schwerste Fraktion des Rohöls und Sumpfprodukt der Vakuumdestillationskolonne einer Raffinerie, hat daher in den vergangenen Jahren besonders an Bedeutung gewonnen. Vakuumrückstand wird meist als Treibstoff in der Schifffahrt auf offener See verwendet. Die Globalisierung und die steigende Nachfrage am internationalen Transport von Gütern hat zu einem starken Anstieg des Schwerölverbrauchs geführt. Schwefel, der in hohem Maße in Vakuumrückständen enthalten ist, bildet bei der Verbrennung in Schiffsmotoren umweltschädliches Schwefeldioxid. Um die steigenden Schwefeldioxidemissionen einzugrenzen, hat die International Maritime Organization eine Reihe von Gesetzen erlassen, von denen das letzte den maximal zulässigen Schwefelgehalt für auf internationalen Gewässern verwendeten Schiffstreibstoffen von 3,5% auf 0,5% reduziert. Diese neuen Schwefelvorschriften sind am 1. Januar 2020 in Kraft getreten und haben zu steigenden Preisen für die Kraftstoffe geführt, die den Schwefelvorschriften entsprechen. Andererseits ist bei Kraftstoffen mit hohem Schwefelgehalt, die den Schwefelgrenzwert von 0,5% überschreiten, ein Preiserückgang zu verzeichnen, der sich auch auf die Gewinnspannen der Raffinerien beim Verkauf von hochschwefelhaltigen Vakuumrückständen auswirkt. Die Entwicklung eines Verfahrens zur direkten Entschwefelung von Vakuumrückständen birgt daher ein großes wirtschaftliches Potenzial. Bestehende Entschwefelungstechnologien würden bei der Verarbeitung von Vakuumrückstand stark unter der Deaktivierung des Katalysators durch hohen Asphalt, Schwermetall und Conradson-Kohlenstoff-Gehalt leiden. Die Hydrodesulfurierung in der Slurry-Phase bietet das Potential, einige dieser Nachteile durch die Verwendung von ungeträgerten, hochdispergierten Katalysatoren und Additiven zu überwinden. In dieser Arbeit wurden Prozessbedingungen, Katalysatoren und Additive hinsichtlich ihrer Entschwefelungsaktivität von hochschwefelhaltigem Vakuumrückstand untersucht und bewertet. Die Experimente wurden in einem 2 l Semi-Batch-Slurry-Reaktor durchgeführt, der die Möglichkeit hatte, Öl und Rückstandsfraktionen getrennt zu sammeln. Bei niedriger Temperatur, langer Verweilzeit und hohem H_2 -Partialdruck konnten unerwünschte Konversionsreaktionen minimiert und Entschwefelungsreaktionen maximiert werden. Das Screening katalytisch aktiver Substanzen ergab einen Katalysator und ein Additiv, die sehr unterschiedliche Auswirkungen auf Umwandlungs- und Entschwefelungsreaktionen zeigten als die restlichen getesteten Katalysatoren. Überkritisches Wasser, als sehr billiges Additiv, unterstützte ausschließlich Konversionsreaktionen und lieferte große Mengen an leichter siedendem Öl, während ein Rückstand zurückblieb, der einen sehr hohen Schwefelgehalt aufwies. Untersuchungen an schwefelhaltigen Modellverbindungen

untermauerten die Abwesenheit von Entschwefelungsaktivitäten des überkritischen Wassers. Ein neuartiger Katalysator zeigte eine sehr starke Hydrierungsaktivität, wodurch die Schwefelbindungen destabilisiert wurden und die Entschwefelung des hochschwefelhaltigen Vakuumrückstandes ermöglicht wurde. Eine Entschwefelung von über 90% wurde erreicht, während bei 400 °C und 310 bar unerwünschte Konversionsreaktionen unter 30% gehalten werden konnten. Die Reaktionsnetzwerke hinter der Konversion mittels überkritischem Wasser und der Entschwefelung mit dem neuartigen Katalysator wurden intensiv untersucht. Die Ergebnisse bildeten die Grundlage für eine Wirtschaftlichkeitsbetrachtung beider Prozesse. Auf Basis einer 50 000 b/d Vakuumrückstands-Veredelungsanlage wurden die beiden Fälle berechnet. Die Kosten des neuartigen Katalysators stellen einen großen Nachteil für die Wirtschaftlichkeit der Entschwefelungsanlage dar. Der hohe Schwefelgehalt des verbleibenden Rückstandes im Falle des Konversionsprozesses mit überkritischem Wasser stellt die Kehrseite des untersuchten konversionsprozesses dar. Das Potential der Verwendung des neuartigen Katalysators bei der direkten Entschwefelung von Vakuumrückständen zur Herstellung von sehr schwefelarmem Treibstoff ist gegeben, obwohl beim derzeitigen Forschungsstand die Katalysatorkosten das Verfahren wirtschaftlich nicht realisierbar machen. Die langfristigen Preistrends für schwefelreiche und schwefelarme Schiffstreibstoffe sowie zukünftige Forschungen zur Verbesserung des neuartigen Katalysators werden das Potential für kommerzielle Anwendungen zeigen.

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Abbreviations

AFM	atomic force microscope
AGO	Atmospheric Gas Oil
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BP	boiling point
BSE	back-scattered electrons
BT	Benzothiophene
CAPEX	capital expenditures
CHPS	Cold High Pressure Separator
COS	carbonyl sulfide
CSTR	continuous stirred-tank reactors
DBT	Dibenzothiophene
DDS	direct desulfurization
DMDS	Dimethyldisulfide
EAC	equivalent annual cost
ECA	Emission Controlled Areas
EBR	ebullated bed reactor
EDX	energy-dispersive X-ray spectroscopy
EGCS	exhaust gas purification systems
EMA	Emission Controlled Area
EST	ENI Slurry Technology
FCC	Fluid Catalytic Cracking
GC	gas chromatography
GC/MS	gas chromatography - mass spectrometry
IMO	International Maritime Organization
IFO	Intermediate Fuel Oils
HDCCR	Hydro-removal of Conradson Carbon
HDM	hydrodemetallization
HDN	hydrodenitrification
HDO	hydrodeoxygenization

HDS	hydrodesulfurization
HFO	Heavy Fuel Oil
HPLC	high-pressure liquid chromatography
HOK	activated lignite (Herdofenkoks)
HS	hydrogen sulfide
HSFO	High Sulfur Fuel Oil
HYD	Hydrogenation
LEL	lower explosion limit
LNG	Liquefied Natural Gas
LSF2020	Low Sulfur Fuel Regulations
LSFO	Low Sulfur Fuel Oil
MARPOL	International Convention for the Prevention of Pollution from Ships (Maritime Pollution)
MDO	Marine Diesel Oil
MGO	Marine Gas Oil
ODS	oxidative desulfurization
OPEX	operational expenditures
PFD	process flow diagram
PID	piping and instrumentation diagram
RFCC	Residue Fluid Catalytic Cracking
ROI	return on invest
SEM	scanning electron microscope
SCW	supercritical water
TIC	total investment cost
ULSFO	Ultra Low Sulfur Fuel Oil
UEL	upper explosion limit
VCC	VEBA Combi Cracking
VGO	Vacuum Gas Oil
VLSFO	Very Low Sulfur Fuel Oil
VR	Vacuum Residue

Symbols

Roman letters

Sign	Description	Unit
C	Capacity	t/a
c	Concentration	mol/l
E_A	Activation energy	kJ/mol
I	Investment cost	€
K_w	Self-dissociation constant of water	-
k	pre-exponential factor	kg/kg*h (depending on reaction order n)
M	Molar mass	g/mol
m	Mass	kg
$n_{H/C}$	molar ratio H/C	mol/mol
p	Pressure	bar
R	Molar gas constant	J/mol*K
r	rate of reaction	kg/kg*h (depending on reaction order n)
T	Temperature	°C
t	Time	h

Greek letters

Sign	Description	Unit
δp	Pressure drop	bar
ΔS	Desulfurization	kg/kg
τ	Residence time	s
ω	Mass fraction	kg/kg

Subscripts

Sign	Description
0	Initial value
<i>A</i>	Reacting specie
feed	Feed
gas	Gas fraction
<i>i</i>	stands for the different fractions residue, oil and gas
<i>n</i>	Number - denotes the number of a state, order of reaction etc.
org	atom chemically integrated into organic matter
oil	Oil fraction
res	Residue fraction

Introduction

Though non-fossil fuels are increasingly gaining importance in the transportation sector, combustion engines driven by crude oil based fuels are still dominant. Especially in the shipping sector, where mostly heavy oils are used, a strong increase in demand is predicted, which is estimated at 200 Mt/a in 2020 [6, 7]. Marine engines mostly run on Heavy Fuel Oil (HFO) mainly composed of vacuum residue. Depending on the crude oil source, the fraction of vacuum residue varies, but globally around 15% of the annual crude oil consumption is vacuum residue (750 Mt/a in 2020 [8]). Naturally, this heavy fraction of crude oil is high in undesired species, especially in sulfur.

On January 1st, 2020 new Low Sulfur Fuel Regulations (LSF2020) came into force reducing the sulfur cap from 3.5% to 0.5% [4]. These regulations are the latest in a series of International Maritime Organization (IMO) measures to reduce marine pollution in response to the threat of air pollution. The LSF2020 emissions legislation means that ships must significantly reduce their emissions both on open seas and in coastal areas.

The question for both refineries and shipping industry now is how to comply with these new regulations. Generally, three options are discussed:

- Switching to a different fuel with lower sulfur content - Marine Gas Oil (MGO) or Marine Diesel Oil (MDO)
- Installation of exhaust gas purification systems (EGCS) on board the ship
- Switching to Liquefied Natural Gas (LNG) powered ships

All three options are associated with considerable costs and changes in infrastructure and therefore present refineries as well as shipping companies with major economic

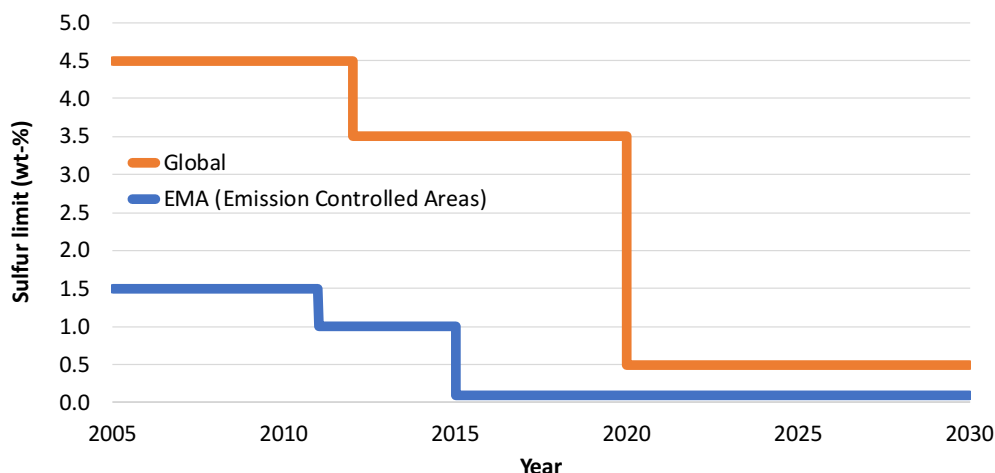


Figure 1.1: Implementation of sulfur limits by the IMO globally and in EMA

challenges. An alternative with fewer downsides would be of great benefit for the sector.

A different option could be the removal of sulfur directly from the vacuum residue which could then be further used as Very Low Sulfur Fuel Oil (VLSFO) complying with the new sulfur regulations. The complete infrastructure for fuel handling, starting at the refinery and ending with the consumption of fuel in heavy engines of ships, would not have to undergo any costly changes. Additionally, the precise removal of sulfur from vacuum residue without conversion to lower boiling products could reduce H_2 consumption during the hydrotreating process thus reducing cost for refineries. This could lead to a less expensive supply chain for maritime fuel, compared to the scenario that the shipping industry switches to lower boiling products like MGO.

Around the world, refineries are equipped with desulfurization units - mostly in the form of hydrodesulfurization (HDS) processes using expensive, highly active fixed bed catalysts - to meet the strict sulfur limits for low boiling fuels like diesel and gasoline [9]. These processes enable the explicit removal of sulfur in the form of H_2S with minimal cracking of the feedstock. Due to the high viscosity and the coke-forming tendencies, vacuum residue causes severe problems when being sent over these fixed bed catalysts. Therefore, different process options are investigated to remove sulfur from vacuum residue, ideally as presented in Fig. 1.2 with no cracking and thus minimal H_2 consumption.

A potential procedure for desulfurization of vacuum residue is possible by alteration of the Bergius-Pier process, which applies a high H_2 partial pressure of above 300 bar, intermediate temperature of 400 °C - 500 °C, together with a dispersed catalyst, in

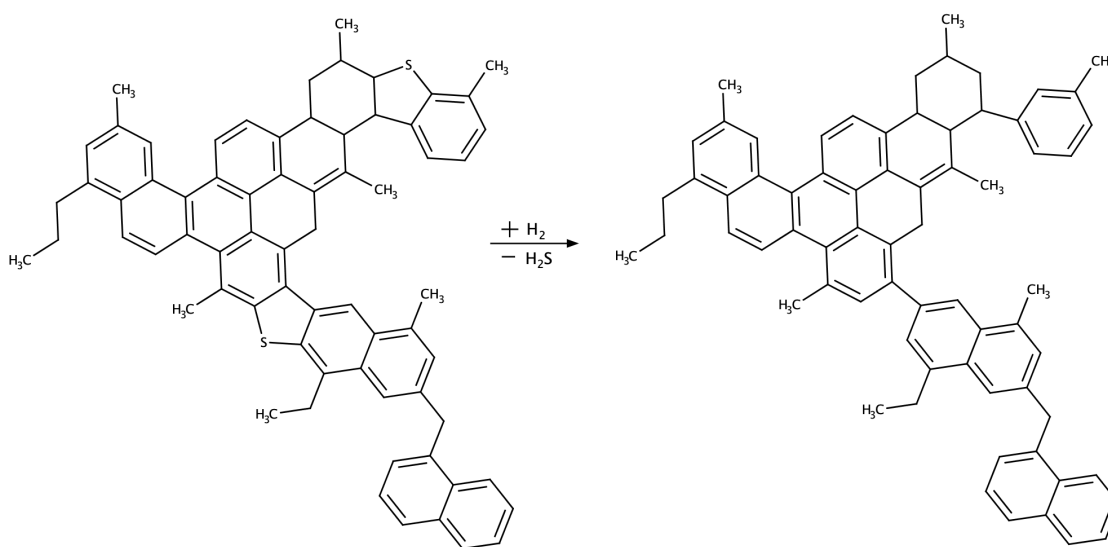


Figure 1.2: The authors understanding of a hypothetical vacuum residue molecule with sulfur and the ideal removal of sulfur via HDS (the author does not claim that these exact molecules exist in reality)

a slurry reactor. The process was originally designed for the liquefaction of coal and has been adopted for the conversion of other feedstocks including vacuum residue [10]. In case of HDS, the aim is to keep conversion at minimum level, while maximizing the sulfur removal at the same time. Thermodynamically, the removal of sulfur is preferred before rupture of simple carbon - carbon bonds, implying that theoretically, HDS should be possible at less severe conditions, compared to conversion processes. Consequently, the choice of an adequate slurry phase catalyst together with optimal choice of reaction conditions could display a route to desulfurization of vacuum residue at minimal conversion and H_2 consumption.

This work focuses on the investigation of HDS of vacuum residue in a slurry reactor. Optimization of the process conditions in a semi-continuous stirred tank reactor was performed and global reaction kinetics of HDS and hydroconversion reactions of high sulfur vacuum residue were studied and are presented in Chapter 6.1. Several catalysts and additives were tested and their suitability for HDS of vacuum residue was evaluated in Chapter 6.2. A novel catalyst for slurry phase HDS was developed and the fundamental reaction mechanism is discussed in Chapter 6.4. In Chapter 7

the economic feasibility of applying this novel catalyst at large scale HDS of vacuum residue is evaluated.

Background

2.1 Crude oil

Crude oil is a natural product and consists of numerous different hydrocarbons ranging from CH_4 to molecules with hundreds of carbon atoms. Because of its natural offspring, the diverse structure also includes heteroatoms like oxygen, nitrogen, and sulfur, as well as metals like vanadium and nickel [11].

The composition of crude oil may vary strongly, also affecting its physical properties including the boiling range, carbon chain length as well as asphaltene content. In its naturally occurring state, crude oil is of low value. It is therefore sent to a refinery, where separation and upgrading into different marketable products like diesel, gasoline, waxes, and heavy fuel oil are performed. In total, refinery products supply a third to half of the worlds energy supply [7]. Removal of undesired heteroatoms, of which sulfur is the most prominent, from crude oil is also one major task for refiners. Marketable HFO, as one fraction resulting from the refining process, is the main focus of the sulfur removal addressed in this work since HFO mainly consists of vacuum residue [12]. Sulfur and sulfur chemistry found in crude oil, together with the path molecules take within a refinery that end up in the vacuum residue fraction, are essential for the understanding of the nature of the vacuum residue and the complexity of the sulfur removal from this fraction. Therefore, in Sections 2.1.1 and 2.1.2 an overview on the nature of sulfur in crude oil and the properties of vacuum residue are given, followed by a short description of a refinery in Section 2.2.

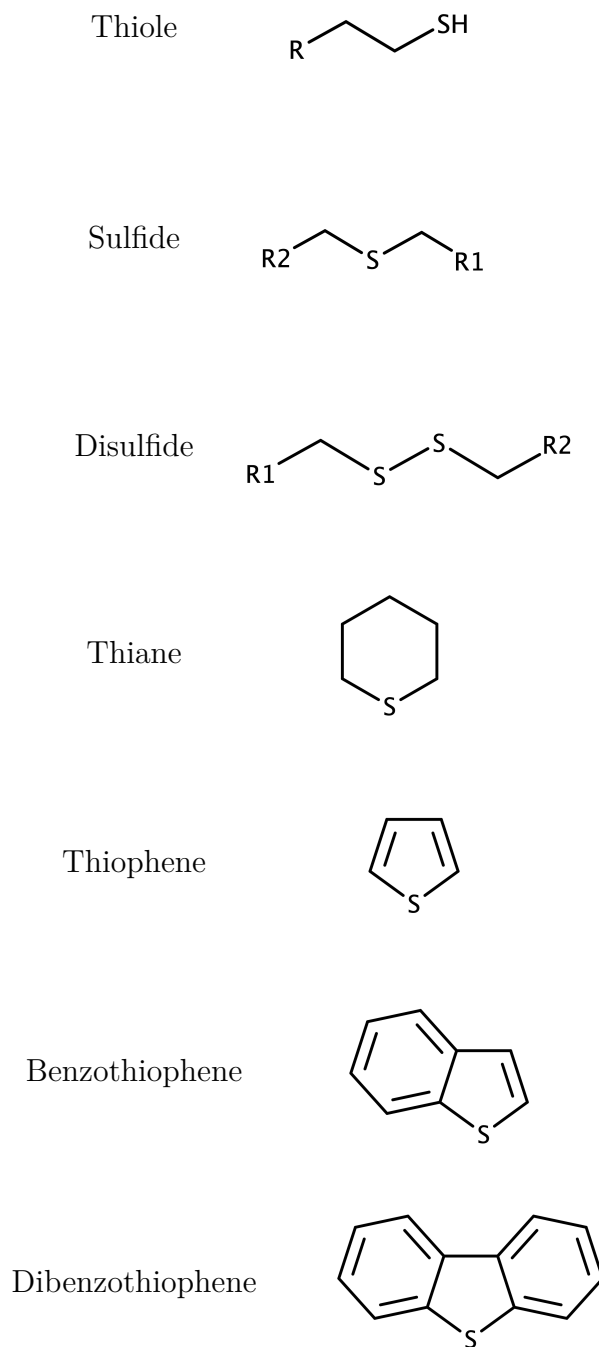


Figure 2.1: Sulfur containing structures in crude oil

2.1.1 Sulfur in crude oil

Of the different heteroatoms found in crude oil, sulfur is often the most concentrated [13]. Sulfur content may vary significantly and correlates strongly with the gravity of the feedstock ranging up to 20 wt%. Below a sulfur level of 1 wt% the crude is referred to as low sulfur; above, as high sulfur. Sulfur may occur as elemental sulfur,

carbonyl sulfide (COS), inorganic sulfur, including hydrogen sulfide (HS) or, the largest fraction, as heteroatoms within the carbon matrix. This largest fraction is comprised of mercaptans, sulfides as well as polycyclic sulfides [14].

Figure 2.1 shows the main organic sulfur bond types existing in crude oil. While most of the elemental sulfur, hydrogen sulfide, as well as carbonyl sulfide, are not included in vacuum residue after distillation, the portion of sulfides, thioles, and polycyclic sulfides increase. The predominant structures present in vacuum residue are BT and DBT derivatives built into complex macro molecules [15].

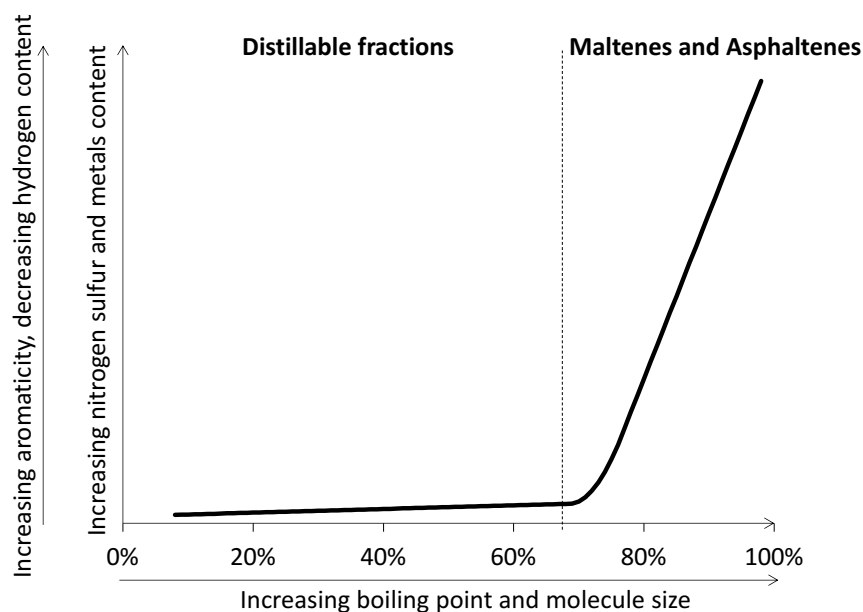


Figure 2.2: Distribution of heteroatoms in crude oil according to the boiling point fraction

2.1.2 Vacuum residue

Vacuum residue is the crude oil fraction with the highest initial boiling point and therefore the bottom product from the vacuum distillation step, which is further described in Section 2.2.1. Depending on the conditions applied in the vacuum distillation, the initial boiling point of the vacuum residue varies but it is mostly above 500 °C. Because it is the bottom product of the distillation, it accumulates most of the undesired and potentially catalyst impairing, as well as environmentally polluting components like sulfur and heavy metals. Vacuum residue is of high viscosity and almost solid at room temperature due to the large molecule sizes. Its chemical composition is complex and because of low or not existing volatility of the constituents, an exact characterization of the material is difficult. The quality of

the vacuum residue is specified by the quality of the crude oil used in the refinery and with decreasing amounts of crude oil reservoirs the crude oil quality is more and more becoming of heavier composition. Therefore, upgrading of the residue is gaining higher importance.

Though the characterization of vacuum residue is difficult, one can distinguish different molecule classes present in heavy oils and residua according to their solubility. Several, different procedures exist for the separation [16–20] and depending on the applied method, the cut point between fractions varies. Therefore, a precise explanation of the used method is important. The method applied in this work is described in Section 5.4.2.2. A simplification indicating, which fraction is soluble in which solvent is presented in Fig. 2.3.

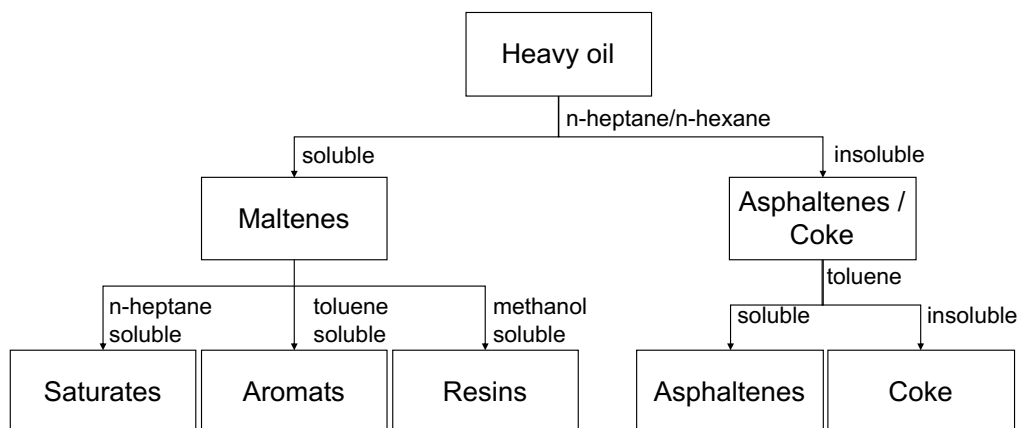


Figure 2.3: Solvent fractionation

From the properties of the solvents, in which the different fractions dissolve, one can conclude the character of the respective fraction.

2.1.2.1 Coke

Coke will mostly not be present in crude oil but can form when retrograde reactions take place and no hydrogen is present to saturate the forming radicals. Coke is a solid carbon structure insoluble in solvents. For most processes, formation of coke is undesired. Especially in HDS reactions and processes, where catalysts are used, the formation of coke is very problematic and process conditions are chosen in such a manner that reactions leading to coke are minimized.

2.1.2.2 Asphaltenes

Asphaltenes are the heaviest fraction (molar mass of 500 - 3,000 g/mol) found in crude oil and are composed of macromolecular carbon structures containing large amounts of heteroatoms (sulfur, oxygen and nitrogen) and heavy metal (nickel, iron, vanadium) giving them a polar character. They are predominantly black or dark brown solids (non-volatile) with a very low H/C ratio, strongly influencing the high viscosity of vacuum residue [21–27]. DIN 51595 defines asphaltenes as the insoluble components of a crude oil sample diluted with 30 times the amount of a non-polar solvent (n-heptane) at temperatures between 18 and 28 °C [16]. Asphaltenes are therefore not an organic group of substances in the sense of the term, because they are not defined chemically by their molecular or chemical structure, but by their physical properties. Therefore, also the molecular and chemical structure of an asphaltene molecule is discussed intensively in literature and several different example molecules with varying characteristics can be found in literature [28–34]. In Fig. 2.4 atomic force microscope (AFM) pictures are shown of different asphaltenes found in crude oil.

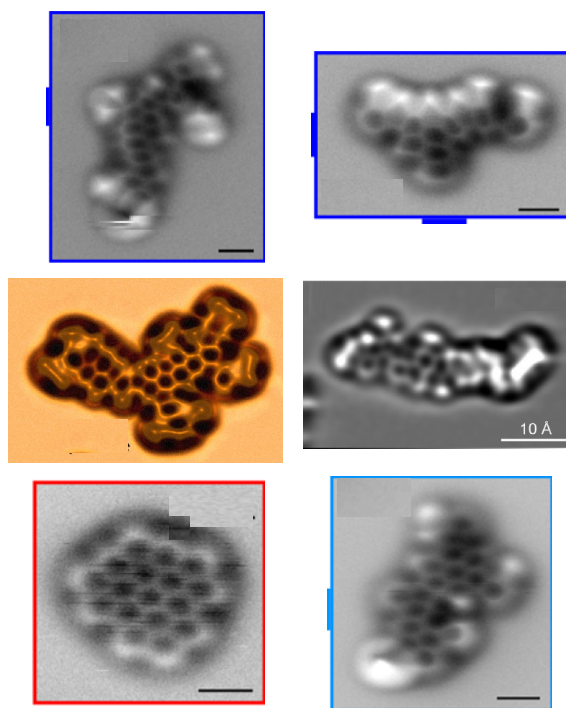


Figure 2.4: AFM of crude oil asphaltenes with permission from [28, 30]

Asphaltenes are composed of condensed aromatics (unsaturated cyclic compounds composed of one or more benzene rings) with aliphatic chains (saturated and unsaturated open chained compounds with no rings) attached to them. In most cases, the condensed aromatics are arranged in layers and can be connected to each other

both within one layer as well as between layers by aliphatic chains. In a stable mixture of asphaltenes and maltenes the maltenes surround the asphaltenic structures and prevent them from building clusters that precipitate. [35–37] The aggregation and three-dimensional structure of asphaltenes together with their aromaticity and aliphatic chains, strongly contributes to the difficulty to remove sulfur from residue [31, 38–43]. The sulfur containing core of different asphaltenes were identified by Grinko et al. [40] and Liu et al. [44]. Macromolecules with a molar mass of between 500 and 3,000 g/mol are possible for asphaltenes from heavy crude oil vacuum residue [45–47].

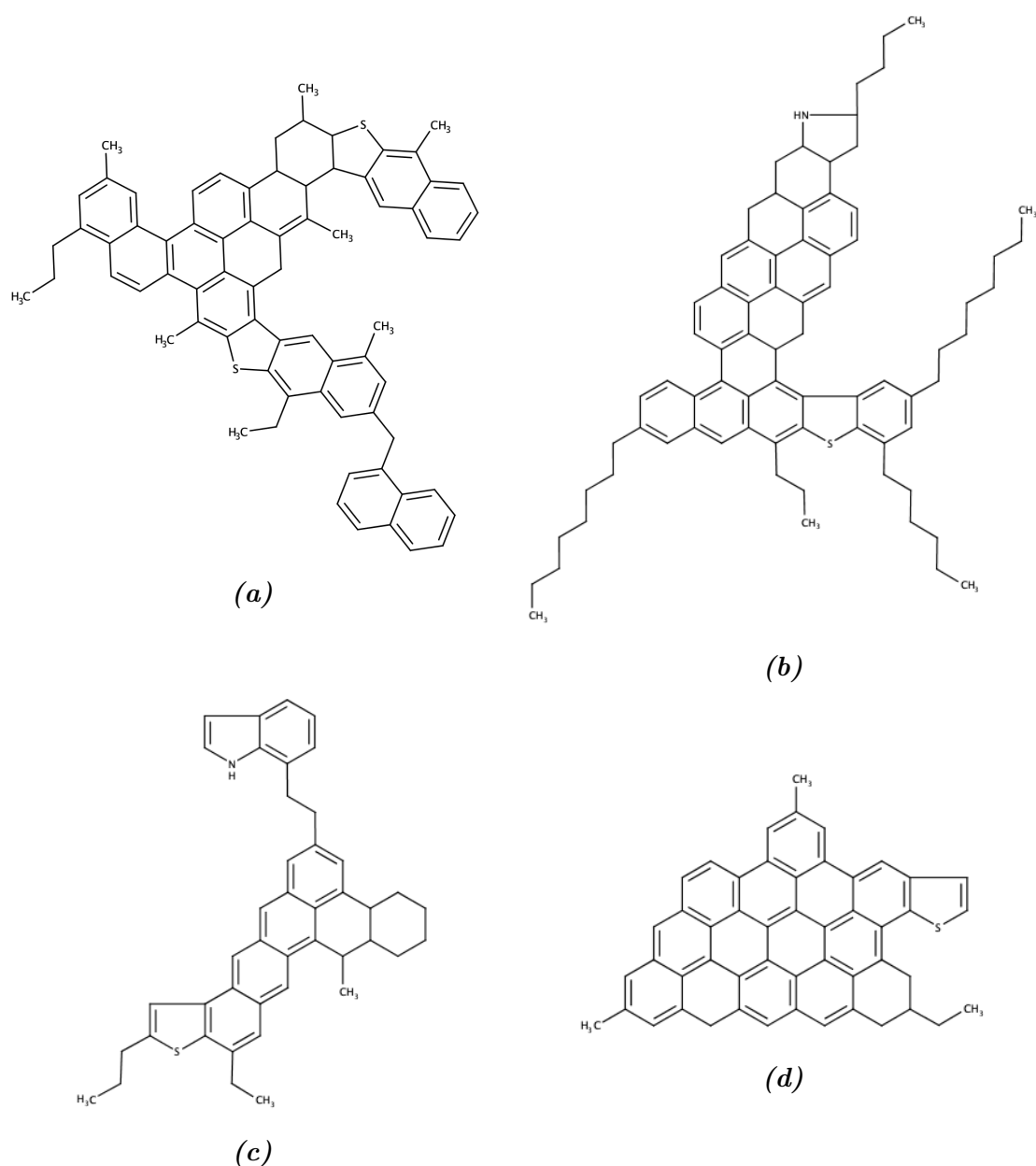


Figure 2.5: Hypothetical structure of different asphaltene molecules (the author does not claim that these exact molecules exist in reality)

Though, as mentioned above, several descriptions of asphaltenes exist in literature, some common characteristics can be identified. These are listed in the following and are further used in this work for the definition of asphaltenes.

- Aromatic core
- Low H/C ratio
- High concentration of heteroatoms
- Thiphenic, benzothiophenic, and dibenzothiophenic sulfur structures
- Aliphatic chains attached
- Molecule size of more than 50 carbon atoms

Based on these characteristics, some structures of hypothetical asphaltene molecules are designed and shown in Fig. 2.5.

Apart from the large size of each asphaltene molecule, formation of molecule aggregates and colloids is reported by several researchers [33, 48–52]. According to Brandt et al. [48], polycyclic aromatic compounds with saturated substituents group together forming sheets of asphaltene molecules. These individual aromatic layers may stack forming larger elementary particles. Interactions within these sheets involve π – π interactions between polycondensed aromatic structures as well as hydrogen bonds [53]. According to Eriksson et al. [49], these particles may reach an estimated molecular weight of 10,000 g/mol. Apart from being coke precursors in thermal processes, these clusters of asphaltenes also precipitate when the mixture is not stable [33]. In analytics, these aggregates are problematic, because the colloids make a precise analysis of the molecular weight of asphaltenes difficult [32]. Asphaltenes are the reason for the high viscosity of heavy and residual oils of around 10^6 Pa*s [50].

2.1.2.3 Maltenes

Maltenes are defined as the n-alkane-soluble fraction of crude oil residue, thus, the remaining fraction after asphaltenes have been precipitated. Maltenes can further be separated into aromatics, resins, and saturates [54]. The aromatics are molecules composed of only armomatic structures, while saturates are completely aliphatic molecules. For resins different definitions exist, all having in common a relatively

similar molecular description to asphaltenes [55]. Potential structures for maltenes are shown in Fig. 2.6.

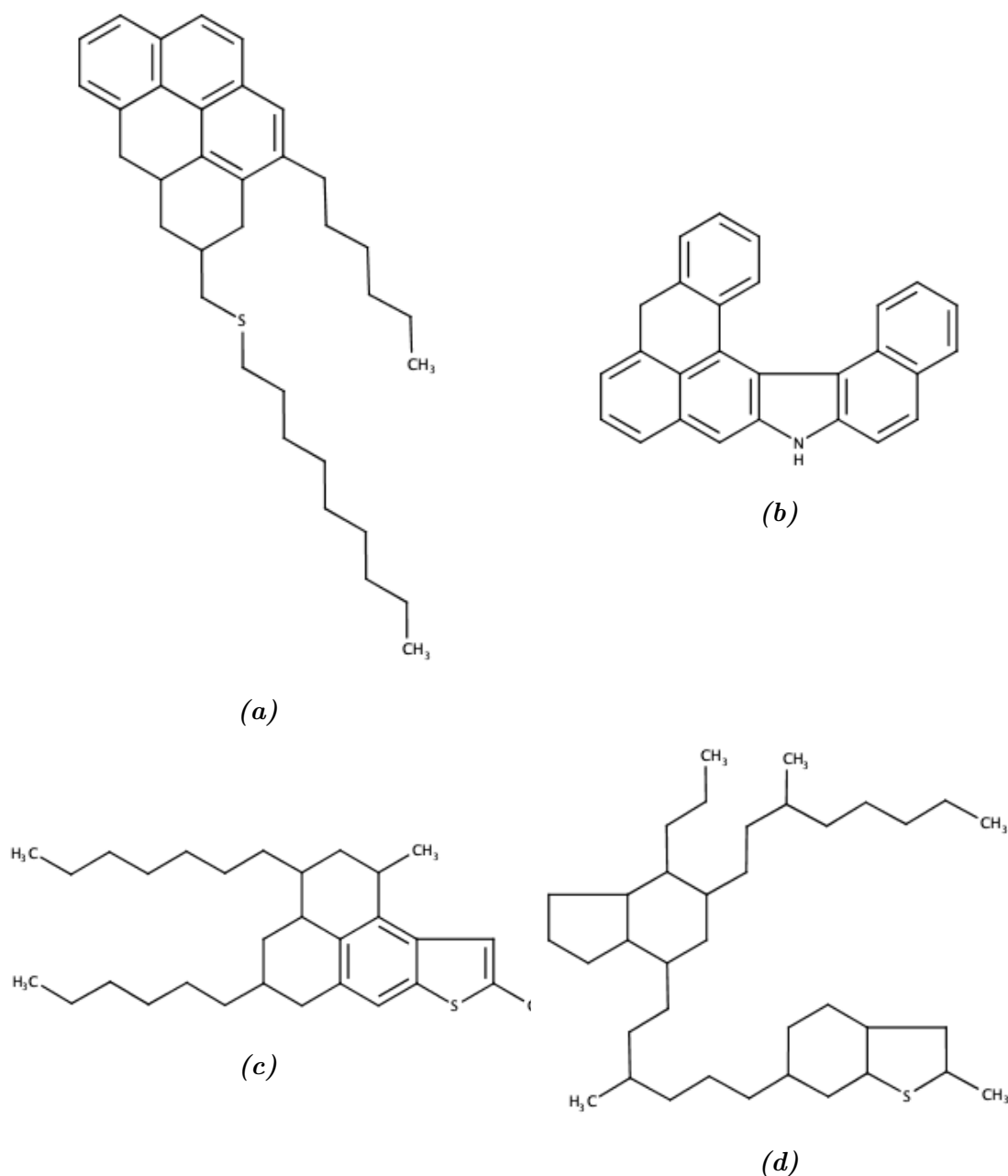


Figure 2.6: Hypothetical structure of different maltene molecules with (a) resin, (b) aromatic, (c) resin and (d) saturate

The similarity of resins to asphaltenes gives them an important role in stabilizing asphaltenes in maltenes [21, 56]. If resins are all converted or removed from the mixture, while asphaltenes are still present, they will precipitate and will not be stable in the mixture [21, 57]. The stabilization is enabled by the nature of the resins. The polar side of the resins agglomerate around the asphaltenes or clusters of asphaltenes and the aliphatic end of the resin extends into the oil phase [58].

2.1.3 Heavy fuel oil

The term heavy fuel oil (HFO) refers to fossile fuels, which are characterized by a particularly high viscosity and high density. The International Convention for the Prevention of Pollution from Ships (Maritime Pollution) (MARPOL) Convention defines HFO as either having a density of more than 900 kg/m^3 at 15°C or a kinematic viscosity of more than $180 \text{ mm}^2/\text{s}$ at 50°C [59]. The heavy oils contain large percentages of heavy molecules such as asphaltenes and maltenes with high degree of aromaticity. Their color is black and at ambient conditions they are nearly solid. Mostly, heavy oils are used as marine fuels but, also older locomotives and oil-fired power plants run on these low value fuels [60].

HFO is produced during refining of crude oil, mostly consisting of the vacuum residue described in Section 2.1.2. In order to achieve different specifications and quality levels, these residual oils are blended with lighter fractions. The resulting blends are known as Intermediate Fuel Oils (IFO) or Marine Diesel and have a higher economic value than the pure residue fraction. The most commonly used grades are IFO 180 and IFO 380 with a viscosity of $180 \text{ mm}^2/\text{s}$ and $380 \text{ mm}^2/\text{s}$, respectively [61]. The fuel is assigned to the heavy oil category, if the residue fraction exceeds that of the distillate blend-in fractions. In general, HFO cannot be pumped at ambient temperature and must therefore be preheated in order to lower its viscosity [60].

An essential distinguishing feature of heavy oils and the reason for the investigations in this work is their sulfur content. With regard to the sulfur content, the classes presented in Tab. 2.1 are distinguished.

Table 2.1: Fuel types and sulfur regulations for the use of heavy oils as fuel on open seas [3, 4]

Fuel type	Sulfur content [%]	Usage on open seas after 2020
High sulfur fuel oil HSFO	< 3.5	only with scrubber
Low sulfur fuel oil LSFO	< 1.0	only with scrubber
Ultra low sulfur fuel oil ULSFO	< 0.1	globally and in ECA

From the year 2020, the maximum allowed sulfur content in fuels used globally on open seas is reduced from 3.5% to 0.5% according to the LSF2020 [4], if no scrubber is installed on board the ship to remove sulfur emissions from the off-gas. The investigations in this work address the reduction of the sulfur content of vacuum residue to comply this new sulfur level of 0.5%.

2.2 Refinery

Crude oil is generally sent to a refinery where it is separated and subsequently upgraded to marketable products like diesel, jet fuel, or gasoline. In order to understand where the vacuum residue fraction results from and where processes dealing with vacuum residue are located within a refinery, a brief overview on a refinery setup is given here. Refineries consist of a variety of different unit operations dealing with fractionation, conversion and purification of crude oil in order to receive high value product streams. Although refineries can differ significantly in their exact structure, they are all designed along the process chain separation (distillation) followed by upgrading and conversion (e.g. desulfurization, conversion, or isomerization). Topping and hydroskimming refineries do not include a vacuum distillation step [62]. Since the vacuum residue is subject of the present work, a simplified flow scheme of a more complex, full conversion crude oil refinery plant is displayed in Fig. 2.7 [63].

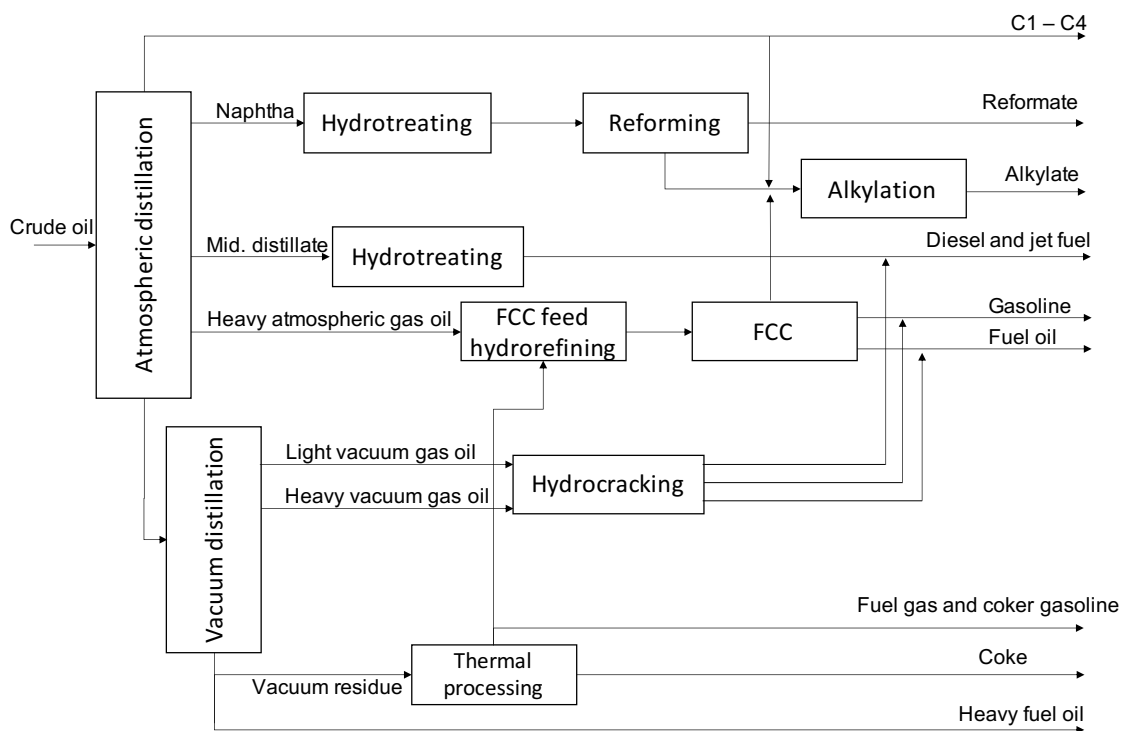


Figure 2.7: Simplified flow diagram of a refinery

2.2.1 Distillation

The core of every refinery is the atmospheric distillation column. After desalting and dewatering, the crude oil is heated and enters the atmospheric distillation just above the bottom tray. The constituents of the crude oil are separated according

to their boiling point and the products are collected from the top, bottom, and side of the column. Desired side streams like naphtha are removed from trays where the temperature corresponds to the cut-points for the corresponding product fraction. Side-draws can be returned to the column to control its temperature and enhance separation efficiency. Also, reflux can be adjusted to control temperature and improve separation. The evaporation heat is supplied by a reboiler at the bottom of the column, which is normally kept below 350 °C to prevent cracking of C-C bonds, which is an undesired process in the distillation due to coke deposition [64]. The reboiler ratio ensures the bottom product quality and that no light boiling components exit through the bottom product. A list of American Society for Testing and Materials (ASTM) products from the distillation with their corresponding boiling points is given in Tab. 2.2 [65].

Table 2.2: *ASTM boiling range of crude oil distillation products*

Fraction	Boiling range in °C
Light naphtha	30-99
Heavy naphtha	88-204
Kerosene	171-271
Atmospheric Gas Oil (AGO)	288-438
Vacuum Gas Oil (VGO)	399-566
Vacuum residue	538+

The bottom product from the atmospheric distillation is sent to the vacuum distillation in modern refineries. In the vacuum distillation, a vacuum of up to 15 mbar and temperatures of 350 °C are applied to separate the heavy fractions. By decreasing the pressure in the vacuum distillation, light and heavy vacuum gas oil can be evaporated without exceeding 350 °C where cracking reactions would substantially start to occur. Lighter fractions can be sent to the distillate hydrotreater or fluid catalytic cracker. The bottom product from the vacuum distillation is called vacuum residue and is further described in Section 2.1.2 [14].

Most of the distillates have to be further upgraded to give a marketable product. Therefore, refiners have developed a variety of processes to treat product streams yielding desired products. The processes can be divided into

- Thermal cracking
- Catalytic cracking
- Hydroprocessing
- Catalytic reforming and isomerization

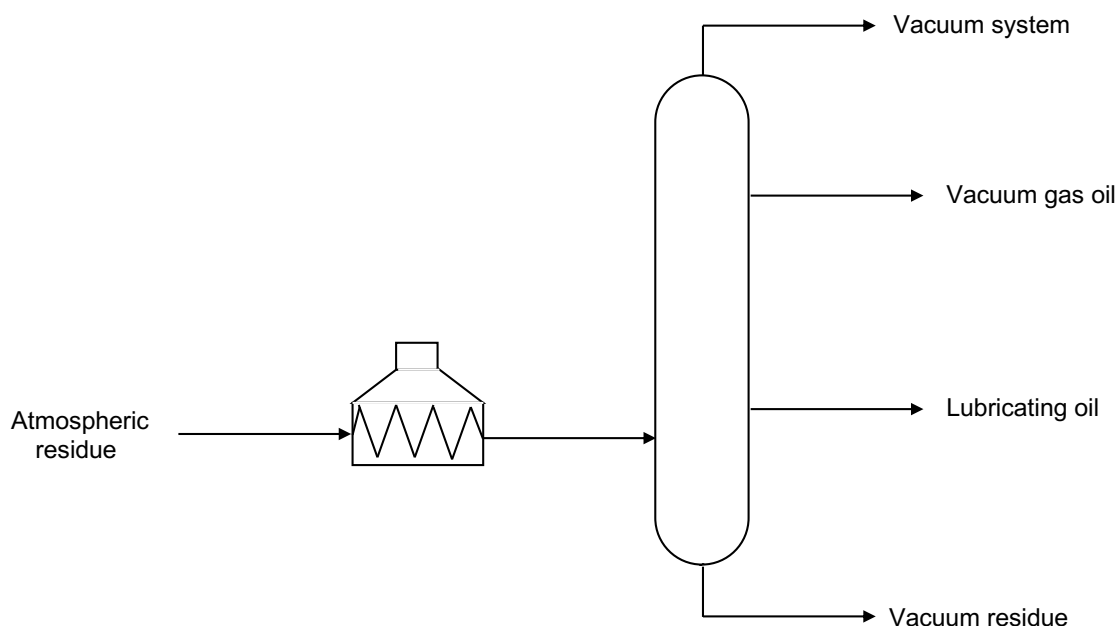


Figure 2.8: Vacuum distillation column and the resulting product streams

- Alkylation and polymerization

Each of the upgrading processes is briefly described in the Subsections 2.2.2 - 2.2.6.

2.2.2 Thermal cracking

Thermal cracking is applied to feedstock and refinery intermediate streams of low quality (in Fig. 2.7 located in the bottom product stream from the vacuum distillation unit) and high molecular weight in order to receive a product stream with lower molecular weight. As the name indicates, thermal energy is used to break carbon bonds to achieve a molecular weight reduction. The chemical process behind thermal cracking is displayed and described in detail in Section 2.4.1. Different process forms exist in this unit operation segment, which are thermal crackers, visbreakers and cokers. The term thermal cracking is mostly used when the process feed is atmospheric residue, while visbreaking refers to upgrading of the vacuum residue. The product streams from both processes are comprised of remaining residue (since both processes do usually not achieve 100 % conversion) and lighter fractions LPG, naphtha and middle distillates. Coking describes a process form at more severe conditions leading to full conversion. The cost of this full conversion is the formation of coke. All three process types have a similar configuration composed of a cracking furnace, a "soaking" vessel (in more complex and modern setups) or coils and a product recovery section. In the cracking furnace, the feed is kept at temperatures above

500 °C for a defined period of time. The "Soaker" enables an extended section where cracking occurs. In the coking process, oil is passed through several coking drums after the furnace. In the coking drums, coke is formed at long residence times while at the same time short chained hydrocarbons are released. Products from the coking process have a higher fraction of unsaturated hydrocarbons compared to other cracking processes. The composition of the products is highly dependent on the feed, cracking severity and residence time in the reaction zone. Solid coke remains in the coking drum while liquid and gas products are sent to the product recovery. In the product recovery section, which is again similar for all three thermal cracking processes, the different streams are separated and sent to further processing steps [65–67].

