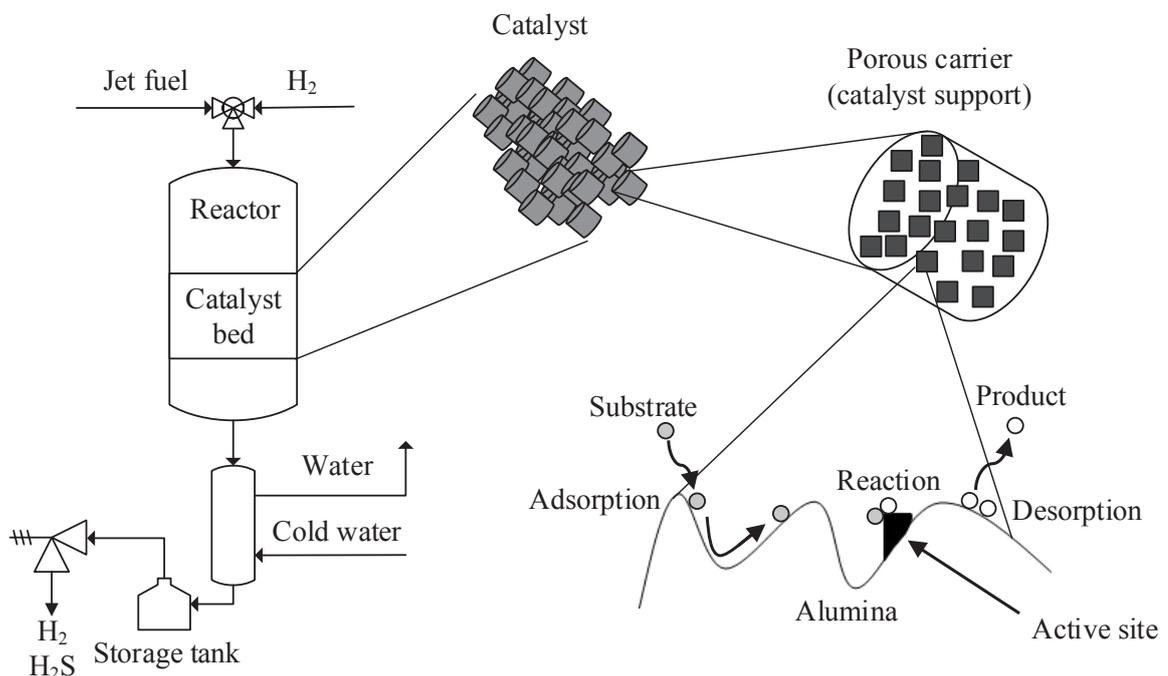


μ HDS system for desulfurization of logistic fuels for fuel cell applications



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Nicklas Jönsson & Johan Karstensson

Department of Chemical Engineering
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by

Nicklas Jönsson and Johan Karstensson

Department of Chemical Engineering
Lund University

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Supervisor: **Associate Professor Christian Hulteberg**
Co-supervisor: **PhD Fredrik Silversand**
Examiner: **Professor Hans T. Karlsson**

Postal address

P.O. Box 124
SE-221 00 Lund, Sweden

Web

www.chemeng.lth.se

Visiting address

Getingevägen 60

address

Telephone

+46 46-222 82 85

+46 46-222 00 00

Telefax

+46 46-222 45 26

Preface

This master thesis was carried out at the Department of Chemical Engineering at Lund University and at Catator AB, in collaboration with FMV. We are grateful for having the opportunity to be part of this exciting project.

Special thanks to Fredrik Silversand and Mikael Persson at Catator AB for all your help and support during this project.

We also want to thank Christian Hulteberg, for your availability and valuable guidance, and Hans T. Karlsson for your time in this project.

Furthermore, we would like to thank Tian, Putte, Fredrik Svensson, Mariano and Yasir for brightening up the workday with fun conversations.

We remember Fredrik Silversand saying, on the subject of catalysis: “The farther into the woods you go, the darker it gets”, which at that point felt striking. Though, we feel we might have found the way out and managed to “see the light at the end of the tunnel”.

Abstract

Logistic fuels such as diesel and petrol, in which Jet A1 is included, are sulfur-containing fuels used for transports. The main problem with logistic fuels, when used in fuel cell (FC) applications, is their relatively high concentration of sulfur compounds. The sulfur compounds might poison the catalysts in all of the downstream processes, including the FC itself.

Hydrodesulfurization (HDS) is an industrial approach for effective desulfurization of fuels by converting complicated organic sulfur compounds into hydrocarbons and hydrogen sulfide (H_2S), which in turn can be trapped in an adsorption cartridge. This thesis focused on a miniaturization of said technology, i.e. a μHDS -system for logistic fuels, in small-scale fuel cell systems.

The goal was to desulfurize Jet A1 for utilization in FC-applications. Through investigation and evaluation of different catalysts and process parameters, a catalytic reactor system was developed. Desirable was to achieve a sulfur level below 10 ppm which is low enough for injection into a FC.

The approach was to set up a micro-scale plug flow reactor (PFR) in which the effects of temperature ($260\text{ }^\circ\text{C} - 450\text{ }^\circ\text{C}$), pressure (2 bar – 8 bar) and LHSV ($1\text{ h}^{-1} - 4\text{ h}^{-1}$), on catalytic activity, was investigated. Incipient wetness impregnation was used for the preparation of six different catalysts, which were tested in said reactor. Detailed investigations were done on a Pt/alumina (PPt-47, manufactured by Stonemill AB) catalyst as well as on a CoMo/alumina catalyst impregnated with citric acid (CA). Their activity was determined based on the conversion of thiophene and dibenzothiophene (DBT). As a final test, Jet A1 was desulfurized using the same two catalysts.

CoMo-CA was consistently the better performing catalyst compared with PPt-47, reaching a sulfur conversion of 98.2 %, compared to 93.2 % when tested with Jet A1 at the most severe reactor settings. A sulfur level of 13.3 ppm was achieved with the CoMo-CA, applicable in a high-temperature FC.

Populärvetenskaplig sammanfattning

μ -Avsvavlingssystem för jetbränsle till bränslecellsapplikationer. Bränsleceller är ett intressant alternativ till förbränningsmotorer då bränsleceller har en högre effektivitet, är miljövänligare samt tystare.

Bränslen som diesel, bensin samt det undersökta bränslet Jet A1, innehåller olika svårreagerade svavelföreningar. Problemet med bränslena är att de har ett relativt högt svavelinnehåll. Svavelföreningarna riskerar att förgifta katalysatorerna i de nedströms kommande processerna, inklusive bränslecellen själv, och måste därför avsvavlas.

Genom att omvandla komplicerade svavelföreningar till vätesulfid, som i sin tur tillfångatas i en adsorptionspatron, är väteavsvavling ett effektivt industriellt tillvägagångssätt att avsvavla på.

Syftet med detta examensarbete har varit att undersöka möjligheten att, på mikroskala, katalytiskt avsvavla jetbränslet Jet A1, till en svavelhalt acceptabel för bränslecellsintag. Detta har inneburit framtagning av en lämplig reaktor och optimering av reaktionsparametrar, tillverkning och utvärdering av katalysatorer samt analys av produkt.

Reaktorsystemet var uppställt i en ugnslignande omgivning. Reaktorn var omsluten av en värmare i ett isolerat kärl och höll konstant temperatur. Samtliga katalysatorer prövades först vid identiska processbetingelser för att jämföra deras inbördes aktivitet. De två bäst presterande katalysatorerna i denna undersökning var CoMo-CA och PPt-47. CoMo-CA består av kobolt, molybden och nickel, på en support av aluminiumoxid, och citronsyra användes för att optimera spridningen av den aktiva fasen vid tillverkningen av katalysatorn. PPt-47 är en ädelmetallkatalysator bestående av endast platina på en support av aluminiumoxid. Denna tillverkas av Stonemill AB.

Vidare användes dessa katalysatorer i detaljerade tester, som kördes på både tiofen och dibensotiofen (DBT), för att avgöra vilka processbetingelser som fungerade bäst. Sist ut testades katalysatorernas förmåga att avsvavla Jet A1 vid ett skarpt försök.

Det högst uppmätta resultatet på Jet A1 var en omsättning av svavel på 98,2 %, vilket utfördes vid de tuffaste processbetingelserna, med CoMo-CA katalysatorn. Sammanfattningsvis kan det konstateras att CoMo-CA genomgående hade en högre svavelomsättning än PPt-47 samt att en svavelhalt på 13,3 ppm uppnåddes. Denna halt är gångbar i en högtemperaturbränslecell.

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1 Introduction

The military shows interest in the use of fuel cells (FC) for various applications. FC's are quiet, have high energy efficiency and low weight, why they are highly interesting for a wider use. Most fuels used by the military are a group of hydrocarbons called logistic fuels and can be diesel, petrol and Jet A1. All of which have too high sulfur content and decomposes the sulfur component into H_2S , up to 3,000 ppm, to be used in FC applications. The fuel has to be desulfurized for several reasons. Initially, stringent environmental regulations within EU [1, p. 80], prevention of catalyst poisoning, protection from corrosion and protection of downstream processes [1, p. 77], [2, p. 1]. A common technique for sulfur removal is called hydrodesulfurization (HDS), which saturates hydrocarbons with hydrogen. Next step in the chain, after hydrotreating, towards an injection of hydrogen to a FC is the removal of formed sulfur before gas upgrading. FC's among other applications are highly sensitive to sulfur and requires low concentration, which normally must be below 1 ppm [2, p. 2]. Because of the good characteristics that follow with a FC in combination with the easily accessible fuel, Jet A1, this led to a cause for investigation.

Sulfur compounds in diesel contribute to environmental problems and EU have set standard directives on maximum allowed sulfur content in exhaust gases. Since this directive from EU, the interest in hydrotreating has grown. Today the EU directives allow a sulfur level about 10-15 ppm in diesel, as seen in Figure 1.1. This requires a procedure called deep desulfurization that produces ultra-low-sulfur diesel (ULSD). [1, p. 80]

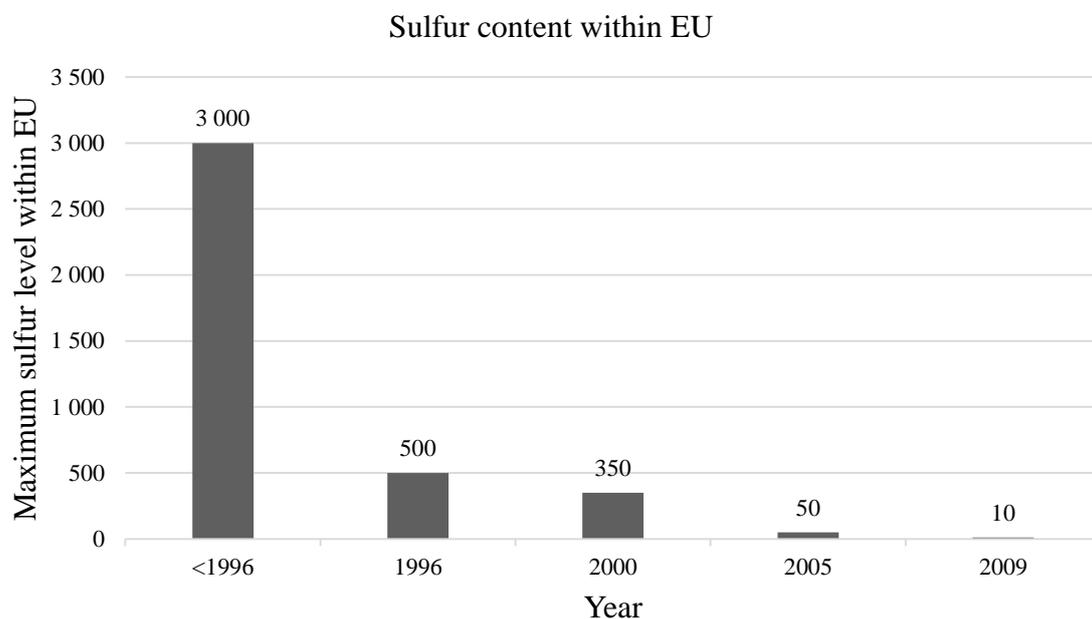


Figure 1.1. Maximum sulfur content (ppmv) allowed in automotive diesel within EU [1, p. 80].

The thesis is based on hydrotreating in order to desulfurise Jet A1 using a catalyst. The goal is to be able to reach sulfur levels <10 ppm, that makes the converted fuel possible to be run in a FC with an effect about 1 kW. This means, choice of reactor system with installation and design parameters, manufacturing of catalysts and analysis of the product. Catalysts for HDS will be

developed and tested on dodecane and paraffin. The most effective catalysts will be tried on Jet A1.

Not only the catalysts itself affects the sulfur conversion. A test matrix with pressure, temperature, liquid hourly space velocity (LHSV) and hydrogen partial pressure will be studied to view at which parameters the different catalysts had an optimum sulfur conversion. This involves two steps, hydrodesulfurization, and H₂S adsorption. The complete process can be seen below, though, only the first was evaluated.

Catator AB was founded in 1990 by a group of researchers at Lund University in Sweden. It quickly became a high-tech company in the field of catalysis and catalytic process design. Their vision is to supply high-quality catalytic systems for efficient energy supply in various applications. This thesis was an assignment coming from the Swedish Defence Material Administration (FMV) to Catator. FMV provides technology for Sweden's security. Their delivery is defence logistics, which means that they, in collaboration with their key partner, the Swedish Armed Forces, design and provide the military with defence materiel and services. Technology and business expertise are their core competences.

1.1 Overall process set-up – from logistic fuel to fuel cell applications

The complete set-up, from logistic fuels to FC injection, involves several steps. First, the sulfur content in the fuel has to be treated through a HDS step. Organic sulfur compounds are converted into hydrogen sulfide (H₂S) and later removed through H₂S adsorption in a second reactor. This is done in a process step where the H₂S-system will trap the H₂S into an adsorption cartridge consisting of zinc oxide (ZnO). After the sulfur removal, the product gas needs upgrading, which is also done through two steps. Autothermal reforming (ATR) is the first one and is used to produce syngas, rich on H₂ and CO. The last step before FC injection, a water-gas shift (WGS) reaction is needed to alter the ratio between H₂ and CO in the syngas. A process overview is visualized in Figure 1.2.

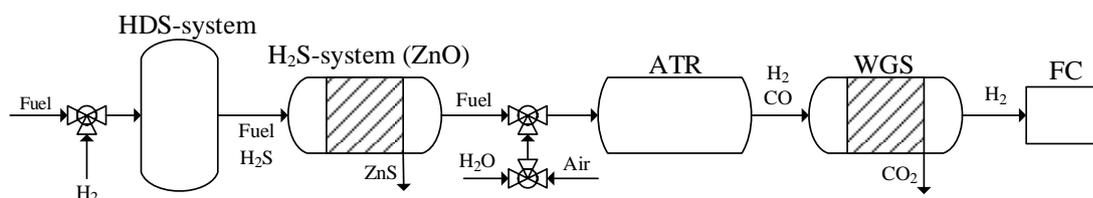


Figure 1.2. Overview of the desulfurization process from logistic fuels to FC.

1.1.1 Logistic Fuels

For FC applications there are a great variety of logistic fuels available. The logistic fuels are products that originate from refineries and consist of hydrocarbon mixtures. Hydrocarbons with a carbon number in the range of C₉-C₂₈, are all included in the diesel fuel category and constitutes of alkanes, cycloalkanes, and aromatics. Jet A1 is a kerosene-type fuel that is manufactured from distillates out of straight-run petroleum, derived from crude oil without chemical reaction or molecular modification [3]. Sulfur is an unwanted, but an inevitable component in logistic fuel, and for most applications, it has to be removed before use. For this, HDS as a removal method is very suitable and industrially implemented on a large scale.

1.1.2 Hydrotreating

Oil fractions in general always contain fractions of unwanted components, especially sulfur, nitrogen, oxygen and metals. These undesired compounds in the oil fractions have to be removed, and this is done via a reductive treatment called hydrotreating. The main objective with hydrotreating is simply to remove heteroatoms and, in general, it does not alter the molecular size substantially. Hydrotreating can be divided into two categories, hydrogenation and hydrogenolysis. Hydrogenation is generally performed by addition of hydrogen to double or triple bonds (π -bonds) to saturate a compound. Hydrogenolysis, on the other hand, involves breaking of the single bonds (γ -bonds), C-S or C-N etc. [1, p. 76]

Oil products can be purified before use for several reasons. Sulfur and nitrogen contribute to air pollutions which lead to acid rain. Catalysts in processes downstream seldom tolerate any presence of sulfur as it is poisoning for the catalyst as well as for the system. Since most oil fractions must be hydrotreated, this has become one of the largest industrial breakthroughs in industrial catalysis. [4, p. 2695]

The name of the hydrotreating process is determined by which heteroatom that is removed, S, N, O or M (metal): hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallization (HDM).

Figure 1.3 below shows HDS reactions of thiophene and dibenzothiophene (DBT) with equilibrium data.

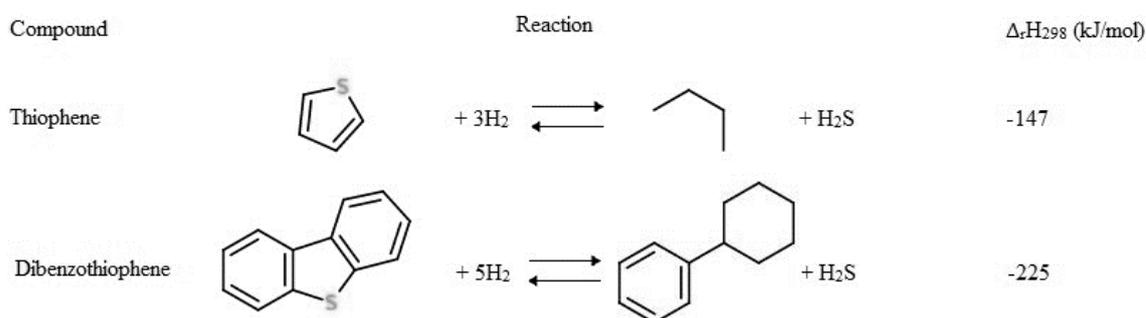


Figure 1.3. HDS reaction of thiophene and DBT [1, p. 76].

1.1.3 Autothermal Reforming

ATR is a combination of partial oxidation (non-catalytic) and steam reforming in presence of a catalyst and produces syngas. Part of the feed along with oxygen is combusted in the reactor with methane, or others, and generates heat (Reaction 1.1 and Reaction 1.2). To protect the catalyst (often platinum-based or nickel-based) from poisoning against sulfur, hydrotreating is required as a pretreatment step to reforming. Into the ATR unit, the sulfur levels should not be above 1 ppm [1, p. 77]. The outgoing gas from the ATR have a high concentration of steam >35 % and low concentration of H_2S , about 1-2 ppmv from natural gas [2, p. 2].



In the reforming zone, formed CO_2 and H_2O react with parts of the feed (Reaction 1.3 and Reaction 1.4). Figure 1.4 visualizes an ATR reactor. The exothermic oxidation reactions provide heat for the endothermic reactions. [1, p. 137]

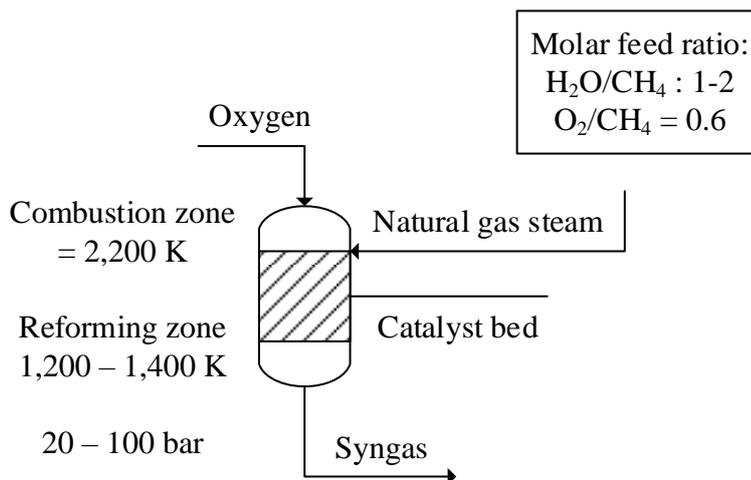


Figure 1.4. A schematic figure for an ATR process of methane with syngas as product [1, p. 137].

1.1.4 Water-Gas Shift Reactor

A widely used industrial method is one called WGS which serves the purpose to alter the ratio between H_2 and CO in the production of different chemicals, such as Fischer-Tropsch and synthetic natural gas (SNG). Reaction 1.5 below shows the principle of WGS.



A typical set-up for the WGS reaction is seen in Figure 1.5 and consist of two reactors: a high-temperature reactor and a low-temperature reactor. Catalysts have been developed to be active around $230^\circ C$, in the low-temperature reactor. Pure gases are needed to avoid poisoning of the catalysts and they are not stable at higher temperatures. [1, p. 164]

All of the processes HDS, H_2S , ATR, WGS, and FC, are sensitive to sulfur poisoning. The WGS can act as a guard bed for downstream processes, in this case, a FC, since it requires a low sulfur level and comes after the WGS. The WGS catalyst is not only very sulfur sensitive, H_2S is strongly adsorbed by the WGS catalyst. [5, p. 537]

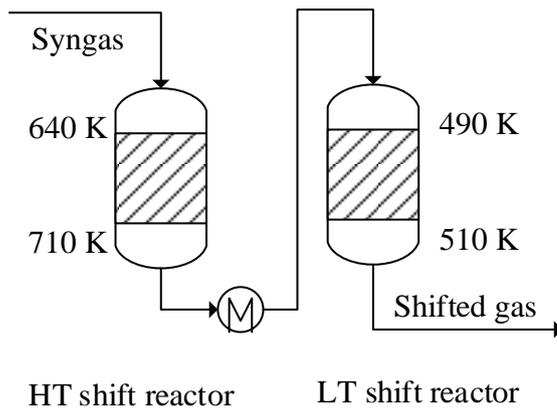


Figure 1.5. Formation of WGS reactors using syngas as feed [1, p. 164].

1.1.5 Fuel cells

A FC is an electrochemical device that converts free energy from a chemical reaction into electric energy [6]. Electrical energy, as well as heat, is directly derived from hydrogen or hydrogen-containing fuels. Oxygen and hydrogen reacts and forms water and energy, as seen in Reaction 1.6, which is the reversed electrolysis process.



The main advantage with FC's is that they can be fed with fuel continuously while still sustaining the electrical power indefinitely, contrary to regular storage cells. Other advantages that batteries follow with FC's are that they have high efficiency, they are silent and come with no pollutant emissions if they run on pure hydrogen [7].

In general, a FC includes the components anode, anodic catalyst layer, electrolyte, cathodic catalyst layer, cathode, bipolar plates/interconnects. There are several different FC's. Table 1.1 shows characteristics of common ones, which gives an indication of the applications for such devices.

Table 1.1. Characteristics of some different FC's [7, p. 2].

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Primary application	Automotive and stationary power	Portable power	Space vehicles and drinking water	Stationary power	Stationary power	Vehicle auxiliary power
Electrolyte	Polymer (plastic) membrane	Polymer (plastic) membrane	Concentrated (30-50 %) KOH in H ₂ O	Concentrated 100 % phosphoric acid	Molten carbonate from LiAlO ₂	Yttrium-stabilized Zircon dioxide
Operating temperature range	50-100 °C	0-60 °C	50-200 °C	150-220 °C	600-700 °C	700-1,000 °C
Charge carrier	H ⁺	H ⁺	OH ⁻	H ⁺	CO ₃ ⁼	O ⁼
Prime cell component	Carbon-based	Carbon-based	Carbon-based	Graphite-based	Stainless steel	Ceramic
Catalyst	Pt	Pt-Pt/Ra	Pt	Pt	Ni	Perovskite
Start-up time	Sec-min	Sec-min		Hours	Hours	Hours
Primary fuel	H ₂	Methanol	H ₂	H ₂	H ₂ , CO, CH ₄	H ₂ , CO
Power density (kW/m ³)	3.8-6.5	~0.6	~1	0.8-1.9	1.5-2.6	0.1-1.5
Combined cycle FC efficiency	50-60 %	30-40 %	50-60 %	55 %	55-60 %	55-65 %

Proton Exchange Membrane Fuel Cell

There are several different fuel cell types, which have different characteristics. Advantages are simplicity, viability and quick start-up. In vehicles, the FC needs to be downsized for use, and therefore the proton exchange membrane fuel cell (PEM-FC), seen in Figure 1.6 [8], -is highly suitable.

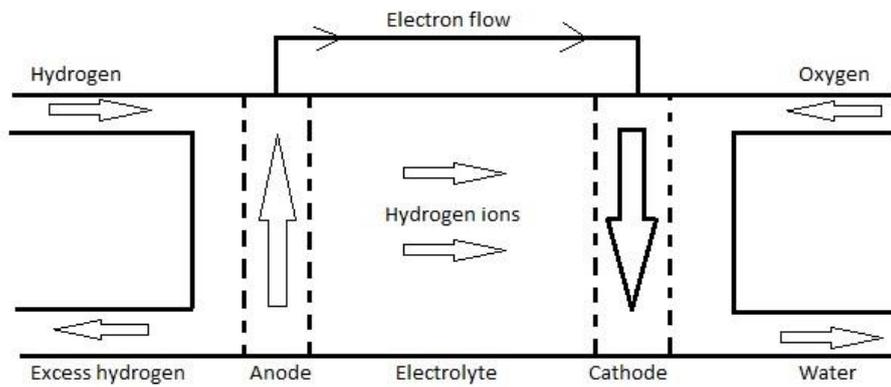


Figure 1.6. A general schematic of an operating PEM-FC [8, p. 28].

2 Hydrodesulfurization

2.1 Commercial HDS systems

There are several commercial and implemented systems for hydrodesulfurization of organo-sulfur compounds. Basic schematics and principles for three large operators are presented in this section. Though, the process parameters differ widely from the catalyst optimization reactors. Most significantly, the HDS are performed using a lot higher pressures. The temperature chosen depends more on the compound that is desulfurized. Too high temperatures, about $>500\text{ }^{\circ}\text{C}$ and above, for too long could cause risk for coking. Coking causes undesired phenomena's such as reduced heat transfer rates, increased pressure drop and lower yields [1, p. 110].

Two-stage processes

The two-stage processes have been developed and commercialized by several companies, such as Shell and Haldor Topsøe, and can be seen in Figure 2.1. For sulfur and aromatics removal, to low levels in diesel fuels, this method is very effective. A fixed bed reactor for each stage is used. To remove sulfur and nitrogen, the gas oil is hydrotreated using a conventional catalyst of the type $\text{CoMo}/\text{Al}_2\text{O}_3$ or $\text{NiMo}/\text{Al}_2\text{O}_3$ in the first step. Further treatment of the gas oil is done in the second step by a sulfur resistant noble metal/zeolite catalyst. In the first step of ultra-deep HDS, reduction of H_2S and increased partial pressure of hydrogen occurs. The second step handles hydrogenation of aromatics. Fine-tuning properties of the diesel fuel in regards to the sulfur and aromatic levels can be done by the second reactor. [9, p. 37]

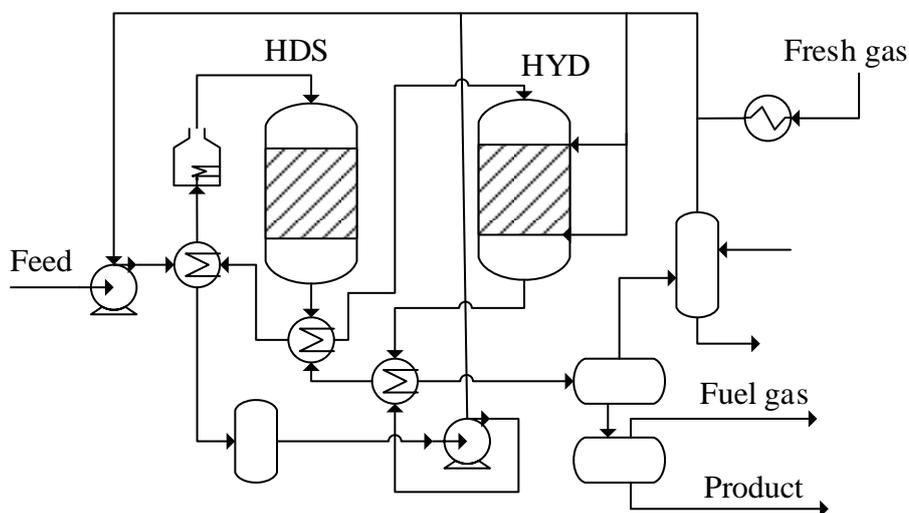


Figure 2.1. The schematic figure for Two-stage processes [9, p. 37].