2.2.3 Catalytic cracking

Catalytic cracking is one of the most commonly used processes to reduce average molecular weight of the oil and upgrading the feed stream to higher quality products. It is mostly performed in a Fluid Catalytic Cracking (FCC) facility, processing high boiling fractions from the atmospheric distillation but also fractions derived from the vacuum distillation unit as displayed in Fig. 2.7. The FCC process is operated with a finely powdered catalyst (nowadays highly active and selective zeolites [68, 69]), which is mixed with the substrate oil. The hot catalyst coming from the regeneration zone leads to cracking reactions of the feed oil. In the reactor, catalyst particles are suspended in a rising flow of feedstock in a fluidized bed so that contact between oil and catalyst is very high, exposing a large portion of the oil to the hot catalyst. In catalytic cracking, a carbonium ion is formed initiating the break down of large chain length molecules. The further reaction path taken by the carbonium ion decides on the product being formed. A detailed description of the cracking process is given in Section 2.4.2. Cracked products leave through the top of the reactor as vapor. Downstream of the reactor, a recovery section is operated to remove the distillate products from the residue. Residue is recycled to the reaction zone. During cracking reactions, the catalyst gradually deactivates and therefore it is sent to a regeneration zone. In the regenerator, carbon on the catalysts surface is removed by contact with air at high temperature. The heat stored in the catalyst then provides the energy for the cracking reaction in the reaction zone. The product oil spectrum exhibits mostly naphtha and lighter boiling products but also a smaller fraction of heavy hydrocarbons [65, 70, 71].

2.2.4 Hydroprocessing

The term hydroprocessing in the context of a refinery includes a number of different processes, all involving the reaction of crude oil with H_2 . The processes can be subdivided into two major groups, which are hydrotreating (downstream of the atmospheric distillation unit in Fig. 2.7) and hydroconversion (downstream of the vacuum distillation unit in Fig. 2.7). The first, hydrotreating, refers to processes that aim at the removal of undesired heteroatoms (sulfur, nitrogen, and oxygen) and heavy metals (nickel, vanadium, etc.) while increasing the hydrogen content of the product but not the boiling range. Often the removal of these contaminants is necessary to prevent downstream catalysts from poisoning or to meet product specifications. The processes are called HDS, hydrodenitritication (HDN), hydrodeoxygenation (HDO), and hydrodemetallization (HDM). The second group, the hydroconversion processes, aims at changing the average molecular weight and structure of the crude oil. Hydrocracking, hydrogenation, hydrodearomatization as well as hydroisomerization processes are all processes that belong in this group [71, 72].

Hydrotreating units are very common in refineries for the removal of impurities from lighter distillate products like naphtha and diesel. The setup is described by example of a naphtha hydrodesulfurization unit. H_2 rich gas from the catalytic reformer is added to the naphtha stream coming from the naphtha splitter. The stream is heated to about 350°C before entering a reactor containing the desulfurizing catalyst. The catalyst is mostly a very active Co-Mo or Co-Mo-Ni catalyst supported on an alumina base. Sulfur is removed from the feed stream under reaction with H_2 forming H_2S . The chemical reaction is described in detail in Section 2.4.3. The product stream is cooled and flashed in a product separator. H_2S is removed with the gas phase stream and can be sent to the Claus unit [73, 74]. Novel hydrotreating processes for the upgrading of vacuum residue exist scarcely in refineries. They will be discussed in Section 3.

Hydrocracking is a relatively new upgrading process within the family of unit operations in a refinery. In the presence of high H_2 partial pressure (50 bar for mild processes and up to 260 bar for residue hydrocracking) the feed constituents are cracked and the forming radicals are saturated with H_2 . The high H_2 partial pressure makes the process costly and therefore, FCC units and thermal crackers have mostly been installed as preferred upgrading step, though the hydrocracking process delivers high value products and can deal with a wide spectrum of different feeds [65].

The process has a similar setup to the hydrotreating process composed of a heater, a recycle gas section, a reactor and a recovery section. Feed oil is preheated and H_2 (both fresh and recycled) is introduced into the hot feed before entering the reaction zone. Often, a hydrotreating catalyst is installed upstream of the hydrocracking catalyst to prevent catalyst poisoning. The hydrocracking catalysts are mostly bi-functional catalysts that can be divided into two types, an amorphous type (non-crystalline) and a zeolite type (crystalline) [75]. The amorphous type are mostly composite oxides with controlled pore structure and surface acidity, which produces high yields of middle distillates. The zeolite type are crystalline aluminosilicate structures with high catalytic activity due to strong acidity but less selectivity towards middle distillates. The difference in selectivity is controlled by the pore size of the zeolite catalysts. Because of a very defined pore size, zeolite catalysts yield smaller hydrocarbons than the amorphous catalysts [76–78]. Downstream of the reactor, the effluent is cooled down and partially condensed. The removed heat is used to heat up the feed stream. In a flash drum, unreacted H_2 is removed from the product stream and recycled to the feed. The liquid phase is often passed to a second separation step, which is operated at a lower pressure (6–7 bar). This pressure reduction leads to the evaporation of light hydrocarbons (mostly C_3 and C_4 compounds), that can be removed as gas. Liquid products are sent to the fractionation column [79, 80].

2.2.5 Catalytic reforming and isomerization

Aside cracking processes that break down large molecules in order to produce smaller, more valuable products, also unit operations exist in a refinery that deal with reformation and isomerization of naphtha fraction. These processes have become increasingly important as they yield high octane naphtha to meet the demand for rising motor gasoline and aviation fuel consumption. The reformation and isomerization step in Fig. 2.7 is indicated only by the reformation step downstream of the hydrogenation reactor for the naphtha fraction. In reformation, a fraction of the hydrocarbons in the naphtha feed reacts, forming hydrocarbons with higher octane value. The octane value is a measurement for how far a fuel can be compressed before self ignition, with the reference point 100 defined as a fuel with 100% iso-octane. Reformation reactions involve formation of cyclic products from n-alkanes, removal of H_2 from cyclic hydrocarbons forming aromatic rings, and isomerization of n-alkanes to iso-alkanes. Example reactions are given in Fig. 2.9.

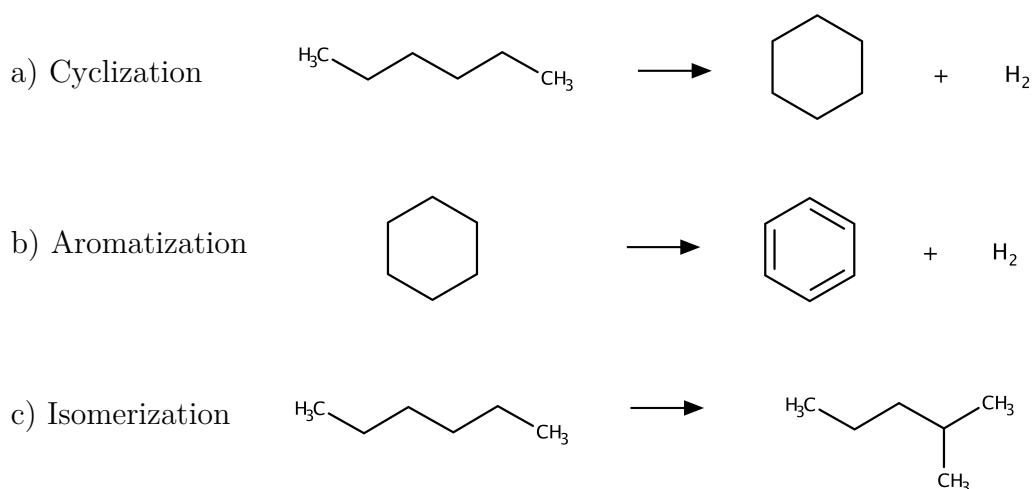


Figure 2.9: Reactions taking place in the isomerization unit

One necessary step within the reformation reactor is the aromatization of cyclic paraffins (paraffines are non-cyclic saturated hydrocarbons). H_2 is released during this reaction, necessary for the hydrotreating section of a refinery. After sulfur and N_2 removal from the bottom product of the naphtha splitter, the reformation units feed is preheated by the heat from the product stream of the reformation unit. Together with unreacted and recycled H_2 , the feed is passed through several (often three or four) reactors subsequently with intermediate heating, to maintain the reformation temperature needed in the reaction sections. The products are cooled down and condensed partially in the heat exchanger supplying heat to the inlet feed. Downstream, H_2 is recovered in a flash unit from which the reformed product stream is retrieved as liquid product. The liquid fraction is sent to a stabilizer column, where butane and lighter hydrocarbons are removed and the bottom product is the debutanized reformate (desired products from the reformation step), which is further sent to the gasoline pool [81]. Especially in the production of low sulfur fuel, the blending with isomerates (products from isomerization reactions) plays an important role due to the low sulfur content in the isomeration products. In order to meet the rising demand of high octane and low sulfur fuels, n-butane is often isomerized to iso-butane in a separate isomerization reactor, mostly using bifunctional catalysts (platinum on chlorided alumina). The isomerization unit in a refinery is very similar to the catalytic reforming. Reactions are also carried out in presence of H_2 , though H_2 is neither produced nor consumed in the process but it is employed to inhibit undesirable side reactions [82].

2.2.6 Alkylation and polymerization

During catalytic cracking, light gases are produced, which are unsaturated to a high extent [83]. In order to increase the fraction of valuable products in a refinery, these hydrocarbons are usually sent to polymerization or alkylation processes for conversion into high octane gasoline species. Polymerization in this context does not mean the build up of long chained molecules, but only linking mostly two monomers. Light olefins (olefins are hydrocarbons containing one or more double bonds) polymerized from propylene and butylene monomers are the products from this unit operation as displayed in Fig. 2.10. Mostly, iso-olefins are produced, but also n-olefins belong to the product range [84].

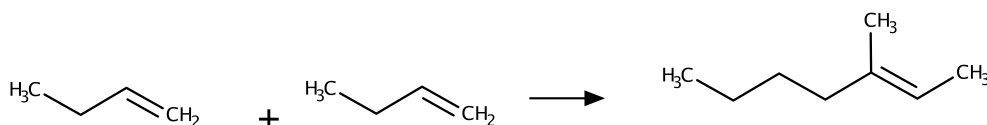


Figure 2.10: Polymerization reaction

Thermal polymerization needs to be operated at 480 – 650 °C, while by applying a catalyst, temperatures can be reduced. Catalysts consist of phosphoric acid on pellets of diatomite. Pressures of 30 – 75 bar are required at temperatures of around 175 – 230 °C [14, 85].

Alkylation in petroleum refining is mostly used for conversion of smaller olefins (<C₆) with iso-butane into highly branched iso-paraffins as displayed in Fig. 2.11 [84].

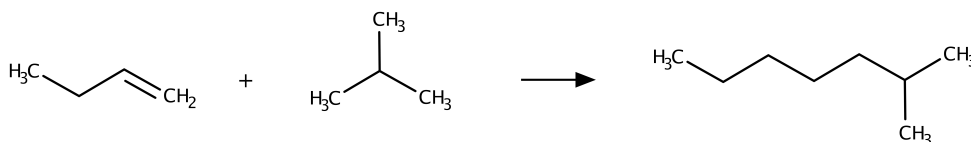


Figure 2.11: Alkylation reaction

Liquid and solid acids are used as catalysts of which hydrofluoric (HF) alkylation and sulfuric acid alkylation are the most commonly used processes [86]. The process using sulfuric acid as catalyst is operated at low temperature of 2 – 7 °C where refrigeration is necessary in order to remove the heat generated by the alkylation reaction [14, 87]. When using hydrofluoric acid for alkylation, the reaction temperature may be higher (up to 50 °C) though the chemistry behind the reaction is very similar to the reaction in sulfuric acid. Main advantage is avoiding refrigeration but

reactors have to resist the very corrosive HF acid. Recovery of the acid is realized in a distillation unit downstream of the reactor [14,88].

2.3 Catalysts and additives

Catalysts play an important role in most modern chemical conversion processes. They lower activation energy and are used to catalyze specific reactions, increasing selectivity. Several catalytic unit operations within a refinery have been discussed in the previous Section 2.2.

In the context of slurry residue upgrading, catalysts can be divided into two groups. The first group is often referred to as additive because of its minor catalytic capacity, while the second plays a catalytic role in hydrogenation or bond breaking [89]. The most prominent representatives of the additives are carbonaceous solids, which provide a large surface area. The surface area is used to adsorb coke precursors. Catalysts are often chosen as oxides or sulfides from group IV to group VIII metals including transition metal-based catalysts, derived from organic acid salts or metal-organic compounds of molybdenum, vanadium, tungsten, chromium or iron. Commonly, these metals are combined as dual catalysts (CoMo, NiMo, and NiW) often supported on a carrier material. Typical supports consist of aluminum oxides, silicone oxides, titan oxides, mesoporous aluminosilicate, and zeolites [90]. Molybdenum, tungsten, and iron based HDS catalysts are sulfided in order to transform them into the active phase [91]. This can be achieved by presulfiding the catalyst with H_2S forming MoS_2 , WS_2 , and FeS_2 . Catalysts used in slurry phase hydroconversion are often dispersed MoS_2 . MoS_2 shows good reduction of coke formation and removal of heteroatoms but needs to be produced from costly precursors [92, 93]. Since catalysts deactivate significantly in slurry processing of vacuum residue, expensive catalysts display a large downside, if they cannot be recycled and regenerated [93, 94]. Research on different catalysts is summarized in Chapter 4.

HOK has been used as additive in coal liquefaction in the Bergius-Pier Technology and later also in the conversion of residue in the VEBA Combi Cracking (VCC) process [95]. Since its catalytic activity is minimal, it has been doted with molybdenum to combine the ability to suppress coke formation with the hydrogenation activity [96].

SCW can also be used as additive in slurry processes. Because of its particular role in this work, supercritical water will be discussed in detail with its unique attributes in Section 2.3.1.

2.3.1 Supercritical water

Water changes its properties above the critical point at 373.95 °C and 220.64 bar. The resulting dense supercritical phases have unique properties that form the basis of innovative technologies and have also led to the search for technical applications as an ecologically clean solvent for chemical reactions [97]. By adjusting pressure and temperature, conditions are reached, where water mixes completely with non-polar substances, while, at the same time polar and ionic substances are dissolved in high concentrations [98]. In addition, the viscosity remains low, even at liquid-like densities, so that mass transport and diffusion-controlled chemical reactions can be accelerated. The phase diagram of H₂O is displayed in Fig. 2.12. Relevant properties of H₂O at supercritical conditions are given in this section.

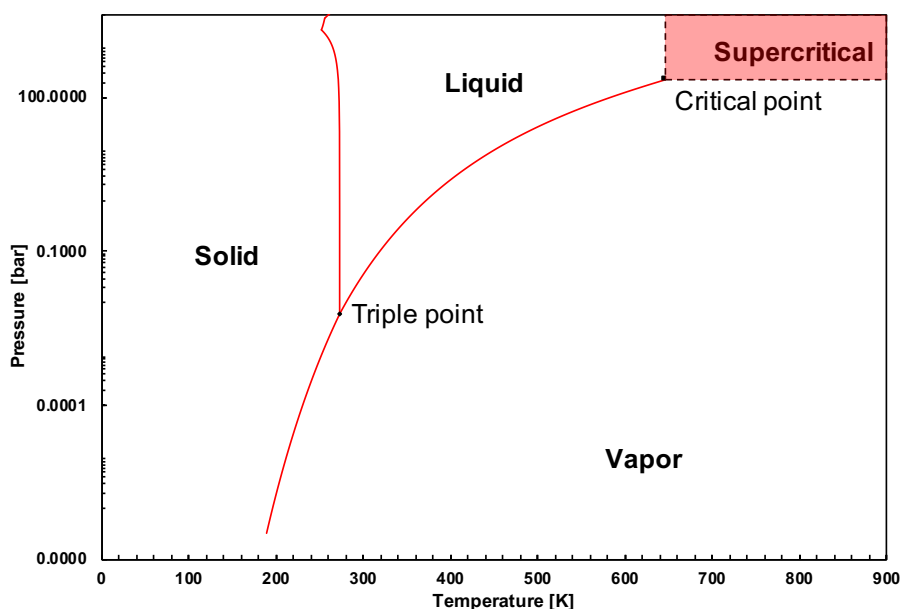


Figure 2.12: Phase diagram of water showing the critical point

2.3.1.1 Self-dissociation

The self-dissociation constant K_w is a measure of how strongly water tends to dissociate forming H^+ or H_3O^+ as well as OH^- ions under given conditions.



With known activity α of the ions, the self-dissociation constant K_w can be calculated according to Eq. 5.10.

$$K_w = \alpha(\text{H}^+) \alpha(\text{OH}^-) \quad (2.2)$$

Calculations for K_w performed by Holzapfel and Franck [99] and later improved by Marshall and Franck [100], laid basis for description of K_w , dependent on temperature and pressure at above critical conditions. According to Iwamura et al. [101], K_w reaches a maximum of 10^{-5} (compared to close to 10^{-7} at ambient conditions) at the critical point and drops drastically afterwards ($> 10^{-22}$ at 450°C). Between 200 and 450°C and above critical pressure, acid and base conditions could be applied without addition of a strong acid or base, simply by adjusting temperature and pressure [101]. This tunable acid-base equilibrium may enable H_2O to play a catalytic role in desulfurization reactions according to Savage et al. [102].

2.3.1.2 Transport properties

Both heat and mass transport properties play an important role in HDS. While mass transfer is generally better in gas phase due to the mean free path [103], heat conductivity in liquids is better than in gases [104]. For example at ambient conditions water exhibits a thermal conductivity of 0.6 W/m K , while gases like H_2 and air show far lower values of 0.18 W/m K and 0.026 W/m K respectively [104]. Water at supercritical conditions combines both advantages, because the density is similar to that of a liquid (322.39 kg/m^3 at the critical point), while maintaining a high diffusion coefficient for H_2 [105, 106]. In comparison to oil, SCW has a more than twice as high thermal conductivity coefficient at 400°C and 300 bar of about 0.4 W/mK [106]. In this manner, both heat and reactants can effectively be transported to and away from the reaction site.

2.3.1.3 Dielectric properties

Water at ambient conditions is not suitable as solvent for crude oil fractions because of the polar character of water. Reason for this is the dielectric constant ϵ which is a measure for the polarity of a solvent. At ambient conditions, water has a

dielectric constant of 80.10 [107], while organic solvents exhibit far lower values (e.g. benzene 2.30, n-hexane 1.89). At SCW conditions, this "constant" drops below five and enables dissolving organic substances like crude oil [108].

2.3.1.4 Supercritical conditions of mixtures

When a mixture of two or more compounds is investigated according to their critical behavior, the phase rule states that a critical point does not exist, but a critical line. If pressure and temperature are above this critical line, the mixture acts as one supercritical phase. In the system investigated in this work, the mixture is composed of vacuum residue, H_2 , oil, and water, while water and H_2 represent the largest fraction according to the number of moles (vacuum residue has a very large molecular weight of $> 500 \text{ g/mol}$) and therefore represents only a few mole in the system), which is the relevant figure for determining the critical line [109, 110]. Therefore, the critical line is mostly defined by the behavior of these two components. Seward and Franck [109] investigated the behavior of the critical conditions for the mixture of $H_2O - H_2$. The resulting critical line for the system $H_2O - H_2$ is displayed in Fig. 2.13.

The critical point of pure H_2 is not displayed in the diagram because it is with -251.95°C and 12.96 bar far outside the displayed range. The critical line between both critical points of the pure components will show an interruption at high pressures and therefore it belongs to the type III phase diagram described by Konynenburg and Scott [111] [110].

2.4 Chemistry and thermodynamics

The chemistry behind conversion and desulfurization of heavy oil is governed by thermal and catalytic rupture of C-C as well as C-S bonds and subsequent recombination reactions of the formed fragments or the addition of H_2 to the fragments. For a deeper understanding of the experimental investigations in this work, a short overview of the chemistry behind different occurring reactions is given.

2.4.1 Thermal cracking

Thermal cracking reactions break longer chain alkenes into shorter alkanes. The basic mechanism behind non-catalyzed cracking is a free radical mechanism where

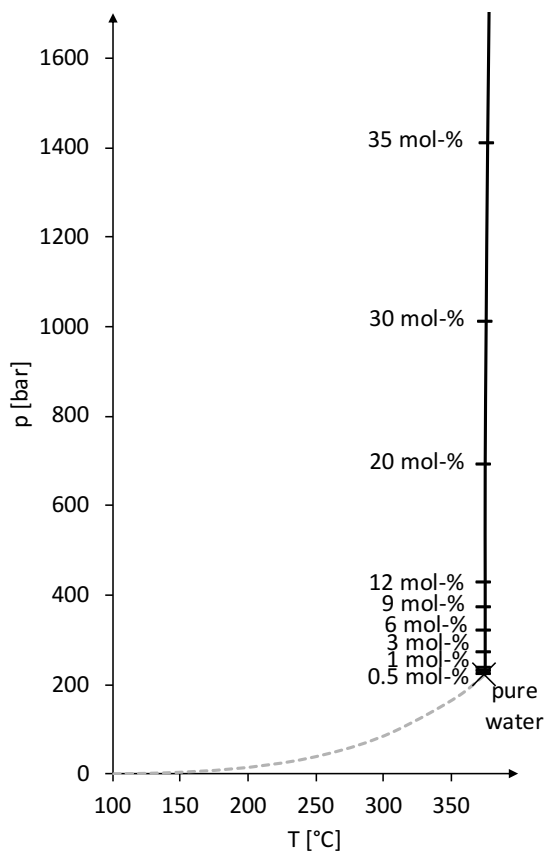


Figure 2.13: Critical curve of the binary mixture $H_2O - H_2$: the black line indicates the critical curve for the mixtures with the labeled molar ratio of hydrogen in water; the dotted curve shows the vapor pressure line for pure water ending in the critical point of pure water

carbon atoms with unpaired electrons, but no electronic charge, display the reactive specie. Thermal cracking involves three steps (initiation, propagation and termination) presented in Eq. 2.3 - 2.5 [112].

Initiation



Propagation



Termination



Free radical chain reaction is initiated by thermal rupture of the weakest C-C bond in the reacting alkane (R-H), forming two free radicals $R_1^\bullet$ and $R_2^\bullet$, each with one unpaired electron. After the initiation step, two different propagation steps are possible for each radical. Once formed by the initiation step, the free radical can go through two different propagation reactions. The two options are hydrogen abstraction and β -elimination of which the former is preferred at higher pressures. In hydrogen abstraction, the radical R_1 removes a hydrogen atom from a different alkane present in the mixture, producing a shorter alkane (R_1-H) as well as one new radical, which propagates the free radical chain mechanism. In the case of β -elimination, the radical undergoes a reaction producing an olefin by breaking the C-C bond in β -position in relation to the location of the unpaired electrons and a radical, which can propagate the chain. Both propagation steps have in common that a free radical is formed propagating the chain reaction. In contrast to the propagation, the termination step describes a reaction involving the combination of two radicals ending the chain reaction [113].

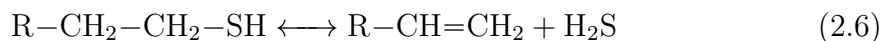
2.4.2 Catalytic cracking

Catalytic cracking has several advantages compared to thermal cracking, including the reduction of the activation energy and the possibility of increasing selectivity. The largest difference in the mechanism between thermal and catalytic cracking, leading to a very different product spectrum, is the formation of a carbonium ion instead of a radical. Additionally, the physical adsorption of the hydrocarbon on a bi-functional catalysts surface (as described in Section 2.2.3) lowers the activation energy necessary for the cleavage of the C-C bond. It is generally accepted that the dual mechanism involves adsorption of a paraffin molecule on a metal site of the bi-functional catalyst, followed by reversible dehydrogenation to form an olefin. In the second step, migration to the acid site of the catalyst takes place. The acid site of a catalysts starts the protonation of the olefin and proceeds by an attack of the proton on the π -electrons of the olefin. The following reactions can either be further cracking on an acid site or hydrogenation on a metal site [114,115].

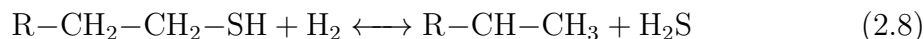
2.4.3 Hydrodesulfurization

Analogue to the cleavage of C-C bonds, the easiest desulfurization mechanism proceeds via β -elimination. Sulfur bound to adjacent the α -carbon atom leaves the

molecule in hydrogenated form as H_2S , leaving behind a double bond, which will at high H_2 partial pressure be hydrogenated directly as displayed in Eq. 2.6 and 2.7.



In catalytic HDS, hydrogenolysis is the predominant mechanism by which sulfur is removed. Hydrogenolysis is a reaction in which the C-S bond is opened with catalytically activated H_2 to form a hydrocarbon molecule and H_2S as displayed in Eq. 2.8.



The steps in catalytic hydrogenolysis proceed analogue to the catalytic cracking of C-C bonds. Elimination can take place on the surface of the carrier material, while hydrogenolysis and hydrogenation take place on the metal sulfide surface of the catalyst.

The mechanism of catalytic HDS has been studied extensively and investigations show, there are the two possible reaction pathways displayed in Eq. 2.6 - 2.8. Reactions might proceed via an active center for direct desulfurization by hydrogenolysis or an active center for the hydrogenation of sulfur compounds initiates the removal. The exact mechanisms on the catalyst surface is difficulty to clarify completely, partly because the catalyst surface is not stable in presence of the reactants and different active centers can be transferred into each other, depending on the interacting gas species [1,2,116]

Thiophene, BT and DBT derivatives, which are as outlined in Section 2.1.1, the predominant species in vacuum residue, are desulfurized via both hydrogenolysis and hydrogenation. H_2 may react directly with the sulfur atom to form H_2S or H_2 can react with the π -bond of the aromatic structure surrounding the sulfur atom. Hydrogenation of the ring destabilizes the C-S bond so that subsequently H_2 can cleave the bond forming H_2S . Alkylation of BT and DBT lowers their HDS reactivity, drastically. The steric hindrance of the alkyl groups are most probably the reason for the lowered reactivity [117,118]. Steric hindrance is an effect resulting from the form and conformation of functional groups in a molecule and may reduce reaction

rates or selectivity of reactions. BT and DBT and their alkylated derivatives are most present in vacuum residue and therefore the HDS reactions are presented for both model substances.

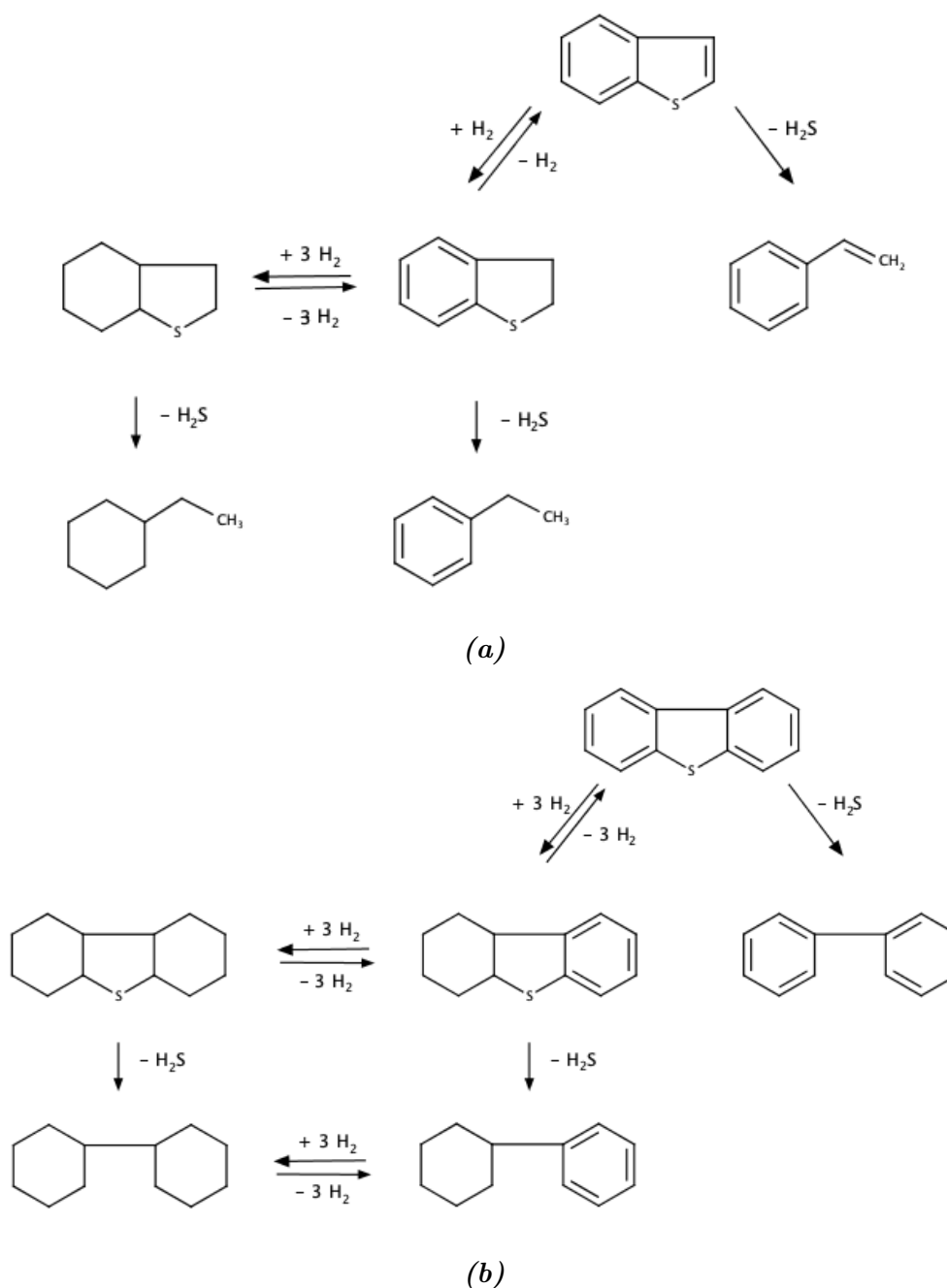


Figure 2.14: Desulfurization reactions via hydrogenation and hydrolysis route for (a) BT and (b) DBT based on [1, 2]

HDS reaction of BT can proceed via two main reaction paths. Either the hydrogenation of the ring (HYD) followed by the removal of H_2S or the direct hydrogenolysis (DDS). Because of the stabilizing function of the aromatic ring, hydrogenation is

difficult, leading to a preferred direct hydrogenolysis of the C-S bond. The reaction network is displayed in Fig. 2.14 [1].

Similar to the reaction of BT, DBT is desulfurized. The reaction network is also given in Fig. 2.14. Hydrogenation of either of the rings followed by the removal of the destabilized sulfur atom displays the first path, hydrolysis of the C-S bond the second. Hydrogenolysis and hydrogenation are promoted by different centers on the catalyst surface as it is explained in Section 2.4.2 [1].

The alkyl chains at different positions have a strong influence on the reaction rate of both alkylated BT and DBT. Alkyl groups positioned adjacent of the sulfur atom shield the sulfur atom and the direct hydrogenolysis is hindered. For instance, in HDS of DBT, the alkyl groups in positions 4 and 6 (displayed in Fig. 2.15 as the most refractory compound) sterically hinder the catalyst [119,120]. The order of stability of the sulfur species is given in Fig. 2.15 based on [15,119,121–123]

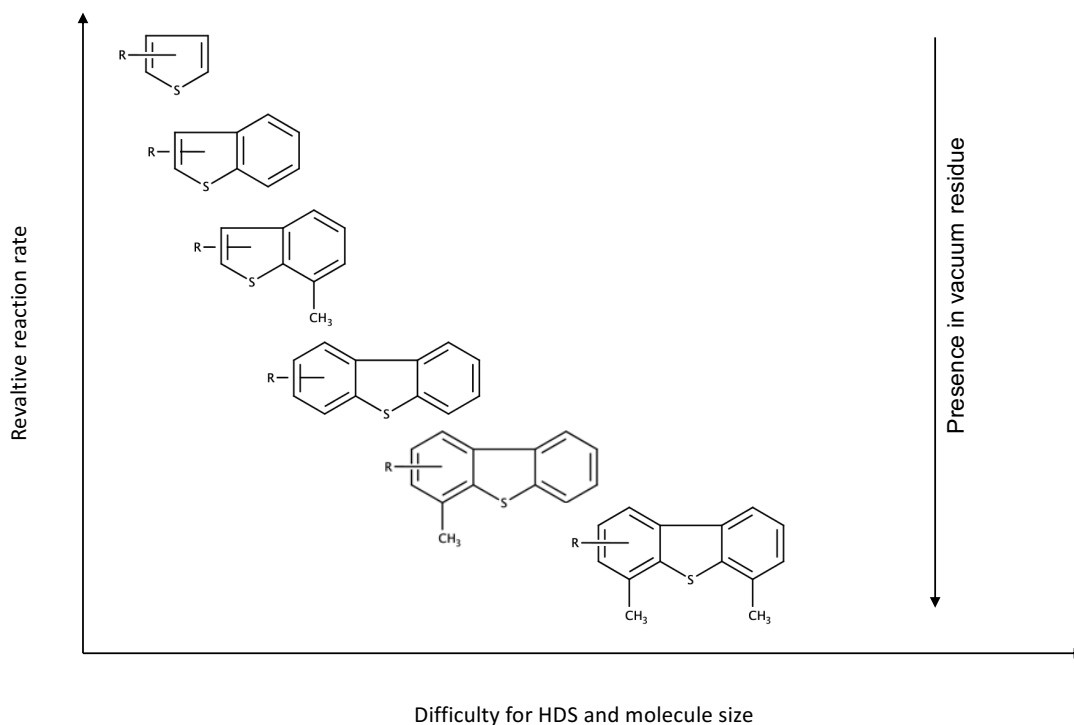


Figure 2.15: Stability of sulfur species based on [15]

Vacuum residue, as the heaviest crude oil fraction, contains large percentages of the most stable C-S bonds.

2.4.4 Bond energy

The chemical bonds of interest for this work are C-C bonds and C-S bonds. When only taking into account the energy needed to break these bonds without taking into consideration the surrounding functional groups, the energy needed for the desulfurization (breaking C-S bonds) is lower than for cracking reactions (breaking C-C bonds) as listed in Tab. 2.3.

Table 2.3: Bond dissociation energies in diatomic molecules [5]

Bond	Bond energy in kJ/mol
C-C	347
C=C	614
C-S	259
S-S	266

Though these bond energies are generalizations for bond energies that can vary, depending on the complete molecular structure and the surrounding functional groups, it can be seen that in a system of simple sulfur and carbon bonds, the sulfur bonds are more easy to break due to a lower bond energy. Influence of the various functional groups can be found in literature [124–126] and be determined via computational methods [127]. For example, as displayed in Fig. 2.16, the exchange of the linear hydrocarbon group containing 5 carbon atoms by a phenyl group, increases the bond energy from 300.8 kJ/mol to 357.3 kJ/mol. A reduction of the number of carbon atoms from 5 to 3 also increases the bond energy slightly to 306.7 kJ/mol.

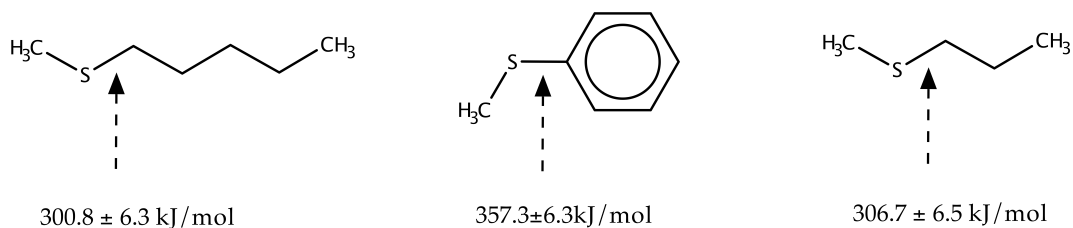


Figure 2.16: Influence of functional group on the bond dissociation energy [126]

It is well known that in systems with the complex composition of residual molecules like asphaltenes and maltenes, these bond dissociation energies fail to include the various steric effects that are a consequence of complex molecules containing three-dimensional structures [121].

2.5 Reaction mechanisms for heavy feedstock hydroconversion and hydrodesulfurization

For a better understanding and mostly as basis for modeling of hydroconversion and HDS reactions, mechanistic models were developed to describe the reaction paths taken by heavy feedstocks during hydroconversion and HDS. For hydrocracking reactions of heavy feedstock, a wide variety of different mechanistic models exist, comprised of very detailed models [23, 115, 128–131]. Detailed models use up to seven different lumps, mostly distinguished according to boiling points, as displayed in Fig. 2.18 [132].

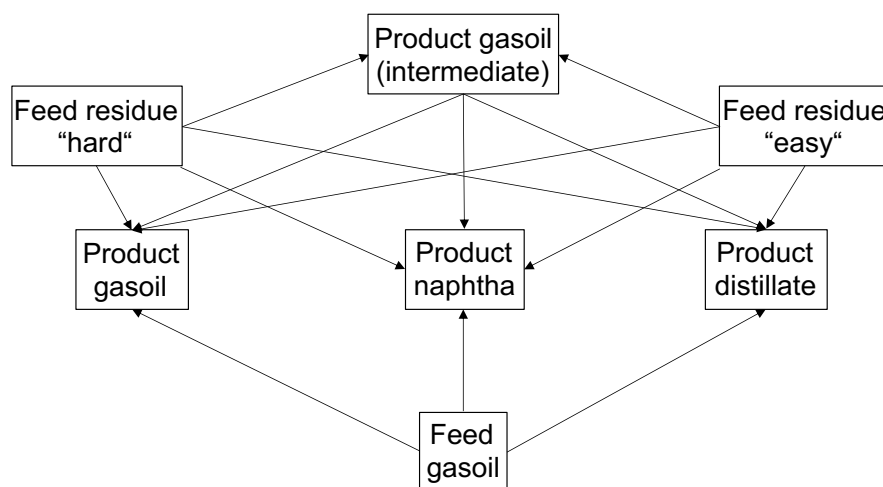


Figure 2.17: Complex mechanistic model of heavy feedstock hydrocracking based on [132]

Very simple models use only four lumps (asphaltenes, maltenes, oil, and gas) have also been reported [23]. With increasing number of different lumps, and thus increasing degree of accuracy, also the number of obtained data points and product specifications, needed to determine kinetic parameters for the model, increase.

Hydrodesulfurization of light fractions have been described with models intensively. Mostly, publications focus on model compounds, especially thiophene and BT based [133–135]. HDS reactions can then be described by the mechanisms presented in Section 2.4.3. For HDS of heavy fractions, only very few works have been reported [134]. According to Ancheyta et al. [134], this is because of the very complex mechanisms and different behavior of the different sulfur structures present in heavy feedstock. Mostly, kinetics and mechanistic models are therefore reduced to two lumps, the sulfur containing feedstock and the desulfurized product [134]. A mechanism for HDS combined with hydroconversion of atmospheric and vacuum residue is reported by Alvarez et al. [134] and the assumed mechanism is presented in Fig. 2.18.

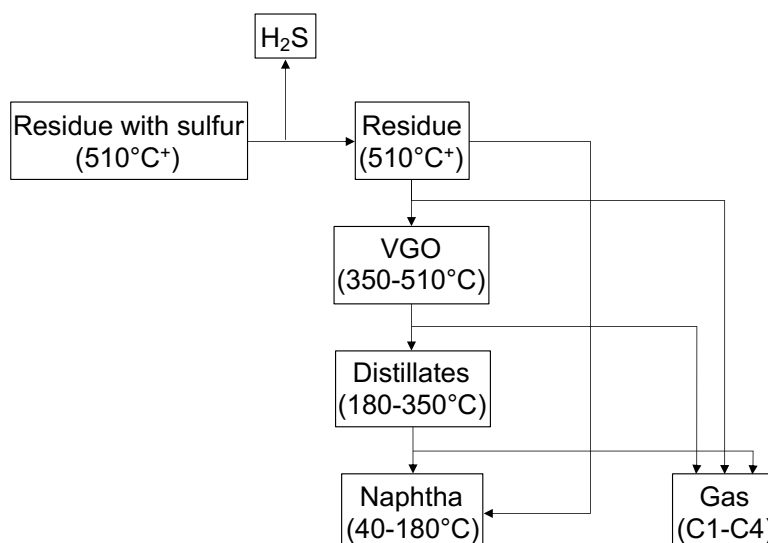


Figure 2.18: Mechanistic model of heavy feedstock hydrocracking and hydrodesulfurization based on [136]

In the displayed mechanism, HDS reactions are only influenced by the sulfur content of the feed. Further, it is assumed that prior to hydroconversion reactions, HDS reactions have removed all sulfur from the heavy feedstock. As presented in. HDS reactions of cracking products are not considered. A different approach is reported by Marek et al. [131], where parallel to the feedstock decomposition, organic sulfur reacts to hydrogen sulfide, as displayed in Fig. 2.19.

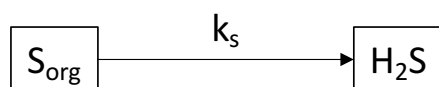


Figure 2.19: Reaction mechanism for desulfurization reactions based on [131]

According to Scott et al. [137], overall HDS reactions of heavy feedstock can be seen as the sum of a number of competing first order reactions, since all model sulfur compounds react with a different reaction rate. Also Marifi et al. [138] described a similar approach. HDS could be described best by a first order kinetic for removal of simple sulfur compounds and a first order kinetic for more complex compounds, that are removed slower. In this work, in Section 6.1.4.1, based on experimental results, a mechanism for the observed HDS and hydroconversion reactions is developed and the influence of cracking reactions on HDS is discussed.

State of technology of hydrodesulfurization and hydroconversion technologies

More and more stringent regulations for sulfur emissions do not only affect the handling of the residue fraction but also most fractions leaving a refinery. In fact, sulfur levels for diesel and gasoline fuels have had regulations on sulfur emissions since 1993 [139]. Aside the regulations for product streams, sulfur displays a catalyst impairing and corrosive contaminant. Both reasons forced refiners to develop processes to reduce sulfur levels since sulfur content in crude oil can vary from 0.05-6.00% [15]. These developed processes are designed for lighter crude oil fractions and have difficulties to cope with the heavy vacuum residue fraction. Therefore, in refineries, vacuum residue is commonly used for heating purposes, blended to comply with HFO regulations, or converted to lower boiling product, mostly via coking. Aside coking, also conversion via hydrogen addition technologies is possible. Both conversion technologies for vacuum residue as well as desulfurization technologies for lighter fractions play a significant role when developing a process for vacuum residue desulfurization. While the reactor and the type of reaction system used in this work is based on the slurry technology, the purpose of this work is hydrodesulfurization. Therefore, the research presented in this work is located in between slurry phase residue hydroconversion processes and (fixed bed) HDS processes for light fractions. For this reason, state of technology for both areas is presented in this chapter.

3.1 Desulfurization technologies for lighter fractions

Sulfur is removed from crude oil and crude oil products within a refinery in different ways. Aside HDS, which is the process mainly used in refineries, technologies like oxidative desulfurization, adsorptive desulfurization, and biodesulfurization can be considered. They play an inferior role in modern refineries and will not be discussed here.

3.1.1 Hydrodesulfurization

Hydrogenation serves many purposes in a refinery including the conversion of low ranked streams into more valuable products, improving product quality or transformation of high molecular weight compounds into liquid products. It is also the main process for sulfur removal. The processes can be further differentiated with regard to the breaking up of C-C bonds as it is discussed in Section 2.2.4. HDS commonly used in refineries for sulfur removal belongs to the process types not aiming at destruction of C-C bonds [72].

Both distillate streams from the atmospheric distillation and vacuum distillation of crude oil and streams from conversion reactions like the FCC or hydrocracking units are desulfurized by HDS in refineries. It is performed either before or after conversion processes like FCC. However, it is always performed upstream of the reformer unit, because of the platinum catalysts used in reforming. Platinum is easily poisoned by sulfur and to prevent fast deactivation, sulfur needs to be removed before this step. The products of the HDS step are desulfurized hydrocarbons and H_2S . Since HDS is applied at several steps during the refining of crude oil and intermediate streams, the exact process details including temperature, pressure, and catalyst vary. Generally, conditions are temperatures of 290-455 °C and pressures of 10-200 bar [15]. A process flow scheme is displayed in Fig. 3.1.

After preheating the feed together with H_2 , the mixture is fed to the HDS reactor. Commonly, HDS reactors are fixed-bed reactors, which must be shut down in order to remove spent and deactivated catalyst. Catalysts deactivation proceeds gradually due to the accumulation of coke, metals, and other contaminants and exchange of the catalyst is needed when the activity falls below a certain level. Aside fixed-bed reactors, also moving and ebullated bed reactors exist for the hydrodesulfurization. The reaction generally takes place as a heterogeneous reaction between the oil in gas phase and the catalyst [140].

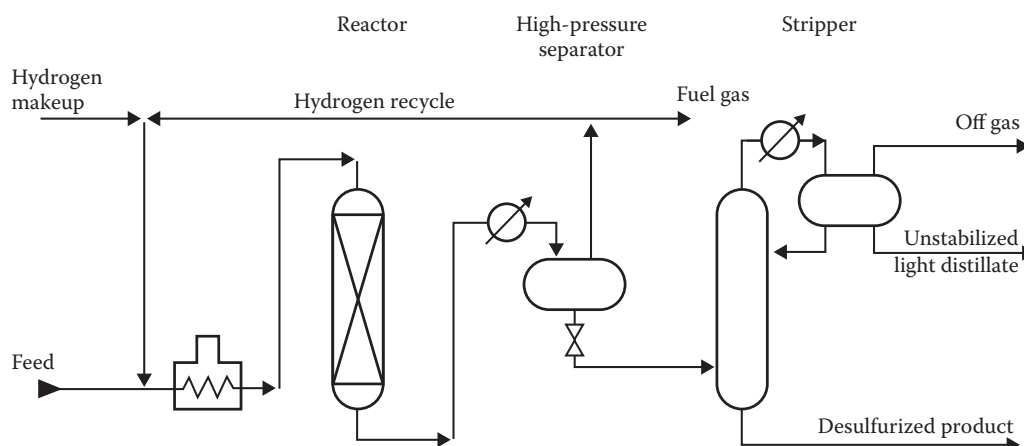


Figure 3.1: Process flow scheme for a HDS unit taken from [15]

Mostly, fixed-bed reactors are operated in cocurrent flow. The mixture of H_2 and feed is heated and sent to the reactor. The desulfurization reaction itself is exothermic, therefore heat must be removed in order to maintain an optimal temperature. By introducing fresh H_2 after every packed bed of catalyst, the temperature can be controlled and the H_2 partial pressure is kept high as displayed in Fig. 3.2 [15, 72].

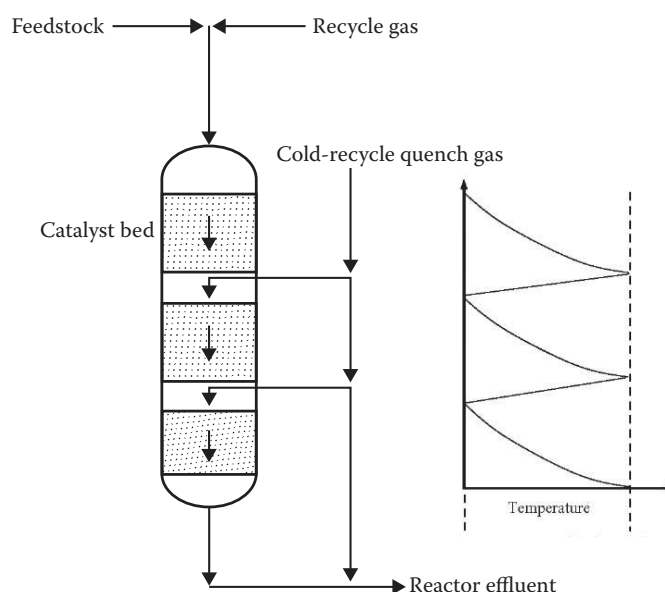


Figure 3.2: Typical fixed-bed reactor for HDS altered from [15]

Alternatively to the cocurrent flow reactor, H_2 and the oil can flow in opposite directions resulting in a counter current flow reactor. In counter current flow processes, the H_2 concentration is at maximum, where only very difficult to remove sulfur is still present in the oil. Consequently, the H_2 concentration is lower, where simple sulfur containing hydrocarbons are desulfurized [15]. This effect results from the fact, that at the beginning simple sulfur bonds, like mercaptanes, sulfides, and disulfides, as

displayed in Fig. 2.1 are hydrogenated at high reaction rate. Further downstream in the reactor, only the stable sulfur containing bonds are still present. This is where fresh H_2 is introduced and H_2 partial pressure is highest. This operation mode is therefore beneficial for removal of highly complex sulfur species. Generally, HDS is very reliable in removing inorganic sulfur or simple organic sulfur species. More complicated polycyclic and aromatic compounds, that include BT, DBT and their derivatives, are difficult to desulfurize in common HDS processes [141,142].

HDS is performed in excess of H_2 related to the stoichiometrically needed amount of H_2 . The relatively high H_2 partial pressure suppresses coke formation and enhances the desulfurization. The total consumption of H_2 is dictated by:

- removal of the sulfur, nitrogen, and oxygen, and formation of their hydrogenated forms
- stabilization and saturation of intermediates formed during the removal of sulfur, nitrogen, and oxygen
- saturation of unsaturated groups and aromatics

Unconsumed H_2 always has to be recycled in order to make the process economically feasible. Therefore, downstream of the reactor a high pressure separator is operated that removes gases from the desulfurized liquid oil. For the recycling of H_2 , the formed hydrogen compounds (mostly H_2S) are removed from the flue gas by scrubbing, mostly using amines. Scrubbing with amines is based on the principle of chemisorption. H_2S reacts reversible with the amine increasing both selectivity as well as capacity in comparison to scrubbing liquids which only dissolve H_2S . The liquid oil is further sent to a stripper to obtain the desulfurized product oil [15].