Syn Technologies

SynAlliance is a group of companies consisting of Shell Global Solutions, ABB Lummus Global and Criterion Catalyst Company, which together have developed Syn Technologies. It includes SynHDS, SynShift and SynSat. For selective ring opening of hard treated aromatics,

SynShift is developed to decrease density, improve cetane number, and reduce aromatics content. SynSat is developed for saturation of aromatics, providing added density reduction and cetane improvement. The reactor system is seen in Figure 2.2. A combination of both is possible for deep hydrodearomatization (HDA) and deep HDS. Hydrogen and oil are processed in the first reactor co-currently to achieve deep desulfurization. H₂S is removed from stripped hydrogen and oil, then it is processed counter-current in the second reactor, with a noble metal-based hydrogenation catalyst. This generates improved HDS performance and relatively high partial pressure of hydrogen in that part of the reactor. [9, p. 38]

In these processes, the removal of H₂S, after the first stage has been proved to be a key strategy for beneficial reaching of ultra-low levels of sulfur as well as aromatics in the second stage. The presence of H₂S affects HDS reactions negatively. [10, p. 208]

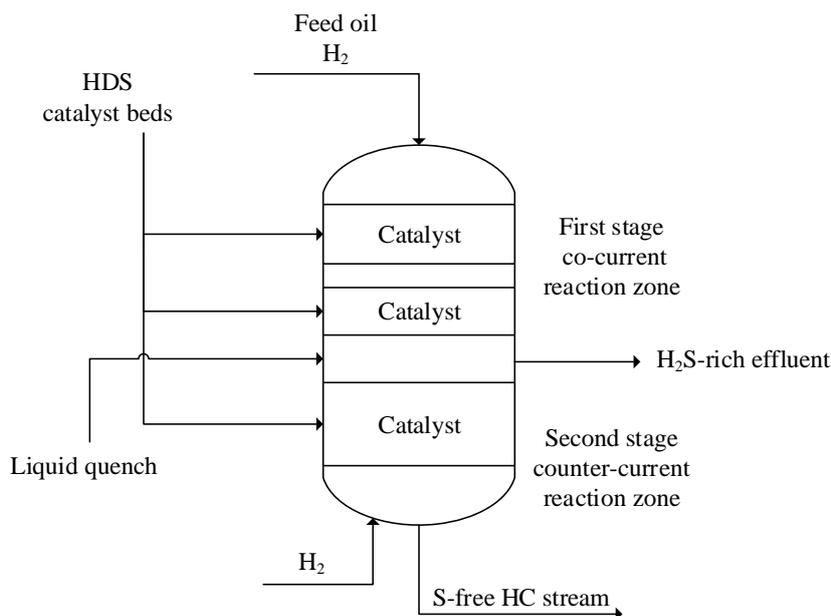


Figure 2.2. SynSat/SynShift process with catalytic hydrotreating reactor [4, p. 2711].

Producing diesel fuel with ultra-low sulfur content (below 10 ppm), in which SynHDS has its focus [9, p. 38], is seen in Figure 2.3.

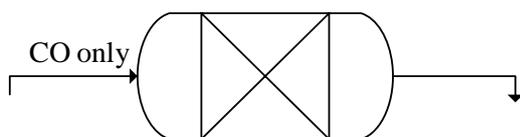


Figure 2.3. Co-current SynHDS reactor [9, p. 39].

Multicatalyst bed

This deep HDS technology was developed for hydrotreating light and heavy fractions of the diesel feed in separate catalyst beds. At about two-thirds of the reactor height, between the first and the second catalyst bed, the feed is injected. Sulfided CoMo/alumina constitutes the top bed in the reactor and NiMo/alumina is in the two lower beds. In the bottom of the reactor, hydrogen is fed below the bottom bed. The HDS reaction occurs in the top bed with CoMo where light organosulfur molecules are desulfurized at high hydrogen partial pressure. Less reactive and heavier organosulfur molecules, such as substituted DBT's, are deeply desulfurized in the first

NiMo bed, counter-currently. Since hydrogen is introduced in the bottom part of the reactor, the deep HDS and hydrogenation take place at quite a low operating temperature. This stage is as good as free from H₂S. In Figure 2.4 the Multicatalyst bed technology can be seen. [9, p. 38]

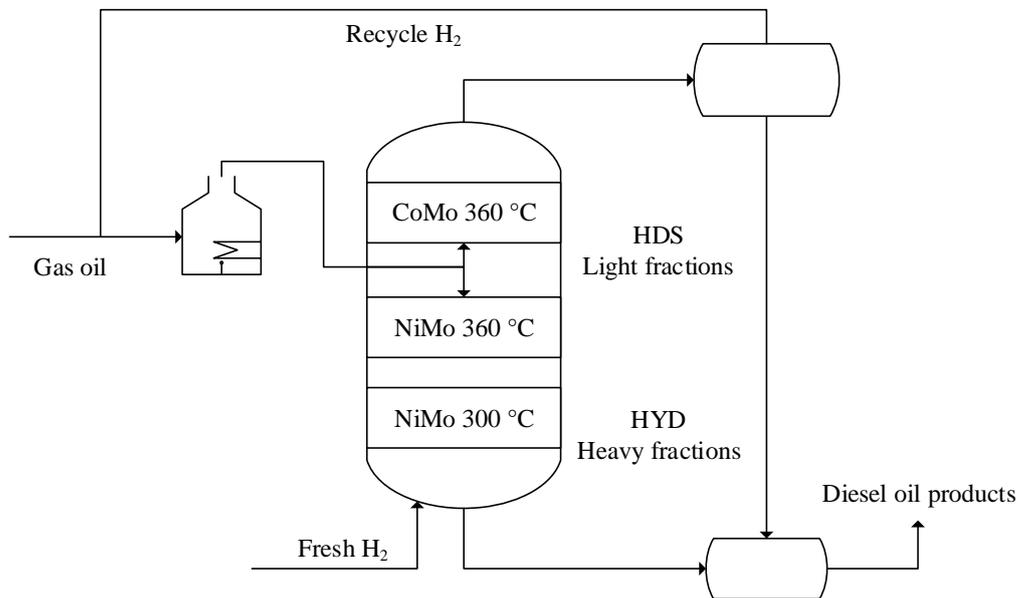


Figure 2.4. Process overview for the Multicatalyst bed technology [9, p. 39].

2.2 Test reactors

During the last 20 years, many technologies and concepts to desulfurize refractory organosulfur compounds have been developed. With these technologies, it is possible to reach levels down to 0.1 ppm, at a high-cost efficiency [9, p. 36].

Numerous of different types of reactors are available and each come with a different purpose of use. They can be divided into two main categories, namely stationary and non-stationary reactors, which both have three subgroups. Some different types and following subgroups are seen in Figure 2.5. For research and development, other reactors than those below are used. [11, p. 21]

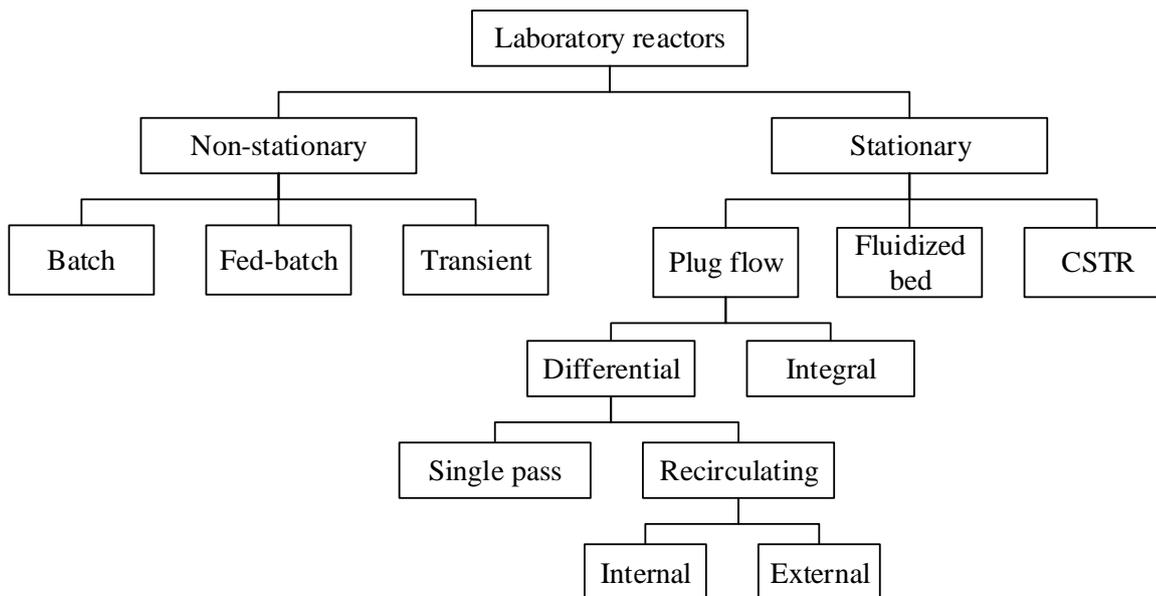


Figure 2.5. Some reactor types with associated subgroups, reproduced with permission [12].

1. Scouting laboratory reactor (catalyst discovery 1st scale)

The main task with the scouting laboratory reactor is basically testing activity in different catalysts without concentration and/or temperature interference. This reactor is good for catalyst discovery and typically has a diameter of 6 mm which enables the reactor to be operated at a constant temperature, often through a sand bath or tube furnace. Since the reactor is small, the amount of catalyst is as well, and it is easy to replace it. [11, p. 21]

2. Catalyst-optimization reactor (catalyst improvement 2nd scale)

The next reactor in line is the catalyst-optimization reactor. It tests satisfactory candidates from the scouting laboratory reactor in a commercial way, with for example pellets or a net, which is good for catalyst improvement. In general, the dimensions are about 25 mm in diameter and between 300-1,000 mm in length. The bed is considerably larger and is operated closer to industrial circumstances than for the scouting laboratory reactor. Temperature and pressure gradients are included. The reaction rate is strongly dependent on pressure and heat evolution inside the reactor, while heat transfer is not affected by the pressure. [11, p. 22]

3. Prototype reactor

The prototype reactor is larger than the two previous reactors. In some contexts, it is applied as a commercial reactor for pilot testing. There are several features accompanied by performing tests using a prototype reactor. The temperature gradient will not be the same along the catalyst-optimization reactor, but for the prototype reactor, it is. Kinetics and economics can be largely affected by a pressure drop, which has to be minimized. The actual gradient and the heat-transfer resistance is inside the bed and should be removed. Reproducing the pressure drop through the reactor by verifying the repacking it multiple times is of interest for the prototype reactor. [11, p. 22]

2.3 Reactor gradients

In non-ideal catalytic reactor systems, a variety of gradients might exist. As for the reactor, a temperature gradient may emerge if highly exothermic or endothermic reactions take place. This gradient implies that the temperature varies in the reactor, particularly in the catalyst bed, i.e. the reactor is not working isothermally.

Another gradient type relevant for the reactor is the concentration gradient. This gradient arises due to radial or axial dispersion of the reactants in the catalyst bed. The axial dispersion is inevitable if there is any conversion of the reactants, but can be minimized. Radial dispersion is more prominent if the reactant flow is laminar than if it is turbulent.

For reactor systems, a common gradient is flow gradient. This gradient might occur if the velocity through the catalyst bed is not constant, that could cause a difference in reaction rates inside the catalyst bed.

Concentration gradients may also appear between the bulk and the catalyst pellet or inside the pellet due to mass transfer limitations.

Concentration and temperature gradients inside a reactor or catalyst particle can influence the rate of reaction, i.e. the apparent catalyst activity [13, p. 311].

2.4 HDS process parameters

Reactor temperature, hydrogen partial pressure, and SV are factors that all affect the performance of hydrotreating systems. Kinetic studies have shown that higher temperature and pressure, as well as lower SV, will increase the HDS rate and reduce the sulfur content. Although, trying to reach ultra-low sulfur levels by further increasing temperature and pressure is not viable since these severe conditions have a negative impact on cycle length and throughput time. It is also limited by design pressure, thermodynamic equilibrium and hydrogen availability. For ultra-low sulfur levels, the optimum operating conditions for the hydrotreating reactor is dependent on the feedstock quality, catalyst type, and thermodynamic limitations.

The thermodynamic constraints are not a limiting factor to the actual removal of sulfur, but rather in the pre-hydrogenation of the polyaromatic compounds in which the sulfur atoms are present. Since these hydrogenation reactions are exothermic they benefit from a lower temperature, and hence it is not favorable to conduct the desulfurization at too high temperatures. At low hydrogen pressure, very high reactor temperature will have a negative effect on the desulfurization of polyaromatic compounds. See Figure 2.6 for an overview on how the different parameters affect the sulfur removal. [9, p. 28]

Table 2.1 displays the conditions at which the process parameters were tested.

Table 2.1. Process conditions [14, p. 3].

Process parameters under study	Temperature effect study	LHSV effect study	H ₂ /oil effect study	Pressure effect study
Temperature (°C)	300-380	340	340	340
Pressure (MPa)	3	3	3	2-6
H ₂ /oil ratio (ml/ml)	200	200	150-500	200
LHSV (h ⁻¹)	4	2-6	4	4

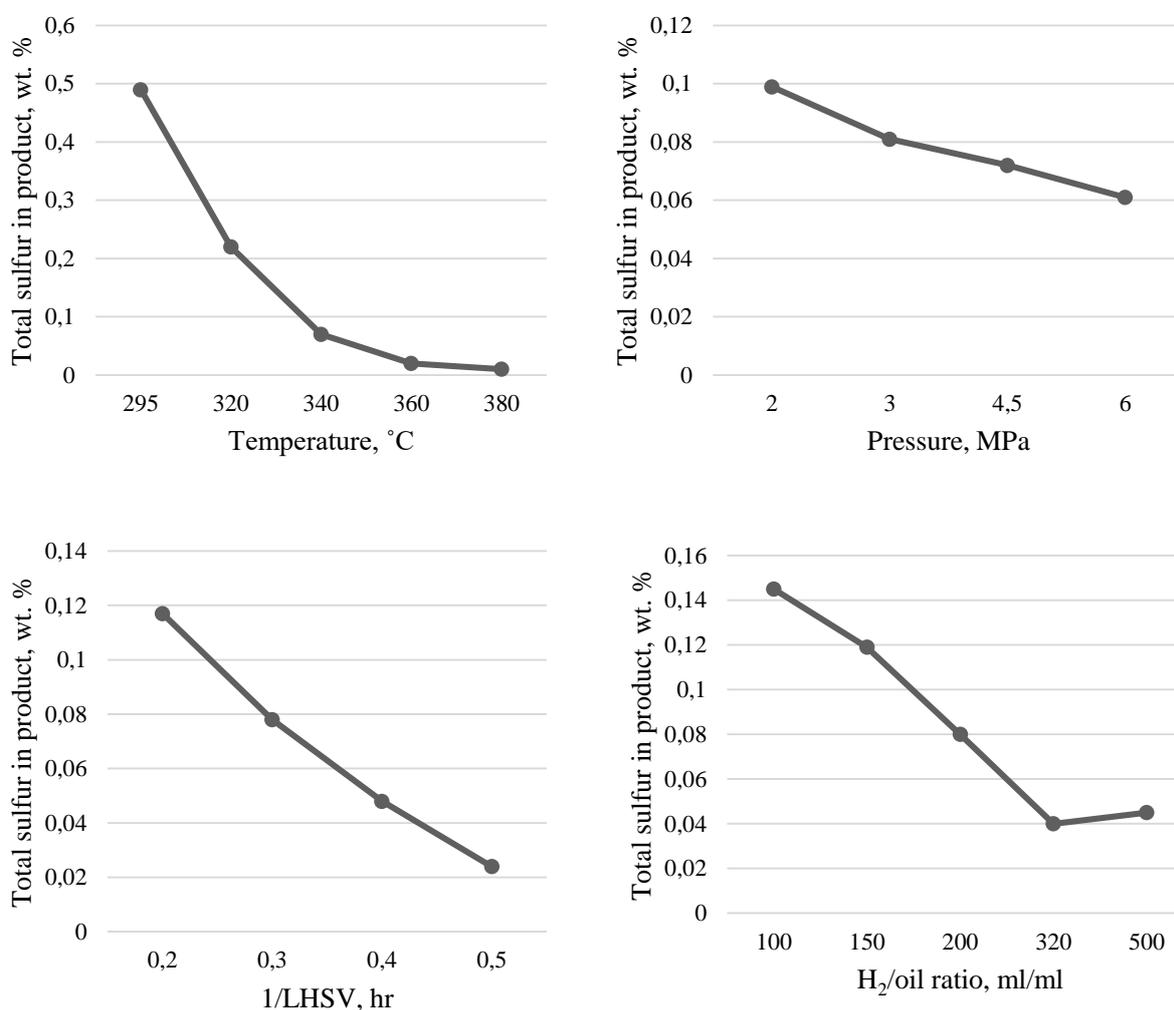


Figure 2.6. The impact of different temperature, pressure, LHSV and H₂/oil ratio in HDS [9, p. 29].

The effects of temperature on the rate of direct desulfurization (DDS) and hydrogenation (HYD) routes of 4,6-DMDBT was investigated by Farag et al. [15]. -The study was conducted over CoMo/alumina catalyst at 29 bar. It concludes that the HYD reaction passes through a

maximum when the temperature is increased from 300 °C to 380 °C and is the primary reaction route at temperatures below 340 °C. Above 380 °C, the DDS route becomes more prominent. This distribution could be due to the thermodynamic limiting of the hydrogenation step [9, p. 29].

Another important parameter to take into account is the LHSV, which is expressed as m³ feed per m³ catalyst per hour. A decrease in LHSV generally leads to a decrease in sulfur content in the product, since it entails a longer contact time between the feed and the catalyst. Although, a decrease in LHSV implies a longer throughput time, and to maintain the same throughput time at a lower LHSV an increase in catalyst volume is required. What is also beneficial with a decrease in LHSV is the fact that the reactor can be operated at lower temperatures which ease the HYD route [9, p. 32].

Changes in hydrogen partial pressure affect which pathway the reaction follows. An increase in hydrogen pressure promotes the HYD pathway and consequently a decrease in hydrogen pressure benefits the DDS pathway. Overall, though, an increased hydrogen pressure increases the HDS rate. Also, by increasing the hydrogen partial pressure, the thermodynamic limitations caused by the saturation of polyaromatics, are removed. Another advantage with higher hydrogen pressure is that it reduces the inhibition effects of for instance H₂S [9, p. 33].

2.5 H₂S adsorption

Desirable features of an absorbent for gas desulfurization are several. Most importantly it should be able to, theoretically, reach sulfur levels below 0.1 ppmv, which is required for downstream processes. Other desirable qualities are acceptable sulfur capacity for the absorbent, for it to be regenerable and for it to be able to endure a large number of sulfidation/regeneration cycles while maintaining the activity and capacity. Also, for FC applications the absorbent has to be nonpyrophoric. In most cases, it is favorable if the cost of the absorbent is low. [2]

The hydrated iron oxide is efficient but has in general been replaced industrially by ZnO. ZnO also is nonpyrophoric and is stable in the range of 350-450 °C in a reducing atmosphere. Another absorbent is manganese oxide (MnO) which is stable at 400 °C, though, it has a higher outlet concentration of H₂S than ZnO which makes this unsuited for use in FC's. The reaction for the absorption of H₂S using ZnO as the absorbent is seen below, Reaction 2.1. [2, p. 2]



The reaction is an equilibrium reaction that is exothermic, and the H₂S concentration is determined by the temperature, partial pressure of H₂O, and to some extent, the ZnO phase. [5, p. 2]

The presence of CO in the feed decreases the sulfur removal in the ZnO since it might form carbonyl sulfide (COS), according to Reaction 2.2 [16, p. 4], [5, p. 3].



In cases when neither H₂O nor CO is present in the feed, while CO₂ is, a risk of formation of COS also occurs. This is seen in Reaction 2.3.



Reactor design

A set-up for H₂S adsorption contains four components: gas mixing system, preheater, reactor and chromatographic analyzer [17, p. 2], [5, p. 2]. The system uses two streams with reactant gases; one containing a mixture of CO, CO₂ and H₂ and the other contains H₂S in helium. Both are controlled by mass flow controllers. Water is introduced through a pump and is vaporized before it is mixed with the two heated gas streams, before entering the reactor. They all enter upstream of the absorbent bed, containing the ZnO. A thermocouple is attached for heating of the reactor. Downstream of the reactor, removal of water vapor is done through two Nafion dryers, and the products are then further led into a gas chromatograph (GC) [5, p. 2]. The set-up is seen in Figure 2.7.

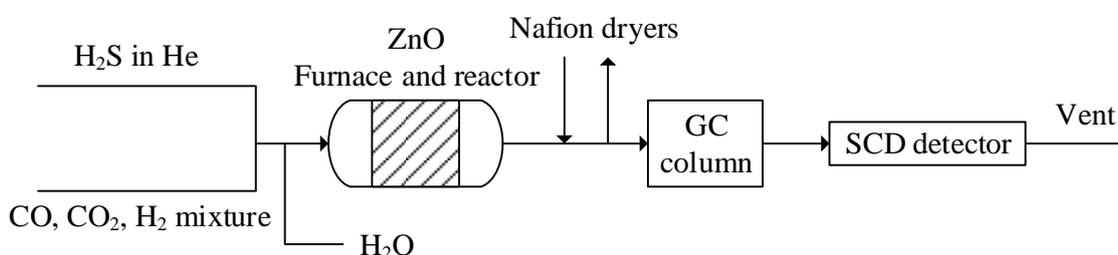


Figure 2.7. Small scale process set-up for H₂S adsorption with ZnO [5, p. 2].

H₂S process parameters

According to Li and King [5], when the temperature where over 315 °C, a sulfur level below 100 ppb was not achieved. Though under 250 °C the kinetics of absorption was slower but still more favorable for ZnS in equilibrium.

The study showed that below 200 °C, the H₂S adsorption was considerable in presence of only H₂ and H₂O. CO₂ did not affect the uptake of H₂S. While CO was present in the feed and with increasing concentration of it, the sulfur uptake decreased drastically. At 150 °C, the same results showed.

At low SV, no proven increase in H₂S capacity was shown and with a high SV (200 °C h⁻¹) the capacity showed a decrease.

Finally, with H₂O present in the feed, the H₂S capacity seemed to increase. With no water in the feed, the sulfur capture showed to be very small. The thermodynamics for the capture of H₂S is visualized in Figure 2.8. [5, pp. 2–4]

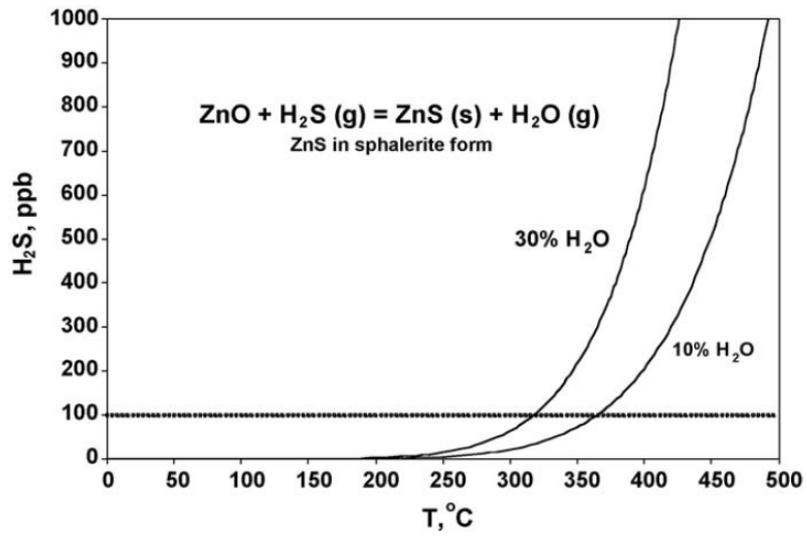


Figure 2.8. Thermodynamics of the H₂S adsorption reaction [5, p. 2].

3 Catalytic hydrotreating

3.1 The concept of heterogeneous catalysis

The main purpose of a catalyst is to open new reaction pathways with lower activation energies than the initial non-catalytic reactions. Heterogeneous catalysis has a large variety of industrial applications and is estimated to be used in over 90 % of all chemical processes [4, p. 1]. When producing chemicals and fuels from raw materials, via catalytic processes they show both economic and environmental benefits. Catalysts are used in many different areas such as chemical industry, food industry, the pharmaceutical industry as well as in the automobile and petrochemical industry. A new field that is growing is the use of catalysts in FC's. Figure 3.1 visualizes the constituents of a catalyst, from the bed and deeper into the support and the active phase [11, p. 13].

Since the catalyst and the products/reactants are in different states of aggregation, the catalysis is heterogeneous. When the reactants/products are in the same state of aggregation as the catalyst, the catalysis is homogeneous [11, p. 3].

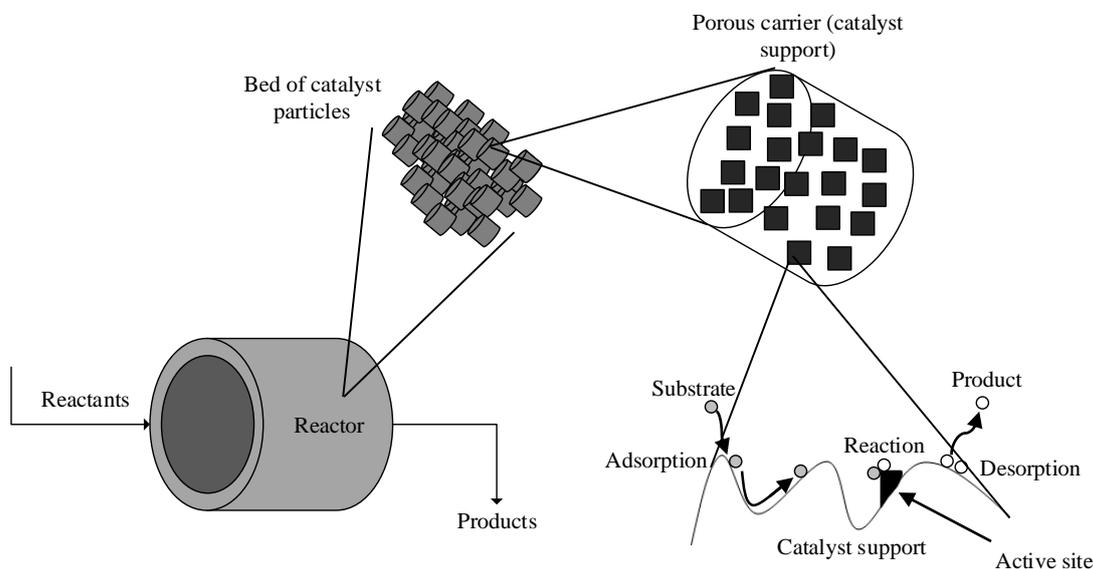


Figure 3.1. The different constituents in heterogeneous catalysis, reproduced with permission. [11, p. 13].

There are four different forms of distribution of active components. Homogeneous, egg-shell, ring and egg-yolk. These are illustrated in Figure 3.2 below [4, p. 481], [12].