3.1.1.1 Hydrodesulfurization catalysts

Generally, hydroprocessing catalysts are composed of transition metal sulfides (mostly Group VIB and VIII metal oxides that are sulfurized to give the active sulfides) dispersed on supporting materials, providing large surface area[90]. Commonly used catalysts are Mo, W, Ni or Co compositions in the sulfide form on a support composed of Al_2O_3 , SiO_2 or carbon materials [91,140,143,144].

Plugging of the catalyst is a severe problem encountered when operating fixed bed HDS reactors because it always leads to expensive shutdowns and possibly complete

renewal of the expensive catalyst bed. Reasons for the plugging of the bed are diverse but mostly they can be traced down to deposition of rust, coke, or metal salts or asphaltenes from heavy feedstock. Also, the exothermic reactions can display the reason for plugging, due to build up of temperature hot-spots leading to coagulation and coking of asphaltenes. Generally, deposition of heavy constituents of the feed may lead to plugging and deactivation of the catalyst. This is the reason, why HDS of vacuum residue displays a very challenging task, which cannot be performed in conventional HDS reactors [15, 121, 145]

3.1.1.2 Hydrodesulfurization technologies

A large number of manufacturers and vendors for HDS technologies exist. The basic principle of the technologies is always as explained in Section 3.1.1. The differences between the technologies lies within the applied catalysts, operation temperatures, and pressures. Some process technologies are also combined with dearomatization, denitrification and demetallization [146, 147]. As a result, product qualities differ, according to the manufacturers. Companies having HDS technologies under license are ConocoPhillips, Haldor Topsoe, Axens and ExxonMobil among others [146–149]. Detailed information on state of the art fixed bed HDS processes for distillate fractions can be found in technical literature as well as on the web pages of the manufacturers [146–149].

3.2 Residue upgrading

Processes dealing with residue utilization are widely used in refineries. Generally, upgrading technologies are divided into carbon rejection and hydrogen addition technologies. Here, focus is put on residue hydroprocessing and its process technologies located in the field of hydrogen addition. These are, in contrast to processes like coking or visbreaking, not as widely used, mostly due to large operating and investment cost [67, 155]. The technologies presented here are all demonstrated at commercial scale while processes still under development or in research are presented in Chapter 4. Several processes are presented in Fig. 3.3 and the corresponding table Tab. 3.1.

While carbon rejection technologies are operated at low pressure and temperatures mostly above 500 °C, hydrogen addition is achieved at elevated pressure and lower temperature. Moreover, processes can be distinguished according to the reactor de-

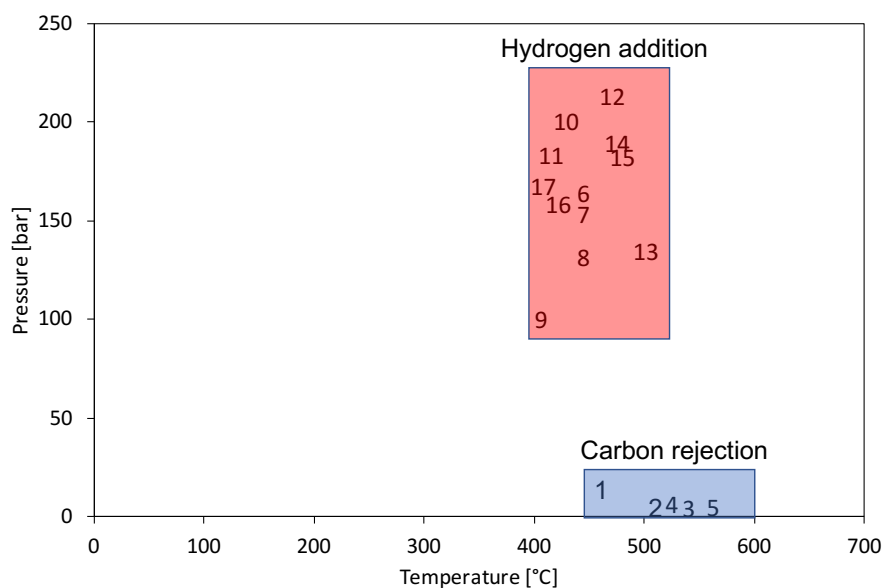


Figure 3.3: Residue upgrading technologies according to their operating pressure and temperature

Table 3.1: Residue upgrading technologies

	No.	Process	Ref.
Carbon rejection			
	1	Visbreaking	[150]
	2	Delayed coking	[65, 67]
	3	Fluid coking	[14, 151]
	4	Flexi coking	[14, 65]
	5	RFCC	[134, 152]
Hydrogen addition			
Fixed bed			
	6	HYCON	[153]
	7	Hyvahl	[13, 63]
	8	OCR	[154]
	9	IMP	[155]
Ebulated bed			
	10	H-Oil	[152]
	11	LC-Fining	[152]
Slurry			
	12	VCC	[95, 156]
	13	HDH plus	[134]
	14	CANMET / Uniflex	[152, 155, 157]
	15	SOC	[128]
	16	EST	[157, 158]
	17	HCAT	[159]
	18	T Star	[152]
	19	MICROCAT	[128, 134]

sign. The three different reactor designs operated for residue upgrading are presented in Fig. 3.4.

Fixed bed reactors are the most common type of reactors used in heterogeneous catalysis. The catalyst bed is mostly filled with catalyst pellets leading to a high

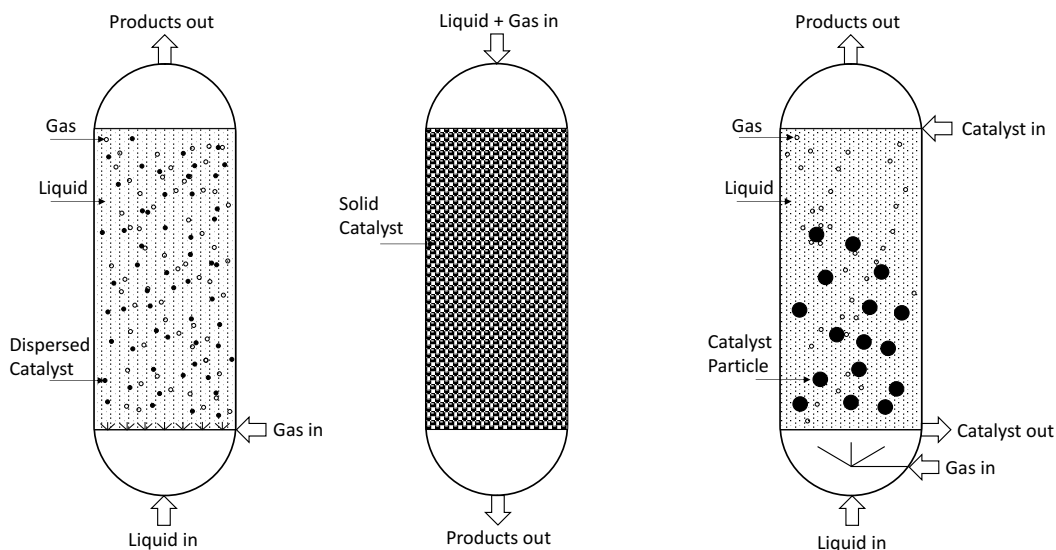


Figure 3.4: Different reactor types - left: slurry reactor; middle: fixed bed reactor (counter-current flow); right: ebullated bed

pressure drop during operation. Temperature control can be difficult because of the often chosen adiabatic operation (no heat removal through the reactor walls). The catalytic section is therefore often divided into segments, in between which cold H_2 is introduced to control the temperature [84]. As a result, the temperature in axial direction shows a profile as displayed in Fig. 3.2 on the right side. The main difference between slurry reactors and ebullated bed reactor (EBR) is that in the former, the catalyst is very finely dispersed and dissolved in the liquid phase, so that it is seen as one phase, while in the EBR the catalyst particles are so big, that they are considered as a separate solid phase. The finely dispersed catalyst together with H_2 and feed vacuum residue form the slurry [160]. A significant advantage of slurry reactors compared to the two other designs is a nearly isothermal operation of the reactor because of the well mixed slurry phase. The resulting absence of temperature gradients in axial and radial directions, which often strongly exist in fixed bed reactors, enables far more severe reaction conditions and therefore higher space yields. Also, the use of a highly active and dispersed catalyst reduces intra-particle diffusion limitations, thus also increasing overall reaction rates. The finely dispersed catalyst also avoids high pressure drop, which is especially problematic with the highly viscous vacuum residue [161,162].

The reactor operated for the investigations in this work is a slurry hydrogenation reactor and therefore, only slurry technologies for the residue upgrading are considered for review on the state of technology. In the following, process technologies

for hydrogen addition are presented. Vacuum or atmospheric residue feedstock is treated at high H_2 partial pressure, mostly in presence of a catalyst in order to receive a product oil of higher value.

3.2.1 VEBA OEL Combi Cracker (VCC)

The VCC technology of the VEBA is based on the coal liquefaction technology and goes back to the 1913 applied patent of Friedrich Bergius. Several changes have been applied to the concept of the coal liquefaction plant resulting in the VCC process now licensed by the American engineering company KBR [163]. The process scheme of the VCC technology is presented in Fig. 3.5.

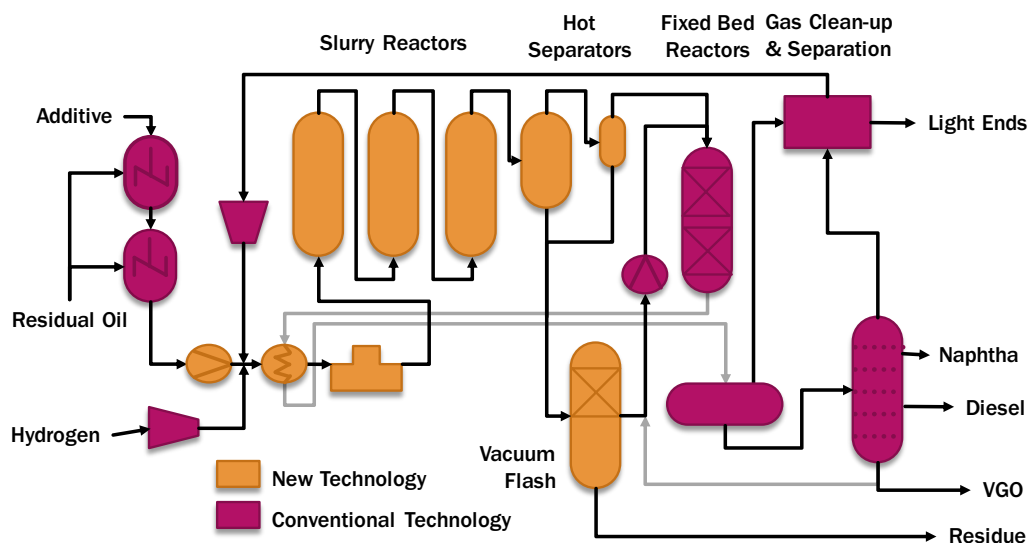


Figure 3.5: Process scheme of the VCC technology for high conversion of residual feedstock taken from [156]

A finely ground additive is mixed with the slurry feedstock and recycle gas as well as fresh H_2 . The mixture is fed to the slurry reactors operated in once through mode. Key aspects of the process are a system pressure of 200 bar and an operation temperature of 450-470 °C in the slurry reactors. The temperature is controlled by addition of cold quench gas (recirculated and fresh H_2) [95, 155]. Full back mixing in the reactor together with nearly isothermal conditions ensure absence of hot-spots and a safe operation at high temperature. A single train is designed for a capacity of 3.6 Mt/a. The process is operated with a carbon based additive. This additive is said to have a number of advantages compared to a common metal HDS catalyst. These include good coke precursor adsorption and asphaltene conversion without the environmental downsides of the need to dispose metal containing spent catalysts [156]. The vapor phase reaction products, together with the recycle gas,

are separated from unconverted residual oil and additive in the hot separators. The residue is sent to a vacuum flash unit to recover additional light products. Both the light products from the vacuum flash and the top products from the hot separators are sent to the fixed bed hydrogenation reactor operated at the same pressure as the slurry reactor but lower temperature. The products are cooled and separated into gases, naphtha, diesel and VGO. Heavy feed conversion of 95% yielding lower boiling products is achieved. The residue from the vacuum flash displays less than 5% of the feed and can be used in combustion, gasification or coking [95, 156].

According to KBR, one VCC plant has been put in operation in 2017 for the upgrading of vacuum residue and VGO in Russia and two more are planned for the next two years in Cambodia and Jordan [156].

3.2.2 ENI EST

The ENI Slurry Technology (EST) technology was developed by Snamprogetti (in 2006 bought by SAIPEM) and EniTecnologie. An oil-soluble molybdenum based catalyst precursor is mixed with the residual feed to protect the acidic cracking catalyst against impurities. The acid catalyst is very prone to deactivation by metal and sulfur contaminants in the feed. The slurry is introduced into the reactor. Operation temperature of the reactor lies between 400-450 °C with a pressure of 150 bar. In the reactor, H₂ is distributed from the bottom and ensures conditions under which the catalyst precursor is transformed into the active phase. This active phase for demetallization and desulfurization is a crystalline layered MoS₂, called molybdenite, of a few nm particle size. The acidic, not further specified catalyst for hydroconversion is protected by the MoS₂ nano-slabs. The in-situ preparation of the catalyst enables the MoS₂ catalyst to be dispersed predominately as single layers with a stable size and shape also for longer runs [157, 164]. A very simplified process flow scheme is shown in Fig. 3.6.

Downstream of the slurry reactor the formed products are separated in consecutive flash units and distillation columns. The catalyst is recycled back to the slurry reactor with the bottom product of a vacuum distillation step. Only 1-3% of the fresh feed have to be purged to prevent accumulation of coke precursors and heavy metal sulfides. The small amount of MoS₂ lost with the purge has to be substituted in order to keep a constant catalyst concentration. Further treating of the purge is possible for recovery of lost catalyst. The high value products from the process are gas, naphtha, atmospheric gas oil and vacuum gas oil [157, 158]. Key figures are:

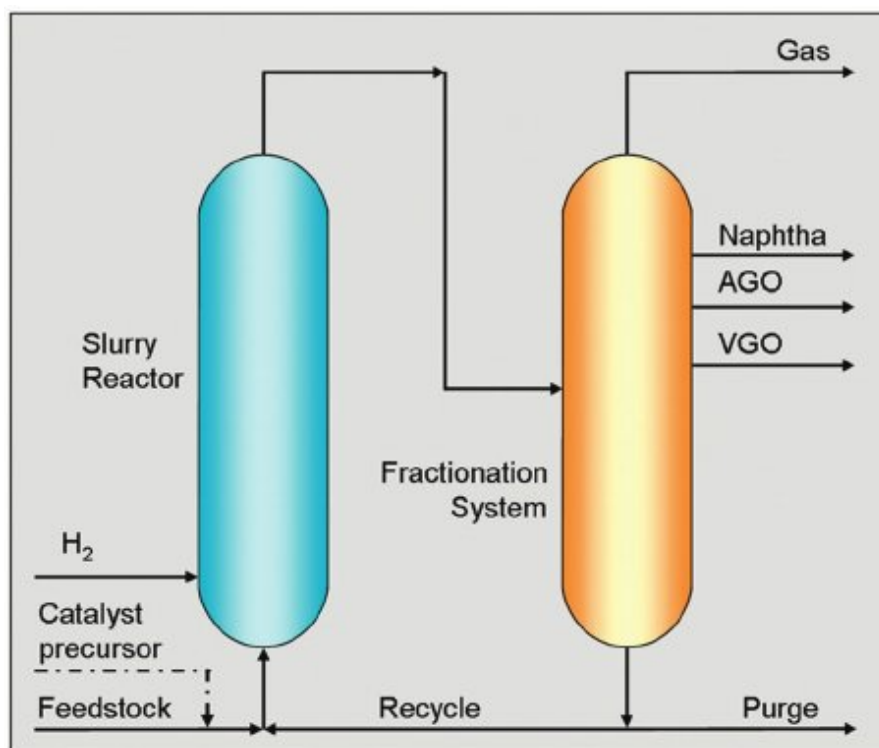


Figure 3.6: Simplified process scheme of the EST technology taken from [157]

- > 97% conversion of heavy feedstock to light products
- > 97% reduction of coke precursors HDCCR
- > 85% removal of sulfur HDS
- > 90% removal of nitrogen HDN
- 99% removal of metals HDM

After the start of research in the early 1990, the start up of a pilot plant followed by a commercial demonstration plant in 2005 led to the first industrial plant in 2013. The industrial plant has a capacity of 23,000 barrels per day. A fire broke out at the EST site in December 2016 forcing the process to be shut down [158, 165]. In 2018 ENI sold a license to the Chinese company Sinopec for a 46,000 barrels per day plant. Heavy refining residue will be processed beginning 2020 replacing an existing pet-coke production [166].

3.2.3 UOP Uniflex

The UOP Uniflex process is based on the CANMET Hydrocracking process developed by Petro-Canada in Montreal in 1986. A conversion process was developed for

the processing of heavy pitch, vacuum residue, atmospheric residue and residue from the visbreaker using an additive doted with iron sulfate. The catalysts function was promotion of hydrogenation reactions and prevention of coke formation while at the same time withstanding the high metal content of the feed. The disposable catalyst is slurried with the feed and H_2 before being fed to the single-stage up-flow hydrogenation reactor. Typically, the reactor is operated at a temperature of 440-460 °C and a pressure between 100-150 bar. The products were further upgraded in an integrated hydroprocessing unit designed for the treating of light and heavy fractions. The cooperation of UOP and Natural Resources Canada began in 2006 in order to improve the technology, resulting in the acquisition of the exclusive rights by UOP in 2007. The Uniflex process was then the result of the UOP's own Unicracking and Unifining processes together with the knowledge on the CANMET technology [152, 155, 157]. UOP significantly improved catalyst performance, engineering design and feedstock flexibility together with input from the Alberta Energy Research Institute. The process flow scheme of the Uniflex process is given in Fig. 3.7.

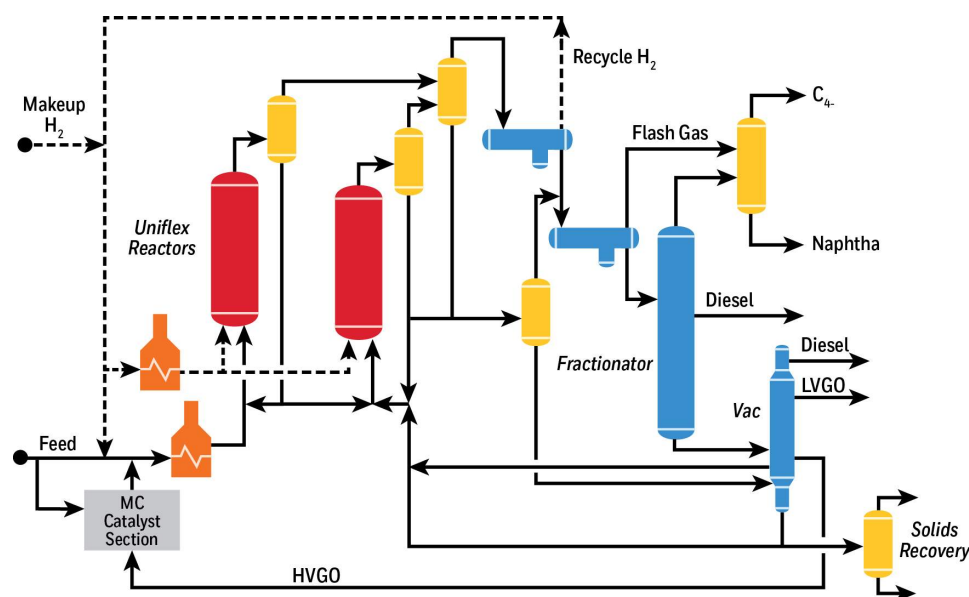


Figure 3.7: Process scheme of the Uniflex technology for high conversion of residual feedstock taken from [167]

Highly integrated schemes with a reactor for product upgrading or recycle of heavy fractions are also supplied by UOP. A new nano-sized catalyst developed by UOP is reported to increase residue conversion to above 98%. UOP nowadays promotes the usage of a molybdenum-based catalyst supported on a carbonaceous base called (MicroCat). Also, here the catalyst is slurried with the feed and enhances asphaltene conversion while preventing coke formation. Gas (recycle and fresh H_2) and

vacuum residue are preheated separately. Only a small fraction of the gas is used to slurry the vacuum residue feed before being fed to the first of two slurry reactors. Nearly isothermal conditions in the reactor together with good back mixing in the up-flow reactor enable higher temperatures than in the CANMET process (up to 470 °C at 138 bar). A series of separation steps (blue and yellow in Fig 3.7) reroute hydrogenation residue to the reaction zone, recycle gas to the feed and the products to the respective fraction [159, 168].

Two Uniflex processes were constructed, including the CANMET plant in Canada, with a total capacity of 1.65 Mt/a. For 2020 another plant is scheduled in Pakistan with a capacity of 0.6 Mt/a [168].

3.3 Summary of the state of technology

The state of research on both HDS technologies and slurry technologies for heavy feedstock conversion were presented in Sections 3.1 and 3.2. The problems encountered, when subjecting vacuum residue to common HDS units were explained in Section 3.1.1.1. Existing slurry hydrogenation technologies were presented and their aim of full conversion of the feedstock under severe conditions was shown in Section 3.2. Residue HDS may be performed ideally combining both slurry hydrogenation and knowledge from hydrodesulfurization of low boiling fractions. Research on these topics is discussed in Section 4.

State of research on hydroprocessing catalysts and additives

Chapter 3 dealt with the state of technology for desulfurization processes, as well as for slurry phase conversion processes for vacuum residue. Aside HDS technologies, there are several other technologies including bio-desulfurization, oxidative desulfurization, selective adsorption or extraction being research for desulfurization [169]. These will not be addressed here. Similar to the state of technology, research has mostly focused on the development and testing of new catalysts, additives, and processes for the hydroconversion of residues and only scarcely on HDS of heavy fractions as the overview in Tab. 4.1 shows. For slurry processes, finely dispersed and often unsupported bulk catalysts and additives are of interest. Since often no clear line between HDS and hydroconversion can be drawn, publications often report desulfurization as well as conversion effects. The purpose of this chapter is to show, what topics research is focused on (mostly hydroconversion) and to identify the gap where this work will contribute knowledge. Extensive reviews on laboratory setups and research [159, 170, 171], as well as on catalysts [172], can be found in literature and, therefore, only several relevant topics will be addressed. The chapter is subdivided into research on supported and unsupported catalysts and additives used in hydroprocessing of residue fractions. Some researches used model compounds, while others used vacuum residue or other crude oil feedstock. In order to structure the reported research, Tab. 4.1 summarizes the research, presented in detail in the following sections.

Table 4.1: Overview on relevant research

Reactor	Topic	Feed	Catalysts	Key finding relevant for this work	Ref.
Fixed-bed	HDS	AR	Mo/Al ₂ O ₃ and NiMo/Al ₂ O ₃	90% sulfur removal; incapable of converting aromatic structures	[173]
Fixed-bed	HDS	MC	NiMoO ₄ and Ni-Co	Removal of methyl groups drastically increases desulfurization	[174, 175]
Fixed-bed	HDS	VR	CoMo	57.4% desulfurization; 15% coke formation	[176]
Slurry	HDS	MC	Sulfides from Nb, Mo, Ru, Rh and Pd	Unsupported catalysts show high HDS performance; MoS ₂ showed best performance	[177]
Slurry	HC	VR	Red mud	Conversion is thermally controlled - no effect of red mud; 51.5% desulfurization only of oil phase	[178]
Slurry	HC	VR	Mo, Ni, Ru, Co, V and Fe	Hydroconversion activity: Mo>Ni~Ru>Co>V>Fe; In-situ generated Mo nano-slabs best activity at low temperature	[179, 180]
Slurry	HC	VR	MoS ₂	>80% conversion and 3% coke formation	[93]
Slurry	HC	VR	MoS ₂	200 h on stream was reached maintaining high activity	[164]
Slurry	HDS	MC	NiMoW and CoMoW sulfides	Co-catalysts promote DDS path; Ni-catalysts promote HYD route	[181]
Slurry	HDS	MC	SCW	Simple MC were desulfurized to high extent; more complex compounds only to less than 5%	[182]
Slurry	HDS	MC	SCW + HDS cat.	HDS is only possible with a catalysts and H ₂ ; SCW alone not suitable for HDS	[183]
Slurry	HC	VR	SCW + HDS cat.	SCW can replace external H ₂ ; SCW suppresses coke formation	[184, 185]
Slurry	HDS	MC	SCW + NiMo/Al ₂ O ₃	In-situ formed H ₂ is more active in HDS than externally added H ₂	[186]
Slurry	HDS	B	SCW	SCW showed same behavior as N ₂	[187]

Topics: HC: hydroconversion; HDS: hydrodesulfurization

Substrates: AR: atmospheric residue; B: bitumen; MC: model compounds; VR: vacuum residue

From the overview table it becomes clear that research on slurry phase HDS of vacuum residue has not been the main focus. Often, model compounds were used to represent sulfur in vacuum residue, which does not represent the real behavior of vacuum residue. The research topics listed in Tab. 4.1 are discussed in more detail in the following sections.

4.1 Supported catalysts

Supported hydrotreating catalysts are very common and are used in most state of the art hydrodesulfurization processes. Though they display state of the art technology, research on these catalysts is still very intense. For an overview, some current developments are presented.

Marafi et al. [173] investigated the effect of operating severity on catalytic hydrotreating of atmospheric residue for industrial hydrotreating catalysts ($\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$) in a fixed-bed reactor. It was found that catalyst type and operating severity (mainly temperature) had a strong effect on the product quality. At temperatures of 420°C the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst removed above 90% of the sulfur but increased the degree of aromaticity. The polynuclear aromatic rings in the asphaltenes could not be converted and became more condensed. The low hydrogenation activity of the catalyst was found to be the reason for the effect on aromaticity and the $\text{NiMo}/\text{Al}_2\text{O}_3$ was shown to have a higher hydrogenation function. The insufficient performance on the hydrogenation of the aromatic core makes these catalysts less attractive for vacuum residue.

Li et al. [174] also focused on Ni-Mo catalysts for desulfurization but on NiMoO_4 fixated on TiO_2 as crystalline phase. The catalysts performance was tested on HDS of DBT. Results showed complete DBT conversion through direct desulfurization (DDS) (path explained in Section 2.4.3). The hydrogenation path Hydrogenation (HYD) of DBT was not proceeded with the catalyst and only direct HDS was observed. HDS of methylated DBT was studied by Landau et al. [175] with Ni-Mo and Co-Mo catalysts. HDS of DBT and dimethyl-DBT was performed in a fixed-bed reactor at H_2 pressure of 54 bar and 360°C . The zeolite H-ZSM-5 was impregnated with the Ni-Co catalyst leading to an increase of HDS rate of DBT and a decrease of HDS on dimethyl-DBT. Under these conditions, no cracking of DBT and dimethyl-DBT was observed. Replacing H-ZSM-5 by a H-Y-zeolite led to significant cracking activity of dimethyl-DBT performed by demethylation of

both benzenic rings and opening of the C–C bond connecting the benzenic rings. The HDS rates of dimethyl-DBT was increased by threefold. Removal of the methyl groups enabled desulfurization via the DDS route.

Ferreira et al. [176] investigated HDM and HDS abilities of commercial catalysts under industrial conditions on different vacuum residues. At 360 °C and 150 bar a presulfided CoMo catalyst supported on alumina was operated in a 500 ml fixed-bed reactor for up to 24 h in continuous mode. A maximum of 57.4% desulfurization was reached but only for low sulfur vacuum residue. Also, 15% coke formation was observed on the HDS catalyst. Molecular size of the different vacuum residues was found to strongly influence the HDS and HDM reactivity.

4.2 Unsupported catalysts

Though supported catalysts constitute the basis for most industrial HDS catalysis, unsupported catalysts are more attractive for slurry hydrogenation and they have been subject of research for the recent years [177]. Hermann et al. [177] studied the applicability of transition metal sulfides from the second group for deep HDS and compared their performance to traditional, supported CoMo/Al₂O₃ catalyst. DBT and 4,6-dimethyl-DBT HDS was studied with Nb, Mo, Ru, Rh and Pd. It was found that HDS activities of the metal sulfides towards the sterically hindered molecule 4,6-dimethyl-DBT closely followed those for DBT. Overall, hydrogenation activities of the unsupported metal sulfides was reported to be far higher than the HDS activity of typical supported catalysts.

4.2.1 Iron based catalysts

Red mud, as a cheap material containing high levels of Fe₂O₃ and Al₂O₃, has been used commercially in the VCC process as reported in Section 3.2.1 but due to its low cost, it is also topic of scientific research nowadays. It is a side product in the production of alumina and mainly consists of iron, titanium, and aluminum oxides, with high silicon, calcium, and sodium oxides content.

Red mud has been tested as cheap catalyst at laboratory scale for the hydrocracking of vacuum residue by Nguyen-Huy et al. [178]. Influence of reaction temperature, reaction time, and catalyst concentration on vacuum residue conversion were investigated. Experiments were carried out in a 100 ml stainless steel stirred batch

autoclave under constant H_2 flow. 1.2 – 3.0 g of catalyst were loaded into the reactor with 30 g vacuum residue (initial boiling point: $454^\circ C$; content: $538^\circ C+$ – 70%, sulfur – 4.4%, nitrogen – 0.48%, C5 asphaltenes – 18.0%, C7 asphaltenes – 10.0%, CCR – 22.9%; and heavy metals: V – 145.1 ppm, Ni – 44.5 ppm). The reactor was pressurized to 90 bar H_2 pressure and heated to $470 - 500^\circ C$ reaching a total pressure of 150 bar. Generally, red mud showed little effect on hydrocracking of the vacuum residue since the conversion reactions of residue are thermally controlled. A slight decrease in conversion was observed because thermal cracking reactions were suppressed and coke formation was decreased by catalytic cracking. Conversion (defined as the percentage of desired product divided by the total amount of introduced vacuum residue) of up to 66.4% were reached. The product distribution within the conversion products was changed in favor of lower boiling products by catalytic cracking. Sulfur reduction is only reported for the converted liquid products and was at 51.5 % and no sulfur reduction is reported for the residue fraction.

4.2.2 Molybdenum based catalysts

Molybdenum based catalysts are very common in HDS. For the processing of residue fractions, research has focused on the development of nano-slabs and finely dispersed Mo catalysts. Also, the development of the ENI EST process largely gained from the developments in this field. Several publications have dealt with the investigation of Mo-based catalysts and their influence on hydroprocessing of residue fractions [93,164,179,180,188–194]. Some key works and their findings are presented here.

Very intensive work on the identification of Mo-catalyst activity (precursor solubility, rate of activation, degree of dispersion, presence of promoters, etc.) and the effect of operation conditions was carried out by Panariti et al. [179,180]. In a first study, a number of different catalysts was tested and their activity in conversion of vacuum residue was evaluated. Conversion in these publications was calculated by subtracting the amount of residues (coke, asphaltenes and deasphalted fraction with $>500^\circ C$ boiling point) from the amount of feed vacuum residue. The observed order of hydroconversion activity was $Mo > Ni \sim Ru > Co > V > Fe$. The study demonstrated that microcrystalline molybdenite generated in-situ by oil-soluble precursors gave the best performance in terms of residue conversion and sulfur removal. Bimetallic precursors showed a slight synergistic effect towards the HDS reaction. Powdered catalyst precursors of micro size had a much lower catalytic activity compared to corresponding catalysts that were made oil-soluble by an organic ligands. As a

reason for this, the authors assume that the powdered catalysts stack in layers, in contrast to the catalysts with oil-soluble ligands, reducing the surface area and thus the performance. Moreover, it was found that in the investigated temperature range (380 - 460 °C), conversion reactions were thermally controlled and therefore, the catalyst concentration had no influence. Coke formation could be suppressed by very low Mo concentrations (200 ppm) but high concentrations (>1,000 ppm) led to the contrary. H₂ pressure had a stronger effect on the inhibition of coke formation and also on the removal of sulfur, Conradson Carbon and heavy metals. The results suggest that the catalytic effect of the reacting system can be emphasized by working at low temperature (<420 °C) and at relatively high Mo concentrations. Under these operating conditions, hydrogenation reactions were favored and coke formation was avoided.

Rezaei et al. [93] focused on the recirculation potential of dispersed MoS₂ slurry-phase catalyst for the hydroconversion of vacuum residue. Experiments were carried out in a semi-batch stirred tank reactor at 450 °C with different catalyst concentrations (100, 300, 600, and 1,800 ppm Mo derived from Mo-micelle and Mo-octoate precursors). Conversion was defined as the fraction toluene soluble of product oil divided by the amount of feed vacuum residue. The recycle was investigated by reusing spent catalysts in subsequent batch runs (three in total). The catalyst was reported to maintain similar reactivity of acceptable level (coke formation (<3 wt%) and residue conversion (>80 wt%). Increased catalyst concentrations led to improved performance of the recycle material. Both Mo-precursors showed similarly low reduction in reactivity after three recycles when using 600 ppm of catalyst.

Bellussi et al. [164] demonstrated the improvement of catalytic performances by combination of hydrogenation, hydrodesulfurization, and hydrodemetallation properties of dispersed MoS₂ with a conventional cracking catalyst. The dual catalyst system utilized the MoS₂ nano-slabs to protect the acidic cracking catalyst against rapid deactivation. Experiments were carried out in a 7.5 l ebullated bed reactor at 130 bar and 430 °C with feed flow rates of 800 – 1 000 g/h. The Mo-catalyst concentration was 2,00 ppm. It was reported that the large number of MoS₂ particles per unit volume are responsible for rapid conversion of the organo-metallic compounds present in the feedstock, thus protecting the cracking catalyst. The MoS₂ particles are said to attach to the coke spots on the cracking catalysts surface, promoting the formation of active hydrogen thus slowing down the rate of coke deposition. More than 200 h on stream producing high quality oil were made possible compared to

6 h with only the cracking catalyst. These works have laid the foundation for ENI's EST process.

Huirache-Acuña et al. [181] tested sulfided trimetallic NiMoW and CoMoW catalysts on DBT desulfurization. The catalysts were prepared by ex situ activation of different tetra-alkylammonium thiotrimetallates precursors and placed in a stirred-tank batch reactor. A Ni(Co)MoW-H catalysts showed enhanced HDS activity compared to bi-metallic and trimetallic CoMo, NiMo(W) and NiMoW-H catalysts. Co-promoted catalysts showed a stronger tendency to promote the DDS pathway while Ni-promoted catalysts showed a stronger hydrogenation effect.

4.2.3 Supercritical water residue upgrading

SCW as a cheap additive (may also play a catalytic role according to several publications) has been examined for the use in upgrading of oil fractions extensively [195]. Though it cannot generally be seen as a catalyst, it is here listed under the section dealing with unsupported catalysts. A detailed overview on research on heavy oil upgrading with SCW can be found in literature [196] and only an overview over a few relevant publications is given here.

Patwardhan et al. [182] desulfurized several sulfur containing model compounds in supercritical water. A semi-batch autoclave was used in which the feed mixture was stirred at 235 bar and 400 °C for 31 min residence time in a 1:1 volumetric mixture with water. Dibenzylsulfide was desulfurized most easily to 60 %, while biphenylsulfide, thiophene and DBT were only desulfurized by less than 5 %.

Vogelaar et al. [183] studied the desulfurization ability of SCW with and without addition of a catalyst. Sulfur containing model compounds (BT, DBT, dephenyl-disulfide and octadecanethiol) were dissolved in gasoil adding up to a mixture containing 0.8 % sulfur. After 30 min at 250 bar total pressure and 400 °C no significant amount of model compounds was converted and the feed mixture was not desulfurized but with the addition of 2 g commercial HDS catalyst (sulfided CoMo/ γ -Al₂O₃) all model compounds except DBT were completely converted. Also, H₂ needed to be added.

The effect of a H₂ rich gas together with different catalysts and SCW on upgrading of heavy oil was studied by Cheng et al. [184, 185]. These studies did not focus on the desulfurization of heavy oil but elucidated the effect of externally added H₂ on cracking reactions in SCW. A H₃(P(Mo₃O₁₀)₄) catalyst was used in a 500 ml steel

batch reactor at 420 °C. The presence of a H₂ rich gas, either CO + H₂ or H₂, could lower the coke formation and increase the retrieved amount of liquid products. An effect on the sulfur content was not reported.

Adschiri et al. [186] compared the effect of externally added H₂ to in-situ formed H₂ on the desulfurization of DBT in SCW with a NiMo/Al₂O₃ catalyst. The findings indicate that in-situ formed H₂ from water gas shift reaction performed better than a system with externally added H₂. It is assumed that H₂ formed from SCW is more active in hydrogenation reactions thus leading to a higher degree of desulfurization. SCW desulfurization is therefore seen as good path to lower processing cost, because H₂ could be replaced by SCW and CO or, as Adschiri et al. [186] reported, by SCW and CO₂.

Morimoto et al. [187] compared the desulfurization capability of SCW with N₂ and toluene at 430-450 °C and 230-300 bar using no catalyst. Experiments were carried out in a 50 ml batch autoclave for 60-120 min. It was found that SCW had the same effect on the desulfurization reactions, coke formation, and liquid yield as N₂. Supercritical toluene was found to perform better in desulfurization, while yielding more liquid products and less coke.

4.3 Conclusion from recent research

Generally, research on hydroconversion and HDS catalysts for residue desulfurization shows that dispersed, unsupported catalysts have a strong hydrogenation ability [177]. Though most publications focus on slurry catalysts for hydroconversion, also catalysts with strong HDS activity have been reported, though these were often only tested on model compounds and not on vacuum residue. Unsupported and supported molybdenum based catalysts have been tested extensively and found to perform well in HDS of heavier fractions but only under severe conditions also leading to high conversion. Research on SCW upgrading does not give a clear picture on how HDS of residue fractions is influenced. The overview on recent activities in the field of hydroprocessing of residue fractions, distillate fractions, and model compounds shows the potential for research in HDS of heavy residues. Concluding from the overview on research, combining unsupported slurry phase hydrogenation catalysts with high H₂ partial pressure and lower temperature than in conversion processes, thus lowering the rate of thermally controlled cracking reactions, may enable HDS of vacuum residue. From Tab. 4.1, it becomes clear that HDS has mostly been

performed on model compounds, while on vacuum residue hydroconversion has been the main interest. HDS of vacuum residue displays the research gap, which this work will fill with knowledge.

Material and methods

5.1 Hydrogenation set-up

A process flow diagram (PFD) of the set-up is given in Fig. 5.1. The setup is designed so that fresh H_2 can be added continuously while volatile products are removed from the reaction zone together with unreacted H_2 . The vacuum residue together with the catalyst or additive is introduced into the 2 l reactor before start of the experiment. The catalyst and unreacted vacuum residue remains in the reactor at the end of the experiment. An installed high-pressure liquid chromatography (HPLC) pump enables the continuous addition of liquids. Because of the continuous addition of reactants and removal of unreacted H_2 together with formed products, the system is neither operated in semi-batch mode nor completely continuous. Therefore the term semi-continuous reactor is introduced, describing the operated system more precisely.

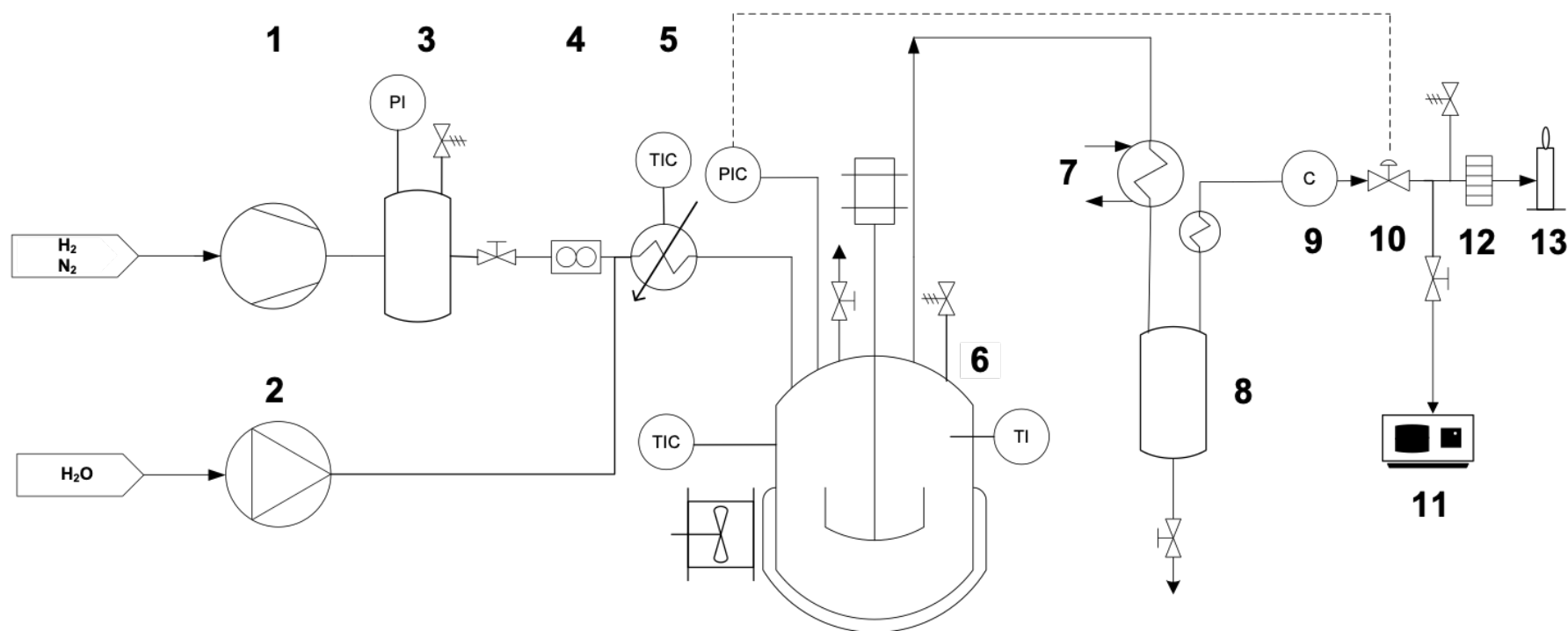


Figure 5.1: P&ID of the setup: 1: compressor, 2: HPLC pump, 3: 2l buffer vessel, 4: thermal flowmeter, 5: gas preheater, 6: stirred 2l reactor, 7: double pipe heat exchanger, 8: 1l high pressure cold separator, 9: Coriolis mass flow meter, 10: pressure control valve, 11: micro-GC, 12: flame arrester, 13: gas flare

Operating pressure in the reactor is reached with a membrane compressor (Sera MV2148). A 2 l buffer vessel downstream of the compressor dampens the reciprocating motion of the compressor so that a flow meter (Bronkhorst InFlow) is able to measure the H_2 flow without disturbance at the reactor inlet. Downstream of the flow meter, the liquid from the HPLC pump is added. The gas preheater is an aluminum block heated by five heating cartridges with a total power of 3.2 kW. A steel pipe (3.2 m of 8×1.5 mm, 1.4571) is wound through the aluminum block which passes the gases (and liquid if added via HPLC pump) through the heating zone. The preheated mixture enters the autoclave through the lid and flows through a dipping tube to the lowest point of the reactor. A more precise overview on the internals of the reactor is given in Fig. 5.2.

The 2 l autoclave (Estanit custom-build) is made from heat-resistant steel (1.7709) with a stainless steel liner (1.4571). It is equipped with a magnetically coupled rotary stirrer. The autoclave is designed for operation conditions up to 400 bar and 500°C . The 6 kW electric heating of the reactor allows heating rates of $8^\circ\text{C}/\text{min}$. The temperature of the autoclave is controlled by a thermocouple inside the autoclave wall, while the temperature inside the autoclave is monitored by four thermocouples in a 30 cm deep thermowell. The thermocouples are distributed in equal distances down the thermowell. During reaction conditions, excess H_2 carries volatile products out of the autoclave through a pipe (6×1.5 mm, 1.4571) attached to the top cover of the reactor.

Vapors are condensed in a 40 cm long water-cooled double pipe heat exchanger. Water flows through the outer pipe at 5°C , ensuring a temperature of below 25°C downstream of the condenser. The condensed liquids flow downwards into a 1 l CHPS. Non-condensable volatile compounds together with H_2 leave through another double pipe heat exchanger which is kept at -10°C to ensure condensation of hydrocarbon products. It is assumed that the low temperature ensures collection of all liquids in the CHPS, thus protecting the Coriolis mass flow meter (Bronkhorst Mini CoriFlow) from contaminants. A constant pressure inside the reactor is guaranteed by adjusting a pressure control valve (Flowsolve 3851P1) with a controller downstream of the mass flow meter. All components have a design pressure of 400 bar. Downstream of the pressure control valve, an in-line detonation flame arrester and a gas flare ensure safe product gas disposal. A sample gas stream is lead to a micro-GC before disposal.

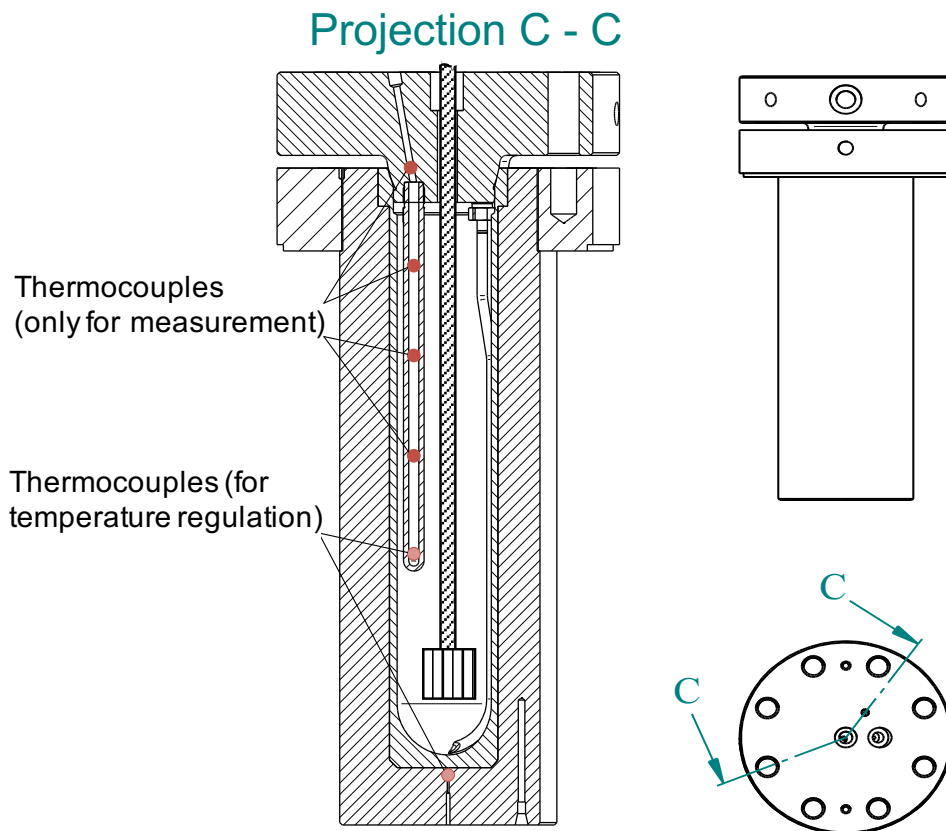


Figure 5.2: 2 l slurry reactor with internals

5.1.1 Liquid addition

For the addition of liquid catalysts and additives like water and Dimethyldisulfide (DMDS), a HPLC pump (Knauer Azura compact HPLC pump with 10 ml Hastelloy pump head) is installed upstream of the gas preheater. The added liquid is passed through the preheater together with H_2 to the reactor inlet. The pump is able to reach flow rates of up to 10 ml/min. A shut-off valve downstream of the pump can be closed when the pump is not in operation.

5.2 Safety precautions

The work with H_2 requires extensive security installations and a cautious handling to ensure safe operation of the experimental setup. Safety precautions focus on preventing situations where the three combustion factors are present:

- ignition source (spark or heat)

- oxidant (O_2)
- fuel (H_2)

The experimental setup is completely enclosed by a ventilated container, that can be accessed via two large doors. Pictures of the complete setup are displayed in the Appendix in Section A.7 The atmosphere inside the container is continuously removed by the ventilation, ensuring that no explosive mixture can accumulate. The H_2 concentration inside the container is permanently monitored. All electronic devices inside the container (apart from the compressor, which is physically separated from the rest by a wall) are installed in explosion protection design.

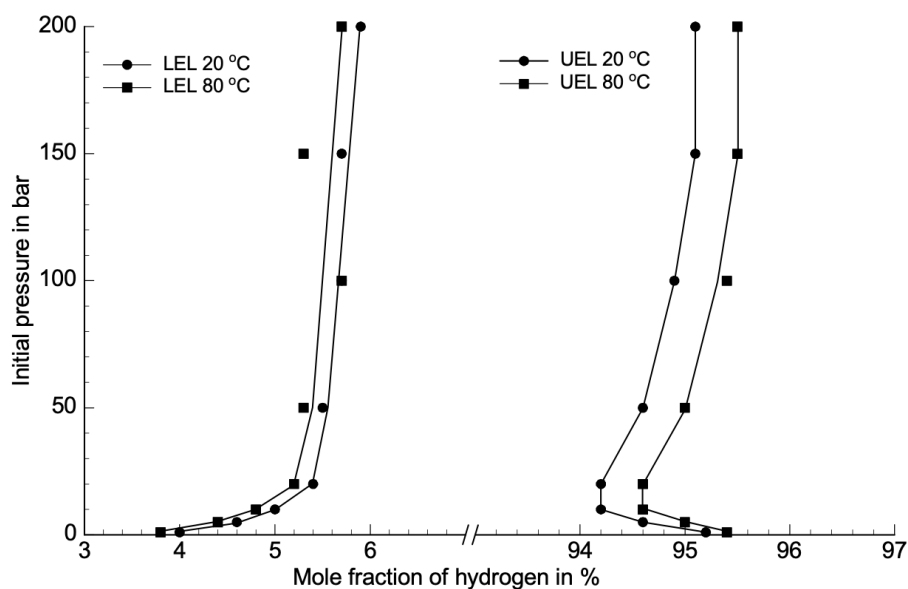


Figure 5.3: Explosion limits for $\text{H}_2\text{-O}_2$ mixtures at different pressure according to Schröder et al. [197] with UEL and lower explosion limit LEL

An explosive mixture can be prevented by either exceeding UEL with the H_2 concentration or by decreasing the H_2 concentration below the LEL as displayed in Fig. 5.3. Since for the purpose of this work a low H_2 concentration was not possible, a the mixture of inside the reactor must contain less than 2.5% O_2 . To ensure that no explosive mixture can form inside the reactor, air is removed from the reactor before H_2 is added according to the procedure described in Section 5.4.1. During an experiment, the pressure inside the reactor was closely monitored and in case of a pressure drop (which indicated a H_2 release into the container), the experiment was stopped, all electronic devices inside the container were switched off, and the leakage point was searched and repaired.

5.3 Materials

5.3.1 Vacuum residue

The vacuum residue used for this work originated from a German refinery in the year 2017. More precise information on the origin of the substrate cannot be given. Measured characteristics of the vacuum residue are summarized in Tab. 5.1.

Table 5.1: Composition of vacuum residue

	Total	Maltenes	Asphaltenes
Composition[%]	100.0	84.9 ± 1.1	15.1 ± 0.9
N[%]	0.4 ± 0.0	0.3 ± 0.0	1.0 ± 0.0
C[%]	83.7 ± 0.1	83.5 ± 0.1	81.8 ± 0.1
S[%]	5.9 ± 0.0	5.5 ± 0.0	8.8 ± 0.0
H[%]	9.9 ± 0.0	10.9 ± 0.2	7.7 ± 0.1
O ^b [%]	0.1 ± 0.0	< 0.01 ± 0.0	0.7 ± 0.0
Ash[%]	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
H/C ratio	1.41	1.57	1.13

^b Oxygen content is calculated by difference:

100 % - (C[%] + N[%] + H[%] + S[%] + ash[%]).

5.3.2 Model components

As model compounds, BT (99%, VWR), DBT (99%, VWR), dibenzylsulfide (99%, VWR) and dibutylsulfide (98%, VWR) were used. The model compounds were dissolved in diesel oil (Ultimate Diesel Aral, sulfur content < 1 ppm) to produce a mixture containing 1 % sulfur to which all components contribute 0.25 %.

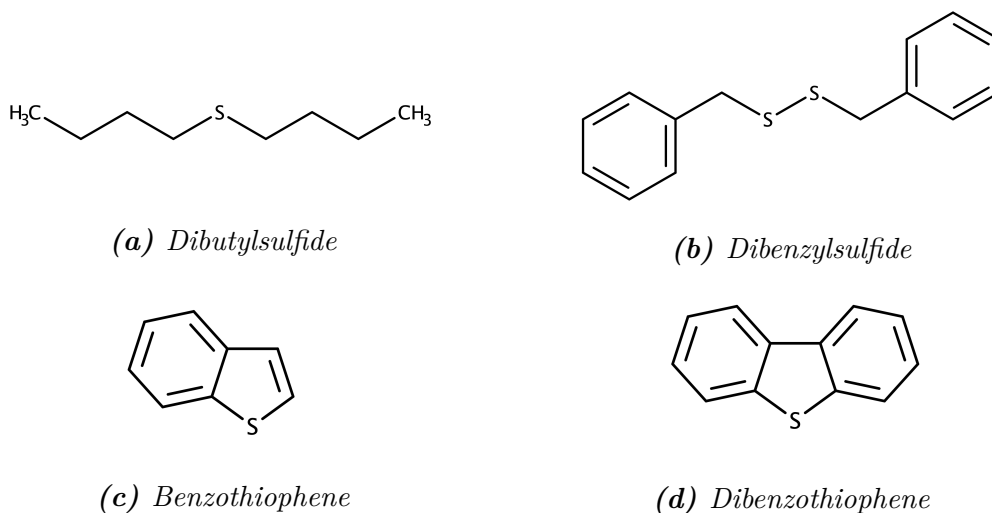


Figure 5.4: Model compounds used to represent sulfur occurring in vacuum residue

5.3.3 Catalysts and additives

Several catalysts and additives were used in this work. In Tab. 5.2 additives and catalysts are listed together with their respective purity.

Table 5.2: Catalysts and additives

Catalyst / Additive	Purity	Catalyst / Additive	Purity
Na_2CO_3	99%	NiMoO_4	98%
WS_2	98.8%	Raney Nickel	in water
HOK	n.a.	Bauxit	n.a.
SnC_2O_4	98%	MoO_3	>85%

The HOK was doted with molybdenum in order to increase its catalytic activity. In an excess of hot aqueous ammonia, 15 g of the solid MoO_3 were dissolved and the solution was poured over 500 g HOK. The mixture was heated and the excess ammonia escaped, leaving ammonium heptamolybdate $(\text{NH}_4)_2\text{MoO}_4$ distributed on the surface of the HOK. By addition of sulfuric acid $(\text{NH}_4)_2\text{MoO}_4$ was transformed back into MoO_3 . The resulting catalytic surface of the HOK doted with MoO_3 was examined with energy-dispersive X-ray spectroscopy (EDX) and back-scattered electrons (BSE) images from scanning electron microscope (SEM) analysis performed at the ZELMI institute of Technische Universität Berlin to see the distribution of the MoO_3 . The obtained signal and image are shown in Fig. 5.5.

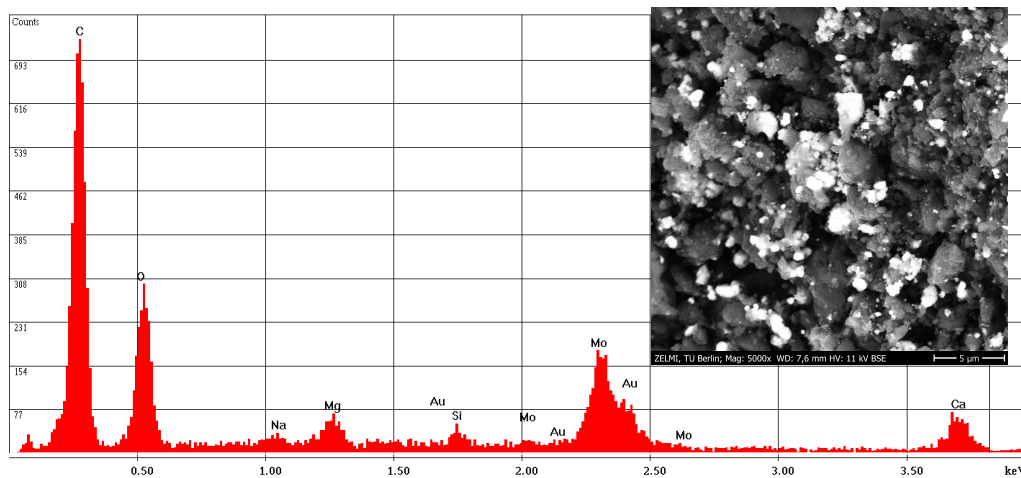


Figure 5.5: EDX signal and corresponding SEM image for determination of the MoO_3 distribution

In the BSE image, the bright spots are heavy elements, molybdenum, and ash content of the HOK. Gold (Au) is part of the preparation method to increase the samples electrical conductivity. The sample is coated with an ultra thin layer (2 nm) of gold deposited on the sample by vacuum coating. The relationship of the peak sizes does not directly represent the mass distribution and therefore the EDX spectrum

only gives an impression of the different elements on the HOK surface, while the BSE image can be used to see the good distribution of the elements on the carbon surface.

5.4 Experimental procedure

5.4.1 Operation of the hydrogenation setup

The experimental procedure including feedstock preparation and product handling was optimized for the processing of the vacuum residue throughout several preliminary experiments. The determined procedure minimizes errors that could occur by different handling of the product fractions and preparation of the feed materials. For some experiments, this procedure had to be altered due to specific feed or product handling, for example, when experiments were performed with SCW. This is indicated concerning Sections 6.3.1 An overview scheme of the general process steps for each experiment is given in 5.6.

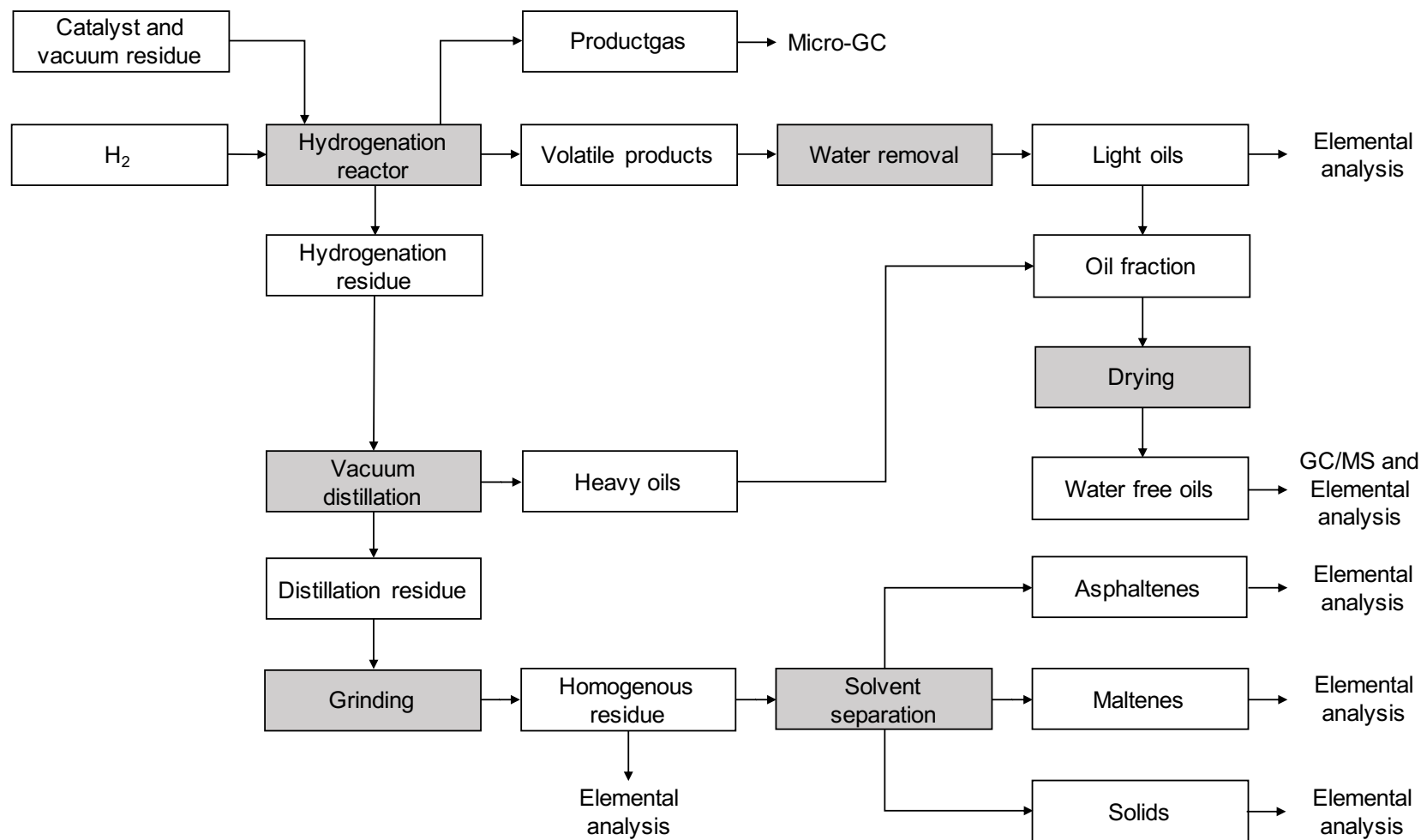


Figure 5.6: Process steps for each experiment

Before the vacuum residue could be introduced into the reactor, it had to be heated to 170 °C so that it had a viscosity that allowed it to be poured. Meanwhile, the reactor was heated up to a temperature of above 100 °C (except for experiments with water, where a temperature of around 90 °C was chosen due to the boiling point of water) to maintain the low viscosity until the reactor was closed. For experiments with a catalyst or additive, the corresponding substance was added while the reactor was open. When all compounds were added, the reactor was closed and the eight nuts sealing the lid were tightened with a torque of 100 Nm. To reduce the risk of an ignitable mixture inside the reactor, N₂ was added to at least 21 bar and the diluted air was released through a valve in the reactor lid. According the calculation in Eq. 5.1, the O₂ content was reduced to below 1 % by this procedure.

$$\text{O}_2[\%] = \frac{21\% \cdot 5l \cdot 1 \text{ bar}}{5l \cdot 21 \text{ bar}} = 1.00\% \quad (5.1)$$

The gas preheater was switched on and H₂ was first added, when a temperature of 480 °C inside the preheater was reached, ensuring a constant H₂ inlet temperature. The exact inlet temperature depends on the chosen H₂ gas flow and varies according to table 5.3.

Table 5.3: Inlet temperature for chosen hydrogen throughput

Flow	Temperature
300l/h	300 ± 5 °C
600l/h	305 ± 5 °C
1200l/h	320 ± 5 °C
1800l/h	332 ± 5 °C

After the setpoint temperature, pressure, and residence time were set in the control panel, the compressor was switched on and H₂ entered the reactor. Temperature and pressure evolution inside the reactor for a typical 3 h experiment are displayed in Fig. 5.7.

Additionally, H₂ flow, pressure regulation valve settings, mass flow out of the system, and additional temperatures and pressures are monitored throughout every experiment. The operator can directly take actions when irregularities are detected. Also, all parameters are logged so that if unexpected deviations in the products occur, the log files can give additional insights on the process and on what might have caused the deviations. Each experiment was carried out at the parameters which are given in the corresponding section. The parameters which can be altered are:

- Total pressure

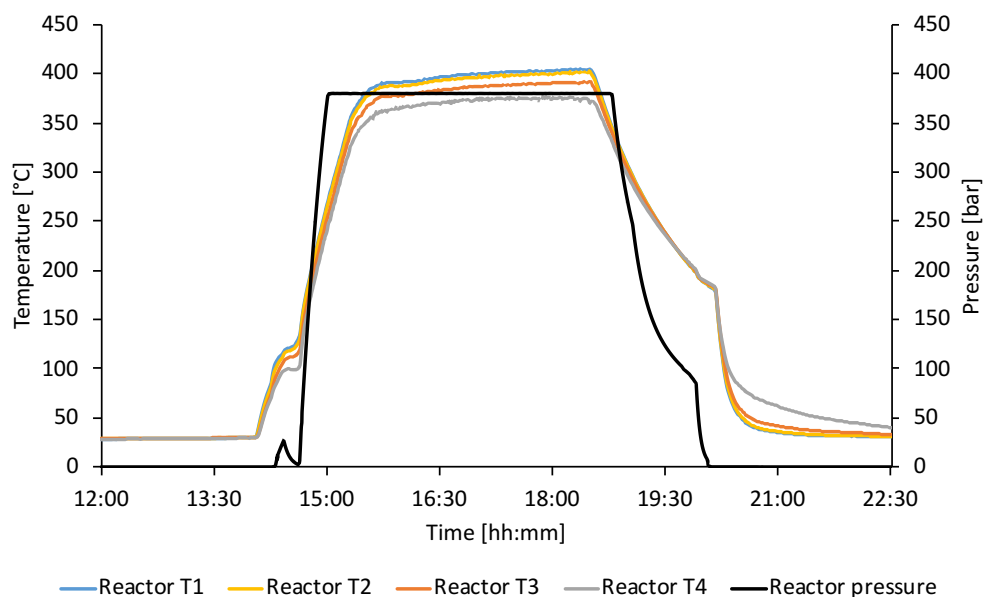


Figure 5.7: Typical temperature and pressure evolution throughout an experiment without SCW

- H₂ throughput
- Residence time
- Reactor temperature
- Agitator rotation speed

All parameters were altered in an order, following an experimental plan (apart from the agitator rotation speed, which was kept constant at 750 rpm for all experiments) to understand their influence on product properties. Additionally, a catalyst and additive could be introduced, to influence the product properties in a targeted way.

After the residence time elapsed, all heaters were switched off and the reactor was cooled via an electric ventilation to a temperature below 330 °C before depressurization of the system was initiated. Depressurization was performed out by setting the pressure control valve to a fixed opening degree of 30 % while subsequently switching off the H₂ supply. At a pressure below 200 bar the valve was opened completely. The depressurization procedure ensured that gas velocities out of the reactor were kept minimal. High gas velocities could result in removal of residue material with the gas stream, potentially clogging the product gas cooler. When ambient pressure was reached, a valve at the bottom of the CHPS was opened and the liquid product fraction was retrieved in a bottle. The reactor was kept at a temperature between 100 °C and 150 °C while opening the lid, to keep the residue product at low viscosity during removal. The stirrer was switched off and the residue was sucked into a

round flask. All experiments, for which an accuracy is given, were carried out twice, to ensure repeatability. Both product fractions were weight before further analysis. For mass balance reasons, the remaining residue, as well as potentially formed coke, were also removed and weight.

5.4.2 Product analysis

The different product fractions were handled each in the procedures, which are explained in detail in Sections 5.4.2.1-5.4.2.4.

5.4.2.1 Distillation

As displayed in Fig. 5.6 the residue fraction was distilled to separate residue from oil. Distillation was performed in a laboratory distillation setup as displayed in Fig. 5.8 at 330 °C and 30 mbar .

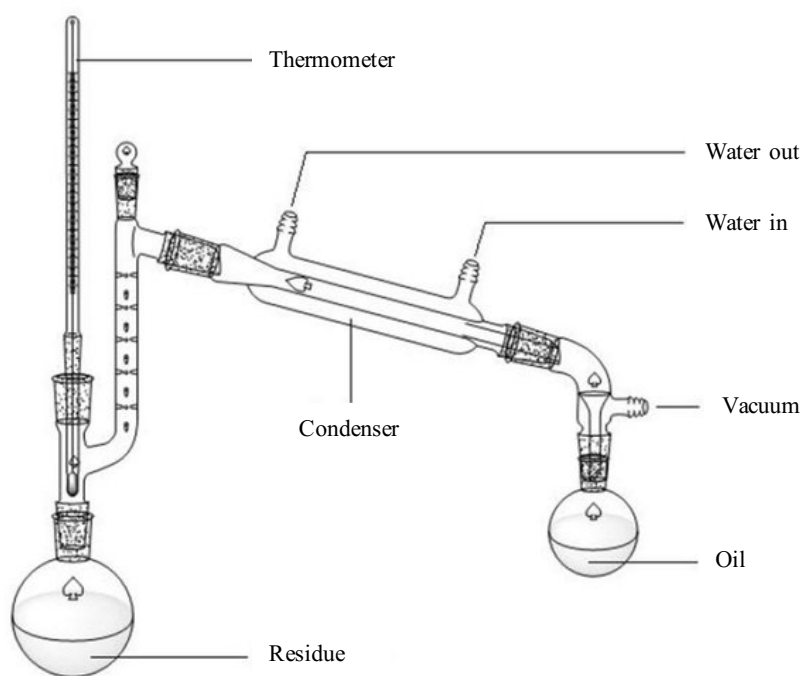


Figure 5.8: Laboratory vacuum distillation based on [198]

With the help of Fig. 5.9 one can read the atmospheric boiling point for a given set of vacuum pressure and temperature 5.9. For 330 °C and 30 mbar, the initial boiling point at atmospheric conditions is 510 °C. By subjecting the residue to the same distillation conditions after each experiment, it was ensured that the remaining

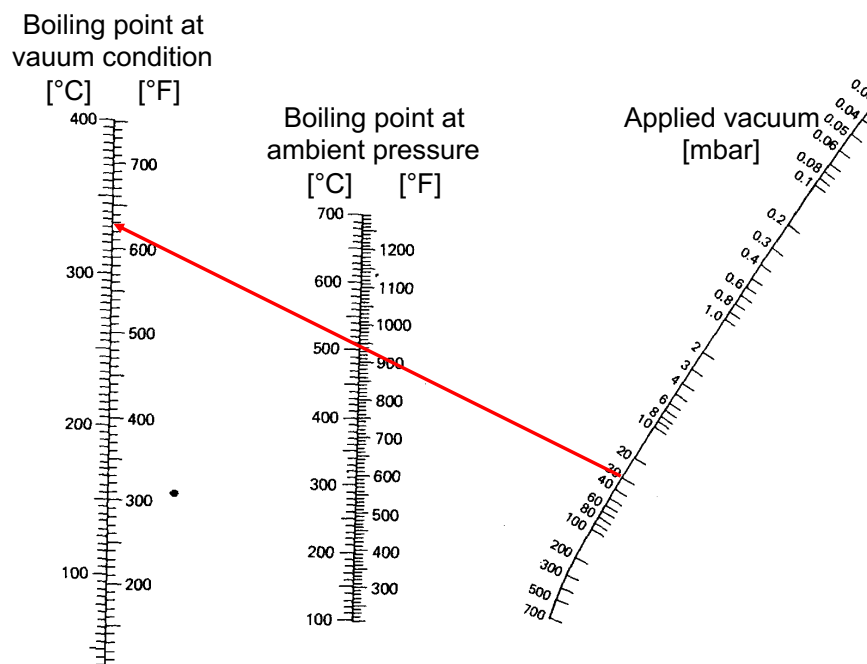


Figure 5.9: Nomograph for the conversion of the boiling point from ambient pressure (middel) to vacuum conditions (left). For a given boiling point at ambient pressure (middel) and an applied vacuum (right), the boiling point at the chosen vacuum conditions can be determined (left) [199]

residue always had the same cut point. This would otherwise not be guaranteed under the different process conditions in the reactor.

For the clarity of the terms, the remaining residue fraction after distillation is always referred to in the following as "residue", while the residue removed from the reactor before distillation is defined as "hydrogenation residue". The heavy oils, which were evaporated and removed during distillation, were collected and mixed with the oil fraction obtained from the CHPS. Handling of the product oil fraction is further described in Subsection 5.4.2.3. The residue was weight before further analysis.

5.4.2.2 Residue fractionation/ solvent fractionation

The distillation residue was ground to powder and a sample was further processed. The method chosen for the fractionation of the distillation residue into solids (toluene insoluble), asphaltenes (toluene soluble, hexane insoluble) and maltenes (toluene and hexane soluble), is analogue to the method described by Kang et al. [200]. A sample of 2 g was taken from the powdered residue and was subsequently dissolved in 100 ml of the different solvents. Precipitates were filtered off and each fraction was weight

and further analyzed in the elemental analyzer (Vario EL III, Elementar) to receive their elemental compositions.

5.4.2.3 Product oil fraction

The light oils obtained gathered in the CHPS were blended with the heavy oils from the distillation step. Together they give the product oil fraction and are in the following always referred to as "product oil" or "oil fraction". The oil fraction was weight before further analysis were performed. For the experiments with SCW, drying (with magnesium sulfate) was necessary to remove all water before the oil could be analyzed in the elemental analysis. Water needed to be removed completely, so that the results were not falsified. Also, a sample was taken and diluted 1:100 in isopropanol for GC/MS analysis. GC/MS analysis of the product oil was performed using a Hewlett Packard G1800C equipped with a VF-5 ms capillary column (30 m, 0.25 mm, 0.25 μ m) and a HP 5890 GC mass selective detector. Helium was used as carrier gas, the injector temperature was set to 280 °C, the column pressure was set at 100 kPa and the initial column temperature was kept at 90 °C for 5 min. Column heating rate was 9 °C/min with a final temperature of 320 °C at which it was kept for 2 min. The samples were injected in split mode. The components were identified using the NBS 75 K library.

5.4.2.4 Gas phase analysis

The product gases from the CHPS passed through a Coriolis flow device (element 9 in Fig. 5.1), which measured the density as well as the mass flow. In the course of the experiments performed in this work, a micro-GC (Inficon 3000 with a molecular sieve column with helium as carrier gas and a Porapak column with argon as carrier gas) became available for a more detailed analysis of the product gas composition. Unfortunately, this device was not available for all performed experiments. For the experiments during which the product gas was analyzed with the micro-GC, the volume flow of the components H_2S , CH_4 and C_2H_6 could be determined. Since the micro-GC was operated downstream of the hydrogenation reactor and CHPS, the time of the gas detection and gas emission in the reactor deviated. In order to identify this time delay between gas emission and detection, the residence time for the reactor at 370 °C was determined experimentally as well as theoretically. The calculation of the residence time distribution was performed by assuming two ideal continuous stirred-tank reactors (CSTR) interconnected by a pipe with no

backmixing. The residence time distribution function for a component i in a CSTR with the volume V and a volume flow into the reactor of $\dot{V}$ can be written as

$$c_{i,out} = c_{i,0} + \frac{1}{\tau} \cdot \int_{t_0}^t c_{i,in} dt - \frac{1}{\tau} \cdot \int_{t_0}^t c_{i,out} dt \quad (5.2)$$

where τ is the ratio between V and $\dot{V}$. The start concentration $c_{i,0}$ is 0 if the tracer compound is not present in the system at t_0 . The solution to this inhomogeneous differential equation for the boundary conditions $t = t_0 : c_i = c_{i,0}$ and $t = t_\infty : c_0 = 0$ is given in Eq. 5.3.

$$c_{i,out} = c_{i,in} \cdot (1 - \exp(-t/\tau)) \quad (5.3)$$

In the case of the hydrogenation setup, there are two consecutive CSTR with deviating volume. $c_{i,out}$ from the reactor is $c_{i,in}$ for the CHPS while $c_{i,out}$ from the CHPS is the concentration detected at the micro-GC. Eq. 5.4 is obtained for the measured concentration $c_{i,out,CHPS}$ at the micro-GC.

$$c_{i,out,CHPS} = c_{i,0} + \frac{1}{\tau_{CHPS}} \cdot \int_{t_0}^t c_{i,in} \cdot (1 - \exp(-t/\tau_{reactor})) dt - \frac{1}{\tau_{CHPS}} \cdot \int_{t_0}^t c_{i,out,CHPS} dt \quad (5.4)$$

The corresponding Matlab code for the calculation is given in the Appendix A including factors to adjust to the real reactor conditions. For the experimental determination, the reactor was filled with 1 l of water to reduce the volume inside the reactor. As trace component to receive the residence time distribution, DMDS was inserted via the HPLC pump. DMDS decomposed in the preheater, theoretically forming only H_2S and CH_4 in equimolar amounts. The measured gas composition is displayed in Fig. 5.10. H_2S is soluble in water (especially at high pressure) and therefore the H_2S curve was not representative for the residence time distribution. CH_4 is nearly insoluble in water and therefore the curve obtained for CH_4 downstream of the reactor and CHPS could be used as indicator for the residence time distribution. The integral under the calculated residence time curve strongly deviates from the actually measured CH_4 concentration. This is attributed to the fact that probably not only CH_4 was formed in the preheater, but also recombination reactions led to the build up of C_2H_4 . Adding both integrals of CH_4 and C_2H_4 together comes very close to the theoretically determined curve with an error of 10%.

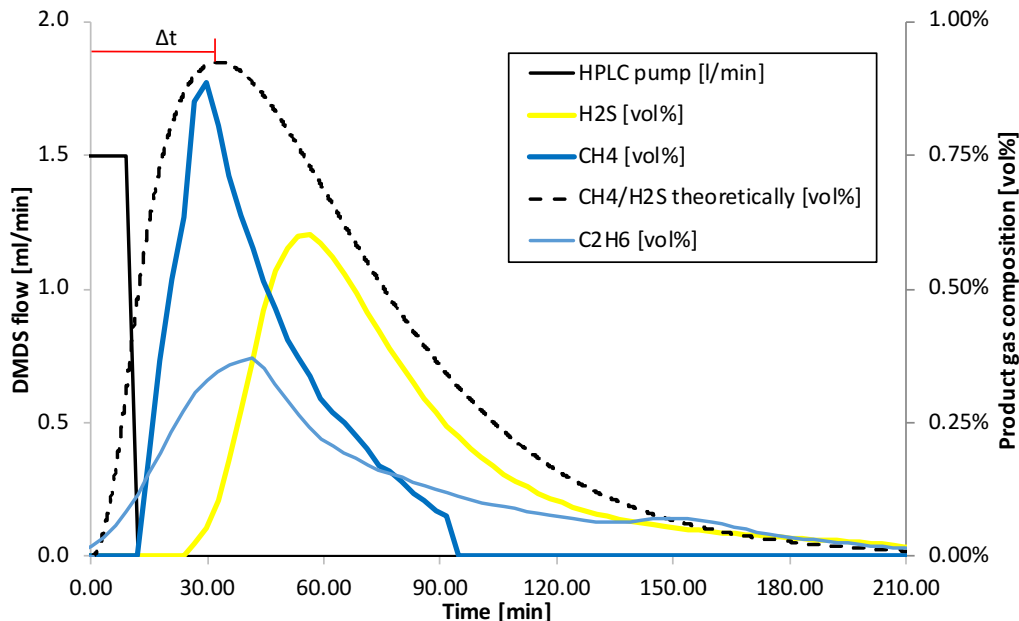


Figure 5.10: Comparison of calculated residence time curve and actually measured values

For the determination of an average time delay between emission and detection, the peak of the residence time distribution was used. Since the theoretically calculated peak and the actually measured one correspond very well, the calculation was used to predict the time delay for experiments conducted above the critical point of water. Above its critical point, water does not serve as a good medium to fill the autoclave, because at supercritical conditions it was gradually removed from the reactor. At 400 °C, conditions at which most experiments were performed, the time delay between production in the reactor and detection downstream was calculated to 33 min.

5.5 Calculations

5.5.1 Product yields

The amount of oil and residue was determined by weighing the respective fractions. For the gas phase, this was not possible and therefore this fraction is calculated by difference according to 5.5.

$$m_{\text{gas}} = m_{\text{feed}} + m_{\text{H}_2} - (m_{\text{res}} + m_{\text{oil}}) \quad (5.5)$$

The amount of hydrogen (m_{H_2}) that reacts with the vacuum residue, thus contributing to the product amount, needs to be taken into account when calculating

the mass balance. The hydrogen balance cannot be closed directly but by calculating the carbon balance first.

$$m_{C,gas} = m_{C,feed} - (m_{C,res} + m_{C,oil}) \quad (5.6)$$

The carbon amount of the product fractions residue $m_{C,res}$ and oil $m_{C,oil}$ as well as for the feed $m_{C,feed}$ are determined by elemental analysis and multiplication with the respective product fraction. The hydrogen balance is closed with the help of the H/C ratio for each fraction ($n_{H/C,i}$), where i stands for the fractions residue, oil and gas.

$$m_{H,feed} + m_{H,H_2} = m_{H,products} = \frac{\sum_{i=1}^i m_{C,i} \cdot n_{H/C,i}}{M_C} \cdot M_H \quad (5.7)$$

For the fractions residue and oil, the H/C ratios are calculated from the elemental analysis results. For the gas fraction it is assumed, that the only volatile products leaving the CHPS are H_2S , CH_4 , C_2H_4 and C_2H_6 as detected by the micro-GC and only a small, negligible amount of higher hydrocarbons. While the amount of H_2S results from the removed sulfur from Eq. 5.15, the rest of the product gas is assumed to be composed of 40% CH_4 , 20% C_2H_4 , 20% C_2H_6 and 20% C_3H_8 which is in the range of the mean throughout the measured products gas compositions. The H/C ratio of the product gas $n_{H/C,Gas}$ is then calculated according to Eq. 6.8.

$$n_{H/C,gas} = \frac{\Delta S_{total} \cdot n_{H/C,H_2S}}{M_S} + \frac{m_{C,gas} \cdot (0.4 \cdot n_{H/C,CH_4} + 0.2 \cdot n_{H/C,C_2H_4} + 0.2 \cdot n_{H/C,C_2H_6} + 0.2 \cdot n_{H/C,C_3H_8})}{M_C} \quad (5.8)$$

The yields for the retrieved product fractions are calculated according to Eq. 5.9-5.11.

$$\eta_{res} = \frac{m_{res}}{m_{feed}} \quad (5.9)$$

$$\eta_{oil} = \frac{m_{oil}}{m_{feed}} \quad (5.10)$$

$$\eta_{gas} = \frac{m_{gas}}{m_{feed}} \quad (5.11)$$

5.5.2 Conversion

For the purpose of this work, it is of interest to identify to which extent the feed vacuum residue is converted to lower boiling products. For this reason, conversion is defined as the fraction of products with a boiling point below the conditions reached in the vacuum distillation (330 °C and 30 mbar), divided by the feed. This is equal to the difference between the feed vacuum residue and the remaining distillation residue as presented in Eq. 5.12.

$$Conversion = \frac{m_{\text{feed}} - m_{\text{res}}}{m_{\text{feed}}} \quad (5.12)$$

5.5.3 Desulfurization

The desulfurization is calculated for each product fraction (except for the gas phase, where ideally, all sulfur ends up as H₂S), as well as for the total product (oil + residue).

$$\Delta S_{\text{res}} = \frac{m_{\text{res}}}{m_{\text{feed}}} \quad (5.13)$$

$$\Delta S_{\text{oil}} = \frac{m_{\text{oil}}}{m_{\text{feed}}} \quad (5.14)$$

$$\Delta S_{\text{total}} = \frac{\Delta S_{\text{res}} \cdot m_{\text{res}} + \Delta S_{\text{oil}} \cdot m_{\text{oil}}}{m_{\text{feed}}} \quad (5.15)$$

Results and discussion

The discussion of the experimental results is subdivided into a section covering all experiments performed without a catalyst (Section 6.1.1), sections dealing with the performance of catalysts and additives (Sections 6.2-6.4), and a section dealing with a comparison of all performed experiments (Section 6.5). All experiments in this work were performed under H_2 atmosphere. The prefix hydro- is left away in the following and the shorter terms conversion and desulfurization or the abbreviation HDS are used instead of hydroconversion and hydrodesulfurization.

6.1 Investigations without catalyst

For the investigations on process conditions (pressure, H_2 throughput, vacuum residue amount, temperature, and residence time), experiments were conducted without addition of a catalyst. This section is subdivided into investigations of operating pressure, H_2 throughput, and vacuum residue amount (Section 6.1.1), investigations on the residence time (Section 6.1.2), investigations on temperature level (Section 6.1.3), and a section, in which a mechanistic model for the desulfurization and conversion reactions together with kinetic parameters were conducted from the experiments. Aim of this section is the identification of a set of parameters which enhance desulfurization, while keeping conversion at a minimum. By deriving a potential reaction model, a further understanding of the influence of chosen process parameters is developed. The identified process parameters were further used in Sections 6.2 - 6.4 as reference point for the investigations on catalyst activity.

6.1.1 Influence of pressure, H₂ throughput, agitator rotation speed, and vacuum residue amount

The influence of pressure and H₂ throughput on desulfurization and conversion reactions of vacuum residue were analyzed. In a first step, the influence of the amount of introduced vacuum residue was investigated, while keeping the ratio between H₂ throughput and vacuum residue constant. The experiments were carried out at 415 °C and 380 bar. Variation was performed between 250 g vacuum residue with 300 l/h H₂ throughput up to 1000 g and 1200 l/h. In a second step, the ratio between H₂ throughput and vacuum residue was varied to investigate the influence of the ratio. Variation of the H₂ throughput, while simultaneously adjusting the introduced amount of vacuum residue, to keep the ratio between H₂ throughput and feed constant with varying feed amount, was found to have no noticeable effect on desulfurization and conversion as shown in Fig. 6.1 (a). Increasing the H₂ throughput for a constant vacuum residue amount (thus increasing the H₂ - vacuum residue ratio) showed a slight increase in desulfurization for the residue fraction, while the conversion stayed nearly unaffected as presented in Fig. 6.1 (b). The ratio between H₂ and vacuum residue was therefore chosen to be kept constant at a high level of 1200 l/h per 1000 g of vacuum residue (increasing the ratio further would have increased the operating cost significantly). The influence of total vacuum residue amount was found not to be relevant (within the tested range of 250 - 1000 g).

The agitator rotation speed influences heat and mass transfer properties. Phase boundaries between gas and liquid are increased with increasing agitator speed as well as turbulences. On the gas side, H₂ transport is not relevant, because pure H₂ is used. To identify the influence of the agitator rotation speed on heat and mass transport, the speed was varied between 200 rpm and 800 rpm at 385 °C, 310 bar, with 1000 g vacuum residue, and 1200 l/h of fresh H₂ for 3 h. The influence of mass transport limitation can be neglected, if a change in agitator rotation speed does not affect the product yields [201]. Therefore, desulfurization and conversion reactions were monitored over changing agitator speed as presented in Fig. 6.1 (c). While for the conversion reactions, no obvious effect of agitator rotation speed could be observed, desulfurization is strongly limited at 200 rpm. Cracking reactions leading to conversion are thermally controlled and H₂ is only used to saturate the reaction products. What is not displayed in Fig. 6.1 (c), is that at 200 rpm, formation of coke was observed, similar to what is displayed in Fig. 6.3. The formation of coke is an indication, that not enough H₂ was present to saturate cracking products and repolymerization reactions took place. This could be a result of mass trans-

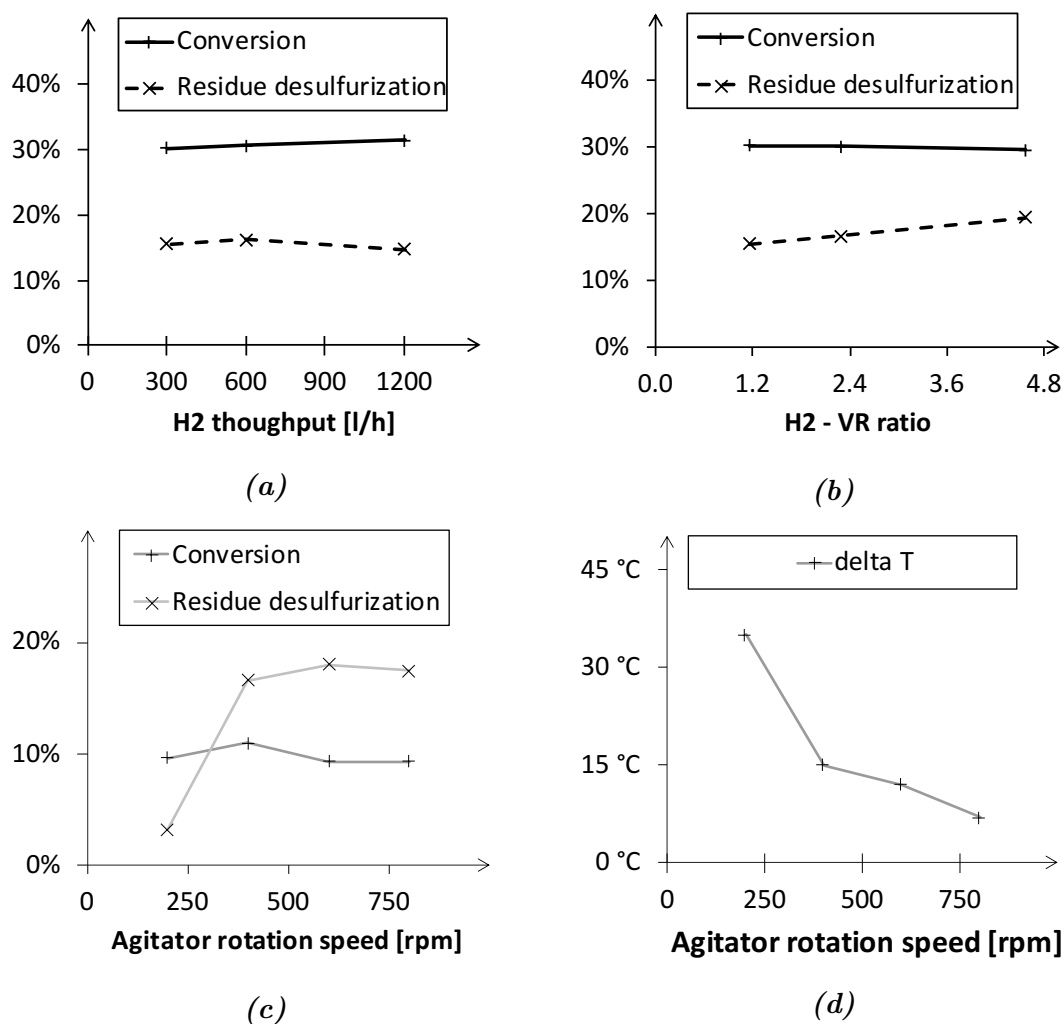


Figure 6.1: Variation of (a) vacuum residue amount while simultaneously adjusting the H₂ to maintain a constant ratio, (b) H₂ - vacuum residue ratio, (c) agitator rotation speed effect on desulfurization and conversion, and (d) agitator rotation speed effect on temperature difference between wall and inside

port limitations. For HDS reactions, the influence of mass transport limitations at 200 rpm can be seen in Fig. 6.1 (c). Above 600 rpm, no change in conversion or HDS reactions could be detected. It is therefore assumed, that at an agitator rotation speed of above 600 rpm, the influence of mass transport limitations can be neglected. In Fig. 6.1 (d), the average temperature difference between heated reactor wall and measured temperature in the reaction medium, with changing agitator rotation speed, is given. For the temperature inside the reaction medium, the average of the bottom two thermocouples, displayed in Fig. 5.2, were used. Only the lower two are surrounded by liquid, while the upper two measure the gas phase temperature. Temperature difference changes throughout operation time, therefore, the difference displayed in Fig. 6.1 (d) was always measured after 1 h residence time. Non stationary heating effects make earlier measurements at residence time below

1 h inaccurate. Fig. 6.1 (d) indicates, that heat transfer is strongly improved by increase of agitator rotation speed. The large temperature difference at 200 rpm may result from the coke deposition, reducing heat transfer strongly. Since a very homogeneous temperature distribution is desired, best results were obtained at the highest agitator rotation speed of 800 rpm. In the further context of this work, an agitator rotation speed of 750 rpm was chosen, to reduce both mass and heat transport limitations. Though higher rotation speed would have been desired, a rotation speed of above 750 rpm resulted in strong vibrations, that could not be tolerated permanently.

Investigations for the variation of pressure were carried out with a sample weight of 1000 g vacuum residue, 1200 l/h of fresh H_2 , without catalyst, at 385 °C reaction temperature and 12 h residence time. The investigated pressures were 310 bar, 200 bar and 100 bar. For the experiments at 100 bar the H_2 throughput had to be reduced from 1200 l/h to 200 l/h because the installed pressure control valve is designed for a Δp of 310 bar and an opening degree of 100 % at 100 bar was not able to discharge the entire amount of H_2 when a throughput of 1200 l/h was maintained. As Fig. 6.2 shows, with increasing pressure from 100 bar to 200 bar to 310 bar, the total sulfur reduction increased. The oil fraction exhibited a relatively constant sulfur content over the entire pressure range, whereas the sulfur removal from the residue fraction increased sharply with reaction pressure. All tests at a reaction temperature of 385 °C showed no coke formation or asphalt precipitation on the reactor wall or stirrer. Also, the conversion could be decreased by applying a higher H_2 partial pressure.

The trend that a higher pressure led to higher desulfurization could also be shown at increased reaction temperature and achieved a total desulfurization of 55 % at 310 bar after 12 h residence time. However, it was also shown that lowering the pressure to 200 bar, at 415 °C, already led to coking in the form of solids deposition on the stirrer as shown in Fig. 6.3. Since the tests at 200 bar had already led to these negative phenomena, a further reduction of the pressure at this reaction temperature was refrained from. A high H_2 partial pressure was therefore necessary for the suppression of coke formation at elevated temperatures. The importance of a high H_2 partial pressure to suppress coke formation is well known [202,203].

For the conversion reactions, a decrease in activity with increasing H_2 partial pressure was observed. An increase in pressure inhibited the formation of smaller, low molecular weight molecules like gas and oil. The rate of cracking reactions is known to decrease with high H_2 partial pressure, as reported by Heinemann et al. [15,204].

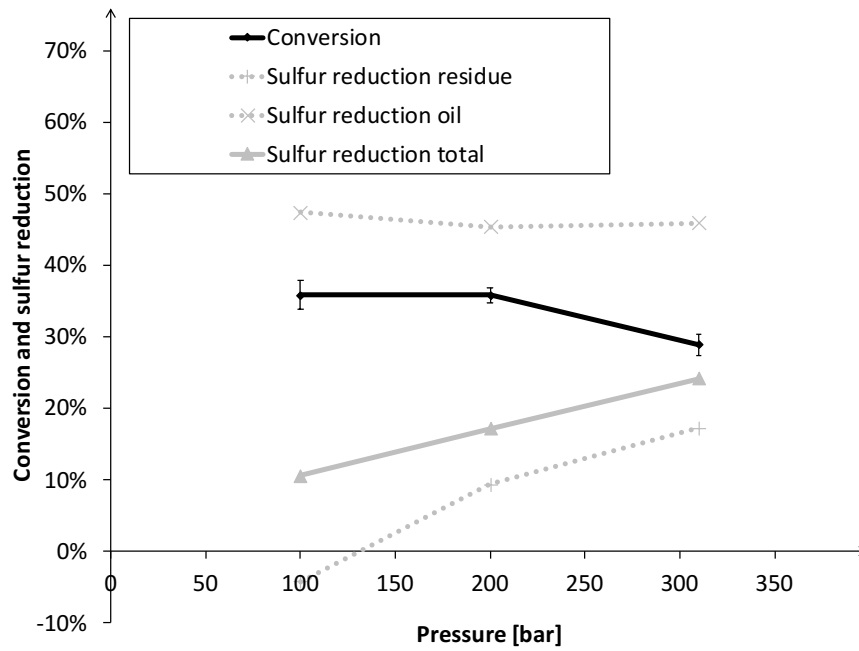


Figure 6.2: Variation of pressure for 12 h experiments at 385 °C



Figure 6.3: Coke deposition on the stirrer formed during an experiment at 415 °C and 200 bar after 12 h residence time

Hydrogenation of double bonds and thus dearomatization, as an equilibrium reaction, is also preferred at high partial pressures due to the reduction of specific volume [205, 206]. The dearomatization may also explain the observed increased desulfurization at higher pressure, although this increase might seem unexplained

due to the formation of H_2S with respect to thermodynamics. The desulfurization of compounds where the sulfur atom is not aromatically stabilized, is far easier than removal of sulfur from aromatic molecules. This desulfurization path is known as HYD route as explained in Section 2.4.3. This has been shown for model compound systems like thiophene - tetrahydro-thiophene [207] as well as for BT - dihydro-BT [208]. Assuming, that most sulfur in vacuum residue is bound in thiophene, BT and DBT based structures, as discussed in Section 2.1.1, the findings from these model compounds display a path to help explain the desulfurization behavior. High H_2 pressure reduces the aromaticity of the feed, thus enabling an increased desulfurization. This correlation has also been reported extensively in literature for crude oil fractions. According to Frost and Cottingham [209] a direct proportionality between operating pressure and desulfurization was observed for the desulfurization of Venezuelan residual fuel in the range of 55 bar to 110 bar. An effect on residue conversion was not reported. For distillate products and heavy gas oil, also an increase in desulfurization degree with rising H_2 partial pressure is reported [210,211]. Higher H_2 pressure leads to a favored HYD route. Benefits of the HYD route in the context of desulfurization of BT and DBT structures are discussed in Section 6.2.1.2.

Concluding from both literature and the experimental findings, high H_2 pressure and throughput are beneficial for desulfurization. Also, high H_2 partial pressure suppresses coke formation and may act inhibitory for the conversion of vacuum residue to lighter fractions like oil and gas. Therefore, for further investigations in the following Sections 6.1.2 - 6.4, a high pressure of 310 bar was used. The ratio between H_2 and vacuum residue was chosen to be kept constant at a high level of 1200 l/h per 1000 g of vacuum residue.

6.1.2 Influence of residence time

To understand the influence of residence time on conversion and desulfurization reactions, as well as to estimate the reaction order for both reactions, the residence time was varied between 3 and 12 h. The system pressure was kept constant at 310 bar with a total H_2 throughput of 1200 l/h per 1000 g vacuum residue feed.

6.1.2.1 Conversion

With increasing residence time, the conversion of vacuum residue to product oil and gas increased, while the amount of remaining residue decreased. The reactions forming lower boiling products are called conversion reactions (definitions of oil and residue fractions as well as the resulting conversion are given in Section 5.4). The yield of conversion reactions is plotted in Fig. 6.4. Conversion increased with residence time for both examined temperature levels.