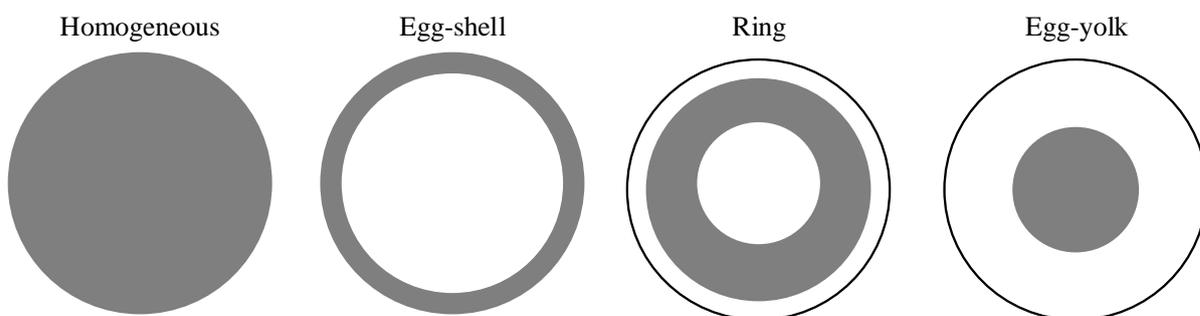


Figure 3.2. Different types of heterogeneous catalysts, reproduced with permission [12].

3.1.1 Catalyst manufacture

The procedure for production of heterogeneous catalysts involves several steps:

- Support preparation
- Active phase preparation
- Post-treatment
- Forming
- Activation

Preparation method, production conditions and quality of source materials heavily affects the catalytic properties. Each production step is necessary to control in order to know the properties of the catalyst, including the physical and mechanical properties of all the intermediates. [18, p. 503]

There are two main categories in heterogeneous catalyst manufacturing: precipitated catalysts and impregnated catalysts, and both contain sub-categories. All categories are seen in Figure 3.3.

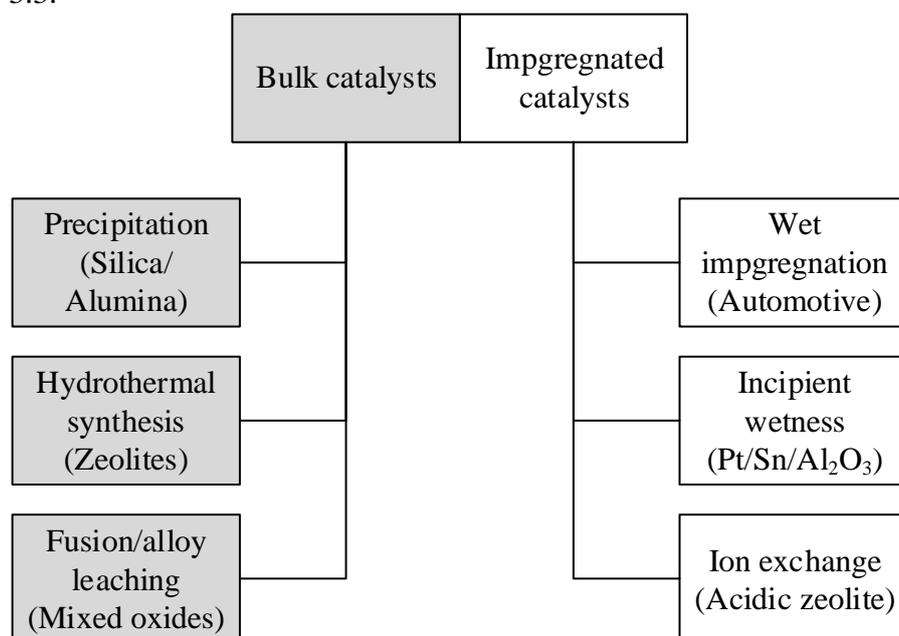


Figure 3.3. The two head categories and their following sub-categories, reproduced with permission [11, p. 27].

For impregnated catalysts, typically an active metal precursor is dissolved in water or an organic solvent and is later absorbed by the carrier material. The idea of the incipient wetness method is to add a solution, with a volume equivalent to the pore volume of the carrier, containing the active phase. The internal pores of the catalyst are then filled up. Depending on e.g. pH, the active metals reaches into the pores with various depth. Later the catalyst is filtered, dried and calcined. Wet impregnation is an alternative manufacturing method that is similar, but demands more water for catalyst production and is therefore disregarded. Figure 3.4 shows the general steps for catalyst manufacture. [11, p. 28]

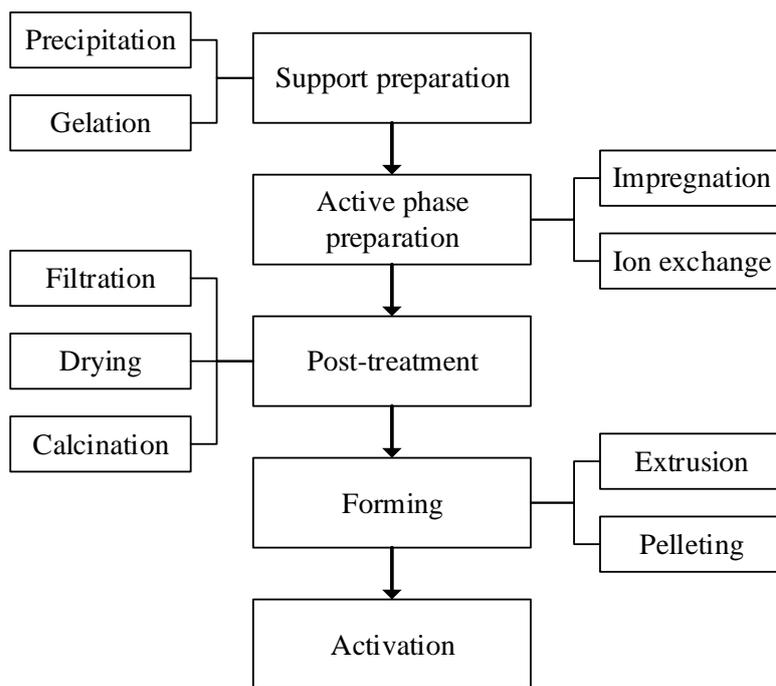


Figure 3.4. Involving steps in catalyst manufacture, reproduced with permission [11, p. 29].

Without affecting the porous system, water is removed from the crystalline solids, or the gel, during the drying step. Drying is done at rather high temperatures (300 to 800°C) in a reducing or inert atmosphere and can also be done with air, in that case, called calcination. This falls under the post-treatment category.

The main purpose of calcination is the removal of thermally unstable compounds such as carbonates, hydroxides or organic compounds. It is done through physical or chemical stabilization of the catalyst or its precursor. The compounds are decomposed, most commonly converted into oxides. New compounds may be formed during a high calcination temperature [4].

Forming is the next step in catalyst manufacture. Pellets are formed into spheres with well-created properties that is essential for supporting their own weight. Extrusion and pelleting are the two methods. In extrusion, forming is done through forcing a binder combined with catalyst together to form a paste. Binder and catalyst powder are pressurized together in the pelleting step.

3.2 Chemistry and catalysis in HDS

3.2.1 Chemistry

A complex mixture of organosulfur compounds is present in most crude oils. The lower boiling point fractions of the oils contain mainly aliphatic compounds, such as thiols, sulfides, and disulfides, which are very reactive and the sulfur atom can be easily removed through hydrotreating. In the higher boiling point fractions thiophenes, benzothiophenes (BT), DBT's as well as their alkylated derivatives are more common. Depending on their molecular structure, the reactivity of these compounds vary, and can be ranked as follows: thiophene > benzothiophene > alkyl benzothiophene > dibenzothiophene > alkyl dibenzothiophenes [4, p. 2696], [9, p. 7]. The reactivity of the heavier compounds can be seen in Figure 3.5.

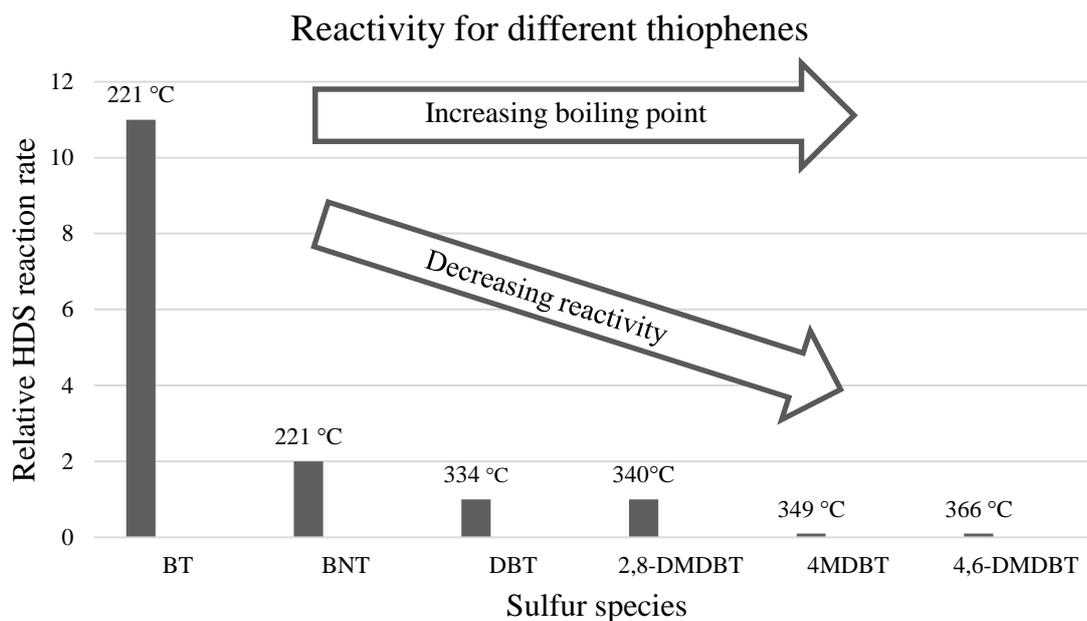


Figure 3.5. Reactivity for different thiophenes [9, p. 7].

The aliphatic thiols can react through elimination, hydrogenation and hydrogenolysis, as seen in Figure 3.6. All reactions occur on the surface of a metal sulfide catalyst. The elimination is an acid-base reaction, while the hydrogenolysis and hydrogenation involve C-S and H-H bond scissions, and C-H and S-H bond formations [4, p. 2696].

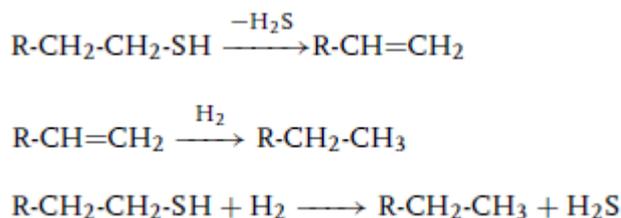


Figure 3.6. Reaction pathways for thiols.

The desulfurization of DBT's follows two parallel routes: DDS and HYD route. The most common pathway, which constitutes 80-90 % of the conversion, is via DDS, Figure 3.7, and it proceeds through two hydrogenolysis steps, forming biphenyl and H₂S.

In the HYD route, Figure 3.8, either of the phenyl groups on the DBT is hydrogenated, forming tetrahydro dibenzothiophene. This is followed by hydrogenolysis, or by elimination and hydrogenation, resulting in an aryl thiol, which is further desulfurized into cyclohexylbenzene [9, p. 8], [4, p. 2697].

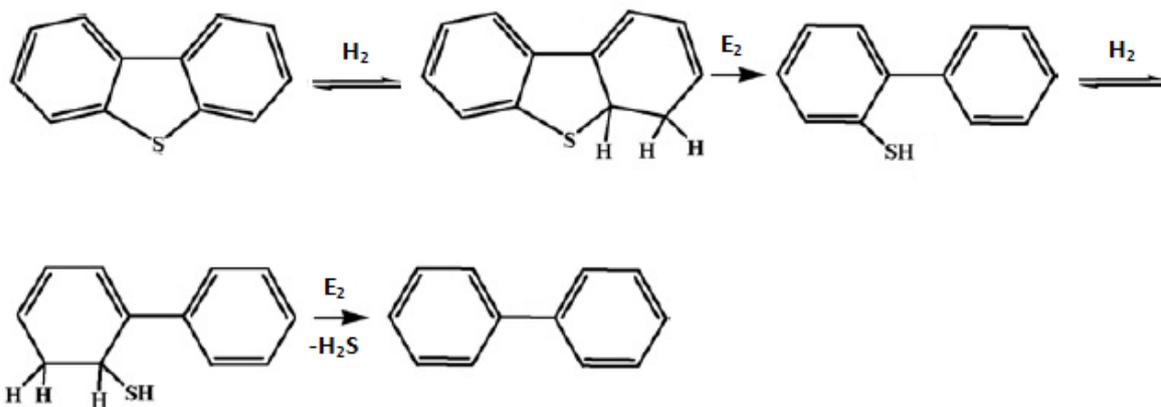


Figure 3.7. DDS route of DBT forming biphenyl and H_2S .