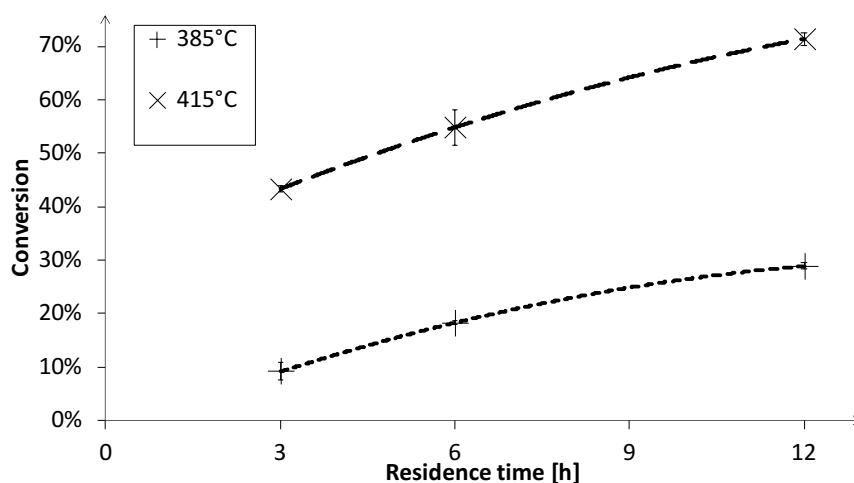


Figure 6.4: Conversion to lighter boiling products plotted over residence time

This correlation is expected, because the longer the feed is exposed to the reaction conditions, the more conversion reactions proceed. Conversion reactions in presence of high H_2 pressure and no catalyst are composed of a thermally induced cracking step, followed by hydrogenation, as described in Section 2.4.1. As shown in Fig. 6.1, conversion was unaffected by a change of H_2 concentration, at the levels of H_2 partial pressure applied in this work. Also, Köseoglu et al. [212,213] as well as Galarraga et al. [214] observed that hydroconversion reactions were considered to be zero order with respect to H_2 . Concluding from both literature and the experimental data, the non-catalytic conversion reactions of the vacuum residue are only dependent on the induced cracking reactions. Since cracking is thermally induced [215], the

total time, during which the feed is exposed to the reaction conditions, directly increases the yield of lighter fractions. A higher yield of conversion products with increasing residence time is also observed in literature [216,217]. Comparing both temperature levels, it can be observed that at 415 °C the conversion was much higher than at 385 °C, which is a well known correlation for endothermic reactions [84,129]. This observation is discussed in detail in Sections 6.1.3 and 6.1.4. Even after 12 h residence time, the conversion at 385 °C did not reach the conversion at 415 °C after only 3 h.

6.1.2.2 Desulfurization

Parallel to the decomposition reactions of the vacuum residue resulting in lower boiling products, HDS reactions removed the organic sulfur from the feedstock as H_2S . Both product fractions, the residue and the oil, were analyzed to determine their sulfur content and the results are presented in Fig 6.5.

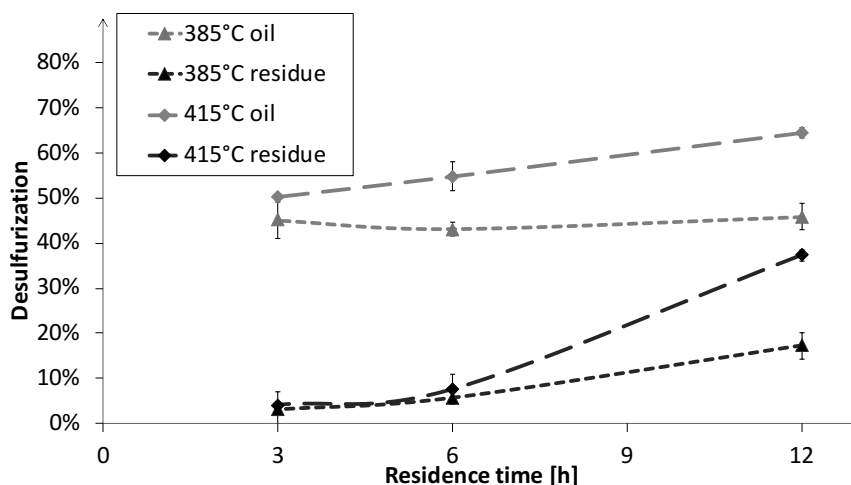


Figure 6.5: Desulfurization of the product fractions oil and residue plotted over the residence time

A stronger influence of residence time could be observed for the reactions at 415 °C, resulting from the fact that the reaction rate increased at higher temperature [218]. An increase in residence time had an inferior influence on the level of sulfur in the oil fraction than on the residue desulfurization. Especially at 385 °C, doubling or quadrupling the residence time had almost no effect on the sulfur level in the product oil. This may be a result of the fact that the product oil is the condensed volatile matter carried out of the reactor continuously throughout the experiment. The product oil fraction was produced by breaking C-C bonds, so that the reaction products were formed of lighter hydrocarbons. During decomposition of the feedstock, by breaking C-C bonds, also C-S bonds were ruptured and sulfur was removed as H_2S . Most

of these lighter hydrocarbons with lower sulfur content were then removed from the reaction zone and were collected in the CHPS downstream of the reactor. In the CHPS, further potential reactions are quenched. Therefore, the sulfur level in the fraction obtained from the CHPS was not further influenced by an increase of residence time, as displayed in Fig. 6.6a.

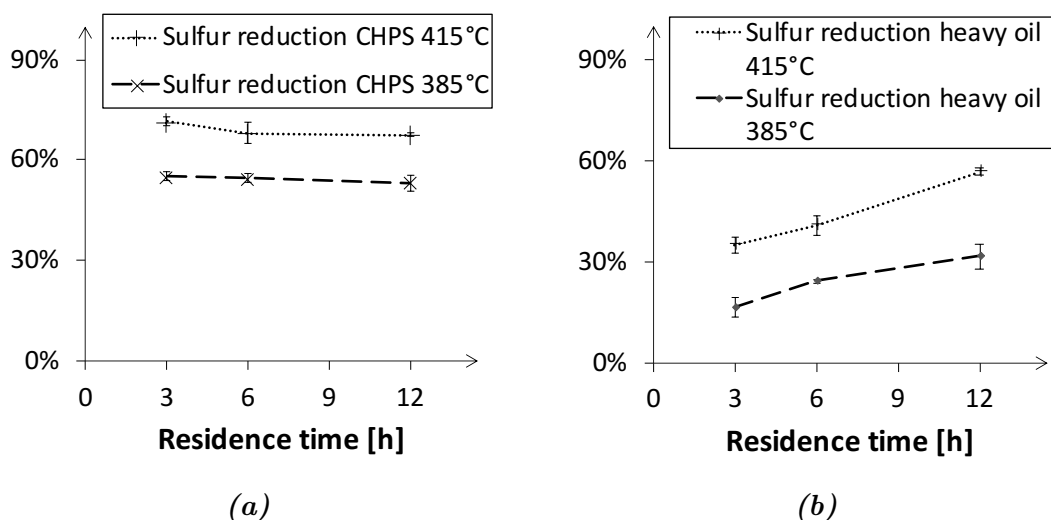


Figure 6.6: Influence of residence time on desulfurization of (a) the CHPS oil fraction and (b) the distilled heavy oil fraction

Only the sulfur containing hydrocarbons remaining in the reaction zone undergo further desulfurization. The residue exhibited an increase of desulfurization with residence time, because this fraction is further exposed to the reaction conditions. In the distillation step, heavy oil, still present in the hydrogenation residue, was evaporated, as explained in Section 5.4.2.1, and merged with the product fraction from the CHPS. This evaporated heavy oil fraction did still undergo desulfurization reactions throughout the whole residence time, unlike the CHPS fraction. The influence of residence time on desulfurization of this heavy oil fraction is displayed in Fig. 6.6b. An increase of sulfur reduction with increasing residence time was observed. As expected, sulfur reduction was increased stronger at higher reaction temperature. Mixing of the heavy oil fraction with the light oils from the CHPS gives the explanation for the slight increase of desulfurization with increasing residence time in the oil fraction at 415°C. The heavy oil fraction only contributes 20-30% to the total oil fraction, therefore, the marginal influence of residence time on heavy oil desulfurization at 385°C does not influence the desulfurization of the total oil fraction, as it does at 415°C.

6.1.2.3 Hydrogenation

The molar H/C ratio of the products may be used as measurement for occurring hydrogenation reactions. Figure 6.7a (a) displays the effect of residence time on the H/C ratio of both the oil and residue fraction. The change is calculated by referring the H/C ratio of the respective product oil to the H/C ratio of the feed vacuum residue.

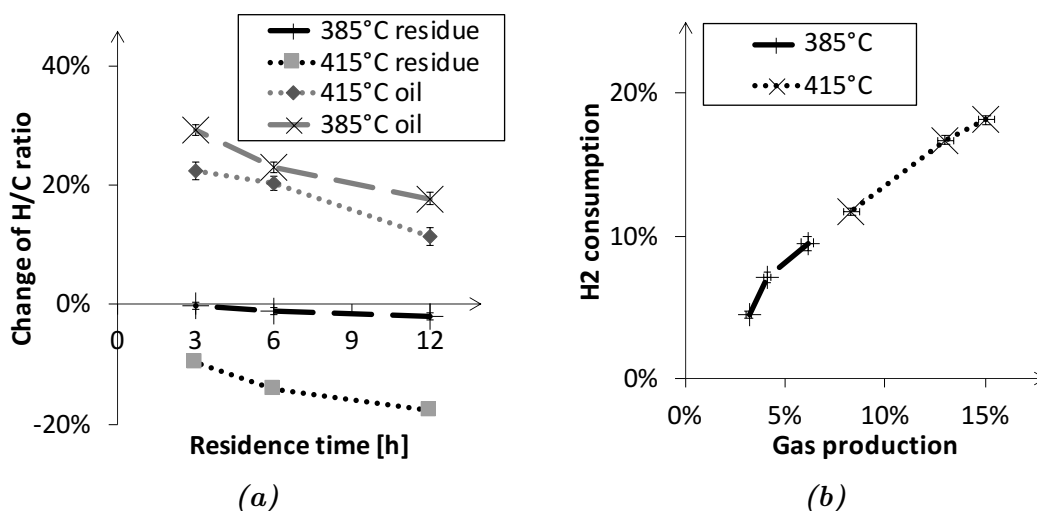


Figure 6.7: (a) H/C ratio plotted over the residence time and (b) increase of H_2 consumption with increasing gas production

With residence time, conversion reactions proceeded. Though H_2 was consumed, as displayed in Fig. 6.7b, the H/C ratio in both the residue and oil fraction decreased. Therefore, H_2 was mostly consumed in saturation of cracking products, that leave with the gas phase, as discussed in Section 2.4.1. Therefore, H_2 consumption increased with increasing conversion, but the residue and oil products did not show an increase of hydrogen content. In fact, the residue and oil fractions were depleted of hydrogen with increasing residence time, as shown in Fig. 6.7a. This is attributed to the fact that non-catalytic hydrogenation is incapable of saturating the highly aromatic core of the asphaltenes and maltenes, which remain after cracking. Hydrogenation and saturation of polyaromatics has a higher activation energy than saturation of simple double bonds that form after cracking [219]. Therefore, the activation energy needed to saturate the aromatic cores was not overcome without a catalyst.

6.1.3 Influence of temperature

In thermo-chemical processes, the influence of temperature is a crucial aspect. Since many different and very complex reactions occur throughout the hydrogenation process, of which some are desired while others are undesired, the influence of temperature on the product characteristics is of great interest. Ideally, the temperature window can then be chosen in a manner, yielding a product with the desired characteristics. Since in this case, the main reactions of interest are desulfurization reactions yielding H_2S and cracking reactions followed by hydrogenation, the effect of temperature on desulfurization and on conversion was closely analyzed. In Fig. 6.8 the behavior of desulfurization and conversion is plotted versus temperature. The black line shows a strong increase of conversion activity with temperature, while the grey line displays the total sulfur removal from both residue and oil (definitions of oil and residue fractions are given in Section 5.4). From the dotted lines, the conclusion can be drawn that the residue was not desulfurized to a stronger extent with increasing temperature, while the oil fraction exhibited a further desulfurization at higher temperatures.

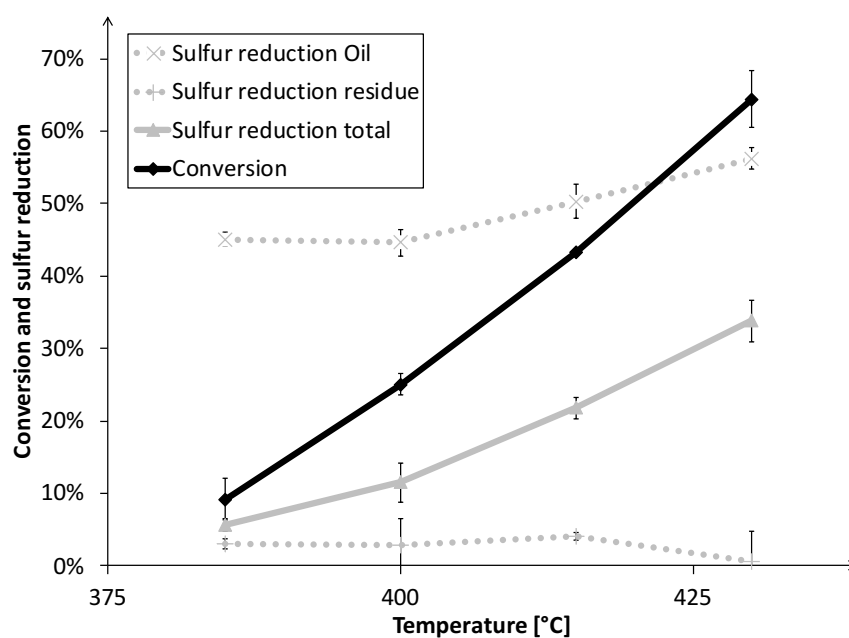


Figure 6.8: Variation of temperature with 3 h residence time

As already discussed in Section 6.1.2.2, cracking of the feedstock may have led to less stable sulfur containing molecules. These could then have been desulfurized more easily. With increasing temperature, cracking of the feedstock was enhanced and a larger fraction of the vacuum residue was converted to low boiling products, that contain less sulfur. Though total desulfurization increased with increasing tem-

perature, the residue did not show an increased desulfurization. This can also be explained by the mentioned effects. While conversion proceeds, less stable sulfur molecules are removed, while only the stable aromatic core remains. This is supported with the H/C ratio, measured in the remaining residue fraction as displayed in Fig. 6.9a. With increasing reaction temperature, the H/C ratio of the residue decreased, indicating that the remaining residue exhibited a highly aromatic character. Also the increase of asphaltenes to maltenes-ratio (displayed in Fig. 6.9b) in the residue supports this assumption. As discussed in Section 2.1.2, asphaltenes exhibit a higher aromaticity, thus containing the most refractory sulfur.

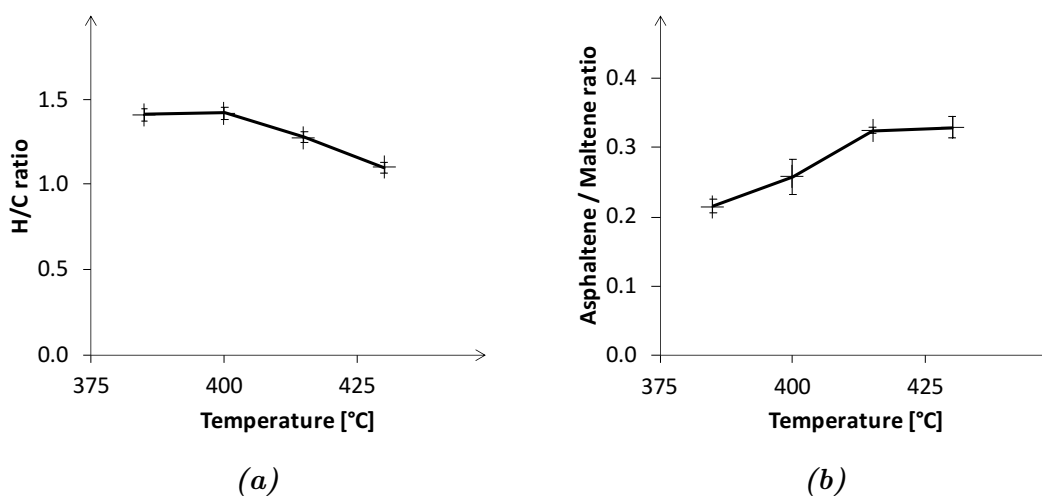


Figure 6.9: (a) H/C ratio of the residue plotted over the reaction temperature and (b) ratio of asphaltenes to maltenes in residue

The investigations of temperature variation on the desulfurization and conversion reactions indicated that an increase of temperature did not support the residue desulfurization, but only conversion reactions. In order to further examine these observations, a reaction mechanism and kinetic parameters are determined in Section 6.1.4.

6.1.4 Determination of a reaction mechanism and reaction kinetics

For a better understanding of how temperature and residence time influence the non-catalytic conversion and desulfurization reactions, global kinetics for both conversion and desulfurization are derived from the obtained data. A reaction mechanism is proposed in Section 6.1.4.1, followed by the determination of the kinetic parameters.

6.1.4.1 Reaction mechanisms

Reaction kinetics describe the rate of a chemical reaction. Vacuum residue is composed of hundreds of different molecules, which undergo different reactions during hydrogenation, making a precise mechanism for the molecular reactions highly challenging to determine. Therefore, a simplified mechanism has to be found that serves the purpose of describing conversion reactions, as well as desulfurization, using global reaction kinetics. The assumed reaction mechanism for the conversion, including three lumped products and the feedstock, vacuum residue, also also considered as a unit (vacuum residue, product oil, gas, and coke), is presented in Fig. 6.10. k_n is the temperature dependent rate coefficient quantifying the rate at which the specific reaction takes place.

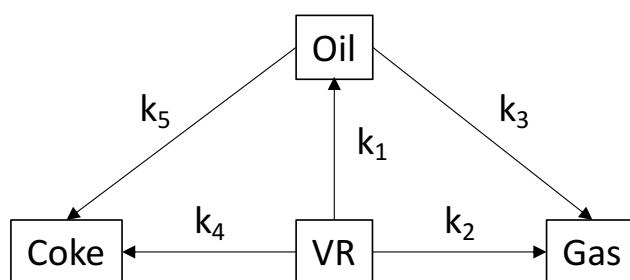


Figure 6.10: Reaction mechanism of the four lumped substances

Feed vacuum residue undergoes conversion reactions yielding either gas or oil. When cracking occurs without hydrogenation of the cracking products, coke may form. There are no reactions back to vacuum residue assumed, while oil can further react to gaseous products as also other researches have reported [131,220] and as presented in Section 2.5. When the temperature range is kept low, while a sufficient H_2 partial pressure is maintained, coke formation may be suppressed [221]. As a consequence, k_4 and k_5 can be assumed as zero. Also, for the purpose of this work, only the conversion reactions reducing the amount of vacuum residue are of interest (further reactions of oil to gas are not of interest), because the aim is the desulfurization of the residue. Therefore, the reaction network can be simplified to Fig. 6.11.

For desulfurization reactions, two different approaches are considered, based on the presented mechanisms in Section 2.5. One simple approach, where no difference between the sulfur in the vacuum residue is made, and one more complex scheme, where HDS reactions are formulated for the light fraction separately from HDS of

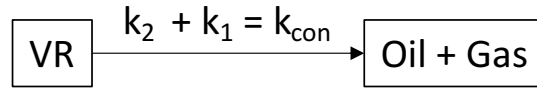


Figure 6.11: Simplified reaction scheme for the conversion of vacuum residue to lower boiling products

the more complex residue fraction. For both, it is assumed that organic sulfur reacts to H_2S .

In the first approach, for reasons of simplicity, no difference is made between occurring sulfur bonds and all possible reactions are reduced to one non-reversible pseudo-reaction, similar to the model used by Manek et al. [131]:

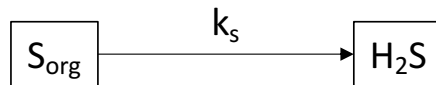


Figure 6.12: Reaction mechanism for desulfurization reactions

The second approach extends the approach by Manek et al. [131] with a second mechanism, which describes HDS for the more complex residue fraction, as suggested by Marifi et al. [138] and displayed in Fig. 6.13.

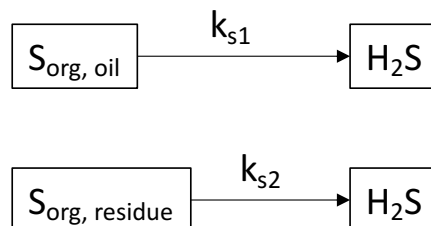


Figure 6.13: Reaction mechanism for desulfurization reactions considering to parallel reactions with different reaction rate

6.1.4.2 Rate expression

Using the Arrhenius model, the rate expression was developed from the general rate expression given in Eq. 6.1, where n_A is the molar amount of component A, ξ is a system variable, and ν_A is the stoichiometric coefficient.

$$\tilde{r}_A = \frac{1}{\xi} \cdot \frac{1}{\nu_A} \cdot \frac{dn_A}{dt} = k(t) \cdot \prod_i c_A^{n_A} \quad (6.1)$$

Generally, rate equations can either be formulated on mass or molar basis. In the context of hydroprocessing and hydrocracking of residue, mostly kinetics are calculated based on mass data [129]. When dividing Eq. 6.1 by the molar mass M_A and using the total mass m_T as reference system, the equation can be rearranged to Eq. 6.2, with ν_A as -1.

$$-\frac{dm_A}{dt} \cdot \frac{1}{m_T} = k(t) \cdot \left(\frac{m_A}{m_T}\right)^{n_A} \quad (6.2)$$

For vacuum residue conversion, Eq. 6.3 was obtained with ω_{VR} as the mass fraction of vacuum residue. Formed products are continuously removed from the reaction zone, while H_2 is constantly feed to the system ensuring an excess of H_2 as reactant. By ensuring excess of H_2 , the conversion reactions are unaffected by the H_2 concentration, as shown in Section 6.1.1.

$$-\frac{d\omega_{VR}}{dt} = (k_1 + k_2) \cdot (\omega_{VR})^{n_C} = k_{con} \cdot (\omega_{VR})^{n_C} \quad (6.3)$$

Analogue to the development of Eq. 6.3, for the desulfurization reactions, Eq. 6.4 was obtained.

$$\frac{d\omega_{H_2S}}{dt} = -\frac{d\omega_{S_{org}}}{dt} = k_S \cdot (\omega_{S_{org}})^{n_S} \quad (6.4)$$

For the temperature dependency of the reaction rate of a single reaction with only one reactant (A), Arrhenius established the following equation, known as the Arrhenius equation:

$$\frac{dm_A}{dt} = k_A \cdot m_A^n = k_0 \cdot \exp\left(-\frac{E_A}{RT}\right) \cdot m_A^n \quad (6.5)$$

In a bi-molecular reaction, the reaction velocity coefficient $k(T)$ corresponds to the proportion of collisions, leading to a reaction. The parameters k_0 and E_A are the

pre-exponential factor and the activation energy. The pre-exponential factor has a different physical meaning depending on the reaction molecularity. In case of a monomolecular reaction, the pre-exponential factor is also referred to as the frequency factor. A connection can be made with the rate at which bonds in a molecule are rearranged, which can also be understood as an oscillation frequency. In multimolecular reactions, the pre-exponential factor can be related to the impact factor, the number of collisions between molecules. In all cases, the unit of k_0 is also the unit of k . By taking the logarithmic of 6.5 the relationship 6.6 is obtained.

$$r_A = \ln\left(\frac{dm_A}{dt}\right) = \ln(k_A) + n \cdot \ln(m_A) = \ln(k_0) - \frac{E_A}{R} \cdot \frac{1}{T} + n \cdot \ln(m_A) \quad (6.6)$$

When further simplifying Eq. 6.6, the linear relationship Eq. 6.7 is obtained.

$$\ln(k_A) = \ln(k_0) - \frac{E_A}{R} \cdot \frac{1}{T} \quad (6.7)$$

6.1.4.3 Determination of kinetic parameters

The kinetic parameters were determined according to the procedure presented in the Section A.1. The factors $k_{\text{con}}(T)$ and $k_{\text{desulf}}(T)$ were determined by variation of the residence time and were derived as the slope of the corresponding reaction order as presented in Fig. A.1.

For the determination of the reaction order, the plots shown in Fig. 6.14 were prepared according to the method presented in Section A.1.

For both temperature levels presented in Fig. 6.14, the R^2 was minimal for the second order reaction, making this the appropriate choice for the global reaction order for the conversion reaction. With increasing residence time, the vacuum residue was cracked and the formed products reacted with H_2 . The rate is unaffected by H_2 concentration as discussed in Sectio 6.1.2. Though several publications report first order kinetics for conversion reactions with respect to the feedstock [220,222], also second order has been reported for heavy feedstocks [129,223]. According to Orochko et al. [223], at high H_2 partial pressure and excess of H_2 , hydrocracking reactions are reported to be irreversible reactions of second order with respect to the vacuum residue concentration.

For the desulfurization reaction order, the total sulfur removal from both the residue fraction and the oil fraction was used. When assuming the more complex mechanism

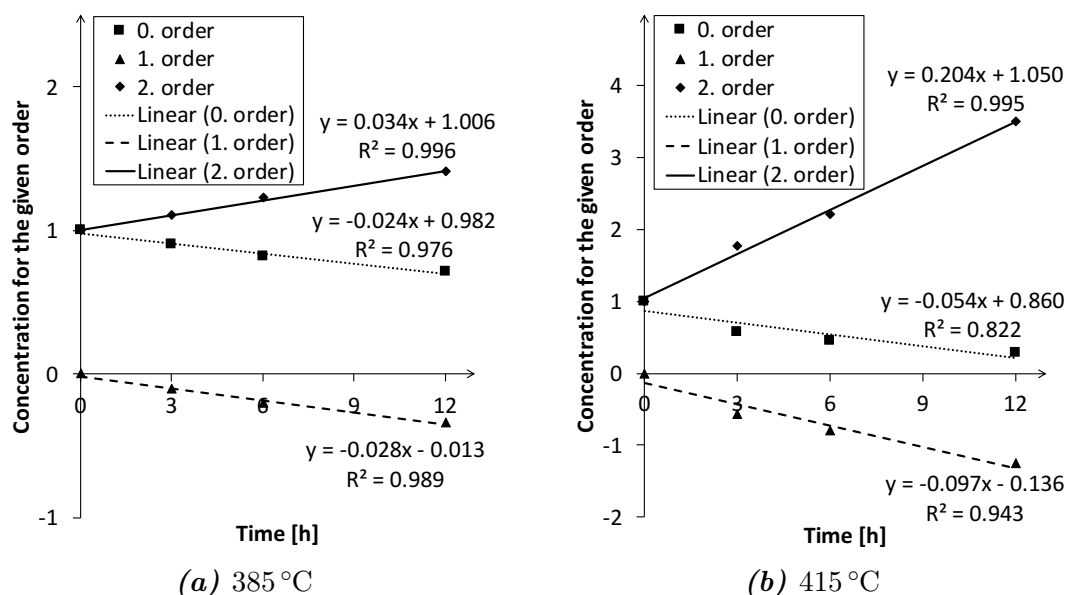


Figure 6.14: Determination of the reaction order for the conversion reaction at 385 °C and 415 °C

with two parallel HDS reactions, as presented in Section 6.1.4.1, the determination of the kinetic parameters led to implausible results. Analogue to the determination of the reaction order for the conversion reactions, the reaction order for the desulfurization was determined, as presented in Fig. 6.15.

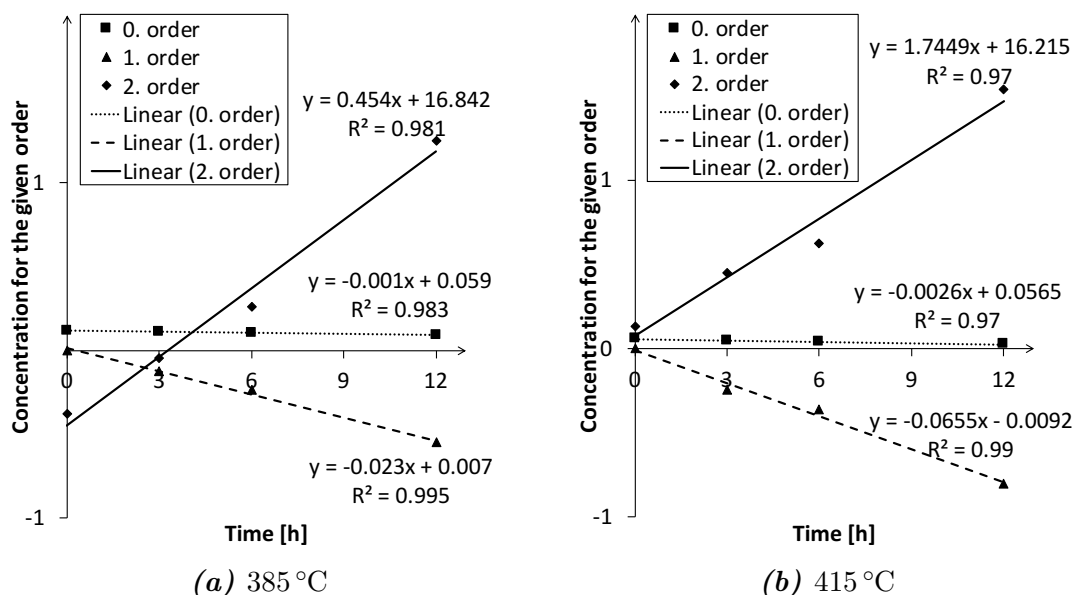


Figure 6.15: Determination of the reaction order for the desulfurization reaction at 385 °C and 415 °C

The linear relationship was found for a reaction order of one, which is in line with one of the three approaches described by Speight et al. [121] to be valid for the desulfurization of heavy feedstocks. Also Girgis and Gates [224] report a first order reaction rate for the desulfurization of a variety of different sulfur model compounds

representing the basic structure of the sulfur bonds present in vacuum residue. All experiments carried out at a pressure of up to 170 bar lead to the proposal of a first order reaction for thiophene, BT, DBT, as well as for two isomers of benzonaphthothiophene. Distillate products are also desulfurized with a reaction order of one according to Ohtsuka et al. [210].

After the reaction orders had been determined as two for the conversion reactions and one for the desulfurization reactions, the Arrhenius method was used for the determination of the activation energies E_A . Together with the logarithmic of the values for $k_{\text{con}}(T)$ and $k_{\text{desulf}}(T)$, which is needed for the determination of the reaction activation energy, E_A , $k_{\text{con}}(T)$, and $k_{\text{desulf}}(T)$ are presented for each investigated temperature level in Tab. 6.1.

Table 6.1: Values for the reaction rate coefficient for the conversion $k_{\text{con}}(T)$ and the desulfurization reactions $k_{\text{desulf}}(T)$ their logarithmic $\ln(k_{\text{con}}(T))$ $\ln(k_{\text{desulf}}(T))$

Temperature	$k_{\text{con}}(T)$	$\ln(k_{\text{con}}(T))$	$k_{\text{desulf}}(T)$	$\ln(k_{\text{desulf}}(T))$
385 °C	0.034	-3.384	0.023	-3.772
400 °C	0.096	-2.351	0.030	-3.507
415 °C	0.204	-1.591	0.066	-2.726
430 °C	0.515	-0.731	0.100	-2.303

Plotting the values for $\ln(k)$ over $1/T$ gave Fig.6.16.

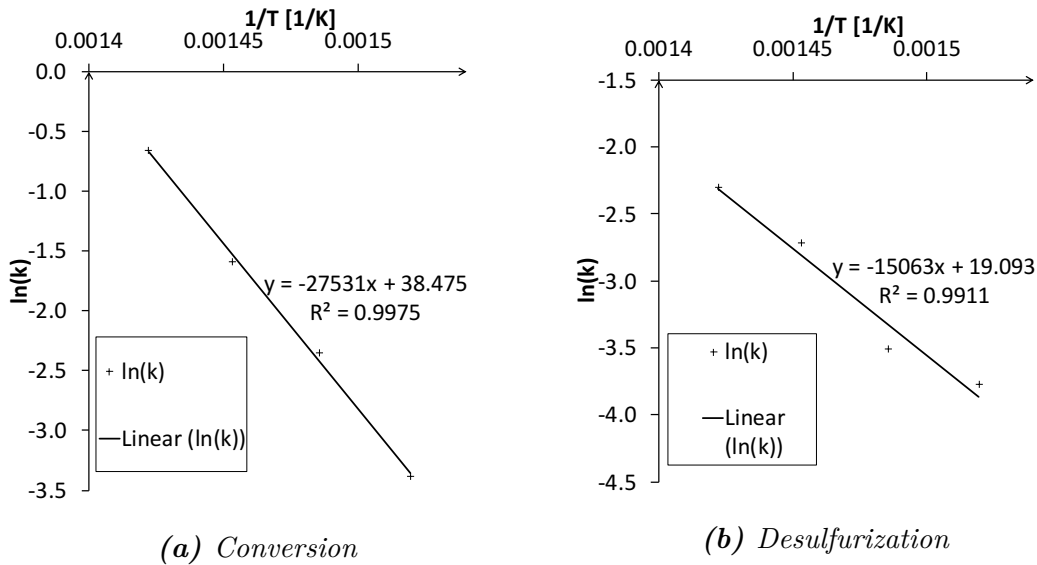


Figure 6.16: Determination of the activation energy for both the conversion reactions and the desulfurization by plotting $\ln(k)$ over $1/T$

The activation energy for conversion reactions was found to be 228.5 kJ and 132.9 kJ for desulfurization reactions. Similar activation energies for heavy oil and residuals are reported by a number of publications [209, 217, 225–227] and are summarized in Tab. 6.2. The activation energy for the conversion reactions is therefore almost twice

as high as for the desulfurization. The rate of reaction is more temperature sensitive for reactions with high activation energy. By choosing a low operation temperature, HDS reactions can be favoured, while limiting cracking reactions [228]. With the knowledge of the activation energies, desulfurization of this vacuum residue should be performed at lower temperatures than conversion of the vacuum residue. Similar results are known from industry and research [15, 173].

Table 6.2: *Literatur values for the activation energy E_A*

Author	E_A conversion	E_A desulfurization	Reference
Taghipour et al.	179.9 kJ/mol	n.a.	[226]
Del Bianco et al.	206.8 kJ/mol	n.a.	[217]
Kirshna et al.	224.8 kJ/mol	n.a.	[225]
Asgharzadeh Shishavan et al.	249.4 kJ/mol	n.a.	[227]
Frost and Cottingham	n.a.	136.0 kJ/mol	[209]
Browning et al.	uses more lumps	147.0 kJ/mol	[229]

Together with the reaction order obtained from Section 6.1.2, a kinetic expression for the conversion as well as for the desulfurization reaction can be formulated according to Eq. 6.8 with the parameters for k_0 and E_A as listed in 6.3. The rate expressions are formulated for weight fractions ω .

$$-\frac{d\omega}{dt} = k_0 \cdot \exp\left(\frac{-E_A}{RT}\right) \cdot \omega^n. \quad (6.8)$$

Table 6.3: k_0 and E_A for conversion and desulfurization

Reaction	k_0	Activation energy	Reaction order
Conversion	38.4 1/h	228.5 kJ/mol	2
Desulfurization	20.4 1/h	132.9 kJ/mol	1

k_0 has the unit 1/h in both cases (which is irritating on first sight because the order is different in both cases) because the rate expression is calculated for weight fractions.

6.1.4.4 Evaluation of the mechanisms and kinetic data

The rate expressions can be validated with a data set from experiments that were not used for finding the variables in the rate expressions. Calculated values are plotted against the experimentally obtained results in Fig. 6.17.

For residue conversion (top of Fig. 6.17) calculated values show good correlation with the experimental data. For 100 % accuracy, all dots would be on the angle bisector. Therefore, the closer data points are located to the angle bisector, the better the

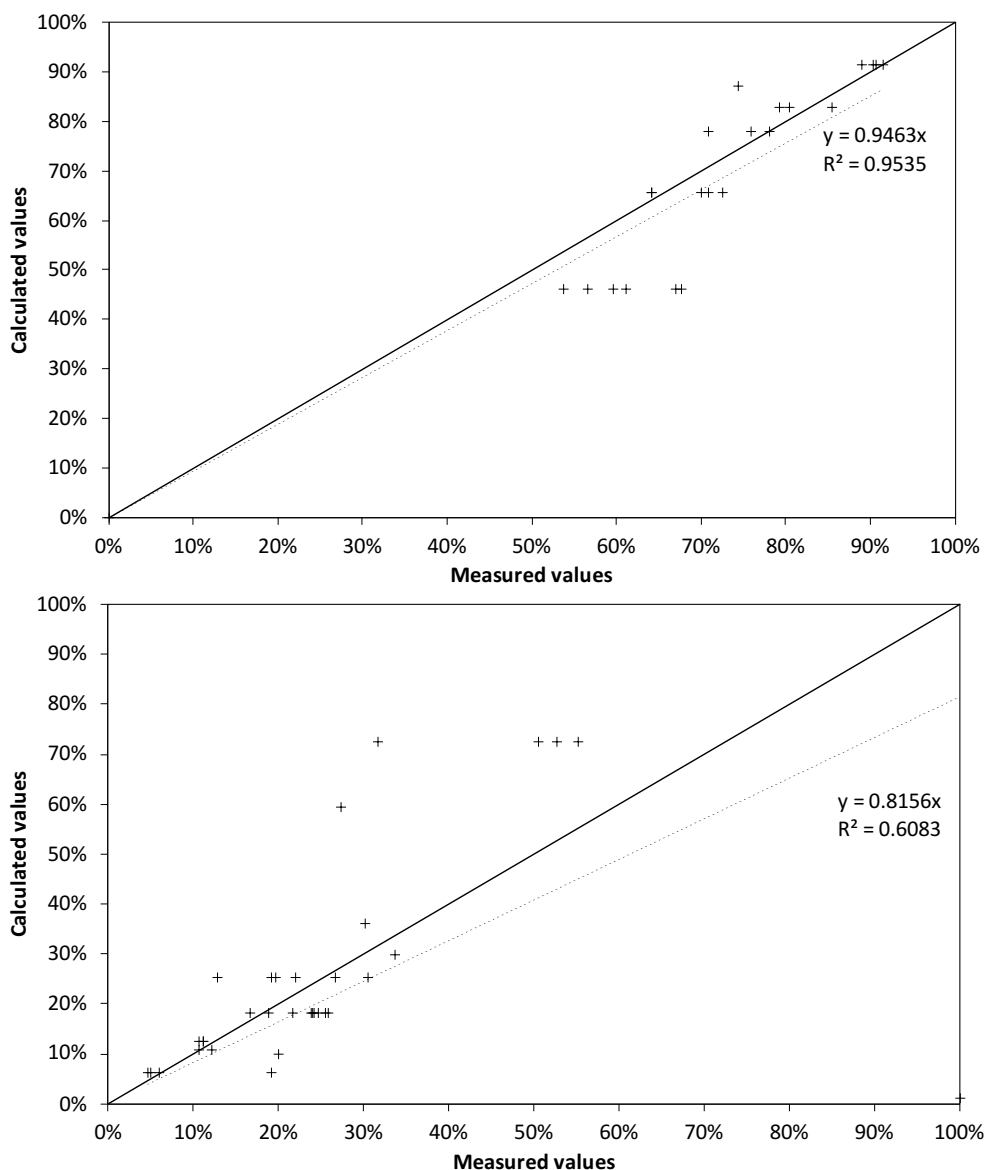


Figure 6.17: Determination of the accuracy of the reaction rate expressions for conversion (top) and desulfurization (bottom)

accuracy of the determined rate expression. For the HDS rate expression (bottom Fig. 6.17) the accuracy is very good at low degree of desulfurization. For predicted higher desulfurization (low sulfur content in the product, values below 2% remaining sulfur) accuracy is very poor. This poor accuracy may be attributed to the fact that the sulfur is released from very different structural molecules. The basic sulfur bonds occurring in vacuum residue are shown in Section 2.1.1. For example, the activation energies for the removal of sulfur from alkylated DBT is much higher than from a simple DBT [230]. Some sulfur bonds might break already during heating up as seen in the H_2S plot in Fig. 6.18. The concentrations for CH_4 and C_2H_6 (products indicating decomposition reactions leading to lower boiling products - conversion) stayed relatively constant over the whole experiment while the H_2S concentration

reached a maximum after 15 min and declined afterwards. Also, a significant amount of H_2S was detected in the product gas before the set-point temperature was reached, indicating that desulfurization reactions occurred already at temperatures below the set-point.

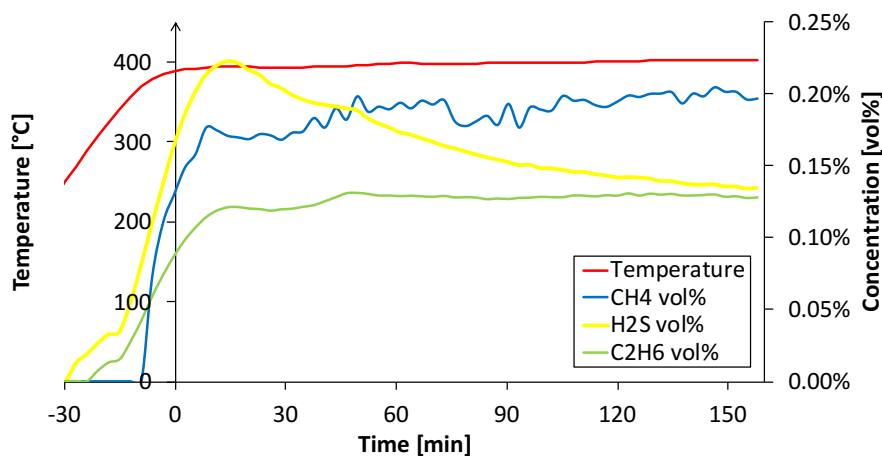


Figure 6.18: H_2S , CH_4 and C_2H_6 concentration measured in product gas for a 3 h experiment at 310 bar and 415 °C

Steric effects make some sulfur atoms more difficult to be hydrogenated and removed as H_2S than others [230]. With increasing residence time, the carbon matrix of the vacuum residue is converted, thus changing the structure and the accessibility of the sulfur atoms. This change in the carbon matrix together with the removal of easily accessible sulfur during the heating phase before start of the residence time, may be strong reasons for the inaccuracy of the rate expression model for predicted high degree of desulfurization. Therefore, several reasons exist, why the desulfurization of vacuum residue could not be put into a simple generic rate expression based on the obtained data, as it was the case for the conversion reactions. Also, several more complex models are reported in literature, based on the assumption of two competing first order reactions (which was also considered here as presented in Fig. 6.13). These competing reactions can be explained with the variety of different types of sulfur compounds in residua, each reacting with a different rate. Scott and Bridge found that for HDS of residuum oil, an overall first order kinetic expression could not represent the observations adequately, but a model of two competing first order reactions was of better accuracy [137]. As shown by Girgis and Gates, first, simple sulfur containing compounds are desulfurized with first order reaction rate. As the reaction evolves, these reactive sulfur compounds become depleted [224]. More stable sulfur species like DBT based structures, potentially also sterically hindered within a large complex asphaltene molecule, remain and the residuum will hold mainly the more difficult-to-remove sulfur [138]. This behavior corresponds very well with the

observed H_2S concentration plot in Fig. 6.18. The more complex mechanism, which was discussed here, based on Fig. 6.13, could also not represent the observed HDS reaction rate. A reason for this might be the influence of the conversion reactions on the rate of desulfurization, as discussed here. Cracking of the feedstock may enable removal of more complex sulfur in the vacuum residue, as discussed in Section 6.1.2. This assumption is supported by Fig. 6.19, where desulfurization of the feedstock is plotted over conversion.

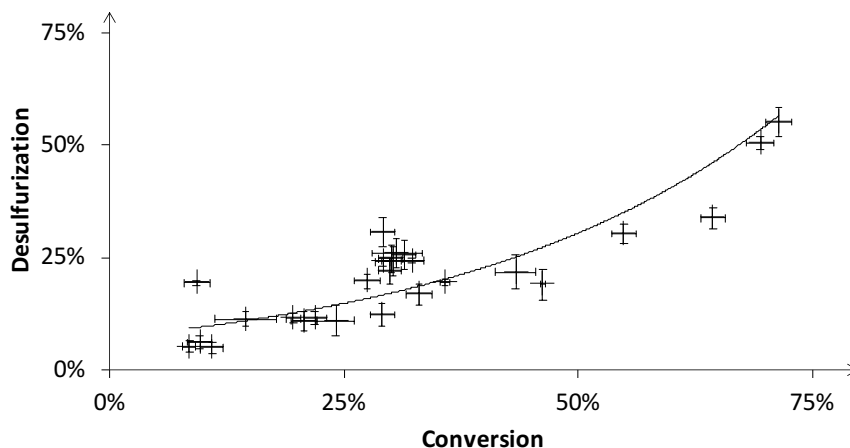


Figure 6.19: Desulfurization over conversion for experiments without a catalyst

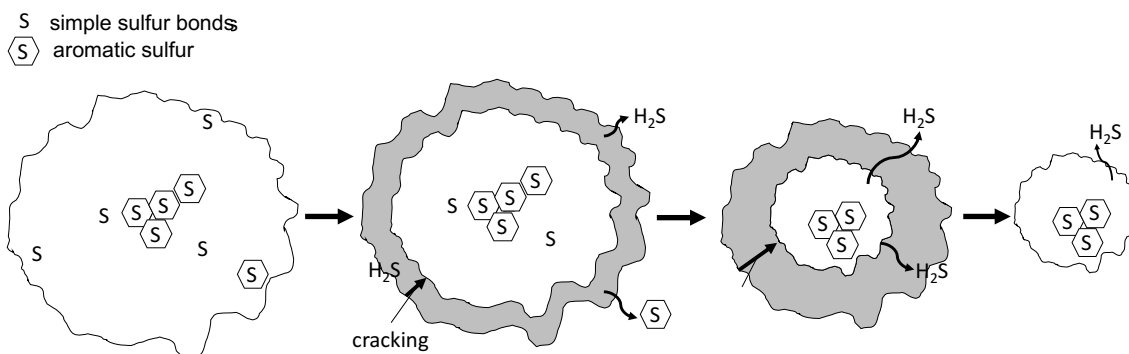


Figure 6.20: The authors understanding of the effect of cracking of the feedstock on the desulfurization, depicted on the example of a colloid of asphaltenes and maltenes. The boundaries between asphaltene and maltene molecules are not displayed. In the grey area cracking reactions have destabilized the carbon matrix

From Fig. 6.19 it becomes clear that without the use of a catalyst, vacuum residue desulfurization is closely linked to the cracking and conversion of the feedstock. In Fig. 6.20 the effect of cracking of the feedstock on the desulfurization is depicted on the example of a colloid of asphaltenes, as it is explained in Section 2.1.2. In the depicted colloid, boundaries between single molecules are not represented and the focus is put on the authors understanding of how cracking leads to access to sulfur. HDS is therefore closely linked to the cracking of the feedstock. The aromaticity

and stability increases from the outer rim of the colloid to the center. Finally, only very stable aromatic sulfur remains in the asphaltenic core of the colloid.

For the development of a more precise model, taking into account the different bond types and steric hindrances of sulfur, as well as the influence of cracking reactions on the desulfurization, a more precise knowledge of the vacuum residue composition and sulfur distribution would be needed, as well as more data, to build such a complex model on [138]. Here, the global kinetics and the retrieved activation energies are precise enough for the identification of set of process parameters, that can be used as basis for the catalyst screening in Section 6.2.

Table 6.4: *Choice of process parameters to achieve good desulfurization and high conversion*

Process parameter	Set-point
Pressure	310 bar
H ₂ throughput	1200l/h · kg
Residence time	3 h
Temperature	400 °C

Concluding from the investigations without catalyst, the set of process parameters, summarized in Tab. 6.4, was chosen for the investigations in the following Sections 6.2 - 6.4.

6.2 Catalyst screening

In Section 6.1 investigations on HDS of vacuum residue showed that catalysts or additives are necessary to desulfurize the feedstock, if conversion is meant to be kept at a minimum, thus increasing selectivity towards desulfurization. In this section, the screening of different catalysts and additives is discussed. Several, mostly cheap catalysts and additives, often known to be active in coal liquefaction or HDS of model compounds, were chosen to be tested for the HDS of vacuum residue. The screening displayed in this section was carried out at 400 °C, 310 bar, 1200 l/h per kg vacuum residue and a residence time of 3 h. All experiments were carried out with 3 wt% catalyst, except for the experiment with SCW, where 100 wt% were added.

Table 6.5: Results from catalyst screening

Catalyst	Conversion	Residue desulfurization	Oil desulfurization
-	24.1%	2.3%	46.5%
NaOH	26.3%	8.6%	55.6%
Na ₂ CO ₃	24.2%	3.3%	46.4%
HOK	23.6%	3.7%	43.3%
MgO on bio-char	15.0%	5.9%	47.0%
Fe ₂ O ₃ on bio-char	15.0%	6.3%	42.9%
MoO ₃	18.6%	5.0%	44.8%
MoO ₃ on HOK	23.5%	9.7%	46.0%
MoS ₂ on HOK	27.6%	17.0%	33.7%
SnC ₂ O ₄	23.8%	6.2%	42.9%
NiMoO ₄	30.9%	39.6%	50.1%
WS ₂	18.4%	8.9%	43.2%
Raney Nickel	15.6%	18.3%	75.6%
Bauxit	18.4%	12.2%	47.3%
SCW	30.2%	-2.5%	44.1%
Catalyst B14	34.8%	63.8%	65.4%

6.2.1 Evaluation of the catalysts screening

The tested catalysts and additives are comprised of cheap adsorbents like Na₂CO₃ and HOK as well as expensive hydrotreating catalysts like NiMoO₄. The results from the screening of the catalysts are interpreted in the following Subsections 6.2.1.1 and 6.2.1.2 according to the characteristics found in the oil and residue phases.

6.2.1.1 Residue fraction

With respect to the aim of residue desulfurization at low conversion, for all performed experiments the degree of residue desulfurization and the conversion are plotted in

Fig. 6.21. There are two data points that strongly deviate from the rest in terms of desulfurization of the residue fraction.

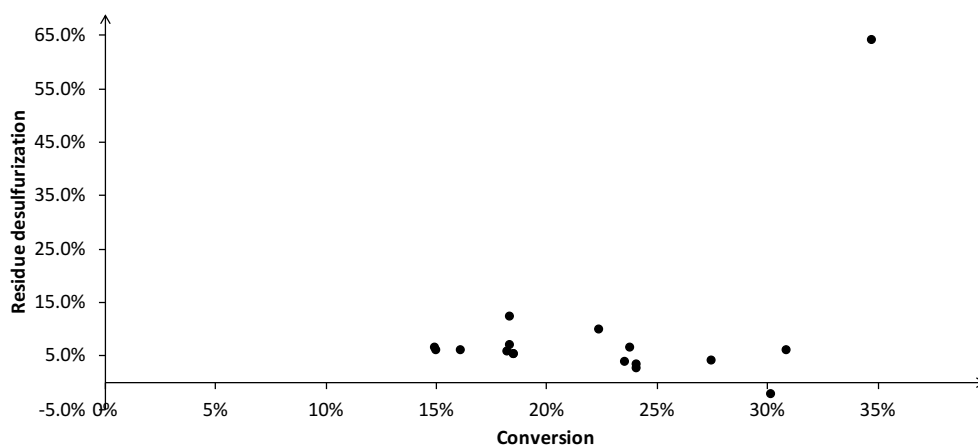


Figure 6.21: Conversion and residue desulfurization for the tested catalysts

The two catalysts / additives that led to these extreme results are catalyst B14 and supercritical water (SCW). While SCW increased the sulfur content in the residue, resulting in a negative desulfurization, catalyst B14 achieved an extremely high rate of desulfurization of above 60%. In order to understand the mechanisms behind these two severe influences on desulfurization, both SCW and catalyst B14 have been the subject of very intense investigations displayed in Sections 6.3 and 6.4. The other catalysts and additives with poor desulfurization results are only discussed briefly here. Removal of sulfur with alkali species from heavy feedstocks was demonstrated by Gordon et al. [231]. The use of NaOH and Na₂CO₃ did not lead to any comparable results and the desulfurization stayed far below what was observed for sodium by Gordon et al. HOK and its doted, catalytically improved forms (doted with MoO₃ and activated with DMDS) are well known as additive in the liquefaction of coal as well as for the conversion of heavy oils in the VCC process as reported in Section 2.3 and Chapter 3. HOK alone predominantly acts as asphaltene catcher by simple physical adsorption (reduction of asphaltene content from 15.4% without HOK to 12.1% with HOK) which then also reduces the sulfur content of the residue as displayed in Fig. 6.41 (b). MoO₃ on the surface of the HOK did not significantly further reduce the asphaltene content. Presulfiding the catalyst to form MoS₂ further reduces asphaltene content. The dotting of the carbon with MoO₃ increased the desulfurization activity from 3.7% to 9.7% and presulfiding further improves the performance to 17.0%. The increase in desulfurization activity by presulfiding molybdenum catalysts is well known and presents state of the art technology in HDS processes [232]. For the desulfurization of the vacuum residue

the presulfided supported molybdenum catalyst does still not reach sufficiently high desulfurization activity. SnC_2O_4 reacts to SnO_2 and CO_2 under the conditions in the reactor. The residue desulfurization stayed far below 10%. NiMoO_4 has been shown to be very active in HDS of model compounds as reported in Chapter 4 and therefore, it was tested on vacuum residue. Nearly 40% desulfurization of the residue was found not sufficient enough to perform further investigations on this catalyst. Also, Raney Nickel, as one of the first commercially applied HDS catalysts, was tested because of its reported good desulfurization ability for complex thiophene based structures [233]. The poor results on vacuum residue are most probably attributed to the complex residue structure and the nature of the asphaltenes and maltenes as presented in the Section 2.1.2. Bauxit was tested as carrier material by Iannebello and Marengo [234, 235]. Compared to HOK it showed a superior desulfurization activity while converting less vacuum residue to lower boiling products. Bio-chars doted with iron and magnesium oxides did not show any significant desulfurization activities compared with simple HOK. Unsupported MoO_3 showed worse results than HOK, but presulfiding the catalyst could possibly improve the performance.

Overall, only catalyst B14 showed good desulfurization activity on the vacuum residue while all other catalysts stayed far behind the target of yielding a desulfurized residue containing less than 0.5% sulfur.

6.2.1.2 Oil fraction analysis

Though desulfurization of the oil fraction was not the aim of this thesis, some important interpretation for the residue desulfurization can be derived from analysis of the oil fraction. The oil phase was in all cases desulfurized to far higher extent than the residue and ranges between 40% and 50% desulfurization (except for the experiments where DMDS was added, and when catalyst B14 is used). In contrast to the residue, oil can be analyzed in a GC/MS to identify the sulfur containing compounds. GC/MS analysis were performed as explained in Section 5.4.2.3. The obtained chromatograms of the oil fractions are very similar regardless of the catalyst. For several catalysts, the oil fraction chromatograms are displayed in Fig. 6.22. Though some peaks vary in size, indicating a slightly different distribution of the product components, the overall compositions are very similar. The chromatograms are dominated by hydrocarbon peaks of which a list with retention times is given in the Appendix A. In order to display also sulfur compounds, only present to smaller extent (especially DBT), both heavy and light oil fractions were analyzed separately. In Fig. 6.23 the chromatograms of the light oil fraction, obtained from the CHPS

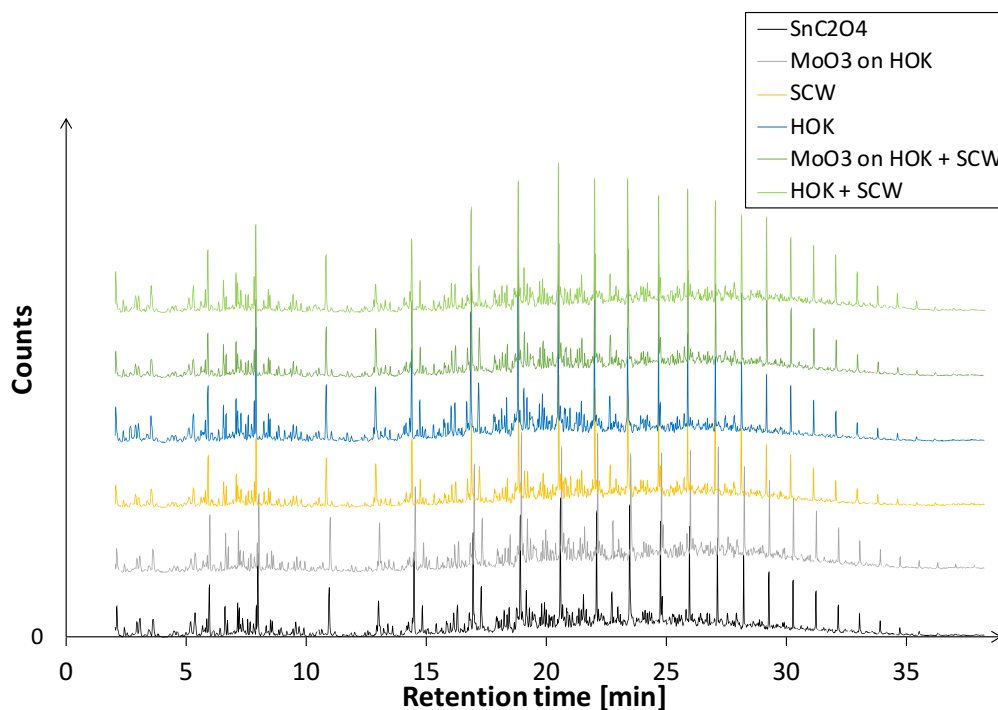
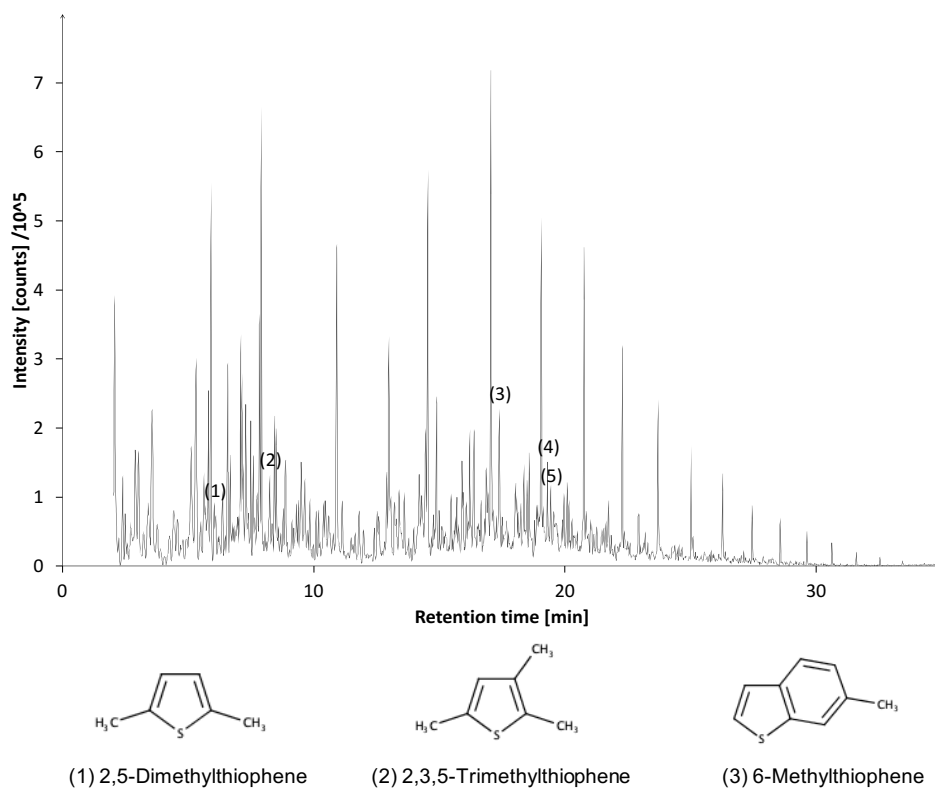


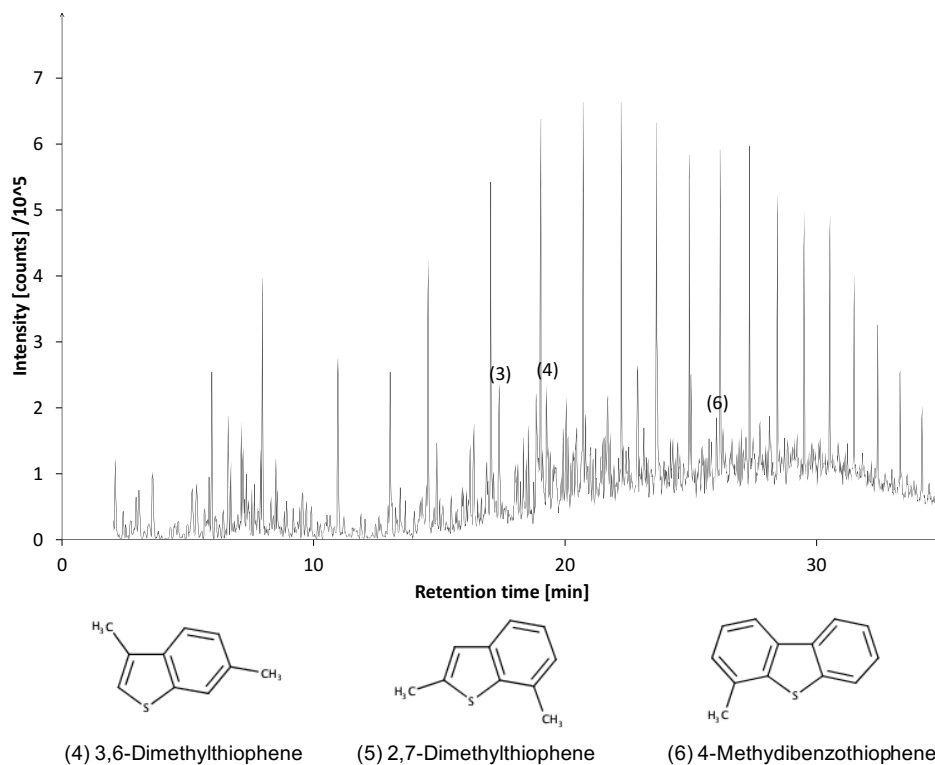
Figure 6.22: Comparison of chromatograms obtained from oil fractions from experiments with different catalysts

(6.23 (a)) and the heavy oil fraction, obtained as distillate from the hydrogenation residue (6.23 (b)) are displayed, both from an experiment with HOK at 3 h residence time, 400 °C and 310 bar. The identified compounds include derivatives from thiophene, BT, and DBT. DBT was only detected in very small concentrations in the heavy oil fraction, while methylated BT (especially, methylated in 2 and 4 position of the benzene ring) displayed the majority of the sulfur compounds.

The refractory sulfur compounds found in the oil most probably remained after cracking of asphaltenes and maltenes. Due to their very stable character, they were still found in the product to large extents. Less stable chemical compounds like sulfides were not found in the product oils indicating that the process conditions, regardless of the chosen catalyst or additive, enabled good removal of these species. Alkylated BT and DBT were found in all the low boiling product fractions regardless of the applied catalyst. The only exception was the product oil from the experiment performed with catalyst B14 which is discussed separately in Section 6.4. Presence of these most refractory sulfur containing structures in the product oils shows that none of the applied process conditions or catalysts could perform real HDS reactions to a higher extent. Thermally controlled cracking reactions most probably led to breaking of the maltene and asphaltene macro molecules releasing stable BT and DBT based molecules. These were carried out of the reaction zone during the experiment,



(a)



(b)

Figure 6.23: GC/MS chromatograms of the light (a) and heavy (b) oil fractions and the identified sulfur species for the experiment with HOK and the process conditions from parameter set 1

because of their low boiling point, compared to the maltenes and asphaltenes. The oil was lower in total sulfur content because the high sulfur asphaltenes and maltenes remained in the residue. Concluding from the chromatograms, hydrogenated cracking products were mostly long chained (and branched) hydrocarbons with no sulfur. Sulfur was only present in methylated thiophene, BT, and DBT, as far as it could be detected. The presence of these sulfur species leads to the conclusion that the tested catalysts were not suitable for HDS of high sulfur vacuum residue (except for catalyst B14). The difficulty lies within desulfurization of the most refractory BT and DBT compounds, especially desulfurization of the alkylated derivatives. It is known that the DDS route described in Section 2.4.3 is often hindered sterically by alkyl groups on the benzene rings adjacent of the sulfur atom in BT and DBT structures [236,237]. Since BT and DBT are mostly built into the macro molecular structure of the asphaltenes and maltenes, the DDS route could not lead to low sulfur levels (at the given reaction conditions). Catalysts yielding oils with high levels of alkylated BT and DBT presumably did not pursue the HYD route.

Desulfurization of the oil fraction belongs to state of the art technologies as reported in Chapter 3 and therefore, sulfur in the oil fraction is not further discussed in this thesis.

6.3 Experiments with supercritical water

From the catalysts screening presented in Section 6.2, SCW was identified as additive that has a strong effect on the conversion of the vacuum residue. Also, in literature it is reported that SCW supports desulfurization reactions [102, 182, 183, 186, 238–240]. Though several publications can be found that apply SCW either for desulfurization or for conversion of residual oil fractions, the addition of SCW to HDS slurry conditions has not been examined. The very complex structure of the asphaltenes and resins, together with the colloids they form, shown in Section 2.1.2, is significantly the reason for the difficult removal of sulfur from vacuum residue. The characteristics of SCW could support HDS with several advantages:

- SCW dissolves organic compounds as reported in Section 2.3.1. The colloids of asphaltenes and resins could possibly be dissolved in SCW, thus enabling better accessibility of the sulfur atoms. This effect has been reported by Khan et al. [241, 242]. For catalytic HDS this could allow the catalyst as well as H_2 to be supplied directly to the sulfur atoms of the aromatic core of the asphaltenes and resins.
- Sulfur in vacuum residue is mostly present in thiophenic, benzothiophenic or dibenzothiophenic structures. These structures are further integrated into aromatic structures of resins and asphaltenes and often have alkyl chains attached, stabilizing the sulfur. Destabilization of the C-S bonds can be achieved by rupture of these alkyl chains or by destruction of the aromatic core. Cracking of residual constituents with SCW is well known [239, 240, 243–245] and may display a path to improved desulfurization when combining catalysts or additives with SCW at high H_2 partial pressure. Bronsted and Lewis acid sites are active in asphaltene destruction [246] and can be supplied by SCW [247]. It has been suggested by Ogunsola et al. [238] that protons provided by SCW possibly promote saturation of heterocycles, destabilizing the heteroatom in the ring. This could accelerate sulfur elimination as well as opening of heterocyclic rings which is comparable to hydrolysis [238].
- SCW has good heat transfer abilities as reported in Section 2.3.1. This may improve the temperature control and enable a very homogeneous temperature distribution.

In a first step, the effect of SCW on conversion and desulfurization of the vacuum residue was analyzed at different temperature levels and compared with the reference

case without additive. In a second step, at a given temperature, the effect of combining SCW with HOK and with HOK doted with molybdenum was investigated. Model compounds representing the sulfur structures in the residue were chosen in order to see the HDS activity on different sulfur structures. In a third step, the same experiments from the second step were performed on vacuum residue to see in how far the findings from model compounds represent the real behavior of vacuum residue.

6.3.1 Experimental procedure

For the experiments with SCW the H_2 flow had to be reduced to 300 l/h. Higher H_2 volume flows through the reactor carried too much of the supercritical mixture directly out of the reactor when the volume expanded at the critical point. Reducing the H_2 flow to 300 l/h could not completely eliminate that water was carried out of the reaction zone. In order to compensate this loss of water, 1.5 ml/min was constantly pumped into the reactor (pump was switched on when the critical point was exceeded) additionally to the 500 ml of water that were introduced into the reactor before the start of the experiment. All experiments in this chapter were carried out at 310 bar and a residence time of 3 h. When cooling down the reactor and depressurizing it, several test runs showed that there are two crucial aspects to be aware of. Both possible paths for cooling and depressurization are displayed in Fig. 6.24.

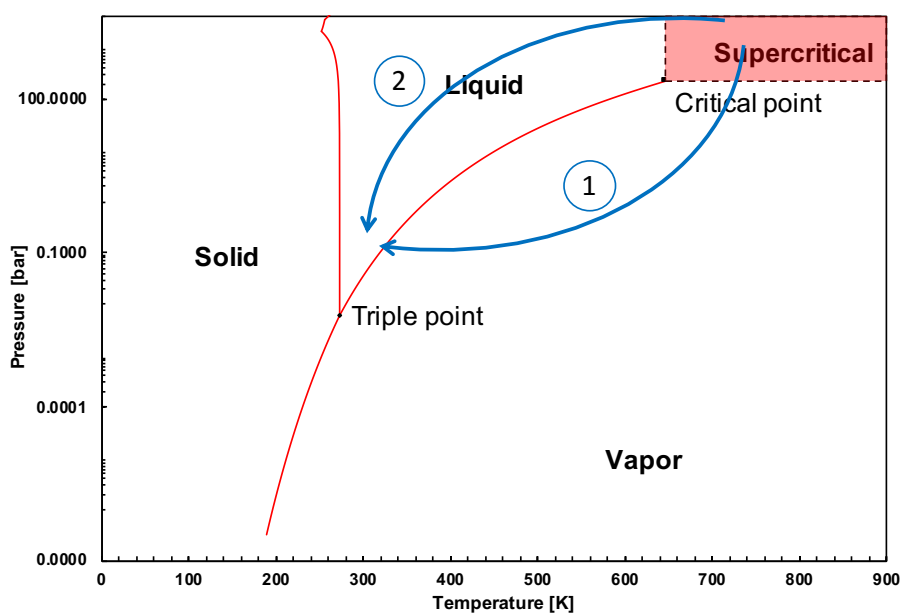


Figure 6.24: Paths for cooling and depressurization with SCW

- 1. When depressurizing the reactor too quickly in order to remove all water in vapor state from the reactor to collect it in the CHPS, coke formation was observed. This is attributed to the fact that the H_2 partial pressure became too low, while the temperature still enabled good conditions for cracking. The formed radicals could not be saturated with H_2 and coking occurred.
- 2. When cooling the reactor to ambient temperature before all water is removed, the supercritical mixture of water and vacuum residue formed a foam. Water is finely dispersed in the vacuum residue and because of the high viscosity of the vacuum residue, water is "trapped" in the vacuum residue. When heating the mixture to above 100°C to lower the viscosity of the vacuum residue and separating water from the organic phase, water evaporates inside the vacuum residue and the foam expands rapidly. The result is shown in Fig. 6.25.



Figure 6.25: Foam produced from SCW and vacuum residues

The procedure chosen in order to not encounter any of the mentioned problems with SCW, was a combination of quick cooling and depressurization. The reactor was cooled to a temperature of 200°C and maintained there during depressurization. At ambient pressure, a H_2 flow through the system was maintained for several min-

utes until all water was removed from the reaction zone. Only when all water was removed, the temperature was lowered further.

6.3.2 Effect of temperature

The influence of temperature on SCW HDS was investigated between 385 °C and 430 °C. With increasing temperature, the rate of conversion reactions accelerated (from 9.2% to 64.4% with no SCW) and more low boiling products were formed as also well known from literature [248–250]. SCW increased this rate of conversion to 77.2% at 430 °C as shown in Fig. 6.26a which is consistent with findings from literature [245, 251, 252]. Decomposition of maltenes showed a quite linear increase with rising temperature, while for asphaltenes an exponential increase in conversion could be observed as displayed in Fig. 6.26b. Both the decomposition of asphaltenes and maltenes was enhanced by SCW, which agrees with the the assumptions derived from Fig. 6.26a that SCW enhances the rate of cracking reactions. On desulfurization reactions, SCW had a negative effect. For all investigated temperature levels the desulfurization with SCW stayed below the desulfurization without addition of SCW as shown in Fig. 6.26c. With rising temperature the concentration of sulfur in the residue increased (from 5.8% to 7.0%) as shown in Fig. 6.26d, indicating that SCW is incapable of supporting the removal of sulfur from highly complex residue fractions. Residual constituents were partly cracked (higher CH₄ production observed during SCW experiments as shown in Fig. 6.31c) leading to higher conversion but the sulfurous core of the residual molecules remained unconverted leading to an increase in sulfur level in the remaining residue fraction. This sulfur containing residual core is difficult to desulfurize due to steric hindrance of the sulfur atoms as well as the stability of predominantly present alkylated BT and DBT based sulfur structures [24, 39]. The observations from the variation of temperature also support the assumed mechanistic pathway displayed in Fig. 6.30. SCW supports cracking reactions but not desulfurization, leading to refractory sulfur containing molecules found in the oil fraction as well as a high sulfur content in the residue fraction.

6.3.3 Combination of catalyst and SCW

The findings from the variation of the temperature showed that SCW increased rupture of C-C bonds (cracking) and enabled better decomposition of very stable and highly complex asphaltene structures. An improved desulfurization activity

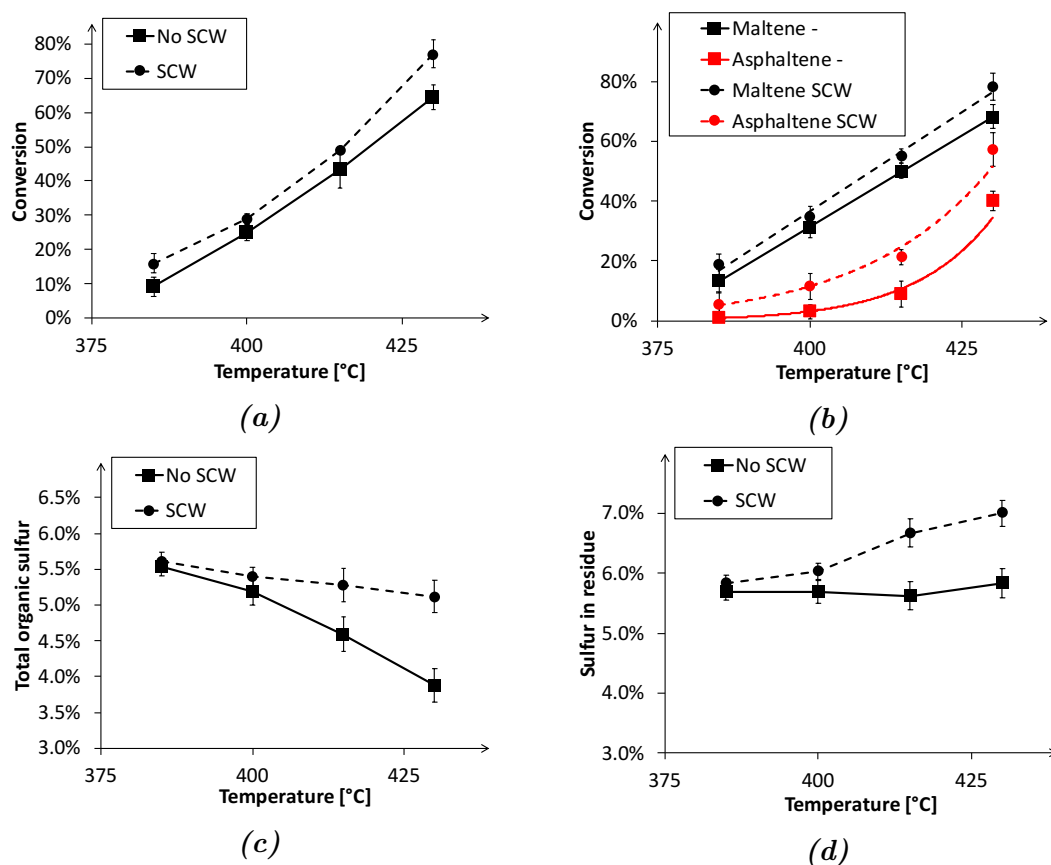


Figure 6.26: Influence of temperature on the (a) conversion reactions, (b) conversion of asphaltenes and maltenes, (c) total organic sulfur content and (d) sulfur content in the residue fraction for experiments with SCW in comparison with no additive

could not be observed. Combination of SCW and additives or catalysts may give better results because of the capability of SCW to dissolve the asphaltenes and maltenes fractions, thus giving the catalyst better possibilities to come into contact with to the sulfur atoms bonds in the core. Experiments with model compounds

Table 6.6: Performed experiments for SCW combinations

	Cat. / Additive	SCW	H ₂ flow [l/h]	Repetitions
Model compounds	-	no	600	2
	-	yes	300	2
	HOK	no	600	2
	HOK	yes	300	2
	Mo-cat.	no	600	2
	Mo-cat.	yes	300	2
Vacuum residue	-	no	600	3
	-	yes	300	3
	HOK	no	600	2
	HOK	yes	300	2
	Mo-cat.	no	600	2
	Mo-cat.	yes	300	2

representing the sulfur containing structures as well as with high sulfur vacuum residue were performed at 400 °C. SCW was tested together with HOK (additive)

and a molybdenum-doped HOK (catalyst). The performed experiments are listed in Tab. 6.6. A pressure of 310 bar, the temperature of 400 °C and a residence time of 3 h was chosen for all experiments.

6.3.3.1 Investigations on model components

Several researchers have reported improved desulfurization results with SCW on model compounds [182, 186, 238, 239] and therefore experiments were performed with model compounds representing sulfurous species also found in vacuum residue molecules. In Fig. 6.27 the results from the experiments with model compounds performed at 400 °C, 310 bar and 3 h residence time are summarized. The least

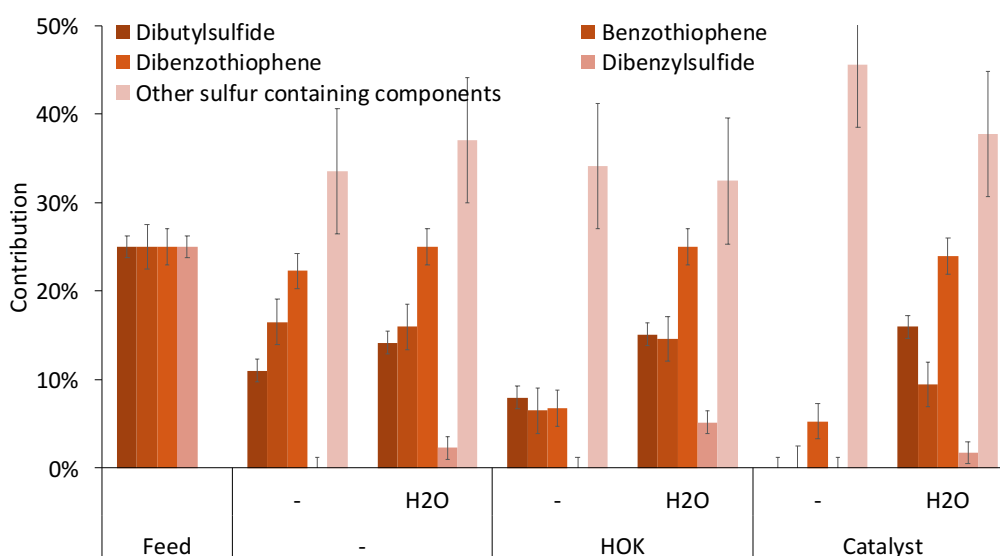


Figure 6.27: Results from experiments with model components

stable component dibenzylsulfide was removed completely without additive or catalyst while for a significant removal of more stable components DBT and BT the addition of HOK or the Mo-catalyst was needed. The most stable component DBT was not completely removed during any experiment performed in this study. The order of stability (DBT > BT > dibutylsulfide > dibenzylsulfide) is well known from literature and corresponds with the obtained results [175, 182]. For all performed experiments, new sulfur containing molecules were formed indicating that cracking and recombination occurred. Addition of SCW decreased desulfurization of the model compound mixture for all performed experiments. The reason for this is most probably the H₂ flow through the system. The mixture of diesel and model compounds was gradually removed from the reaction zone after the critical point was exceeded. The model compounds were not exposed to the reaction conditions throughout the

complete residence time of the experiment and therefore desulfurization results were lower than without addition of SCW where the model compounds were exposed to the reaction conditions throughout the whole 3 h. This reveals the difficulty encountered when operating a semi-continuous or continuous reactor with SCW. Though the experiments with SCW could not show a positive effect on the desulfurization, experiments with HOK and the Mo-catalyst exhibited relatively high rates of desulfurization of 41.6% and 49.0% respectively. Especially, the experiments with the Mo-catalyst removed almost 100% of the very stable DBT, indicating this catalyst should also be very active in desulfurization of vacuum residue.

6.3.3.2 Investigations on vacuum residue

In contrast to the findings from the model components, application of the same process conditions, catalysts, and additives on vacuum residue did not show a clear picture. Desulfurization and conversion results are presented in Fig. 6.28. While

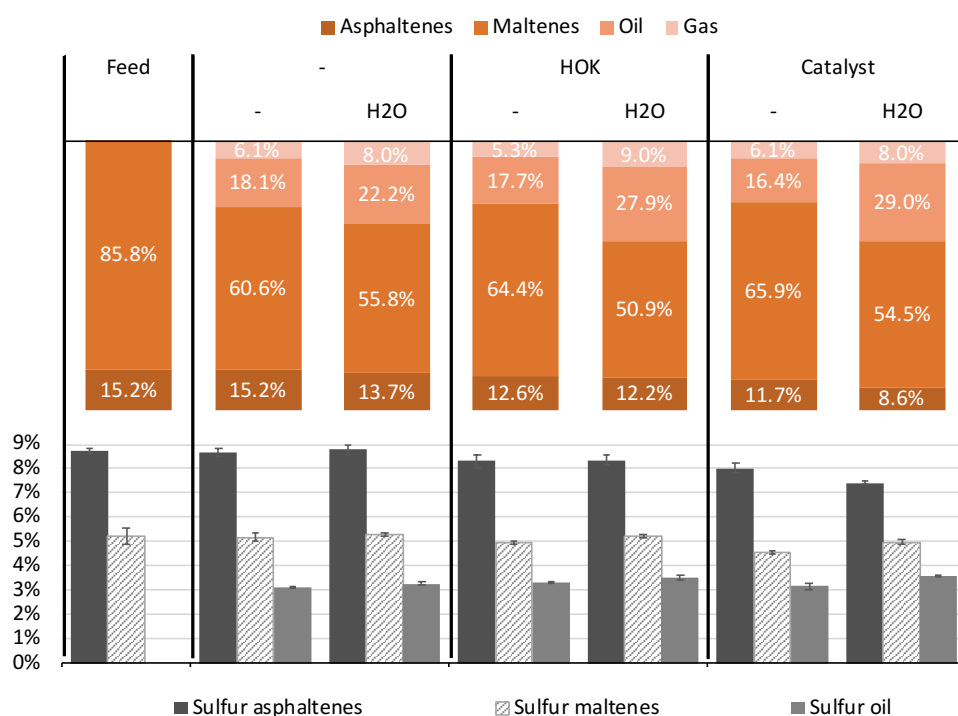


Figure 6.28: Results from experiments with crude oil based vacuum residue; Top: product fractions asphaltenes, maltenes, oil and gas; Bottom: the sulfur distribution among the fractions

the increase of conversion by addition of SCW could clearly be shown (no catalyst: 24.1% to 30.2%, HOK: 23.6% to 36.6% and Mo-catalyst: 22.5% to 37.0%), for the desulfurization of the residue, no obvious effect could be identified. The sulfur level in the asphaltenes was only slightly affected by the Mo-catalyst (Feed-Vacuum

Residue (VR): 8.9%, no catalyst: 8.7%, HOK: 8.4% and Mo-catalyst: 8.0%) but could be reduced further by combination with SCW (SCW-Mo-catalyst: 7.4%). Sulfur in the maltenes fraction could be reduced by the addition of HOK and the Mo-catalyst (Feed-VR: 5.3%, no catalyst: 5.2%, HOK: 5.0% and Mo-catalyst: 4.5%) but combination with SCW decreased this desulfurization of the maltenes fraction (SCW-no catalyst: 5.3%, SCW-HOK: 5.2% and SCW-Mo-catalyst: 5.0%). This contrary effect may result from conversion of asphaltenes to maltenes while leaving the sulfurous core intact when adding SCW, thus contributing to the sulfur in the maltenes fraction. The total degree of desulfurization was far lower than observed for

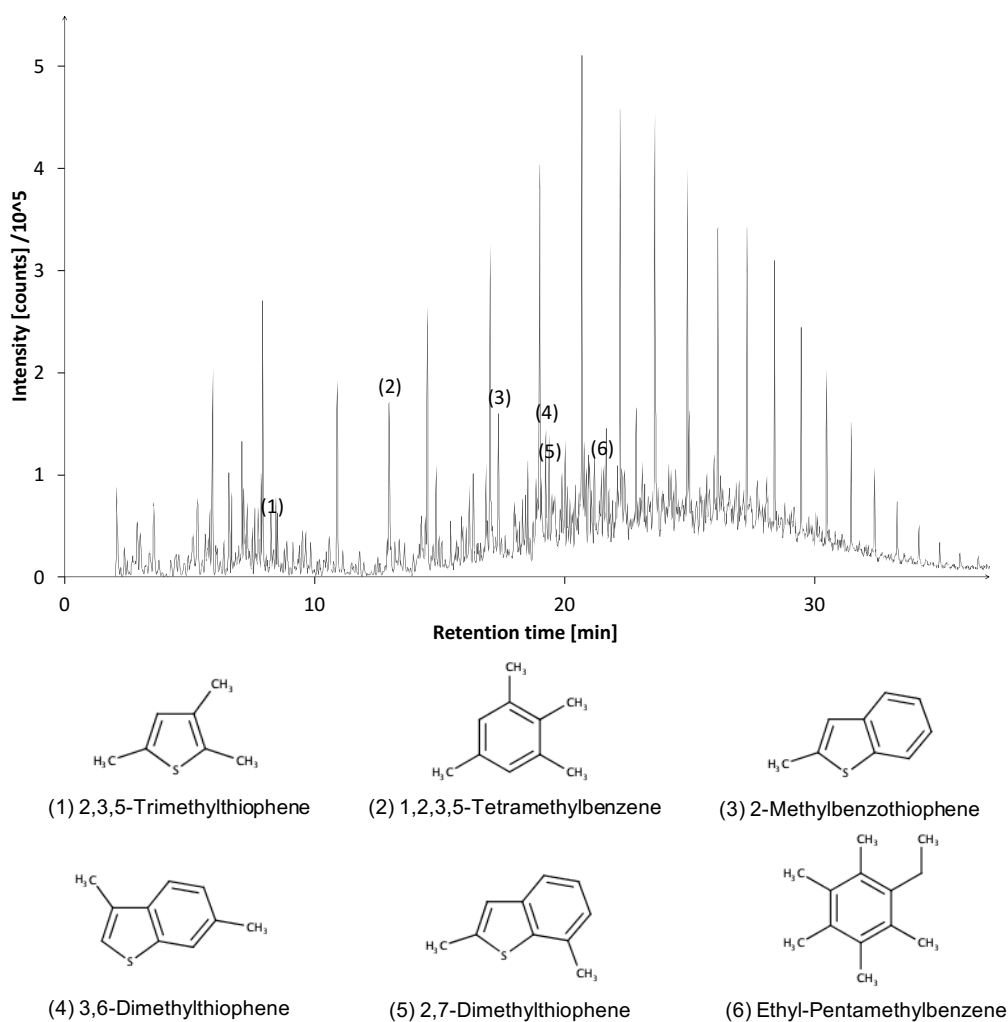


Figure 6.29: GC/MS analysis of the oil fraction obtained from an experiment with SCW and selected identified molecules showing the sulfur and aromatic character of the product oil

the model components. Though C-S bonds in model components, especially DBT, and BT also occur in vacuum residue, the complex structure of asphaltene-maltene colloids cannot be represented by the model components dissolved in diesel. Steric effects, colloidal structure and stability of the asphaltenes and maltenes display

the reason for the difficult desulfurization of vacuum residue according to literature [39,121,253]. The addition of SCW may support breaking this complex agglomeration of residual constituents, dissolve asphaltenes and resins separately as described by Khan et al. [241,242]. Since SCW only seems to support cracking reactions, asphaltenes were converted to maltenes with high sulfur content. Consequently, the residue (composed of maltenes and asphaltenes) presented high sulfur content. Further cracking produced less complex, lower boiling components also containing stable sulfur compounds, as revealed by GC/MS analysis of the product oil and presented in the Fig. 6.29. Refractory BT derivatives were found in the product oils from experiments with SCW. Selected molecules identified in the oil fraction that resulted from SCW cracking of the vacuum residue are displayed in Fig. 6.29. Cracking of the complex feedstock constituents reduces complexity and stability of sulfur containing molecules. The author's understanding of the mechanistic pathway of the asphaltene decomposition with SCW is displayed in Fig. 6.30. Dimethyl-BT and benzene derivatives are both products from cracking reactions identified in the product oil fraction as displayed in Fig. 6.29.

6.3.3.3 Gas phase analysis

The gas composition of the product gas supports the proposed reaction path and is presented in Fig. 6.31. The H_2S release over time gives information on how the desulfurization reaction rate changes throughout the residence time while CH_4 and C_2H_6 are a measurement for the decomposition reactions. Desulfurization of the model compounds without addition of SCW took place in the early stages of the residence time as shown in Fig. 6.31a while CH_4 and C_2H_6 were not detected in the product gas (no cracking of the model compounds).

For crude oil based vacuum residue, the rate of desulfurization (H_2S) as well as decomposition (CH_4 and C_2H_6) was steady over the complete residence time when no SCW was added as shown in Fig. 6.31b - 6.31d. This difference in H_2S release observed for model compounds and vacuum residue underlines the increased complexity in desulfurization of vacuum residue compared to model compounds. The constant release of CH_4 and C_2H_6 throughout the whole residence time indicates that cracking reactions occurred parallel to desulfurization. In contrast to the the comparably simple model compounds, these parallel occurring desulfurization and cracking reactions indicate that more stable sulfur was made accessible while the complex asphaltenes and maltenes were decomposed. Sterically hindered sulfur within the complex macro molecules of the residue could only be removed when the

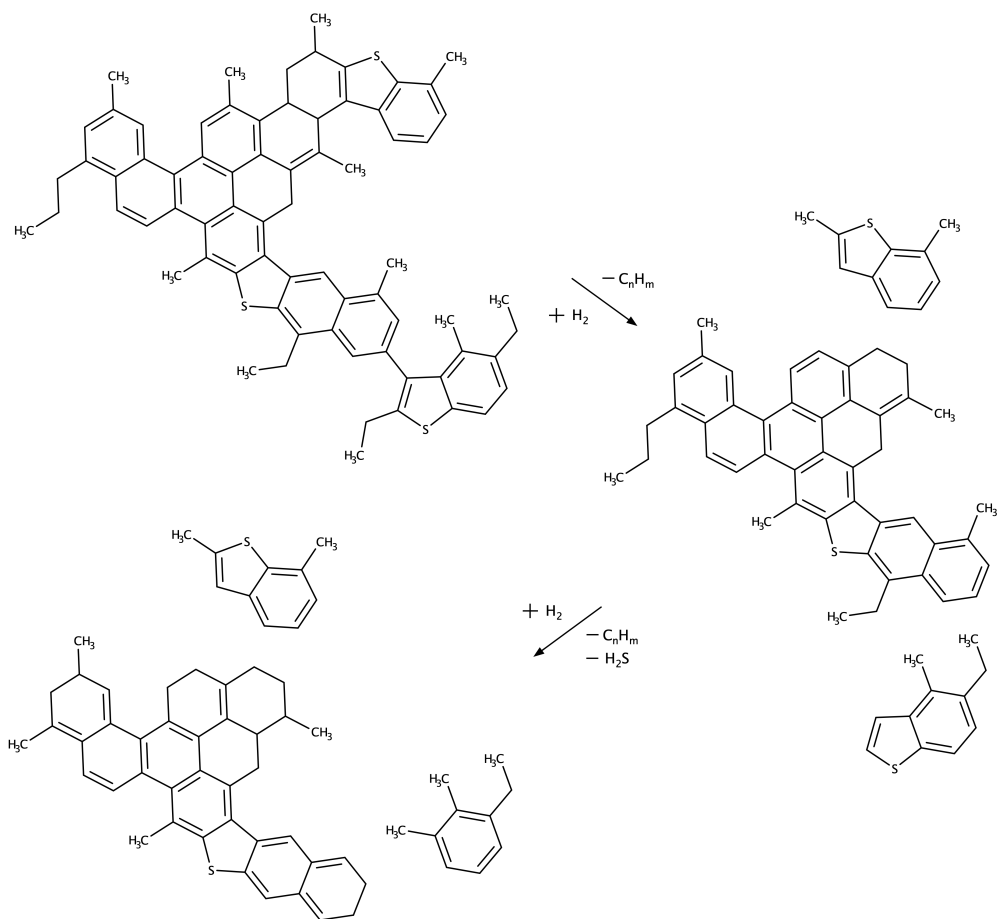


Figure 6.30: The authors understanding of the mechanistic pathway for an asphaltene molecule reacting under SCW conditions (The author does not claim that the displayed asphaltene molecule exists in reality)

feedstock was decomposed as shown in Fig. 6.30. When SCW was added, the H_2S concentration was low for the model compounds because of the low degree of desulfurization. The CH_4 and C_2H_6 plots obtained from vacuum residue experiments, support the assumption that cracking reactions were strongly enhanced by SCW. Additionally, the observation can be made that parallel to the increasing CH_4 and C_2H_6 concentration, H_2S concentration also increased. This observation supports the assumption that cracking of the feedstock makes more refractory sulfur atoms in the vacuum residue accessible. The H_2S concentration in the SCW case stayed below the H_2S concentration in the reference cases without SCW until a residence time of about 90 min. This can only be explained by the solubility of H_2S in water. During the first half of the experiments, formed H_2S could be dissolved in the water that accumulated in the CHPS. Only when saturation was reached, H_2S was detected downstream of the CHPS. The gas compositions and gas evolution over time correspond very well with the findings from the product fraction analysis and

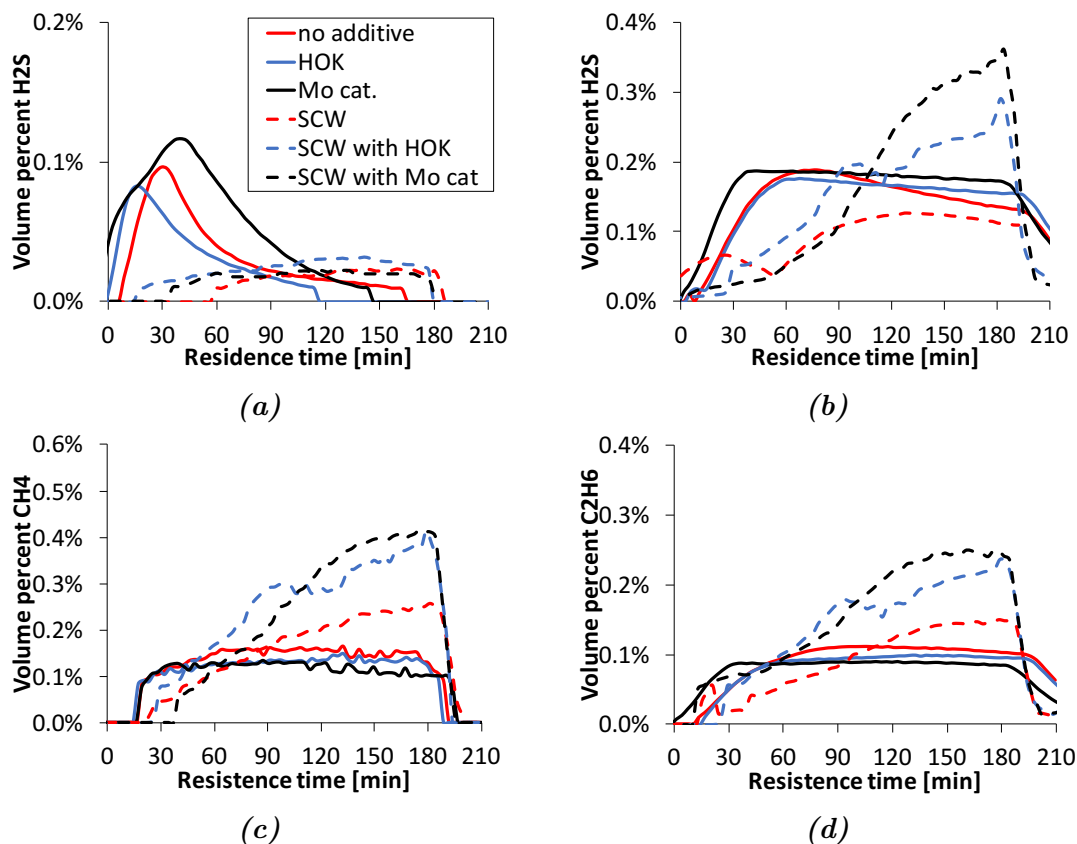


Figure 6.31: Gas composition throughout the residence time for a) H₂S for model compounds, b) H₂S for vacuum residue, c) CH₄ for vacuum residue and d) C₂H₆ for vacuum residue

underline especially the roll of SCW. Cracking reactions are enhanced by SCW thus leading to an improved accessibility of sulfur in the stable asphaltenes.

6.3.3.4 Analysis of the catalyst and additive

SEM images, Brunauer-Emmett-Teller (BET) analysis and elemental analysis of the HOK and catalyst were conducted to give insights on how the added materials reacted under process conditions and how the addition of SCW affected the surface properties. In spite of findings from literature, where SCW is reported to increase the surface area of activated carbons [254, 255], the surface area of HOK decreased when being exposed to the SCW process conditions. It decreased from 300 m²/g to 150 m²/g after 15 min in SCW down to 60 m²/g after 3 h. The high pressure and temperature in the autoclave may cause sintering of the carbon material leading to a decrease in pore volume [256]. The effect can also be seen in the SEM images displayed in Fig. 6.32, although at a different scale than results from the BET analysis.

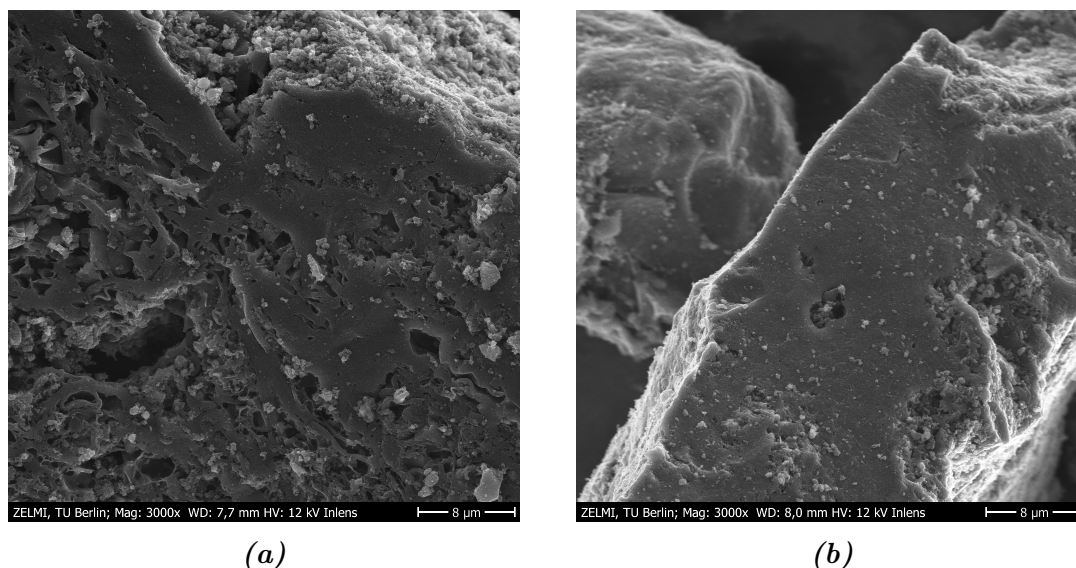


Figure 6.32: SEM images of (a) virgin HOK (300 m²/g) and (b) HOK after being exposed to the process conditions (60 m²/g)

The investigations on the desulfurization abilities of SCW can be summarized as follows. The results show that SCW does not support the opening of C-S bonds but enhances decomposition reactions of the residue fractions involving C-C bond cleavage, especially of asphaltenes. Similar observations are reported by different researches when only applying SCW without a continuous H₂ flow to the system [142, 185, 187, 251, 252]. The high H₂ partial pressure suppresses coke formation, which is observed by most researches who do not apply H₂. The degree of desulfurization of the model compounds was strongly reduced by the addition of SCW, while on crude oil based vacuum residue, SCW showed only a positive effect the conversion reactions. Combination of catalyst and SCW was found to enhance the decomposition of asphaltenes. Also, increasing the reaction temperature does not lead to higher desulfurization but only to stronger decomposition of the residue. A proposed mechanistic pathway takes into account that both in refractory low boiling products as well as in the residue, high levels of sulfur are present after hydrogenation reactions under SCW conditions. Though SCW does not directly affect the desulfurization reactions, the cracking of the residue structures may result in removal of alkyl chains which could sterically hinder the DDS route promoted by the Mo-catalyst.