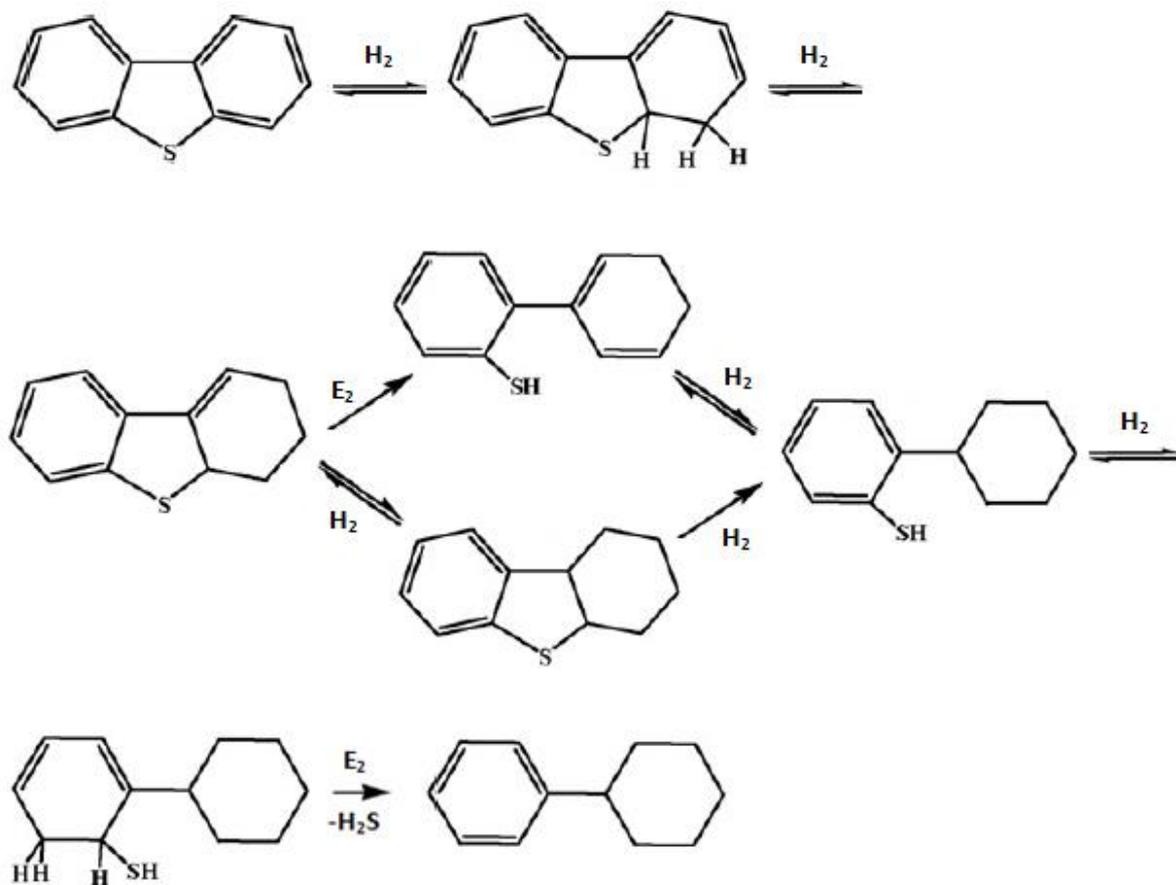


Figure 3.8. HYD route of DBT forming cyclohexylbenzene and H_2S .

The HDS mechanism for thiophene at low hydrogen pressure is still debated, while the reaction pathway at high pressure is well established. The thiophene reacts through HYD forming tetrahydrothiophene, which thereafter can react through the elimination of hydrogen to form butadiene, or through hydrogenolysis to form butane. At atmospheric pressure some authors believe that the reaction occurs similarly to that at high pressure, while others suggest a direct hydrogenolysis to butadiene and H_2S [4, p. 2696].

Hydrodesulfurization of BT, Figure 3.9, follows the HYD pathway. Initially the benzothio-
 phene is hydrogenated, and subsequently, the sulfur is removed through hydrogenolysis [4, p.
 2698].



Figure 3.9. Hydrodesulfurization of BT, forming styrene.

Effect of H₂S -formation

One product of the HDS reactions is H₂S. The formation of H₂S inside the reactor has an overall
 effect on the HDS-activity of the sulfided catalyst, as seen in Figure 3.10.

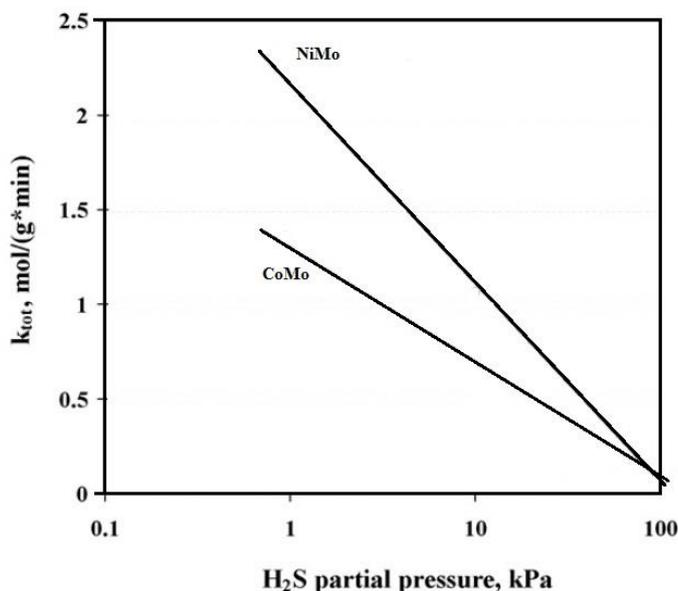


Figure 3.10. Inhibiting effects of H₂S [9, p. 10].

The catalytic activity is dependent on the number of sulfur vacancy sites on the catalyst surface. The problem that arises when H₂S is forming in the reactor is that these molecules also adsorb to the vacancy sites, leaving less of active sites available for the thiophenic compounds. Hence, the inhibiting effect is more prominent on the DDS-route, than on the HYD-route. There is also a difference between different catalyst types, and Egorova and Prins have reported that the inhibiting effect of H₂S is stronger on NiMo than on CoMo [9, p. 9].

Despite all negative influences presented, some studies have shown that a low partial pressure of H₂S has a positive effect on the HDS-activity since it contributes to sulfidation of the catalyst surface [9, p. 10].

3.2.2 Catalysis

In hydrodesulfurization processes, catalysts are used to enhance the sulfur removal. The two main components of hydrotreating catalysts are the support and active metals. Industrially, the

most widely used catalysts consist of molybdenum, supported on γ -alumina, promoted with nickel or cobalt [9, p. 17]. In this report, these CoMo/alumina and NiMo/alumina catalysts have been reviewed regarding catalyst structure and activity.

The role of the promoter and its location in the catalyst structure has been explained by Topsøe et al. [19]–[21] in the Co-Mo-S and Ni-Mo-S phase models. The constituents of these structures are nano-sized crystals of MoS_2 , with Co or Ni atoms located at the edges of the MoS_2 layers, in the same plane as the Mo atoms, as seen in Figure 3.11. For the Co-Mo-S phase model, it has been found that the relative amount of Co has a linear correlation with the HDS activity of the catalyst [9, p. 18].

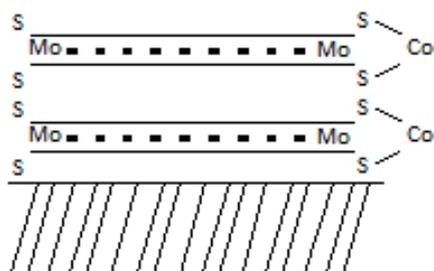


Figure 3.11. Model of edge location of Co atoms in sulfided Co-Mo/alumina [4, p. 2706].

Two types of the Co-Mo-S catalyst that has been identified, based on the extent of linkage between the Mo atoms and OH-groups on the alumina surface, are called type I and type II. The type I catalyst exhibit more Mo-O-Al linking, which makes it harder to completely sulfide, resulting in fewer active sites, and a lower HDS activity. The type II version of the Co-Mo-S or Ni-Mo-S catalyst has weaker Mo-O-Al links and can be completely sulfided leading to higher HDS activity. In the type II catalyst, the underlying MoS_2 , in the Co-Mo-S phase consist of multiple slabs that are not linked to the alumina support. A high dispersion of these slabs at the edge of the catalyst structure lead to the possibility of accommodating more Co atoms forming high activity type II catalysts [9, p. 18]. Another explanation for the catalytic activity was presented by Mössbauer, where the extensive linking in the type I catalyst is believed to sterically hinder reactant molecules to approach the catalytic sites [4, p. 2707].

Catalyst structure

Cobalt and nickel may be present in three different ways, respectively, after sulfidation of the catalyst. Sulfidation is a method for activation of the catalyst where the active Co-Mo-S phase is formed. As for cobalt, it may be as Co_9S_8 crystallites on the support, as ions on the MoS_2 crystallite edges, in the Co-Mo-S phase, or anions in tetrahedral sites in the γ -alumina lattice. Correspondingly nickel may be present in the Ni-Mo-S phase, as segregated Ni_3S_2 or as ions in the support [4, p. 2705]. The relative occurrence of cobalt as Co-Mo-S phase or Co_9S_8 is dependent on the structure of the oxidic precursor, on the sulfiding temperature and on the relative concentrations of cobalt and molybdenum. Small amounts of cobalt lead to the formation of mainly Co-Mo-S phase, resulting in an increase of thiophene HDS activity. If the Co/Mo or Ni/Mo ratios are increased, initially the catalytic activity will increase. Although if the ratios become too high, Co atoms will have to be put on top of other Co atoms or they have to form other Co_9S_8 crystallites, which will cover the MoS_2 edge area. Since the Co_9S_8 crystallites have a low catalytic activity, the overall HDS activity will decrease. The maximum activity is usually observed at ratios of 0.3-0.5, at Mo loadings around 10-15 wt% [4, p. 2705]. The formation of

Co₉S₈ particles can also be caused by high sulfiding temperatures. Optimal temperatures for sulfidation of Co-Mo/alumina or Ni-Mo/alumina are in the range of 400-500 °C [4, p. 2704].

3.2.3 Aspects on the choice of catalysts

CoMo/alumina and NiMo/alumina

CoMo and NiMo, with Cobalt and Nickel being the promoter and Molybdenum the active metal, supported on alumina, are the most widely used HDS catalysts industrially. The type II sites on these catalysts are very active, although to be able to reach ultra-low sulfur levels the process needs to be run at high temperature, low SV and high hydrogen partial pressure. These operating conditions lead to rapid catalyst deactivation, shorter cycle lengths and reduced throughput [9, p. 17].

NiMoW/alumina

To increase the hydrotreating activity of CoMo and NiMo catalysts different additives such as tungsten has been investigated. Both tungsten and molybdenum belong to the transition metals and have similar chemical properties. NiMoW/alumina-catalysts has proven better than conventional NiMo/alumina and CoMo/alumina in desulfurization processes, and especially in the aspect of hydrogenation of aromatics. This type of catalyst has been used industrially, although only to a limited extent since tungsten is relatively expensive. [4, p. 2695].

CoMo/alumina-titania

Hydrotreating catalysts often consist of a carrier, a promoter and an active metal. For the CoMo/alumina catalyst, alumina is the carrier, cobalt is the promoter and molybdenum are the active metal. The purpose of the carrier is to provide a high surface area and to maximize the dispersion of the active phase on said area. Alumina exhibits several desirable qualities, e.g. relatively high surface area, both acidic and basic sites and good stability. It is also relatively cheap, making it a common carrier material [9, p. 19].

Studies on different carrier materials have been conducted, and Ramirez et al. [22] reported promising results when performing HDS on thiophene using coprecipitated alumina and titania carriers. They found that the catalyst activity increased when the Ti/(Al+Ti) ratio was increased. At 0.95 the HDS activity was 1.5 times higher than that of pure alumina.

CoMo-CA/alumina

When preparing catalysts through the incipient wetness method, certain impregnation techniques can be utilized to enhance the properties of the catalyst. The impregnation step affects the structure of the active phase as well as the dispersion of it on the carrier surface. Adding a chelating agent, such as citric acid (CA), to the impregnation solution have been shown to have a positive influence on the formation of the active Co(Ni)-Mo-S II phase. The chelating agent increases the sulfidation temperature of Co and Ni, to above that of Mo. This leads to MoS₂ crystallites forming first, and Co(Ni)-atoms can be sulfided on the edges of these, forming the highly active Co(Ni)-Mo-S phase. Another way in which the chelating agent may improve the formation of this phase is by preventing strong interactions between the metals and the support material. These strong interactions with the support surface can lead to a dissociation of poly molybdates, which is the species involved in the highly active Co(Ni)-Mo-S phase, into mono molybdates. [9, p. 21]

Pt/Pd and Pt

Noble metal catalysts, e.g. Pt and PtPd supported on amorphous silica-alumina (ASA) has proven to be a promising alternative to the conventional CoMo or NiMo catalysts. These catalysts reduce both sulfur and aromatics content due to high hydrogenation and desulfurization activity. They are, however, limited by their sulfur resistance and are most suitable for pre-treated fuels with low sulfur content [4, p. 2715]. Unlike the other catalysts, no activation is needed. Therefore, the sulfidation step can be disregarded for noble metal type catalysts which lead to a significantly easier preparation process.

4 Material and method

In this section, the experimental method for desulfurization is described. A brief explanation of the approach, and how the experiments were performed, follows. Seven potential catalysts for desulfurization of logistic fuels was chosen for evaluation and was then manufactured. Recipes for all of the catalysts are reported in [Appendix I](#). Previous to manufacturing, assembling and ordering of the needed chemicals for the catalysts was done, a compiled list is reported in [Appendix II](#). For most catalysts, except for the noble metal based ones, an activation step called sulfidation was required. Assembling of the reactor systems was done with help of Catator. System test run and calibration was done to evaluate if the system was intact and able to run at required pressures. Most steps were conducted at Catator while the reactor was constructed at Herman Andersson Plåt AB. Two reactor systems were used, a semi-batch system and a PFR system. All results are based on experiments run in the latter system.

4.1 Catalysts

There are two types of hydrotreatment catalysts that are most common. They consist of an alumina support that is impregnated with two types of catalytic elements, one type is Ni or Co and the other type being molybdenum oxide or tungsten oxide. The Ni or Co is converted to sulfide by sulfiding, while molybdenum or tungsten oxides converts to disulfides [23, pp. 138–139].

Below, a list of the seven different catalysts, that from literature was believed to yield the best conversion of sulfur, can be seen. Five of them involved experimental work in form of manufacturing, with γ -alumina (Al_2O_3) as support, and testing. The Pt catalyst, named PPt-47, is a commercial catalyst manufactured by Stonemill AB. It was received from Catator. A product datasheet for PPt-47 is available in [Appendix IV](#). Sulfidation time was 4 h for all catalysts except one batch of CoMo and NiMo which was sulfided for 6 h. This was done to see if the time of sulfidation had an impact on the sulfur conversion. Calculations were performed to receive a standard value which was done as a blind test without a catalyst. Seven different types of catalysts were chosen from the literature study and regarded for testing in the reactor system. These are listed in Table 4.1.

Table 4.1. All of the reviewed catalysts.

	Reviewed	Prepared	Tested
CoMo	✓	✓	✓
NiMo	✓	✓	✓
Pt-Pd	✓	✓	✓
NiMoW	✓	✓	✓
PPt-47			✓
CoMo-CA	✓	✓	✓
CoMo/Al-Ti	✓		

The CoMo/Al-Ti catalyst was reviewed in the literature study but was never prepared or tested due to difficulties in preparation. The other five catalysts were prepared according to recipes in [Appendix I](#), and together with PPt-47, tested in the reactor system.