6.4 Experiments with catalyst B14

From the screening experiments presented in Section 6.2, the inorganic catalyst B14 resulted as most promising for the desulfurization of vacuum residue while maintaining minimal conversion to low boiling products. Desulfurization of the residue of above 60% was reached while only converting about 30% of the substrate to lower boiling fractions which were desulfurized to the same degree as the residue as displayed in 6.5. The analysis of the product fractions showed great differences compared to the products from all other experiments, not only concerning the sulfur content, but also in composition and physical properties, indicating a different mechanistic pathway by which the reaction proceeds. Experiments were carried out to improve the desulfurization degree and to gain more knowledge on the mechanistic pathway. The findings are subject of patent law proceedings and therefore, the catalytic substances cannot be named here. In this Section, the experimental results will be presented, as well as the author's understanding of the new catalyzed mechanistic pathway behind the vacuum residue desulfurization.

6.4.1 Experimental results

Table 6.7: Desulfurization results with catalyst B14

T [°C]	Residence time	Catalyst [wt%]	Conversion [%]	Res. desulf. [%]
400	3 h	3.0	34.8	63.8
400	3 h	7.5	42.4 ± 2.3	89.9 ± 0.3
400	40 min	15.0	25.3 ± 1.8	87.4 ± 3.0
385	40 min	15.0	24.8 ± 2.3	81.0 ± 0.1

The catalysts screening in Section 6.2 showed that for the standard process conditions with 3% catalyst, 400 °C, 310 bar, and 3 h residence time the catalyst B14 showed superior desulfurization capacities, having a moderate conversion activity at the same time. The catalyst concentration was increased as shown in Tab. 6.7 to 7.5% in order to achieve a higher desulfurization of the residue. The increase in catalyst concentration showed that the desulfurization activity could be increased. Almost 90% desulfurization of the residue was observed. At the same time, when taking into consideration the H₂S release over time shown in Fig. 6.33 for the 3 h experiment using 7.5% catalyst it is possible to see that after about 20 min the H₂S content in the product gas decreased.

There are two important observations with regard to residence time which are shown in Fig. 6.33. In Fig 6.33 (b) the mass flow undergoes strong fluctuation which is a

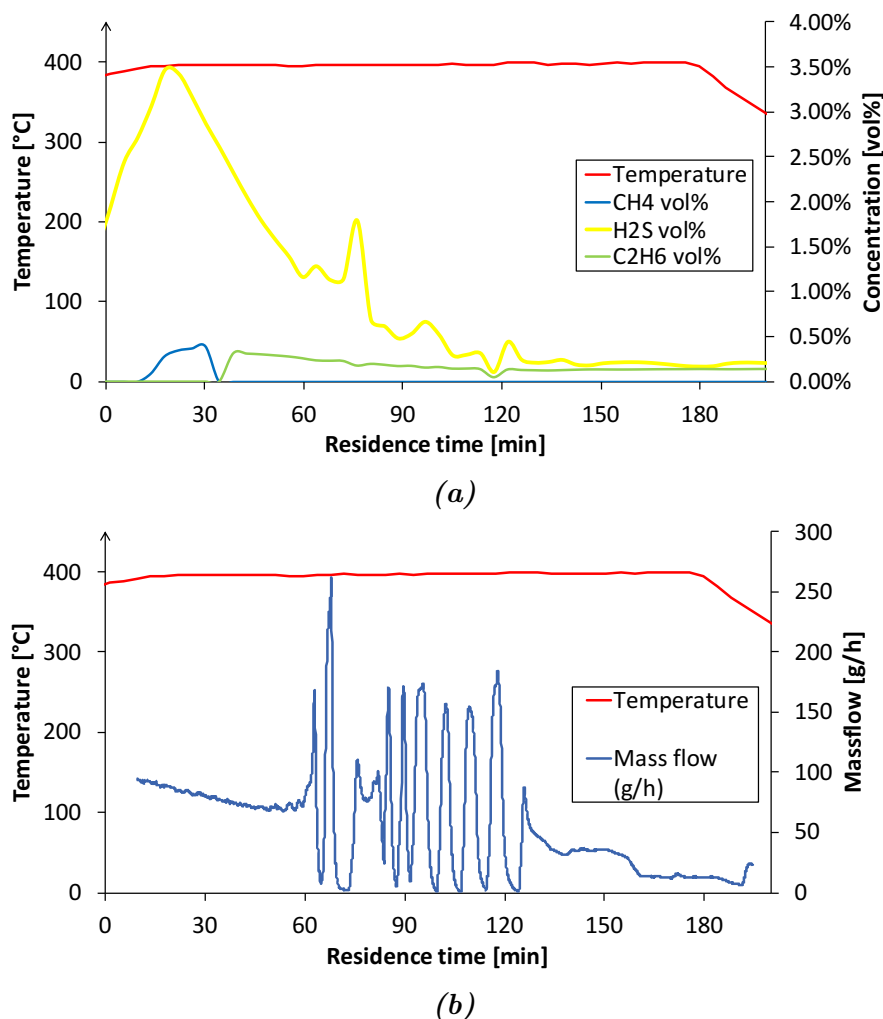


Figure 6.33: Behavior of gas composition over time with use of 7.5% catalyst B14 (a) H₂S, CH₄ and C₂H₆ (b) total mass flow out of the system

result of intermittent plugging of the product gas cooler. Removal of the plugging occurs once the pressure difference between reactor and CHPS becomes large enough. The plugging builds up after about 1 h residence time and is composed of the added catalyst and hydrocarbons (whether of the converted fraction, asphaltenes or maltenes could not be identified). Also, it is observed in Fig. 6.33 (a) that most H₂S release occurs in the first 60 min. When comparing the product gas composition in Fig. 6.33 (a) with that of an experiment with no catalyst also performed at 3 h residence time given in Fig. 6.18 we see a more than tenfold higher H₂S concentration throughout the first 40 min (peak at 3.5 vol.-% in contrast to 0.23 vol.-%). Also, the product gas components indicating cracking and conversion reactions (CH₄, C₂H₆) are nearly not present in the product gas (far below 0.5 vol.-%) when using catalyst B14. Both the H₂S and hydrocarbons release support the assumption that catalyst B14 has a much higher selectivity towards desulfurization than conversion.

In Fig. 6.34 the repeatability of the experiment with respect to the gas evolution over time is presented. The exact course of the gas evolution of the components H_2S , CH_4 and C_2H_6 slightly deviate but the general trend could be reproduced. The H_2S peak was observed at low residence times and a plugging built up after nearly 1 h residence time. Both CH_4 and C_2H_6 are only present to very small amounts in both experiments. The fluctuation of H_2S concentration is a result of the plugging in the condenser.

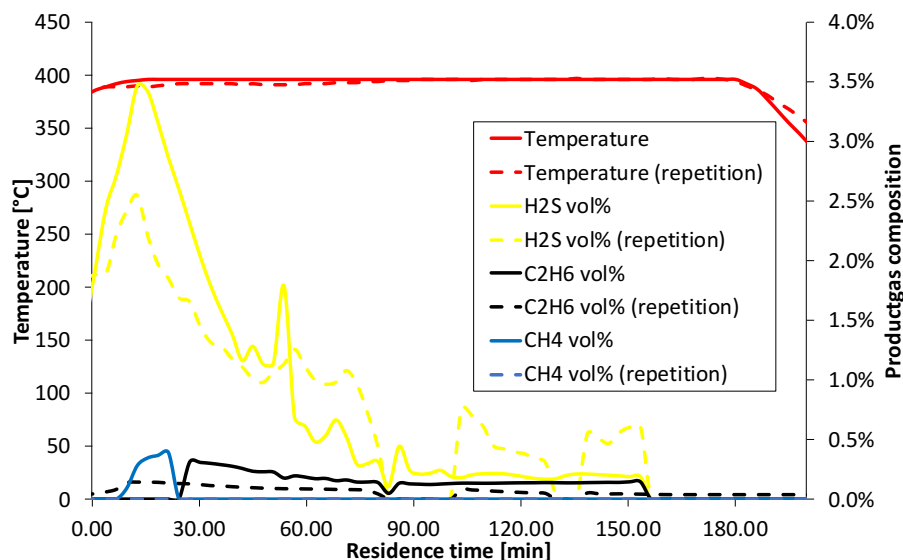


Figure 6.34: Repeatability of the detected gas composition with catalyst B14

A further increase in catalyst concentration to 15% shifts the build up of the plugging to smaller residence times. Therefore, additional experiments with catalyst B14 were performed with a residence time of 40 min to avoid plugging. Doubling the catalyst amount enables similar desulfurization of the residue in shorter time at far lower rate of conversion as presented in Tab. 6.8. When lowering the temperature to 385 °C only a slight decrease in conversion was observed, while the desulfurization is strongly reduced. Therefore, for further investigations, 400 °C and a residence time of 40 min were selected.

Table 6.8: Variation of the catalyst composition for B14

A [%]	B [%]	Sum [%]	Conversion [%]	Res. desulf. [%]
3	12	15.0	25.3 ± 1.8	87.4 ± 3.0
2	13	15	32.2	80.5
6	9	15	30.7	77.5
1	2	3	26.7	56.0
0	12	12	36.5	78.8

The catalyst is composed of substances A and B. In order to identify the influence of each of them, the ratio and total amount was varied at 400 °C, 310 bar, and 40

min residence time. The effect on conversion and desulfurization is shown in Tab. 6.8. Generally, the data show that a combination of A and B resulted in a better behavior than each of them alone. Also, it is possible to see that moving higher and lower than the initially chosen ratio for A and B gave worse results (decrease of residue desulfurization from 87.4% to 80.5% or 77.5%).

After the optimal relation between A and B was determined, measures were undertaken to prevent the plugging of the condenser. With addition of 3% HOK no plugging was observed. Desulfurization was increased to 93.7% while the conversion remained below 30%. Similar improvements were observed when the catalyst was finely powdered before being introduced to the reactor. The results are summarized in Tab. 6.9.

Table 6.9: *Improvements for catalyst B14 at 400 °C*

Improvement	Residence time	Cat. [%]	Con. [%]	Res. desulf. [%]
Reference	40 min	15.0	25.3 ± 1.8	87.4 ± 3.0
Addition of HOK	40 min	15.0	29.5 ± 2.1	93.7 ± 1.4
Finely powdered cat.	1 h	15.0	29.8 ± 1.0	95.5 ± 2.5

The improved results might have been achieved by a larger catalytic surface area available, thus reducing mass transport limitation.

6.4.2 Interpretation of the observations

In order to understand the improved desulfurization results by catalyst B14, further analysis of the retrieved products were performed. All fractions were analyzed and their compositions were identified (asphaltenes, maltenes, solids, substance plugging the pipes).

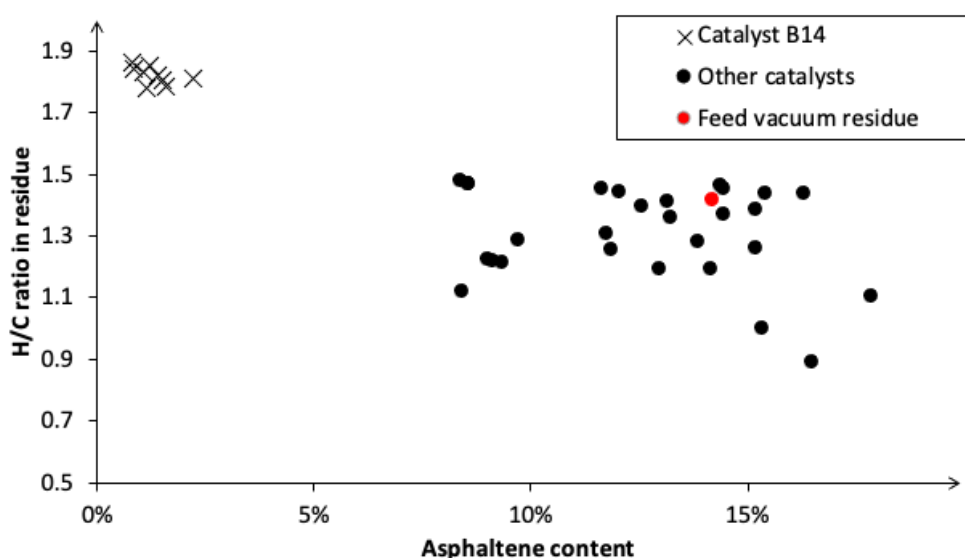
The residue was nearly free of asphaltenes and the H/C ratio was increased drastically as summarized for selected experiments in Tab. 6.10. Also, the residue was composed of a fraction with low viscosity and a second fraction which was solid. The amount of solids was difficult to determine, because parts of the solids were found in the pipes, on the autoclave walls, as well as in the retrieved residue fraction. Therefore, the error in the determination of the solid fraction is very high.

The elemental analysis of the solids (both the remaining solids in the reactor and the solids plugging the pipes) showed that they were composed of inorganic elements to more than 50%, indicating that most of the added catalyst remained in this fraction. On the other hand, the organics in the maltene and oil fractions added

Table 6.10: Residue analysis from catalyst B14 with * as the molar ratio

No.	H/C* residue	Asphaltene content [%]	Solids [%]
Vacuum residue	1.41 ± 0.01	15.13 ± 0.89	0.0 ± 0.0
B14.2	1.86 ± 0.11	$<1.00 \pm 2.16$	12 ± 3.7
B14.3	1.80 ± 0.05	1.10 ± 1.01	10 ± 3.2
B14.5	1.82 ± 0.03	1.40 ± 1.47	14 ± 2.1
B14.9	1.79 ± 0.10	1.60 ± 1.51	9 ± 1.4

up to 100% indicating that no catalyst ended up in these fractions. In Fig. 6.35 the H/C ratio is correlated with the asphaltene content of the residue fraction for different experiments.

**Figure 6.35:** H/C ratio of the residue fraction and asphaltene content

It is obvious that experiments performed with catalyst B14 led to a significant change in the H/C ratio and also the content of asphaltenes as shown in Tab. 6.10. The clear correlation between asphaltene content and H/C ratio can be seen in Fig. 6.35. It is well known that asphaltenes have a low H/C ratio because of the high aromatic character [26, 257, 258]. This aromatic character is, among other reasons, significantly responsible for the stability of the sulfur bonds in the asphaltenes [40, 44]. Measurement of the residues molar mass were performed with a vapor pressure osmometer (Knauer) and shows that no significant change in molecular size occurred. The feed vacuum residue has an average molar weight of 540 g/mol while the residue retrieved from the experiment with catalyst B14 had a molar weight of 520 g/mol. One can conclude that the aromatic structures found in the residue, and strongly in the asphaltenes, are hydrogenated, in comparison to the crude oil, leading to the formation of mostly aliphatic bonds. These aliphatic molecules show a different solubility than the asphaltenes and are therefore characterized as maltenes as explained

in Section 2.1.2. The analysis of the product fractions indicates that the catalyst B14 has a very high selectivity towards the hydrogenation of the residue fractions, thus decreasing the aromatic character and resulting in nearly total removal of the asphaltenes. At the same time, cracking reactions are kept minimal (because cracking is mostly induced thermally, the choice of low temperature keeps cracking at minimum), as it is possible to see from the low conversion displayed in Tab. 6.7, 6.8, and 6.9 as well as the nearly constant molecular molar weight. The low degree of cracking is also seen in the low hydrocarbon content in the gas phase as shown in Fig. 6.36.

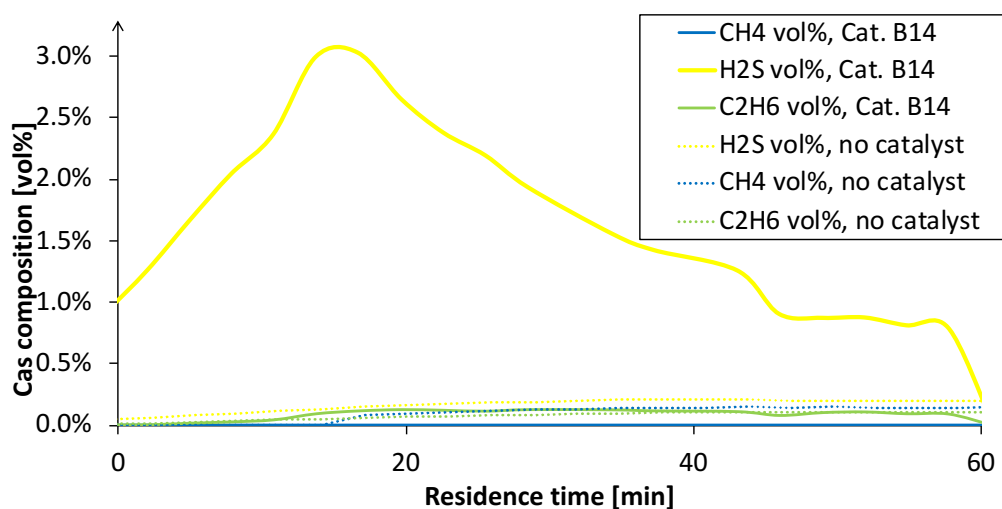


Figure 6.36: Comparison of the H_2S content in the product gas during experiments with catalyst B14 and with no catalyst

Since the molecular size is not decreased severely, there still remains a large fraction with an initial boiling point of $>500^\circ\text{C}$. Also, a very strong reduction in sulfur content can be observed. All findings together support the hypothesis that desulfurization in the presence of catalyst B14 takes place via hydrogenation of the aromatic structures found in vacuum residue. Due to this, double bonds are converted into single bonds with lower energy, making the sulfur bond weaker and enabling desulfurization. This is also known as the HYD route as demonstrated by several authors on model compounds [38, 259] and also discussed in Section 2.4.3. The understanding of the mechanism for vacuum residue is displayed in Fig. 6.37. The figures displayed here represent the author's current understanding of the chemical structure of asphaltenes and hydrogenated as well as desulfurized asphaltenes. The author does not claim that these exact molecules exist.

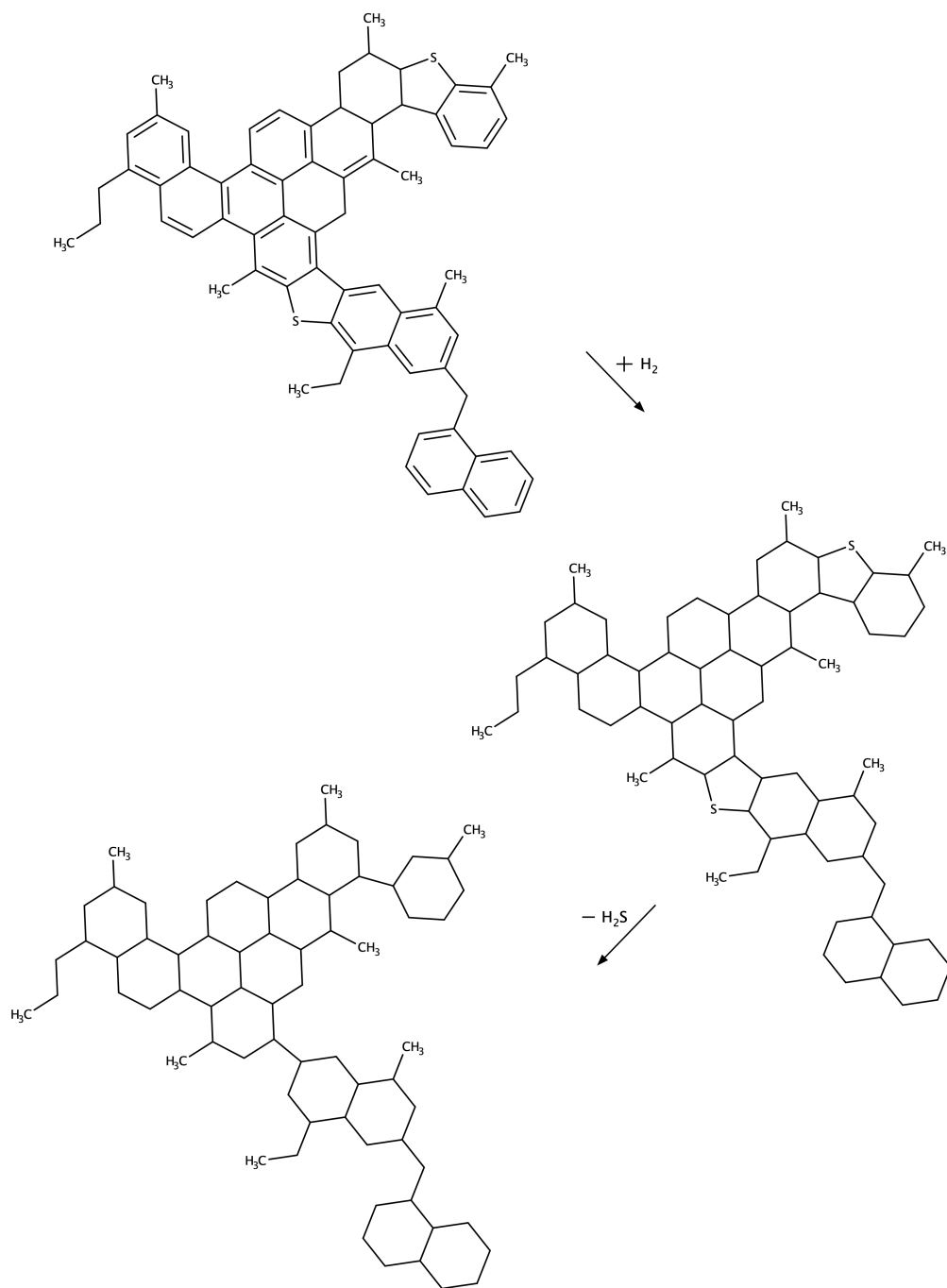


Figure 6.37: Reaction path proposed for the desulfurization using catalyst B14

Assuming a completely aliphatic system as shown in Fig. 6.37, the bond energy discussed in Section 2.4.4 becomes a large role in understanding the desulfurization. In a simple aliphatic system with no resonance bonds, the sulfur bond is weaker and sulfur can be removed more easily [207, 208]. Carbon bonds are more stable and therefore the conversion stays low at the chosen temperature level. When recalling the two mechanisms of HDS displayed in Section 2.4.3, it can be concluded that with catalyst B14 a mechanism based on the hydrogenation route (HYD) followed by hydrogenolysis is present. If this is assumed, the path gives another reason why the desulfurization with catalyst B14 is able to reach such low sulfur levels. While the DDS route of sulfur in the residue is often sterically hindered by alkylated BT and DBT [260–262], the HYD route displays the only path for removal of sulfur to low levels. Common supported HDS catalysts pursue the DDS route [174, 263] and therefore sulfur cannot be removed to such extent from sterically hindered refractory asphaltenes and maltenes. Since the product oils obtained from experiments with catalyst B14 are free of alkylated BT and DBT, one can conclude that the extremely good hydrogenation ability enables the HYD route of sterically hindered sulfur in the residue. A list of identified compounds from GC/MS analysis is given in the Appendix in Tab. A.3.

The above discussed effects are all on the molecular level. As shown in the Section 2.1.2 asphaltenes form clusters in which the π - π interactions between the aromatic rings strongly contribute to the stability of the clusters. These clusters of asphaltenes inhibit desulfurization reactions [264]. Therefore, the removal of almost all asphaltenes enables a deeper desulfurization. Generally, in literature, it is accepted that large amounts of aromatic compounds in oil inhibit HDS reaction substantially [169, 259]. Reduction of the feeds aromaticity and hydrogenation of the asphaltenes may support the improved desulfurization. The low viscosity of the product and the presence of a solid inorganic phase at the reactor bottom suggests that recirculation of the catalyst is possible because of good separation of catalyst and product.

6.5 Data analysis

In total more than 130 experiments were conducted and for each experiment up to 50 different product specifications were analyzed. A list of the product specifications is given in the Appendix A.1. In Sections 6.1.2 to 6.4 the effect of experimental parameters on product composition was analyzed and how, by adjusting these parameters, desired product specifications could be reached. In this section, a correlation between the product specifications, regardless of the path that was chosen to achieve the products (e.g. choice of temperature, catalyst or pressure), is mapped out to identify certain product specifications that correlate strongly with sulfur removal.

6.5.1 Total sulfur removal and sulfur removal from the different product fractions

Analysis of the product fractions oil and residue, showed that both fractions were desulfurized differently (in most cases). When plotting the desulfurization of the oil fraction and residue fraction over the complete sulfur removal for every experiment, the graph shown in Fig. 6.38 is obtained. In most cases, the product oil contained far less sulfur than the corresponding residue fraction. The reason for this may lie within the complexity of the residue fraction and the stability of the sulfur structures in asphaltene and maltene molecules.

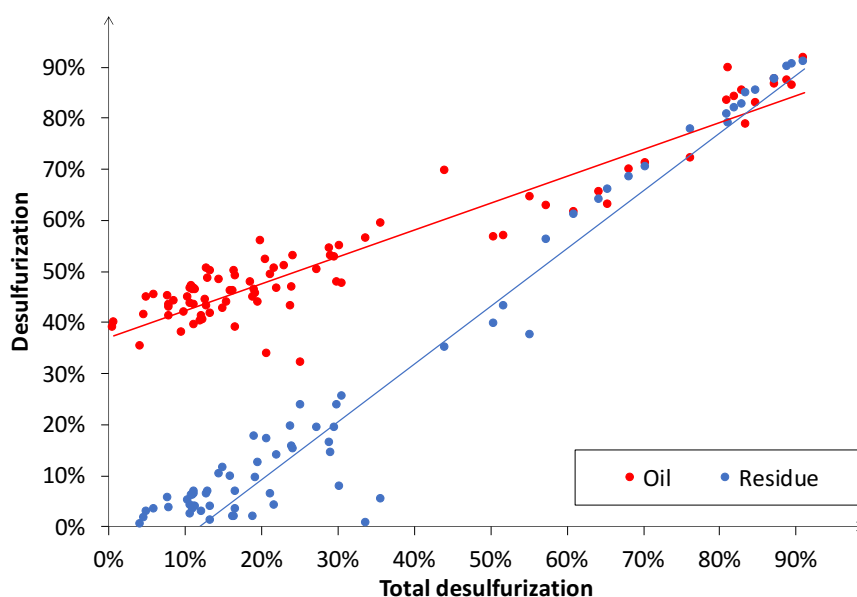


Figure 6.38: Desulfurization of oil and residue over total desulfurization

For a low degree of total desulfurization, the difference between the sulfur level of the product oil and residue was found to be large. Though the residue was only desulfurized to a very low extent in these cases, the oil exhibited a reduction in sulfur of around 50%. For higher levels of desulfurization, both residue and oil became more alike concerning the degree of desulfurization. Two interpretations can be concluded from the plot in Fig. 6.38. First, formed oil is generally of far lower sulfur content than the feed vacuum residue. Converting vacuum residue to lower boiling products forms smaller hydrocarbons that contain a lower sulfur content. Mostly remaining sulfur in the oil fraction was only present in very stable DBT, BT and their derivatives as discussed in Section 6.2.1.2. Second, at high levels of desulfurization both the product oil and the residue are desulfurized similarly strong. This may be attributed to the fact that only catalyst B14 reaches these high levels of desulfurization. The mechanistic pathway discussed in Section 6.4.2 also gives the possible reason for the desulfurization of the stable DBT, BT structures which are then not found in the oil fractions.

6.5.2 H₂ consumption, conversion and sulfur removal

In Fig. 6.39 the correlation between H₂ consumption, residue desulfurization, and conversion is displayed. One possible way of finding structures and correlations in a set of data is by running a K-means algorithm on the data set [265]. By doing so, the set of data is grouped into k subsets (clusters) of which each cluster has one centroid. Each data point is assigned to the centroid to which all attributes of the data point are most similar (closest). In the following, several identified clusters are presented and the information obtained from them is discussed. The 3D plot shows three characteristics plotted in a scatter diagram. For illustrative purposes, x-y diagrams are also presented.

Three clusters are identified, each representing very distinct product specifications. The centroids for the three clusters are given in Tab. 6.11 and are shown in Fig. 6.39 a) as circles and in the 2D-plots as X.

Table 6.11: Centroids for the clusters conversion - sulfur reduction residue - hydrogen consumption

No.	Conversion [%]	Color	Sulfur red. residue [%]	H ₂ consumption [g/kg]
1	24.77	blue	7.87	11.05
2	55.47	red	2.72	15.32
3	31.63	green	76.77	31.89

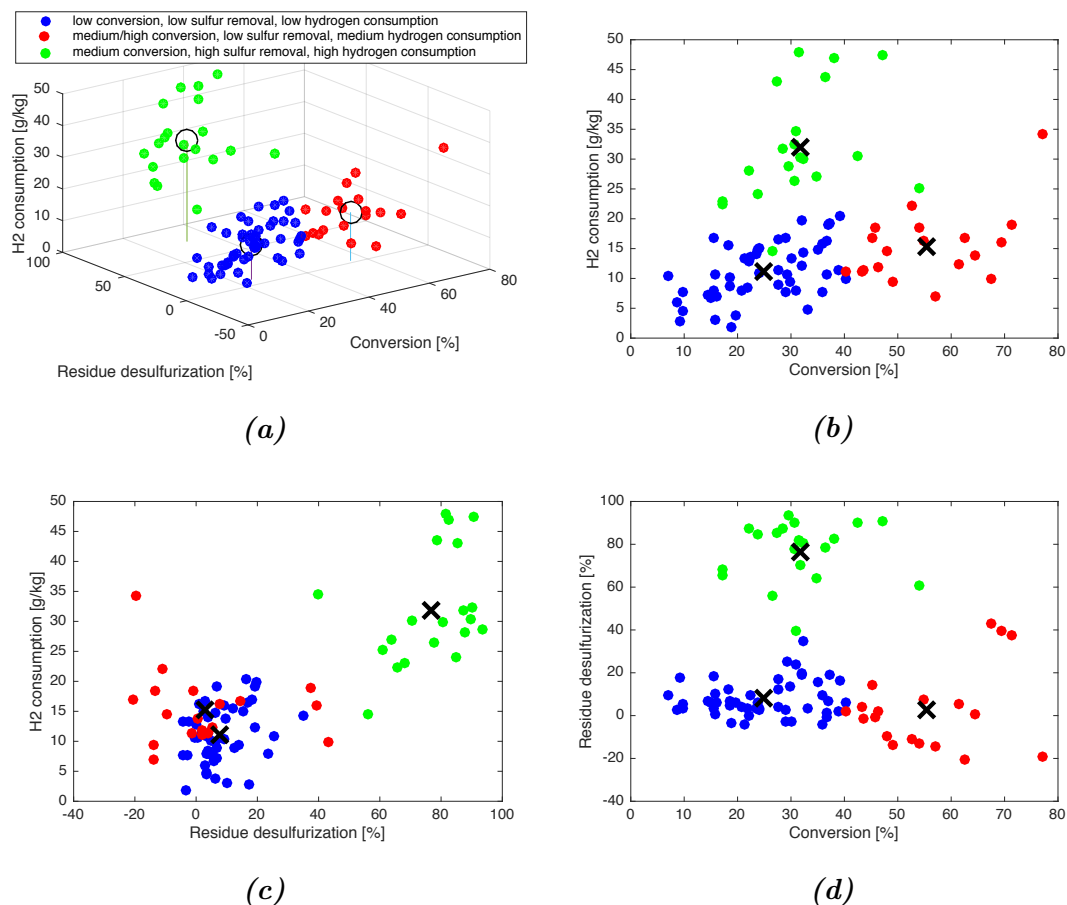


Figure 6.39: Clustering data for a) 3D-plot of H_2 consumption, conversion and sulfur removal in residue fraction, b) 2D-plot of H_2 consumption over conversion, c) 2D-plot of H_2 consumption over sulfur removal in residue fraction and d) 2D-plot of sulfur removal over over conversion

The points presented in blue, first cluster, correspond to experiments that consumed low amounts of H_2 while converting low amounts of feed vacuum residue to lower boiling products and yielded a residue fraction containing high amounts of sulfur. Experimental results allocated in this region display the least promising results. When taking a closer look at the experiments located in this area the observation can be made that mostly experiments performed at low temperature (400°C and below) without catalyst or with very inactive catalysts fall into this cluster.

Second cluster (red) groups data points that have in common a medium to high conversion at low sulfur removal together with medium H_2 consumption. In this area, mostly experiments with supercritical and at elevated temperatures of 415°C and 430°C are located. All experiments of this cluster show a tendency that is not of interest for the aim of precise vacuum residue desulfurization, but for the conversion of vacuum residue. With the aim of the production of low boiling products from vacuum residue, catalysts additives and process conditions of experiments allocated within this cluster are advantageous. The consumed H_2 is mostly needed to saturate

radicals formed in the cracking of C-C bonds [266,267]. Therefore, H₂ consumption is higher compared to the first cluster. Since desulfurization reactions are not promoted in experiments within this cluster, the remaining vacuum residue has a very high sulfur content.

The third cluster is of highest interest. Here, a very high desulfurization of the residue took place and an almost sulfur-free vacuum residue, complying with the sulfur regulations, was received. On the other hand, the cost at which this desulfurization is achieved, can be identified. Though the feed undergoes low conversion, high H₂ consumption is needed to remove the majority of the sulfur from the residue. All data points allocated within this cluster were conducted with the usage of the catalyst B14 in different configurations and with choice of different process parameters. The assumed mechanistic pathway pursued with catalyst B14 is most probably the reason for the high H₂ consumption and is discussed in Section 6.4. The H₂ consumption is in the range of what is reported for high conversion processes like the VCC process, where 395 Nm³/t (corresponds to 35 g H₂ per kg vacuum residue) are necessary for nearly full conversion of the vacuum residue feedstock [268].

6.5.3 Asphaltene and maltene conversion

The procedure for the analysis of the residue fractions maltenes and asphaltenes is complex and involves high consumption of solvents and therefore this was only performed for a subset of experiments. In Fig. 6.40 both residue fractions are plotted over the degree of conversion. The share of maltenes decreased strongly and steadily with increasing conversion indicating that maltenes were mostly cracked and the products contributed to the oil and gas yield. The asphaltene fraction was only marginally influenced by an increased conversion, underlining that the complex asphaltenes were very stable. Even at process conditions that reduced the maltene content from initially 85% to only 20% leading to observed conversions of around 80%, the asphaltene fraction was only slightly reduced. Only the experiments with catalyst B14 showed strong asphaltene reduction at low degree of conversion.

When also the effect on the desulfurization is taken into account the regression analysis used in Fig. 6.40 will become difficult to handle. Therefore, classification is used again to identify regions and parameters that strongly correlate. In Fig. 6.41 results from this clustering are displayed.

Dividing the data into three clusters gives good insights. The blue data points are all from the experiments with catalyst B14, while the green and red can be distinguished

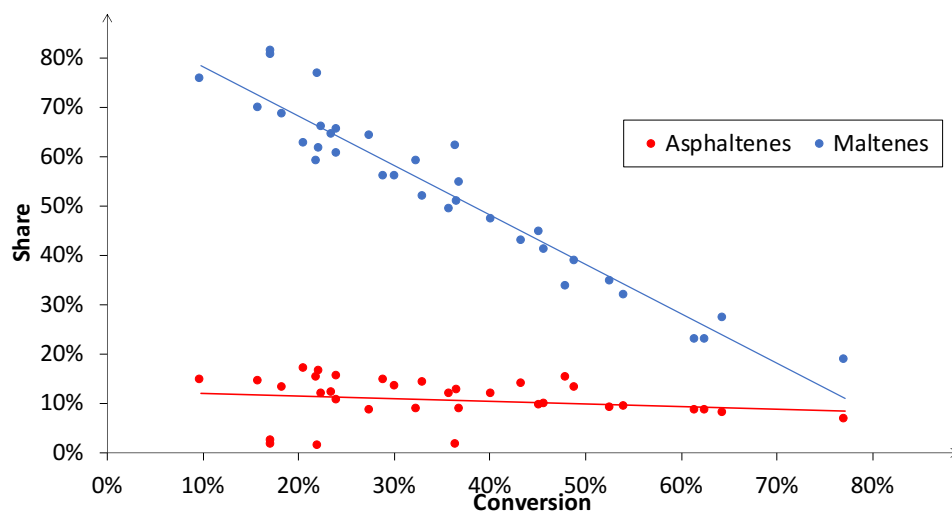


Figure 6.40: Influence of residue fractions on conversion

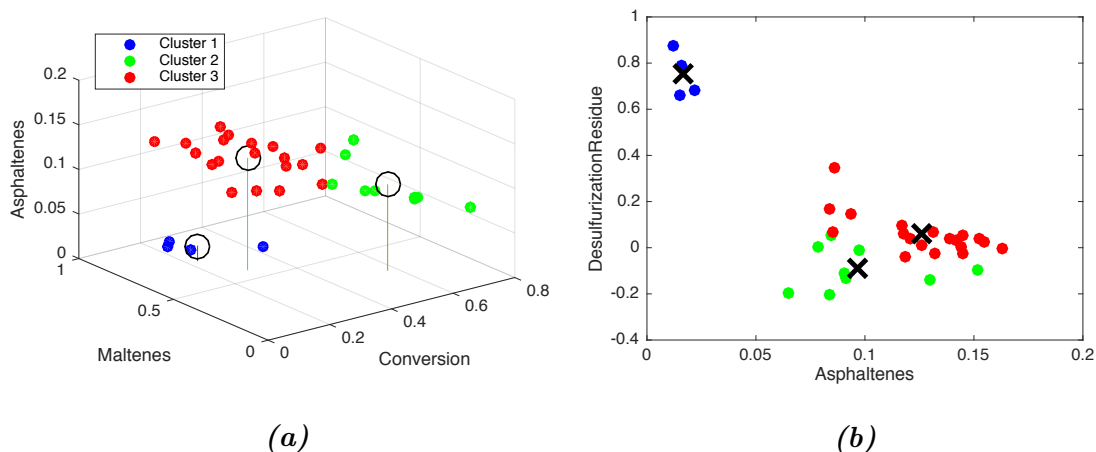


Figure 6.41: a) Clusters in residue transformation b) Desulfurization of residue over asphaltene content

by the temperature level applied during the experiments. Most interesting are the experiments which maintained a high maltene content (leading to low conversion) while reducing asphaltenes which then correlated strongly with the sulfur removal from the residue fraction. This area is located in the far right lower corner of Fig. 6.41 a). The experiments which mostly fulfilled these specifications are the ones using catalyst B14.

6.5.4 Denitrification

In commercial HDS units, also denitrification of the feed takes place. In Fig. 6.42 the nitrogen content of the residue product is plotted over the sulfur content of the residue.

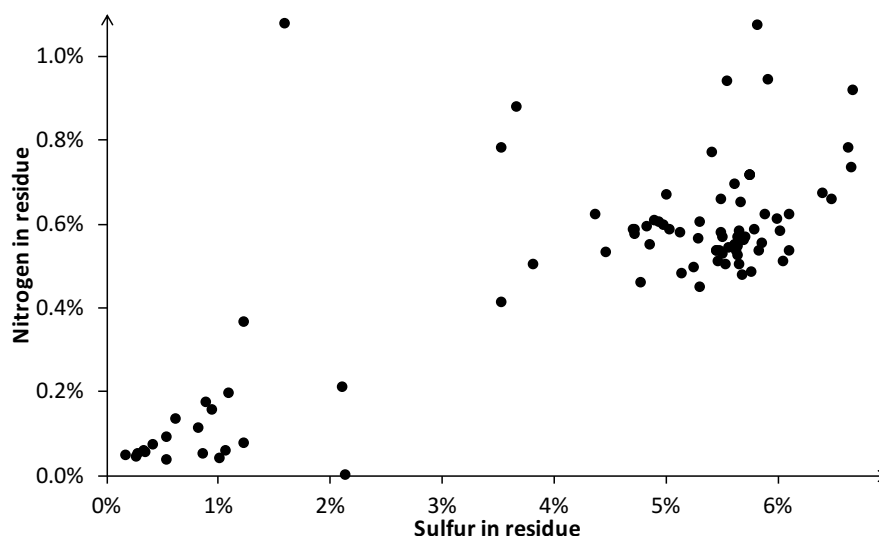


Figure 6.42: *Correlation of desulfurization and denitrification*

Also, for the process conditions and catalysts examined in this thesis, good desulfurization correlated very well with the removal of nitrogen. Denitrification was therefore also strongly enhanced by catalyst B14. In literature it is reported that denitrification is necessary for the desulfurization [172]. The fact that catalyst B14 reduces nitrogen content to a better extent than the other catalysts may therefore also display a reason for the good desulfurization.

6.5.5 Conclusion from the data analysis

The general trend, when neglecting the experiments with catalyst B14, shows that cracking leading to formation of lower boiling products is the key for desulfurization of the feedstock. Thus, the catalysts and additives supporting cracking of C-C bonds enable better desulfurization. Desulfurization of the feedstock does not necessarily correlate with the production of a low sulfur residue, but strongly with production of low boiling fractions with lower sulfur content. The only catalyst not following this trend is catalyst B14. All analyzed data support the interpretations that with catalyst B14 a completely different desulfurization mechanism takes place, compared to all other catalysts and additives. Also, the data support the developed mechanistic pathway as it is displayed in Section 6.4.2.

Economic evaluation of findings

Several different catalysts and process conditions for slurry hydro-desulfurization of vacuum residue have been tested and the experimental results are presented and discussed in the previous chapters. Analysis of the product fractions have been used to identify optimal conditions for the hydrodesulfurization of vacuum residue with high sulfur content. The objective of this chapter is an economic evaluation of the findings at technically relevant scale in order to identify and classify the results within the context of the current market situation. Two scenarios were chosen for the economic analysis which are hydrodesulfurization with catalyst B14 and SCW upgrading. The two scenarios are based on the mass balances and findings from the lab scale reactor and use additional data for the calculation of the CAPEX. The first scenario aims at utilizing catalyst B14 for the removal of sulfur, while the second scenario uses SCW as additive, mostly producing lower boiling components and a high sulfur residue.

We return to the refinery described in Section 2.2 and locate the vacuum residue slurry hydrodesulfurization process in the residue stream leaving the bottom of the vacuum distillation column. For the two scenarios calculated here, boundary conditions are chosen and several assumptions are made. These boundary conditions and assumptions are defined in the following Section 7.1 followed by the calculation of the capital expenditures (CAPEX) and operational expenditures (OPEX) in Section 7.2. The results of the economic calculations are presented in Sections 7.3 and 7.4 and both cases are compared and evaluated in Section 7.5.

7.1 Boundaries and assumptions

In order to perform an economic analysis, the system boundaries have to be determined and several assumptions have to be made complementing the data from the experimental section. The system boundaries are displayed in Fig. 7.1.

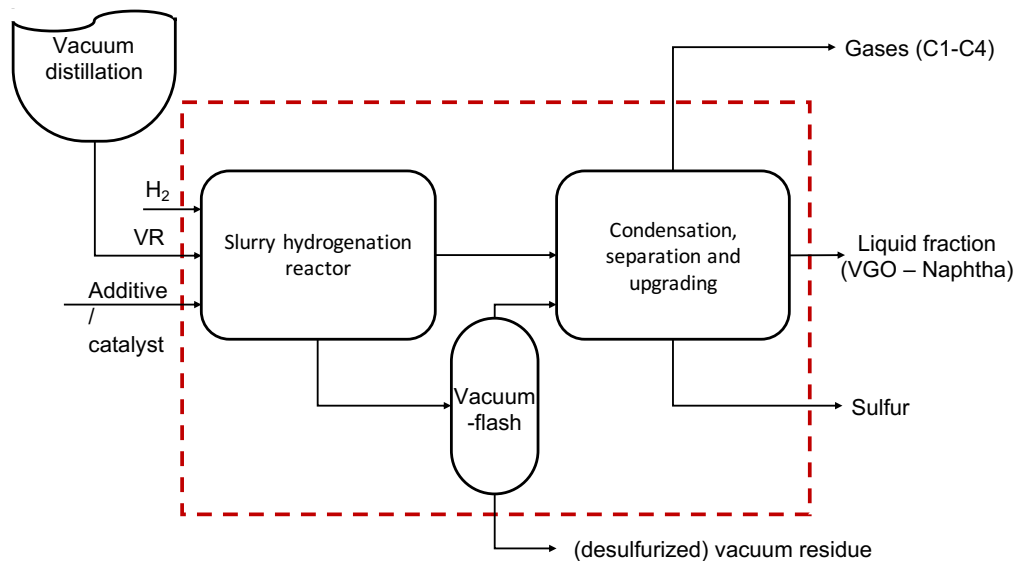


Figure 7.1: Boundaries of the economic evaluation

The capacity of the residue desulfurization unit is chosen to be $2.16 \cdot 10^6$ t/a assuming that about 5-10% of a 500,000 barrel per day refinery is vacuum residue. This corresponds to 59.2 t/day for 8,000 hours of production assumed every year. The figures are based on the Baton Rouge Refinery in Baton Rouge, Louisiana, USA [269] and the economics are calculated for the USA location.

It is further assumed that the residue upgrading unit is integrated into an existing refinery so that an infrastructure for vacuum residue supply as well as utilization of distillate streams exists. In Tab. 7.1 the experimental results, the cost calculations are based on, are summarized.

The feed vacuum residue for the process is the vacuum residue used for the experimental investigations in this thesis. The product fractions are subdivided into gas (gas - H_2S), naphtha (oil), and vacuum residue (residue) as displayed in Tab. 7.1. Further distinguishing the oil fraction into naphtha, diesel and vacuum gas oil is not performed. For the naphtha fraction it is assumed that it can be introduced into the naphtha pool after hydrotreating. This is assumed because the H/C ratio of the product oil is very similar to that of naphtha (naphtha 1.9, product oil 2.00 and 1.87).

Table 7.1: Key figures from the experiments the economic calculations are based on

		Catalyst B14	SCW
Process parameters			
	Residence time	1 h	3 h
	Temperature	400 °C	430 °C
	Pressure	310 bar	310 bar
	Amount of catalyst	15%	100%
Residue			
	Fraction	70%	23%
	H/C	1.98	0.89
	S content	0.3%	7.0%
Oil			
	Fraction	21%	59%
	H/C	2.00	1.87
	S content	0.2%	3.3%
Gas			
	Fraction	9%	18%
	H/C	3.00	3.00
	H ₂ S	56 g/kg	23 g/kg

For the vacuum residue fraction it is further assumed that when reaching the sulfur level of <0.5% it can be sold as VLSFO. Other specifications for the fuel quality are not taken into account. The amount of H₂ consumed during the upgrading process is a crucial figure and is calculated via Eq. 6.8 based on the experimental findings. The sulfur content of the product fractions as well as the degree of desulfurization and thus the H₂S production are also taken from experimentally obtained data as listed in Tab. 7.1. Sulfur, removed from the organic feed as H₂S, is reacted to elemental sulfur in a Claus unit. The ratio of catalyst to vacuum residue is estimated based on the experimental findings. From the experimental semi-continuous setup no insights on possible recirculation of the catalyst could be gained. A sensitivity analysis calculating the process cost based on varying catalyst recycle is performed.

7.2 Cost estimation for the large scale process

7.2.1 Capital cost

In order to calculate the capital investment cost of a plant or unit operation the first step is the development of a basic process flow diagram for the identification of the main components which can then be used for the CAPEX calculation. The basic flow diagram is displayed in Fig. 7.2.

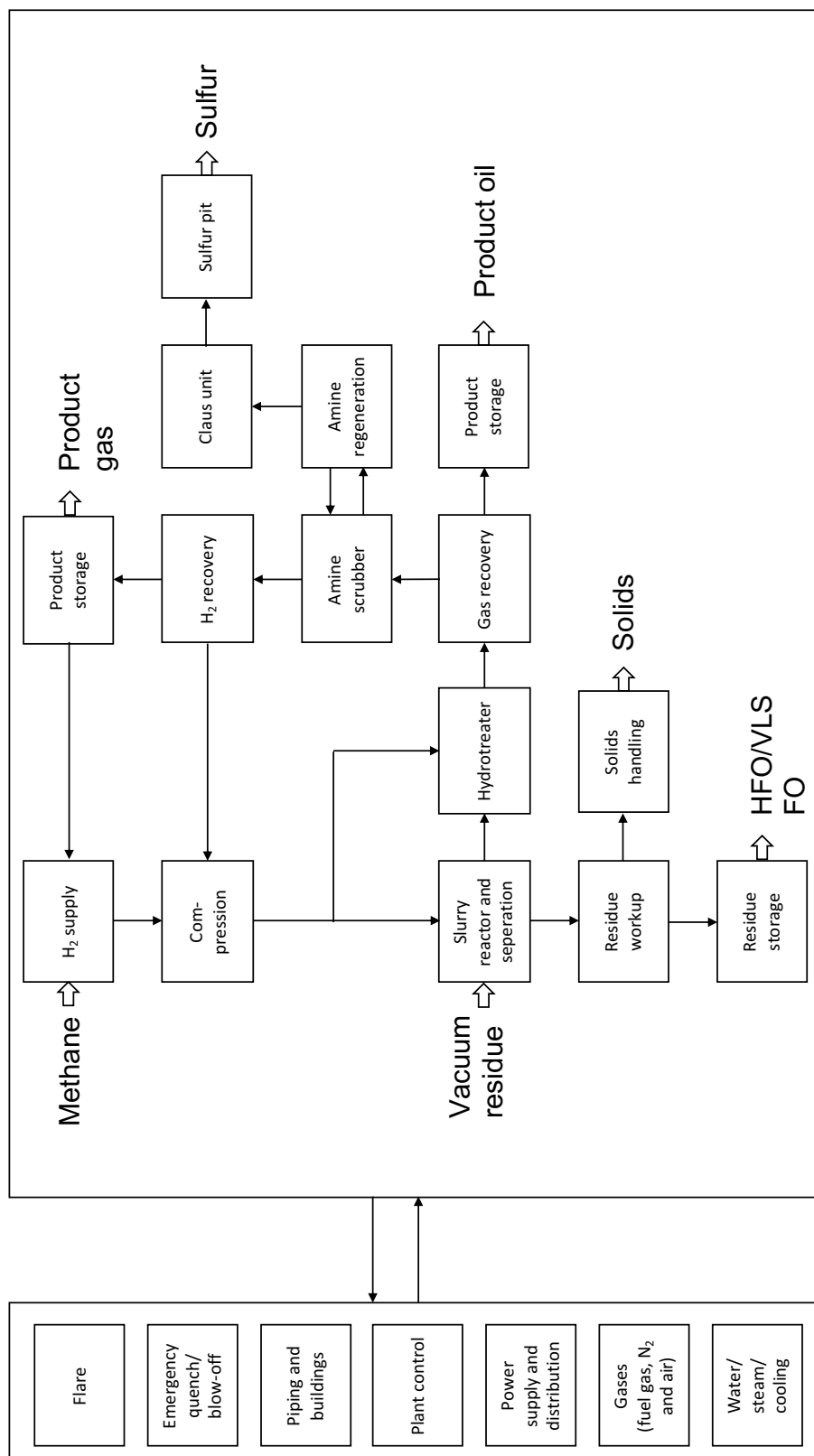


Figure 7.2: Basic flow diagram of the residue desulfurization process

Based on the developed setup of the complete process, the estimation of the CAPEX was performed. Cost for the unit operations were calculated based on a project the partner company h-tec heavy oil GmbH performed for a residue hydroconversion plant designed for a US location. The key unit operations are the same for both the catalyst B14 and SCW cases. Only some unit operations vary in size, mainly because of the large volume needed for the SCW and the differences in the product distribution. Both the residence time and volume affect the space-time-yield, thus influencing the size of the high pressure reactors. As summarized in Tab. 7.1 the residence time with SCW was 3 times higher than with catalyst B14. A factor of 6 (comprised of extra volume needed for water and the increased residence time) for the sizing of the high pressure unit operations is therefore considered when calculating the CAPEX for the SCW case. Also, in the case of SCW a larger fraction of light products is produced needing a larger hydrotreater. For the cost calculation, data was taken from a plant designed for vacuum residue conversion based on the Bergius-Pier technology. The influence of capacity on investment costs was taken into account by degression exponents. The investment costs for a plant with a deviating capacity (I_2) can be estimated according to the eq. 7.1 based on the investment cost from the Bergius-Pier plant (I_1) and the relationship between the new (C_2) and old (C_1) plant size. The exponent m can be found in literature for the different unit operations and is commonly 0.6 [270].

$$I_2 = I_1 \cdot \left(\frac{C_1}{C_2} \right)^m \quad (7.1)$$

The calculated cost are based on a project from the year 2004 and are projected to 2019 using eq. 7.2 taking into account the cost in 2004 (I_{2004}), the inflation (i) and the number of years since 2004 (n).

$$I_{2019} = I_{2004} \cdot (1 + i)^n \quad (7.2)$$

An average inflation of 2% is assumed. The principle components necessary for the large scale plant together with the corresponding capacity and resulting cost for 2019 are given in Tab. 7.2.