The alumina, which is the support material in all catalysts prepared at Catator, was received from the department of Chemical Engineering at Lund University. BET-analysis was conducted for 24 h, with a degassing temperature of 150 °C. The measured pore volume of the alumina was 0.3538 cm³/g at pressure ratio (P/P⁰) = 0.9951. The BET surface area was 300.10 m²/g. A summarized analysis with results from the BET-analysis is reported in [Appendix V](#).

For all but the noble metal catalysts, the final preparation step was to sulfide the catalyst in order for the active phase to form. The sulfidation was conducted at 400 °C for 4 and 6 h using a flow of H₂S(g) in N₂(g) (5,000 ppm) with a flow of 10 l/h and H₂ (g) with a flow of 40 l/h, resulting in 0.1 % ppm H₂S.

4.2 Reactors

The focus on this thesis work, with regards to the reactor system, was to optimize temperature, pressure and LHSV. A basic flow-sheet of the reactor, as well as the intervals of the process parameters used, is seen in Figure 4.1. As a rule of thumb, the catalyst bed in the reactor should contain about 10 catalyst pellets in a row in the reactor. Both reactor systems were designed accordingly. A GC was used for analysis.

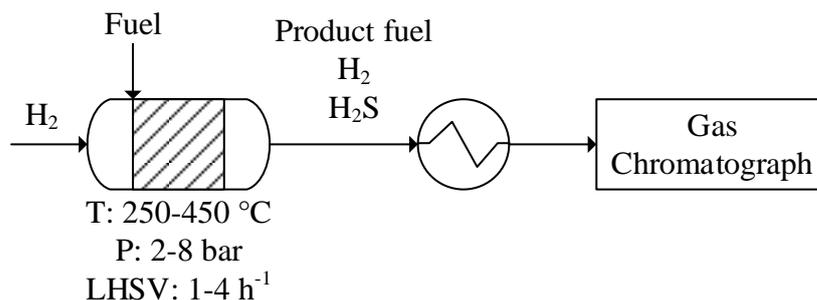


Figure 4.1. Schematics of the HDS system.

4.2.1 Semi-batch Hydrodesulfurization system

The initial reactor was a semi-batch reactor. For each run, 52 ml of dodecane and thiophene to consist of 1,000 ppm sulfur, was added to the reactor. This solution was evaporated by the heater in the bottom of the reactor and mixed with a continuous flow of hydrogen. The semi-batch reactor had an inner diameter of 34 mm and a length of 150 mm and contained a 30 mm catalyst bed. Above the catalyst bed, reacted fuel was ejected for analysis. Non-reacted fuel and hydrogen were cooled down by water and recirculated. An overflow valve was installed above the catalyst bed to control the pressure and ensure that not too high pressures are reached. To inert the system from oxygen after a change of catalyst, a nitrogen pipeline was connected through a mixing valve and injected through the same spot as the hydrogen. Six thermocouples were connected; in the bottom of the reactor, in bottom and top of the catalyst bed, in the bottom and in the top of the condenser and the last one was connected to the water outlet. The fuel was emptied in the bottom of the reactor. Figure 4.2 shows detailed schematics for the semi-batch reactor, with a complementary list that describes the function of each part in the reactor system.

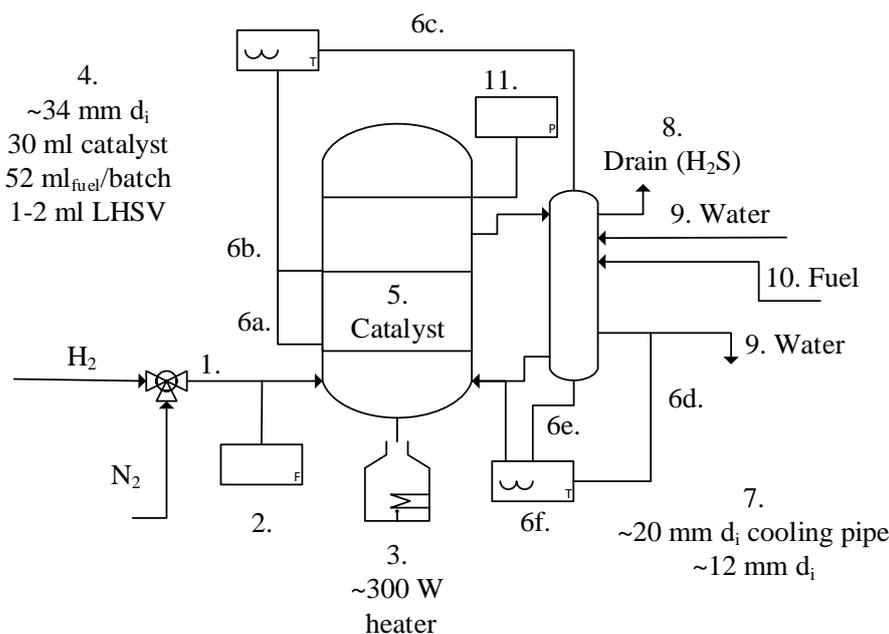


Figure 4.2. Semi-batch reactor set-up.

1. Inlet streams of hydrogen and nitrogen. The partial pressure of the hydrogen can be altered. The inlet flow of nitrogen is used to inert the system from oxygen after each catalyst change.
2. Mass flow indicator.
3. ~300 W heater for evaporation of the fuel.
4. Reactor vessel. The reactor was made of stainless steel with an inner diameter of 34 mm and 150 mm long and constructed as a semi-batch reactor. To change the catalyst, the top of the reactor was cut off and welded together.
5. Catalyst bed. Inside the reactor, a steel net is attached on which the catalyst pellets are placed. The catalyst bed is approximately 30 mm high.
6. Thermocouples for temperature measurement. a and b are connected to the bottom and top of the catalyst bed respectively. f measures the temperature in the bottom of the reactor. d measures the outlet temperature of the cooling water. e measures the temperature of the condenser inlet. c measures the temperature at the top of the condenser.
7. Recirculation vessel. An outlet drain for formed H_2S .
8. Drain for reacted fuel. The formed H_2S is emptied into a gas bag for analysis.
9. Cooling water.
10. Fuel inlet.
11. Pressure relieve valve.

While performing tests, the reactor was wrapped in isolation, and tubes for water cooling was attached. In Figure 4.3, the set-up is seen.



Figure 4.3. Semi-batch HDS reactor system.

4.2.2 PFR Hydrodesulfurization system

The semi-batch reactor system was replaced by a PFR system. The PFR system was installed in order to alter temperature and pressure independently as well as better control during analysis. Schematics and a complementary list for the reactor set-up are seen in Figure 4.4 and the complete assembled reactor system is seen in Figure 4.5. The inner diameter of the reactor was 34 mm. The reactor was inserted into an isolated vessel, with a surrounding heater, that enclosed the system and created oven-like surroundings. This was used to alter the temperature during testing without any loss of heat. Hydrogen and fuel were fed at the top of the reactor, led through the catalyst bed, and emptied in the bottom. The fuel was pumped into the reactor using a high-performance liquid chromatograph (HPLC) pump. A thermocouple was connected to the centre of the catalyst bed.

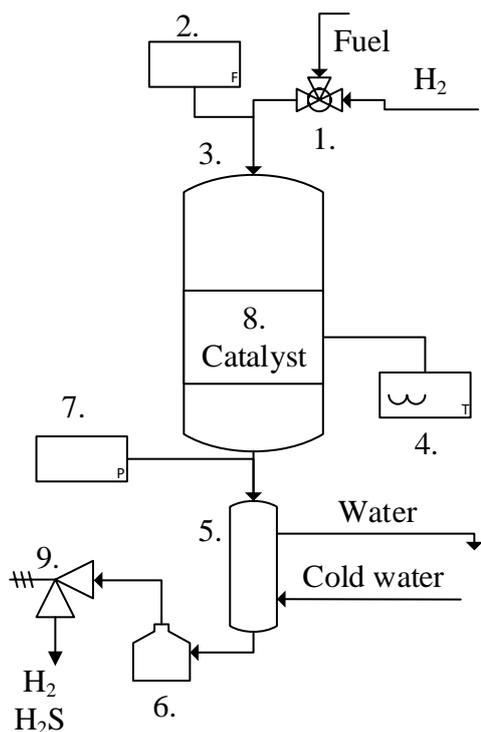


Figure 4.4. Schematics for the PRF reactor.

1. Mixing valve for fuel and H₂. The fuel was pumped into the reactor.
2. Mass flow controller for the H₂.
3. PFR reactor with an inner diameter of 34 mm. The top of the reactor was cut off and then welded together in order to switch the catalyst.
4. Thermocouple connected to the center of the catalyst bed.
5. Cooling system using water to cool the reacted fuel back to liquid state.
6. Storage tank of 109 ml where the fuel was separated from the H₂ and H₂S.
7. Pressure gauge (manometer) for pressure monitoring.
8. Catalyst bed, consisting of 30 ml.
9. Pressure relieve valve, down to atmospheric pressure.



Figure 4.5. PFR system. The oven (to the left) in which the reactor (to the right) was inserted.

4.3 Fuels

Four different kinds of fuel were used during the experimental work:

- Thiophene with dodecane
- Thiophene with lamp kerosene
- DBT with lamp kerosene
- Jet A1

The blends of paraffin or dodecane and thiophenic compounds were mixed to consist of 1,000 wt ppm elemental sulfur. Jet A1 was obtained from Catator having a sulfur content of 970 wt ppm, with an assumed composition of 20 % thiols and sulfides, 50 % thiophenes and BT, and 30 % substituted BT's.

The thiophene/dodecane mixture was used initially during the screening of the catalysts. Due to a shortage of dodecane, further testing, i.e. process optimization, on the most promising catalysts was done using lamp kerosene/thiophene mixtures.

The lamp kerosene/DBT mixture, as well as Jet A1, was then used to test the two most promising catalysts.

The properties of the involved compounds are seen in Table 4.2.

Table 4.2. Properties for dodecane and the organosulfur compounds.

	Molar mass (g/mol)	Sulfur content (wt%)	Density (g/cm³)	Boiling point (°C)
Dodecane	170.34	-	0.75	216
Thiophene	84.14	38.10	1.05	84
BT	134.2	23.89	1.15	221
DBT	184.26	17.40	1.25	333

4.4 Testing

The most important aspect of investigation in this thesis work was to find the best performing catalysts, but it was also of interest to optimize reactor settings, where the catalytic activity was sufficient, with regards to pressure, temperature and LHSV.

The testing of the catalysts was performed similarly to Figure 4.6.

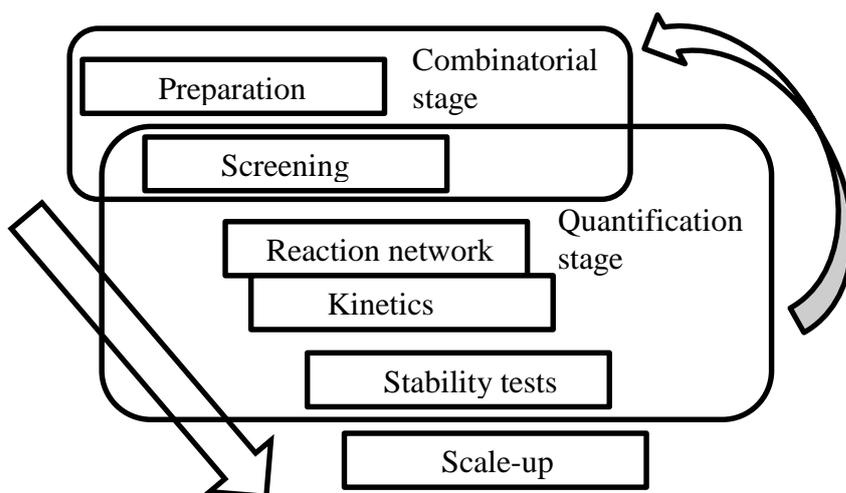


Figure 4.6. A system for catalyst development [4, p. 2020].

In the first step, a screening was performed for catalyst comparison. The H₂:fuel ratio was about 1:3. For the screening process the reactor was running at a standard operating point (SOP) specified in the list below:

- Pressure 6 bar
- Temperature 400 °C
- LHSV = 2 h⁻¹
- H₂ inflow 10 l/h

The fuel used was the dodecane/thiophene mixture and the catalysts were compared with respect to thiophene conversion. The two most promising catalysts proceeded for further investigations.

For the purpose of optimization of reactor settings, the two catalysts that were chosen in the screening step were used. The fuel used was the kerosene/thiophene mixture, and thiophene conversion was again the deciding factor.

- Temperature optimization: the system was run with LHSV = 2, a constant pressure of 6 bar, while altering the temperature between 250-450 °C with an interval of 50 °C.
- Pressure optimization: the system was run with LHSV = 2, a constant temperature of 400 °C, while altering the pressure between 2-8 bar with an interval of 2 bar.
- LHSV optimization: the system was run at 400 °C, 6 bar, while using LHSV = 1 and LHSV = 4.

Finally, testing on Jet A1 was carried out at optimal process conditions with the two best performing catalysts with regards for sulfur conversion.

4.5 Analysis

Three different methods for analysis have been used, one method for each sulfur compound. Thiophene was analysed using a photoionization detector (PID), DBT was analysed by a GC with a flame ionization detector (FID) and Jet A1 was analysed through Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

In the screening process, the product gas was injected to a GC for analysis of the sulfur content. As a detector, a PID was used. A PID ionizes aromatic and unsaturated compounds by using vacuum ultraviolet radiation. It measures the amount of collected electrons produced by the ionization. The PID has little or no response for saturated hydrocarbons. [24, p. 582]

The analysis on the detailed attempts with DBT was done through GC-FID. In the flame, CH radicals as CHO^+ ions and electrons, are produced from carbon atoms. A current is produced by eluted analytes, converted to a voltage and amplified, then the high-frequency noise is filtered and finally converted to a digital signal. The sensitivity for FID is about 100 times higher than for a thermal conductivity detector (TCD). [24, p. 581]

The product from the Jet A1 test was too crude to be analyzed through the regular PID and FID detectors. Instead, it was sent for a total sulfur analysis to the department of Physical Geography and Ecosystem Science at Lund University. ICP-MS has twice as high temperature than a combustion flame, allowing for more elements to simultaneously be excited and measured. The problem is that the number of emission lines is large and that there is no monochromator with the required resolution to separate the plurality of lines of all elements in the sample. [24, p. 486]

5 Results

Screening

The results from the screening process, with respect to sulfur conversion and thiophene peak area, are presented in Table 5.1.