The total investment cost (TIC) for the SCW plant are 23.5 % higher, mostly because of the larger volume needed in the high pressure reactor. The depreciation time is assumed to be 15 years with an annual interest rate of 7%. The equivalent annual

Table 7.2: Unit operations in the large scale plant together with the corresponding capacity for each unit operation and the resulting cost

	Unit operation	Unit	Capacity Cat. B14	SCW	Price [M€] Cat. B14	SCW
Process						
	Revamp VR prep.	t/h	300	300	67.7	67.7
	Slurry reactor	t/h	270	600	144.7	472.0
	Hydrotreater / -cracker	t/h	46	158	113.9	225.2
	Hydrogen compression	m ³ /h	350 000	350 000	68.3	68.3
	Residue work up	t/h	216	108	23.9	15.1
	Emergency quench and blowdown	t/h	270	270	13.6	13.6
	Flake solidification	t/h	32	97	14.1	14.1
	Heavy slop storage	t/h	270	270	3.9	3.9
	Sour water stripping	m ³ /h	25	25	24.1	24.1
	Amine regeneration	m ³ /h	25	25	29.0	29.0
	Sulfur recovery and tail gas	t/h	20	20	103.7	103.7
	Hydrogen recovery	m ³ /h	350 000	350 000	42.5	42.5
	Gas recovery	t/h	50	50	49.5	49.5
Utilities						
	Raw water supply	m ³ /h	1 000	1 200	27.2	30.7
	Steam and condensate	t/h	390	390	38.2	38.2
	Cooling water	m ³ /h	10 000	10 000	8.9	8.9
	Plant and instrument air	m ³ /h	7 200	7 200	7.9	7.9
	Fuel gas system	kg/h	62	62	2.6	2.6
	Nitrogen system	m ³ /h	30 000	30 000	2.5	2.5
	Waste water treatment	m ³ /h	260	460	33.3	48.6
	Power distribution	MW	100	100	160.7	160.7
	Power generation	MW	21	21	9.9	9.9
Off-Sites						
	Sulfur pit	t/h	20	20	1.1	1.1
	Solids handling	t/h	32	97	178.1	178.1
	Flare system	t/h	896	896	8.7	8.7
	Intermediate and product storage	t	10 000	10 000	64.1	64.1
	Control system	-	1	1	20.6	20.6
	Interconnections	t	8 000	9 000	105.8	119.0
	Buildings	m ²	6 642	6 642	7.1	7.1
	Fire protection	-	14	14	8.6	8.6
	Site preparation	ha	19	27	115.5	115.5
Total					1 499.3	1 961.1

cost (EAC) are calculated according to eq. 7.3 where j is the interest rate and n the number of years.

$$EAC = TIC \cdot \frac{(1+j)^n \cdot j}{(1+j)^n - 1} \quad (7.3)$$

The resulting EAC for the case using catalyst B14 are 164.6 M€/a and for the case with SCW 215.3 M€/a.

7.2.2 Variable cost

The variable cost are composed of the cost for consumed educts like the H_2 and vacuum residue as well as cost for maintenance and operating staff.

H_2 and vacuum residue consumption are based on experimental findings as listed in Tab. 7.1. A catalyst recycle ratio of 95% is assumed reducing the amount of fresh catalyst to 5% of the experimentally determinant amount. The resulting OPEX are summarized in Tab. 7.3.

Table 7.3: OPEX for both cases

Component	Unit for consumption	Consumption		Annual cost [M\$]	
		Cat. B14	SCW	Cat. B14	SCW
Vacuum residue	t/h	270	270	216	216
H_2	t/h	9.7	9.2	47.5	44.9
H_2O	t/h	-	13.5	-	<0.1
Catalyst	t/h	2.0	-	454.9	-
Electrical power	MW	50	50	18.0	18.0
Fuel gas	MWh	60	140	13.5	31.6
Maintenance	% of CAPEX	3	3	22.6	29.6
Staff	Person/year	60	60	7.2	7.2
Contingency	% of OPEX	1.5	1.5	2.8	2.6

Both processes yield low boiling fractions as well as residue. In the case of catalyst B14 the residue product is desulfurized and complies with the sulfur regulations. Smaller amounts of gas and low boiling fractions are a side product of the desulfurization process. In the case of SCW the residue fraction contains high amounts of sulfur while the main products of the process are low boiling liquids and gas. Based on the experimental findings the product distributions are calculated and presented in Tab. 7.4

Table 7.4: Produced products for both cases

Product	Produced amount [t/h]	
	Cat. B14	SCW
C1 C2	6.9	31.8
C3 C4	2.3	10.6
Naphtha	56.7	159.3
Sulfur	15.1	6.2
Residue <0.5% S	186.3	0.0
Residue >0.5% S and purge	13.5	62.1
Total	281.8	292.7

7.3 Economic analysis of the desulfurization process with catalyst B14

Based on the figures and calculations presented in the previous sections, the results for the economic analysis for a 50 000 b/d plant using catalyst B14 are presented here. Figure 7.3 shows the cost that are necessary to process 1 t of vacuum residue with a sulfur content of 5.85 wt.-%. The cost are displayed as red bars, while the revenues are in blue. The green bar displays the minimum price (464.07 €) at which the remaining desulfurized residue (690 kg) from 1 t processes vacuum residue feed needs to be sold to cover all expenses. Consequently, this means that 1 t of desulfurized vacuum residue has the minimum production cost of 672.56 €.

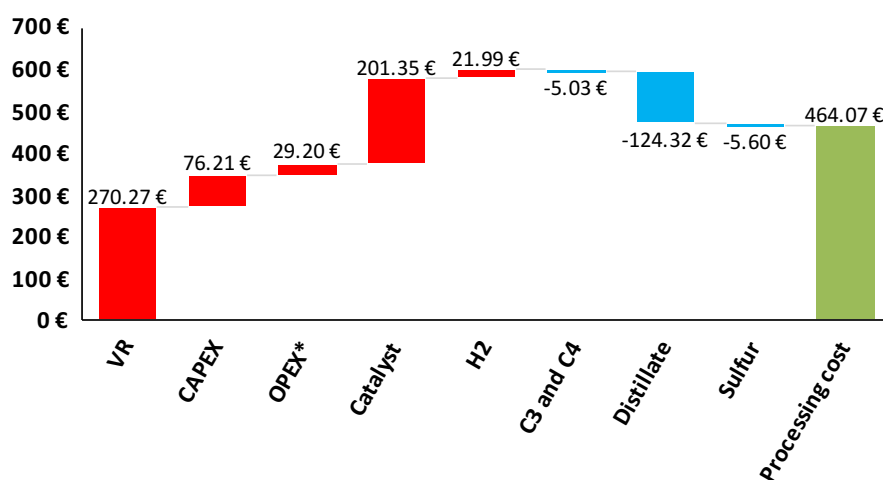


Figure 7.3: Economics of the vacuum residue upgrading using catalyst B14

Since the possibility to return spent catalyst to the process while maintaining a high catalytic activity could not be validated experimentally, the sensitivity of the price of 1 t desulfurized vacuum residue with respect to the recirculation rate of the catalyst is presented in Fig. 7.4.

The green area marks the price range projected for VLSFO (very low sulfur fuel oil - HFO with a sulfur content of < 0.5%) after the IMO regulations come into order based on several studies [271–273]. The price for VLSFO is reported to increase due to a shift in demand from High Sulfur Fuel Oil (HSFO) to VLSFO. The shift in demand is difficult to predict, but most likely, not all ship owners will install scrubbers on board their fleet in order to be able to run on HSFO after 2020. The red line in Fig. 7.4 displays the production cost based on the experimental findings depending on the catalyst recycle ratio. In the bottom diagram, the further catalyst performance improvements are taken into account reducing the necessary total catalyst

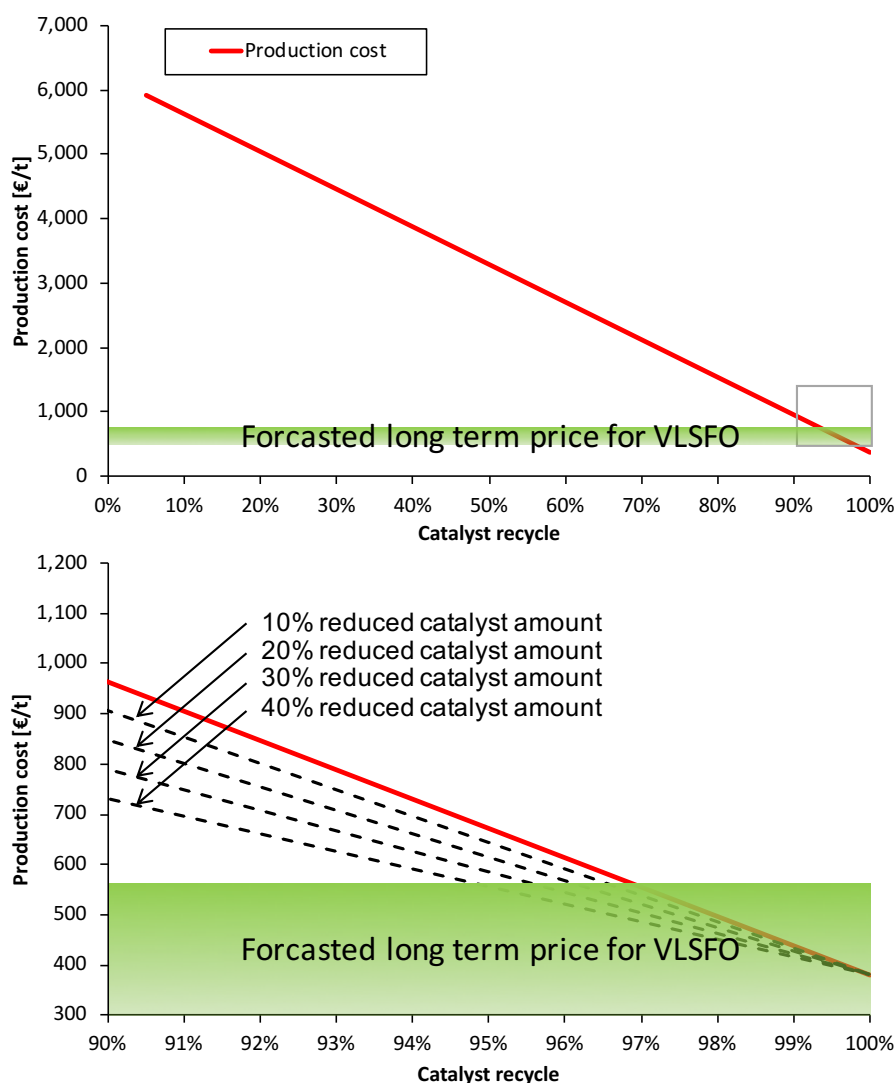


Figure 7.4: Top: sensitivity analysis for the recycle ratio of catalyst B14 Bottom excerpt of the region 90 - 100% recycle with dotted lines as optimization potential in catalyst amount reduction

amount. The dotted lines display cases in which the catalyst is improved in such a manner that the total amount can be reduced by 10%, 20%, 30% and 40%. At this stage of research, there are a number of uncertainties and several optimization potentials that can lead to these improvements. The analysis shows that by reducing the needed catalyst amount by 40% a purge of 5% spent catalyst could still enable economic performance of the process.

7.4 Economic analysis of SCW upgrading

When SCW is used, the main product of the process is not desulfurized residue but lower boiling fractions with higher market value. Downside of SCW upgrading is the remaining residue with a sulfur content of 7%. This residue can only be used

thermally on site or as basis for HFO. Figure 7.5 displays the cost revenue balances for the SCW case in a waterfall diagram.

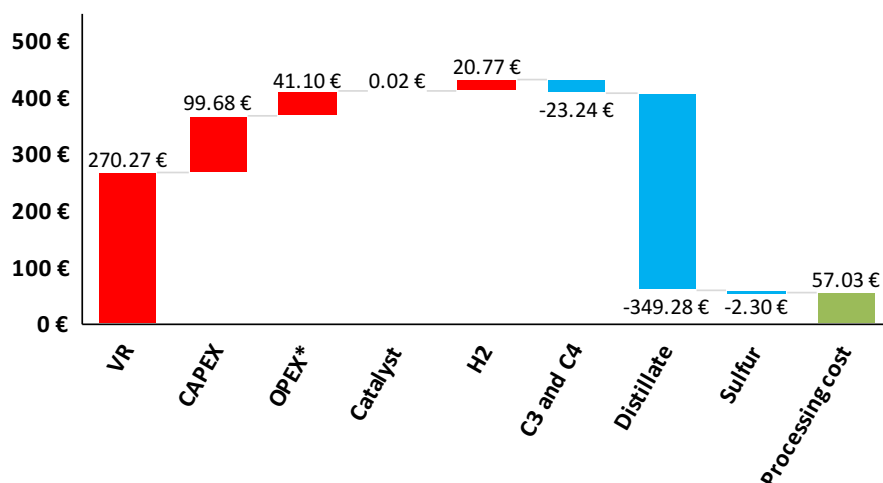


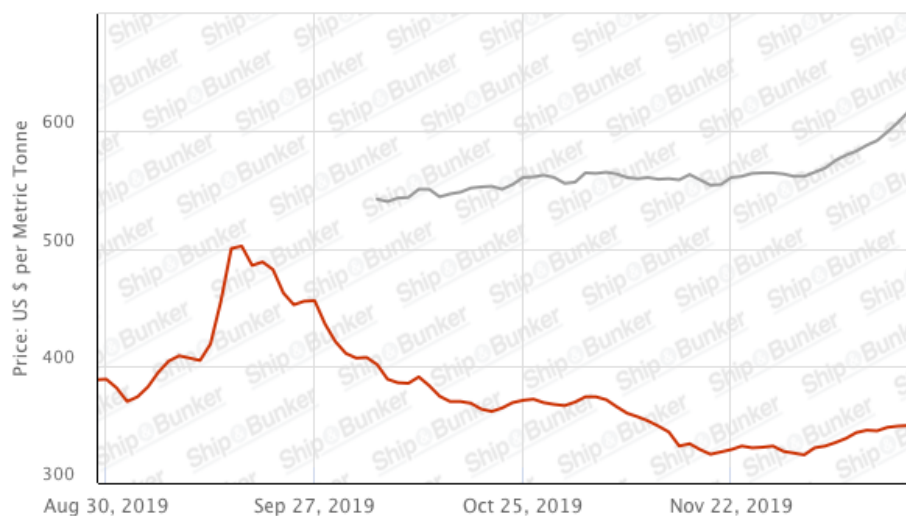
Figure 7.5: Economics of the vacuum residue upgrading using SCW

The higher CAPEX due to larger equipment size and the higher OPEX (excluding hydrogen and catalyst) due to elevated operation temperature compared to the first economic case can be seen in Fig. 7.5. In total, the processing cost still stay below those of the first case because water as catalyst is significantly less expensive than catalyst B14. Revenues from distillate fractions and sulfur still do not cover all expenses so that the remaining high sulfur residue (230 kg/t) must still achieve a market value of at least 57.03 € (247.96 €/t).

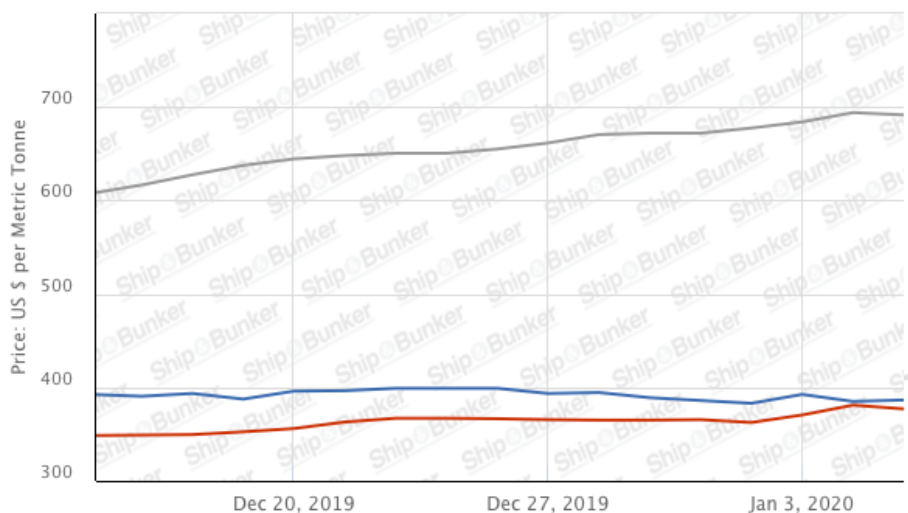
7.5 Evaluation and comparison

Throughout the last months of the year 2019, just before the IMO regulations came into effect, the fuel price for HFO dropped dramatically while the price for VLSFO increased steadily. As displayed in Fig. 7.6 (a), the price gap between VLSFO and HFO steadily increased in average at the 20 largest ports world wide. Also in 2020 the price further increased for VLSFO as displayed in Fig. 7.6 (b) but here we also see an increase in HFO price.

In January 2020 the VLSFO price reached almost 700 \$/t (629 €/t) making the desulfurization process economically more attractive. Based on this price and a HFO price of 380 \$/t (342 €/t) the economics of the two processes for the 50,000 barrel per day plant are compared in Tab. 7.5. For each of the upgrading processes (catalyst B14 and SCW) two scenarios are presented.



(a)



(b)

Figure 7.6: Price development for HFO 380 (red), HFO 180 (blue) and VLSFO (gray) in (a) 2019 and (b) 2020 [274]

Table 7.5: Economic comparison of both cases

		Cost	Income	Revenue	ROI
Cat. B14	95% recycle	1 294 M€/a	1 229 M€/a	-65 M€/a	-4.3%
	95% recycle and				
	40% catalyst reduction	1 120 M€/a	1 229 M€/a	109 M€/a	7.3%
SCW	77% Conversion	933 M€/a	979 M€/a	47 M€/a	2.4%
	100% Conversion	959 M€/a	1 098 M€/a	135 M€/a	6.7%

The economic analysis shows that the desulfurization of the residue using catalyst B14 has potential in the current market situation. In comparison to the SCW upgrading scenario, catalyst B14 may have an economic advantage, if catalyst performance and recycling are improved. Catalyst cost would have to be reduced by at

least 2/3 of the assumed price in order to reach a return on invest (ROI) of 15%, which is generally the minimum return on invest (ROI) for large projects in industry. For the SCW upgrading process not even the complete conversion of the of the feed vacuum residue to lower boiling products could improve the economic performance to an ROI of 15%. Market ready solutions exist aiming at complete conversion with slurry hydrogenation reactors, but the economic incentive is not strong enough to see these solutions prevail. Since the market situation is not easy to predict and insecurities concerning the VLSFO price development dominate the market, refineries will currently not install equipment to produce fuel complying with the new sulfur regulations. Additionally, refineries assume that the extreme price differences observed at the moment will not endure. For example the company UOP assumes ship owners to gradually equip their fleet with scrubbers to enable the utilization of HFO after 2020 and that this will affect the price situation as displayed in Fig. 7.7. A well-founded statement will only be possible after prices have found a stable level as assumed in Fig. 7.7.

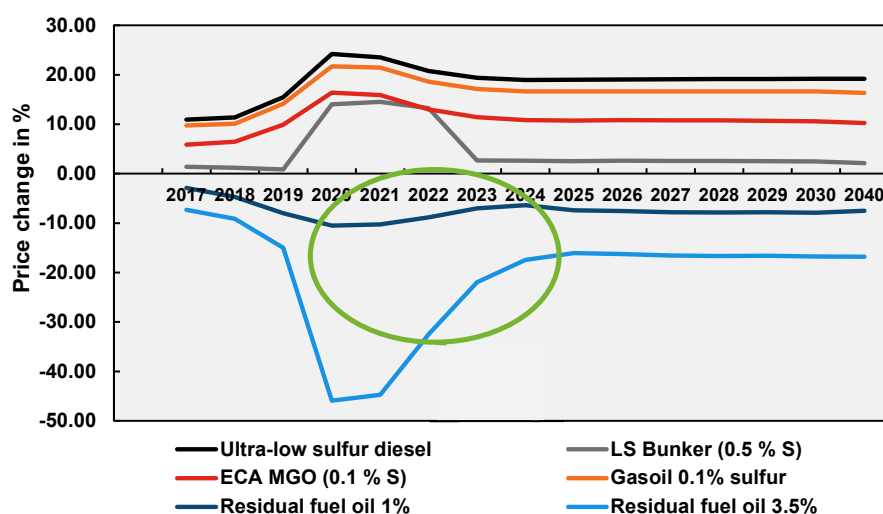


Figure 7.7: Long term price trend for bunker fuels [168]

Concluding from the economic assessment presented in this chapter, the current market situation grants advantages for refineries that are able to supply VLSFO. Both residue upgrading processes presented here do not achieve large enough revenues to make the ROI attractive. Catalyst B14 bears large potential for improvements and may become economically attractive, if its performance is improved and the needed amount reduced. On long term, the ship owners will decide which direction the market will take and only when a stable VLSFO and HFO price level has been reached, refiners will make decisions on how to deal with the residue. Having an economically feasible solution at hand by that time will be extremely valuable.

The economic calculations in this chapter show that catalyst B14 has the potential to play a significant roll in the future, if further investigations on the catalysts performance improvement show positive results.

Summary and outlook

The aim of this work was to identify process conditions and catalysts or additives for slurry phase vacuum residue hydrodesulfurization under less severe conditions than for hydroconversion and to identify the mechanistic pathway for hydrodesulfurization of the feedstock.

The effects of process conditions pressure, H_2 throughput, reaction time, and temperature on desulfurization and conversion reactions were analyzed intensively. The calculation of a rate expression for both desulfurization reactions and conversion laid basis for choosing the temperature within optimal range for desulfurization, while keeping conversion at a minimum. By systematic analysis of the influence of all process parameters, it was found that long residence time, at low temperature, and high H_2 partial pressure and throughput were beneficial for desulfurization reactions. On the other hand, conversion reactions were enhanced by choosing all parameters, except for pressure, at the upper range within the examined region.

Table 8.1: Choice of process parameters to achieve good desulfurization and high conversion

Process parameter	Desulfurization	Conversion
Pressure	high	low
H_2 throughput	high	high
Residence time	high	high
Temperature	low	high

A basic set of process parameters for the screening of several promising catalysts was chosen based on the observations summarized in Tab. 8.1. While both conversion reactions and desulfurization benefit from high H_2 throughput and residence time, pressure and temperature could be adjusted to either promote desulfurization or conversion. With the knowledge of optimal process conditions for the desulfurization of vacuum residue, 400 °C, 310 bar, 1200 l/h H_2 throughput, and 3 h residence time

were chosen for the screening of catalysts. Several catalysts and additives were investigated for their ability to desulfurize vacuum residue at these conditions.

The catalyst screening revealed SCW as additive that enhances conversion reactions, while catalyst B14 was identified as very good desulfurization catalyst. The mechanisms behind conversion of vacuum residue with SCW and desulfurization with catalyst B14 were investigated and discussed. While in literature, SCW is also discussed as additive for desulfurization, the investigations in this thesis showed very clearly that SCW promotes cracking reactions and not desulfurization. Experiments with sulfur containing model compounds revealed the stability of especially BT and DBT structures and the fact that they are very prone to SCW supported desulfurization. Combining SCW with a molybdenum containing catalyst could only marginally increase the desulfurization of model compounds in comparison to SCW without the catalyst. The same process conditions and catalysts applied to model compounds were then used with crude oil based vacuum residue. Strong differences between the desulfurization of model compounds and vacuum residue show that reactions with model compounds are not capable of representing the desulfurization of crude oil based vacuum residue. Desulfurization of asphaltenes and maltenes is more complex because of the large aromatic cores, branched alkyl chains shielding the sulfur atoms, and $\pi - \pi$ interactions between aromatic sheets. Only by cracking of these highly complex residue constituents, sulfur bonds are destabilized and made accessible for sulfur removal. The strong $\pi - \pi$ interactions between the aromatic sheets of asphaltenes and maltenes can be reduced by SCW as also shown by other researches. The increased conversion of vacuum residue to oil and asphaltenes to maltenes observed when using SCW has also been shown by other researchers, but in this work the formation of coke can be completely suppressed by high H_2 pressure. Because SCW enhances only the conversion and not the desulfurization, the remaining residue fraction exhibits an increased sulfur content. Desulfurization abilities of SCW are negligible, but its positive effect on cracking reactions can be utilized in processes where conversion of high boiling vacuum residue to low boiling and more valuable products is the aim. Increasing the process temperature to $430^\circ C$ resulted in a conversion of 77% with the downside of a remaining residue with 7% sulfur content. Based on the compounds identified in the oil phase as well as the composition of the residue, a mechanistic pathway was suggested.

Catalyst B14 exhibited a very strong desulfurization effect and therefore it is currently subject to patent law proceedings which prevent the catalytic substances to be named here. The catalyst is formed insitu by addition of two materials that have

a very strong hydrogenation effect. This strong catalytic hydrogenation resulted in complete removal of asphaltenes by hydrogenation of the aromatic core. H/C ratio of the substrate was intensively increased to nearly 2. Desulfurization with catalyst B14 proceeds via the HYD route. The bond energy of C-S bonds in an aliphatic system is lower than in aromatic systems, enabling deep hydrodesulfurization at low temperatures of 400 °C where thermal cracking reactions are not as dominant. A potential reaction path for the desulfurization of an asphaltene molecule under these conditions was developed based on the identified product properties. By variation of the ratio and total amount of the two catalyst precursors, the catalysts composition was optimized. Reduction of residence time and increase of the total catalyst amount could promote desulfurization reactions while at the same time lowering the occurrence of cracking reactions. Desulfurization of above 90% was reached at only 30% conversion when 15 wt% of the catalyst precursor was introduced into the system at 400 °C, 310 bar, 1200 l/h H₂, and 1 h residence time.

In order to identify the economic potential for both experimentally demonstrated routes (SCW for vacuum residue hydroconversion and catalyst B14 for vacuum residue hydrodesulfurization), economic assessments for both hydroprocessing paths were developed for a 50,000 barrel per day vacuum residue upgrading facility. CAPEX for the SCW hydroconversion plant are higher than for hydrodesulfurization with catalyst B14, mostly because of the larger and more expensive equipment needed. On the other hand, OPEX for the hydroconversion process with SCW are comparably low, because no expensive catalyst is of need. Still, revenues from low boiling products cannot compensate the complete processing cost and the remaining vacuum residue with high sulfur content would need to be sold at a price above the current (and also long term) HSFO price. For hydrodesulfurization with catalyst B14, the OPEX are extremely high, if no recirculation of the catalyst is assumed. Sensitivity analysis for the influence of total catalyst amount and recycle on the desulfurization cost showed potential for this technology, if catalyst activity can be maintained at high recirculation and lower catalyst/vacuum residue ratio. The fact that catalyst B14 has a very strong hydrogenation activity results in high H₂ consumption. Though the aim of low conversion is achieved, the high H₂ consumption exceeds that of the SCW hydroconversion process. In spite of the assumption that H₂ consumption intensively dictates the processing cost, production cost are mainly influenced by CAPEX and catalyst cost.

Price fluctuations at the fuel oil market as consequence of the LSF2020 regulations prevent refineries from making investment decisions though currently (January 2020)

the price gap between HFO and VLSFO almost reaches 300 €/t. The gap is expected to decrease in the upcoming years leading to larger economic challenges for vacuum residue hydrodesulfurization processes.

The aim of finding a catalyst and process conditions for hydrodesulfurization of high sulfur vacuum residue in a slurry reactor system was reached. The mechanism behind this route was identified, revealing the downsides of the catalyst. Very high catalyst/vacuum residue ratio and high H₂ consumption lead to economic unfavorable conditions for the technology. The economic assessment and comparison with a technology for vacuum residue conversion showed both advantages and downsides of the hydrodesulfurization catalyst B14. Future research needs to focus on improving catalyst performance to make it an interesting option for refineries. Intensive studies on the molecular level could help identify optimization potentials. Investigations on the long term activity of the catalyst and recycle potential should also be addressed in order to reduce cost. Though plugging of the downstream equipment could be prevented by addition of HOK and powdering of the catalyst precursors, this phenomenon needs to be investigated more thoroughly. SCW hydroconversion uses a cheap and environmentally sustainable additive to enhance conversion. The downside of the high sulfur containing hydrogenation residue of this process could possibly be minimized by using SCW at even higher temperatures, normally applied for hydroconversion processes.

Appendix

A

Appendix

A.1 Determination of kinetic parameters

In a batch-reactor, kinetic data can be retrieved by varying residence time and reaction temperature subsequently in different experiments, while measuring the concentration or amount of the respective substance. The amount of reaction products must be kept low to minimize their effect on the reaction rate. In the here used system, formed products are continuously removed from the reaction zone, ensuring minimal influence on the reaction. The used procedure for acquiring the rate of reaction is based on [275]. The reaction order was determined by variation of the residence time. In order to find the reaction order, an order was assumed and the corresponding function of the respective component was plotted over time as indicated in the following equations.

$$n = 0 \quad c_A(t) = c_A(0) - kt \quad \rightarrow \quad \text{plot } c_A \text{ over } t \quad (A.1a)$$

$$n = 1 \quad c_A(t) = c_A(0)\exp(-kt) \quad \rightarrow \quad \text{plot } \ln\left(\frac{c_A}{c_{A0}}\right) \text{ over } t \quad (A.1b)$$

$$n \geq 2 \quad \left(\frac{1}{c_A(t)}\right)^{n-1} = \left(\frac{1}{c_{A0}}\right)^{n-1} + kt(n-1) \quad \rightarrow \quad \text{plot } \left(\frac{1}{c_A(t)}\right)^{n-1} \text{ over } t \quad (A.1c)$$

(A.1)

The plot with a linear relationship represented the reaction order and the slope of the plotted line gave k .

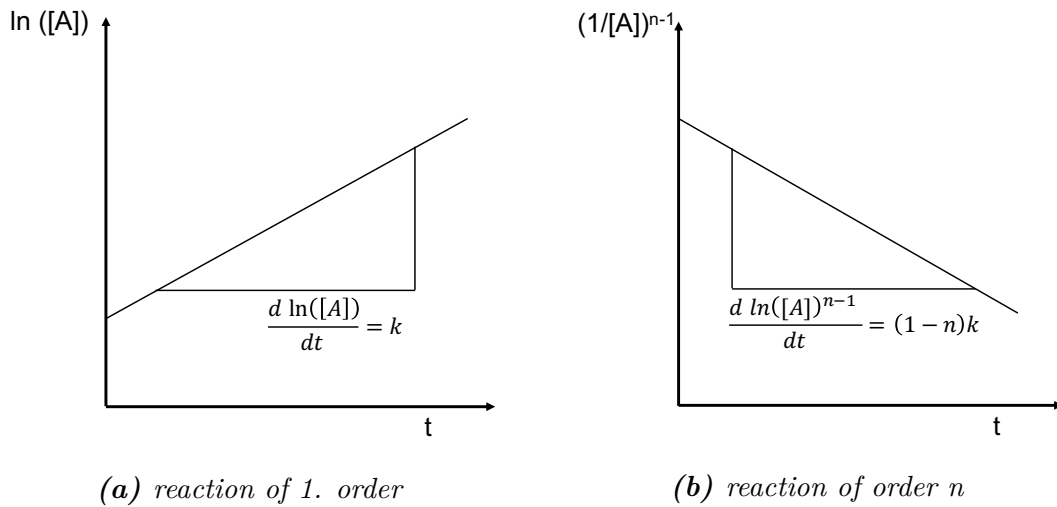


Figure A.1: Determination of the reaction order

Measured data for $\ln(k_A)$ can be plotted over $1/T$ to obtain the slope of the resulting plot as activation energy (E_A) divided by the ideal gas constant (R) as displayed in Fig. A.2.

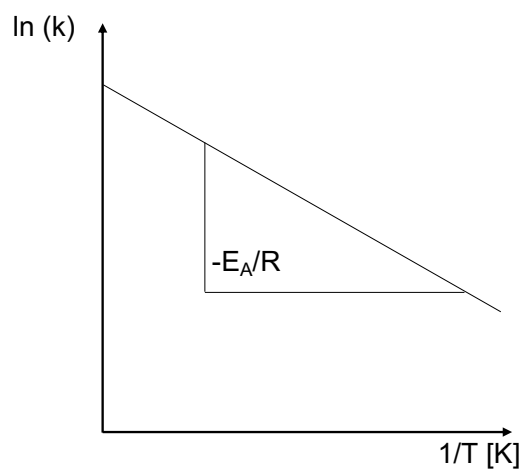


Figure A.2: Determination of the activation energy (E_A)

The intersection between the the graph and the y-axis gives k_0 so that all parameters for the rate expression are determined.

A.2 List of product specifications

Table A.1: List of product specifications; not for every experiment all product specifications were retrieved

Spec. No.	Specification
1	Fraction hydrogenation residue
2	Fraction HPCS
3	Fraction gas
4	Fraction residue
5	Fraction distillate oil
6	Fraction product oil
7	Fraction asphaltenes
8	Fraction maltenes
9	$\omega_{C,hydrogenationresidue}$
10	$\omega_{C,HPCS}$
11	$\omega_{C,residue}$
12	$\omega_{C,oil}$
13	$\omega_{C,asphaltenes}$
14	$\omega_{C,maltenes}$
15	$\omega_{C,solids}$
16	$\omega_{H,hydrogenationresidue}$
17	$\omega_{H,HPCS}$
18	$\omega_{H,residue}$
19	$\omega_{H,oil}$
20	$\omega_{H,asphaltenes}$
21	$\omega_{H,maltenes}$
22	$\omega_{H,solids}$
23	$\omega_{S,hydrogenationresidue}$
24	$\omega_{S,HPCS}$
25	$\omega_{S,residue}$
26	$\omega_{S,oil}$
27	$\omega_{S,asphaltenes}$
28	$\omega_{S,maltenes}$
29	$\omega_{S,solids}$
30	$\omega_{N,hydrogenationresidue}$
31	$\omega_{N,HPCS}$
32	$\omega_{N,residue}$
33	$\omega_{N,oil}$
34	$\omega_{N,asphaltenes}$
35	$\omega_{N,maltenes}$
36	$\omega_{N,Solids}$
37	Conversion
38	H/C ratio oil
39	H/C ratio residue
40	H/C ratio asphaltenes
41	H/C ratio maltenes
42	H/C ratio total
43	Cahr formation
44	GC/MS analysis of oil
45	GC/MS analysis of distillate fraction
46	GC/MS analysis of HPCS fraction
47	H ₂ S
48	CH ₄
49	C ₂ H ₆
50	H ₂ consumption
51	Molar mass

A.3 GC/MS of oil

Table A.2: Table of identified compounds from the oil fraction from experiment with HOK

Retention time	Compound
3.54	Octane
5.11	dimethyl-Heptane
5.30	Xylene
5.90	Nonane
6.56	methyl-Nonane
7.81	trimethyl-Benzene
7.91	Decane
10.87	Undecane
12.95	tetramethyl-Benzene
13.64	tetrahydro-Naphthalene
14.48	Dodecane
16.14	Hexatriacontane
16.30	dimethyl-Hexadecane
17.05	Tridecane
17.31	methyl-Benzothiophene
19.03	Tetradecane
19.19	dimethyl-Benzothiophene
19.98	trimethyl-Dodecane
20.65	Pentadecane
22.25	Hexadecane
22.89	methyl-Tridecane
23.57	Heptadecane
24.94	Octadecane
25.02	Pentatriacontane
26.17	Nonadecane
28.46	tetramethyl-Heptadecane
29.51	Tetracosane

A.4 GC/MS of oil

Table A.3: Table of identified compounds from the oil fraction from experiments with catalyst B14

Retention time	Compound
4.02	dimethyl-Cyclohexane
4.42	Octane
5.28	ethyl-Cyclohexane
6.59	Nonane
6.79	ethyl-2-methyl-Cyclohexane
7.05	methylethyl-Cyclohexane
7.26	propyl-Cyclohexane
7.95	ethyl-methyl-Benzene
8.49	methyl-propyl-Cyclohexane
8.80	trimethyl-Benzene
8.84	Decane
9.91	butyl-Cyclohexane
10.91	decahydro-Naphthalene
12.36	Undecane
13.05	decahydro-methyl-Naphthalene
13.69	pentyl-Cyclohexane
15.52	Dodecane
16.59	undecyl-Cyclohexane
17.88	Tridecane
18.18	Bicyclohexyl
18.85	butyl-Cyclohexane
19.21	tetradecahydro-Benzocyclodecene
19.82	Tetradecane
20.75	Cyclohexane, octyl-
21.15	dimethyl-ethanediyl-Cyclohexane
21.50	Pentadecane
21.59	Undecadiene
22.42	n-Amylcyclohexane
23.00	Hexadecane
24.40	Heptadecane
25.71	Octadecane
26.94	Hexatriacontane
28.10	Eicosane
29.22	Tritetracontane

A.5 Data preparation

Data preparation includes checking the collected data for consistency, accuracy and whether it is cleaned from faulty values. The first step is to store the data in the form of a matrix consisting of vectors that include the experimentally gained data points. A matrix has to be exported containing all vectors between correlations are to be found. During this step it is also necessary to check for the correct formatting of all data points and of the consistency of this formatting. Clustering will work best on data which is normalized. This means that the different vectors should be in the same order of magnitude. The collected data is then checked concerning the completeness of the included data sets.

Once the data is prepared and exported in a manner in which the clustering algorithm can process it, the code can be run on the data. Although data preparation can rule out many potential errors, it is essential to evaluate the results and check their meaning in order to extract useful information from the clustering.

A.6 MATLAB scripts

Residence time %%

```
Densityin = 1.06; % g/l
Molmass = 94.2; % g/mol
Flowratein = 1.5; % ml/min
H2flow = 650; % l/h
duration = 10; % min
Molvolume = 22.413962; % l/mol
Vr(1) = 1; % l
Vr(2) = 0.7; % l
p310 = 310; % bar
T400 = 400; % ?C
Tk400 = T400+273.15; % K
T20 = 20;
Tk20 = T20+273.15;
Time = 10000;
shutofftime = 600;
deadtime = 6; %min

stepsize = 1; % sec

Molflowin = Flowratein*60*Densityin/Molmass; % mol/h
Molflow(1) = 2*Molflowin; % mol/h
Molflow(2) = 2*Molflowin; % mol/h
Molflow(3) = H2flow/Molvolume - 3*Molflowin; % mol/h
Molflowtotal = sum(Molflow); % mol/h

for i = 1:3
    Concentrationin(i)= Molflow(i)/Molflowtotal; % molfraction
    n_dot(i)=Molflow(i)/3600;
end

n_dot_tot=sum(n_dot);
V_dot_p310_T20 = Molvolume*n_dot_tot/p310;
V_dot_p310_T400= Molvolume*n_dot_tot/p310*Tk400/Tk20;
V_dot(1)= V_dot_p310_T400;
V_dot(2)= V_dot_p310_T20;

%at start time concentrations in R1
for i= 1:3
    c_dot_1_(i)=n_dot(i)/V_dot(1);
end

numbr = size(Vr);
for i= 1:numbr(2)
    tau(i)=Vr(i)/V_dot(i);
end

c_old(1)=0;
c_old(2)=0;
```

```

c_old(3)=(p310)/Molvolume;

for i=1:2

    for t= 1:Time

        if t<shutofftime;
            c(i,t)=c_old(i)+1/tau(1)*(c_dot_1_(i)-c_old(i));
        else
            c(i,t)=c_old(i)+1/tau(1)*(0-c_old(i));
        end
        c_old(i)=c(i,t);
    end
end

for t= 1:Time

    if t<shutofftime;
        c(3,t)=c_old(3)+1/tau(1)*(c_dot_1_(3)-c_old(3));
    else
        c(3,t)=c_old(3)+1/tau(1)*(12-c_old(3));
    end
    c_old(3)=c(3,t);
    c_dot_tot_out1(t)=c(1)+c(2)+c(3);
end

for i=1:3
    for t=1:Time
        volpercent(i,t)=c(i,t)/c_dot_tot_out1(t);
    end
end

c1=c';
c_dot_tot_out1 = c_dot_tot_out1';
volpercent=volpercent';

for i=1:3
    c_out_old(i)=c(1,1);
    for t=2:Time

        c_out(i,t)=c_out_old(i)+(1/tau(2))*(c(i,t)-c_out_old(i));
        c_out_old(i)=c_out(i,t);
        time(t)=t/60 + deadtime;
    end
end

time=time';
c_out=c_out';
All=[time, c1, c_out];

```

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Clustering %%

```
%Set k to the number of clusters
%load data

prompt = 'How many parameters are to be clustered? Cultering beginnes
  with 7th column';
pro = input(prompt, 's');
A = readtable(pro);

[row,col]=size(A);
X = table2array (A(:,7:col));
k=3;
idx = kmeans(X,k);

[idx C] = kmeans(X,k);

BB = A.Properties.VariableNames;
B = BB(:,7:col);
A2 = [X idx];

figure;
plot(A2(idx==1,1),A2(idx==1,3),'b.','MarkerSize',25)
hold on
plot(A2(idx==2,1),A2(idx==2,3),'g.','MarkerSize',25)
if k>2
plot(A2(idx==3,1),A2(idx==3,3),'r.','MarkerSize',25)
end
if k>3
plot(A2(idx==4,1),A2(idx==4,3),'y.','MarkerSize',25)
end
plot(C(:,1),C(:,3),'kx',...
      'MarkerSize',15,'LineWidth',3)
%legend('Cluster 1','Cluster 2','Cluster 3',...
%      'Location','NW')
%title 'Conversion and H add'
xlabel(B(1,1));
ylabel(B(1,3));

figure;
plot(A2(idx==1,2),A2(idx==1,3),'b.','MarkerSize',25)
hold on
plot(A2(idx==2,2),A2(idx==2,3),'g.','MarkerSize',25)
if k>2
plot(A2(idx==3,2),A2(idx==3,3),'r.','MarkerSize',25)
end
if k>3
plot(A2(idx==4,2),A2(idx==4,3),'y.','MarkerSize',25)
end
plot(C(:,2),C(:,3),'kx',...
      'MarkerSize',15,'LineWidth',3)
%legend('Cluster 1','Cluster 2','Cluster 3',...
```

```

%      'Location','NW')
%title 'delta S and H add'
xlabel(B(1,2));
ylabel(B(1,3));

figure;
plot(A2(idx==1,1),A2(idx==1,2),'b.','MarkerSize',25)
hold on
plot(A2(idx==2,1),A2(idx==2,2),'g.','MarkerSize',25)
if k>2
plot(A2(idx==3,1),A2(idx==3,2),'r.','MarkerSize',25)
end
if k>3
plot(A2(idx==4,1),A2(idx==4,2),'y.','MarkerSize',25)
end
plot(C(:,1),C(:,2),'kx',...
      'MarkerSize',15,'LineWidth',3)
%legend('Cluster 1','Cluster 2','Cluster 3',...
%      'Location','NW')
%title 'Con and delta S'
xlabel(B(1,1));
ylabel(B(1,2));

if k>3
figure;
plot(A2(idx==1,3),A2(idx==1,4),'b.','MarkerSize',25)
hold on
plot(A2(idx==2,3),A2(idx==2,4),'g.','MarkerSize',25)
if k>2
plot(A2(idx==3,3),A2(idx==3,4),'r.','MarkerSize',25)
end
if k>3
plot(A2(idx==4,3),A2(idx==4,4),'y.','MarkerSize',25)
end
plot(C(:,3),C(:,4),'kx',...
      'MarkerSize',15,'LineWidth',3)
%legend('Cluster 1','Cluster 2','Cluster 3',...
%      'Location','NW')
%title 'Con and delta S'
xlabel(B(1,3));
ylabel(B(1,4));
end

figure;
labels = {'label 1','label 2','label 3'};
scatter3(A2(idx==1,1),A2(idx==1,2),A2(idx==1,3),'MarkerEdgeColor','b',...
         'MarkerFaceColor','b')
hold on
scatter3(A2(idx==2,1),A2(idx==2,2),A2(idx==2,3),'MarkerEdgeColor','g',...
         'MarkerFaceColor','g')
if k>2

scatter3(A2(idx==3,1),A2(idx==3,2),A2(idx==3,3),'MarkerEdgeColor','r',...
         'MarkerFaceColor','r')

```

```

end
if k>3

scatter3(A2(idx==4,1),A2(idx==4,2),A2(idx==4,3),'MarkerEdgeColor','y',...
'MarkerFaceColor','y')
end

stem3(C(1,1),C(1,2),C(1,3),'MarkerEdgeColor','k','MarkerSize',15);
stem3(C(2,1),C(2,2),C(2,3),'MarkerEdgeColor','k','MarkerSize',15);
if k>2
stem3(C(3,1),C(3,2),C(3,3),'MarkerEdgeColor','k','MarkerSize',15);
end
if k>3
stem3(C(4,1),C(4,2),C(4,3),'MarkerEdgeColor','k','MarkerSize',15);
end

%legend('Cluster 1','Cluster 2','Cluster 3',...
%      'Location','NW')
legend('Low conversion, low sulfur removal, low hydrogen
consumption','medium/high conversion, low sulfur removal, medium
hydrogen consumption','medium conversion, high sulfur removal, high
hydrogen consumption',...
'Location','N')
%xlabel(B(1,1));
xlabel('Conversion [%]')
ylabel(B(1,2));
zlabel(B(1,3));

```

*Error using input
Cannot call INPUT from EVALC.*

*Error in Clustering (line 6)
pro = input(prompt,'s');*

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A.7 Experimental Setup



Figure A.3: Compressor for H_2 compression

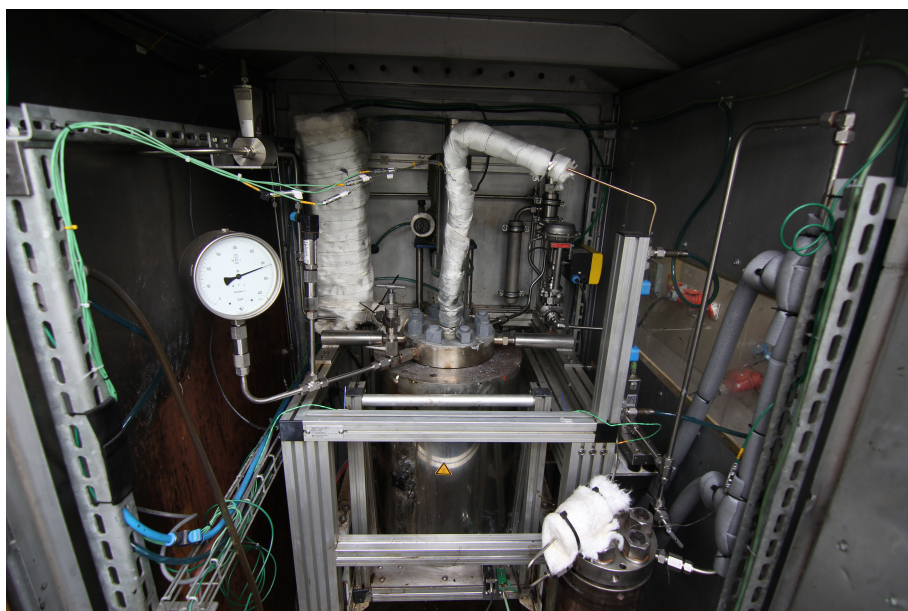


Figure A.4: Reactor with stirrer, preheater, separator, and measuring devices

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