A reference point was obtained by running the system without a catalyst in the reactor. The peak for thiophene was 83.92 Vs, the complete result of this analysis is reported in [Appendix III](#). Five blank tests were taken to see if there were fluctuations of the results in the PID. A standard deviation of 0.238 was received. Figure 5.1 shows the results for the screening.

All samples were taken when the reactor had run for approximately 10 minutes.

Table 5.1. Screening results for each catalyst including reference point.

	PtPd	CoMo	NiMo	Ni-MoW	CoMo-CA	CoMo (6 h)	NiMo (6 h)	Pt-47	Ref. value
Area (Vs)	21.59	2.51	3.40	6.22	1.92	2.11	2.32	0.99	83.92
Sulfur conversion (%)	74.27	97.01	95.96	92.59	97.71	97.48	97.24	98.81	-

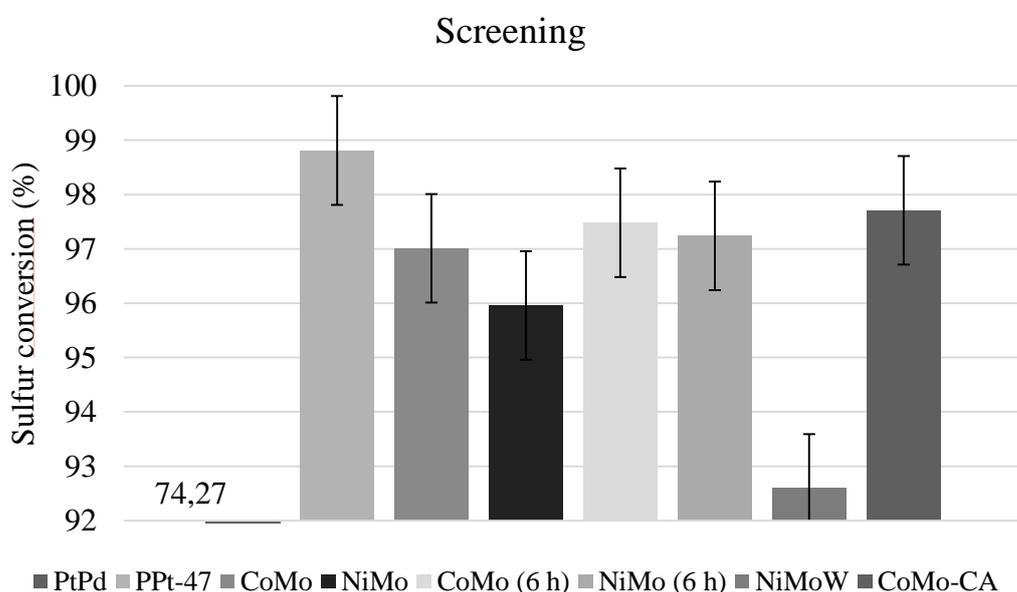


Figure 5.1. Comparison of all the catalysts in the screening.

Based on the standard deviation, the only distinct differences can be seen for the PtPd and NiMoW catalysts.

Detailed attempts

The PPt-47 catalyst had a conversion of sulfur about 98.8 % and CoMo-CA 97.7 %. Based on the screening results of the catalysts, those two were chosen for further evaluation.

In Table 5.2 and Table 5.3, the results from the detailed attempts on the PPt-47 and CoMo-CA catalysts are seen. The second SOP value is shown in a separate column. The process parameter shown in the table is the only parameter that differs from the SOP. For LHSV 1, 2 and 4, samples were taken after 60 minutes, 30 minutes and 15 minutes respectively, after the SOP. A comparison between the two catalysts can be seen in Figure 5.2 for thiophene.

Table 5.2. The detailed attempt on the Pt catalyst.

PPt-47										
Thiophene										
	8 bar	4 bar	2 bar	LHSV 1	LHSV 4	450 °C	350 °C	300 °C	260 °C	SOP
Area (Vs)	8.63	27.43	39.99	4.56	28.34	13.10	30.47	36.60	41.54	9.91
Sulfur conver- sion (%)	89.72	67.31	52.35	94.57	66.23	84.39	63.69	56.39	50.50	88.19
						90.23*				

Table 5.3. Detailed attempts on the CoMo-CA catalyst.

CoMo-CA										
Thiophene										
	8 bar	4 bar	2 bar	LHSV 1	LHSV 4	450 °C	350 °C	300 °C	260 °C	SOP
Area (Vs)	4.43	11.75	33.23	1.47	19.17	9.68	19.95	27.34	36.6	6.82
Sulfur conver- sion (%)	94.72	86.00	60.40	98.25	77.16	88.47	76.23	67.42	56.39	91.87
						95.05**				

*, **: These conversion values have been calculated, using linear regression, to fit the values of the other temperatures. Calculations are reported in [Appendix VI](#).

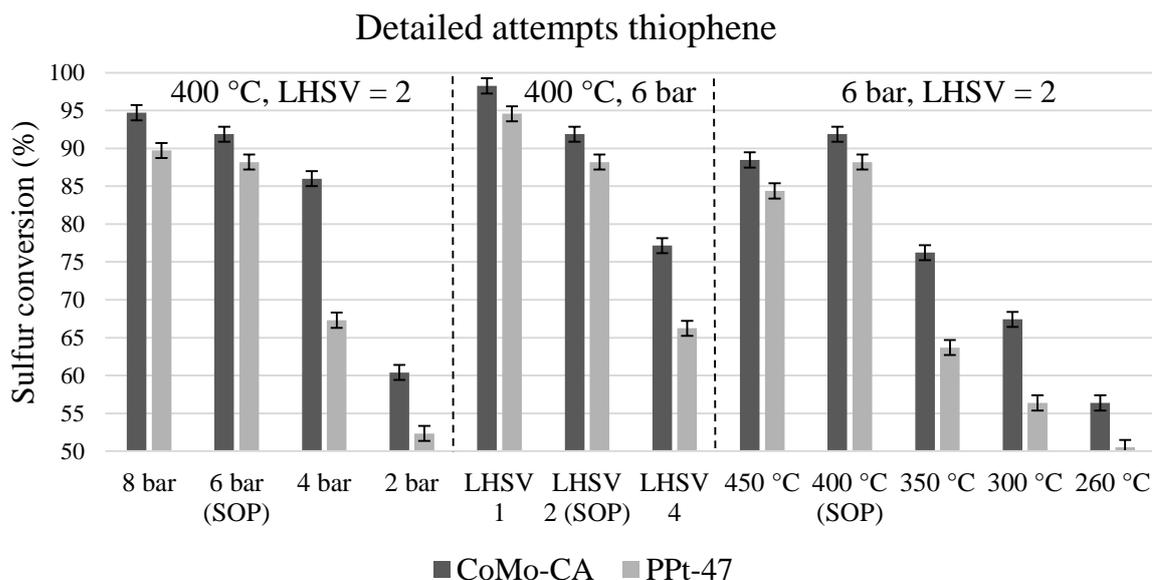


Figure 5.2. Comparison of sulfur conversion between CoMo-CA and PPt-47 on thiophene.

The detailed attempts continued with tests on DBT instead of thiophene. Since DBT is a less reactive compound than thiophene, it was tested both at the SOP and also at tougher conditions. The toughest condition was 8 bar, 450 °C and LHSV = 1. The reference peak for DBT was 70,183. In Table 5.4, the results can be seen as well as the time for extraction of samples. The time shown are the time after the SOP sample was taken. Figure 5.3 shows a comparison the both catalysts when tested with DBT.

Table 5.4. Detailed attempts on the CoMo-CA catalyst on DBT.

CoMo-CA				
DBT				
	LHSV 2 (0.5 h)	LHSV 1 (1 h)	LHSV 1 (5 h)	SOP
Counts	6,395	4,060	5,168	2,947
Sulfur conversion (%)	90.89	94.26	92.64	95.80

Analysis through a GC gave a peak with an area of 4,060 for DBT, resulting in a conversion of 94.3 %.

The results for the PPt-47 catalyst, when desulfurizing DBT, is seen in Table 5.5. Corresponding sample times applied for the PPt-47 catalyst as for CoMo-CA.

Table 5.5. Detailed attempts on the PPt-47 catalyst.

PPt-47				
DBT				
	LHSV 2 (0.5 h)	LHSV 1 (1 h)	LHSV 1 (5 h)	SOP
Counts	9,119	4,591	8,961	6,332
Sulfur conversion (%)	87.01	93.46	87.23	90.98

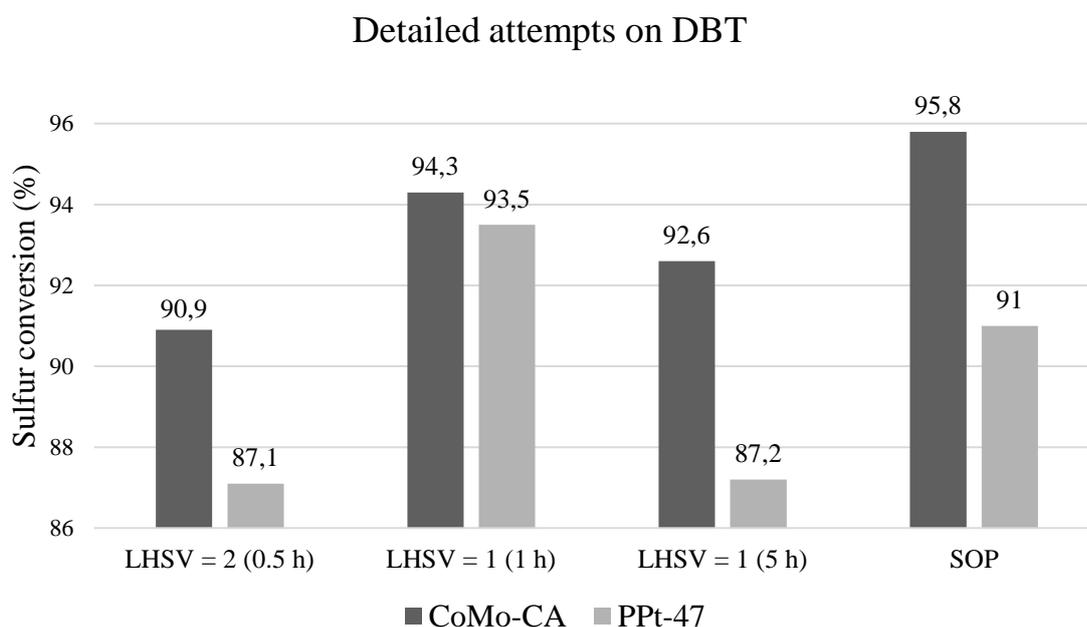


Figure 5.3. Comparison of sulfur conversion between CoMo-CA and PPt-47 on DBT.

Jet A1

As a final test, both CoMo-CA and PPt-47 were used to desulfurize the Jet A1, which were tested at 8 bar pressure, 450 °C with three different LHSV's. The results from this analysis in seen in Table 5.6. A reference value of 748 ppm was used as a comparison to the samples for Jet A1. In Figure 5.4, a comparison between the both catalysts can be seen.

Table 5.6. Detailed attempts of CoMo-CA and PPt-47 on Jet A1.

Jet A1							
	CoMo-CA			PPt-47			Ref. value
	LHSV 1	LHSV 2	LHSV 4	LHSV 1	LHSV 2	LHSV 4	
Sulfur amount (ppm)	13.30	35.11	82.81	51.19	83.88	78.65	748.09
Sulfur conversion (%)	98.22	95.30	88.92	93.15	88.78	89.48	-

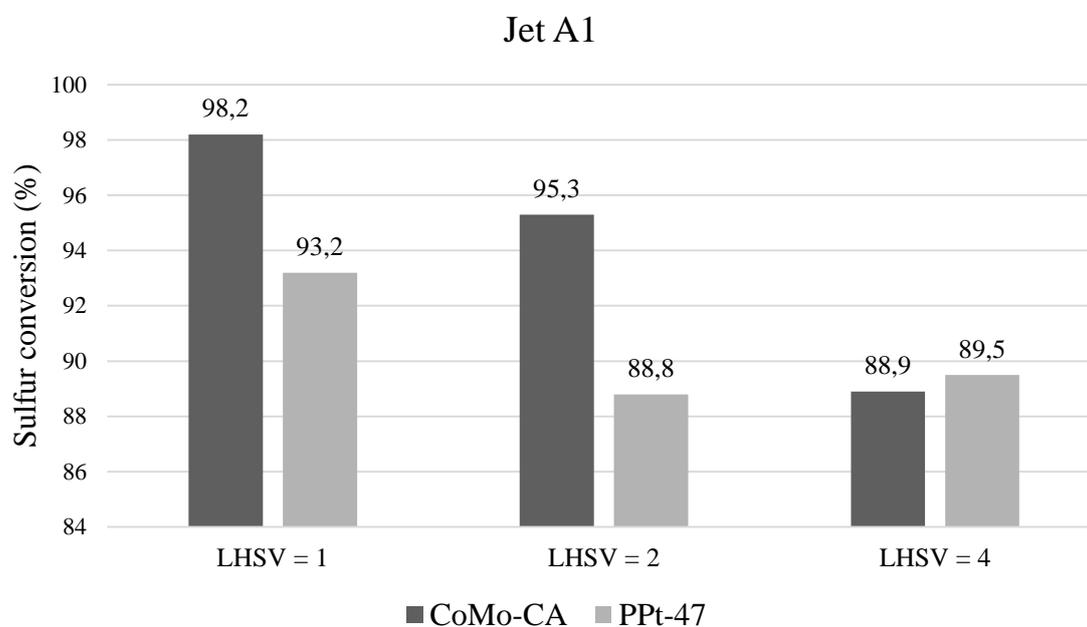


Figure 5.4. Comparison of sulfur conversion between CoMo-CA and PPt-47 on Jet A1. The conversion of 98.2 % corresponds to a sulfur level of 13.3 ppm.

6 Discussion

To be able to reach as low sulfur levels as in industrial processes, harsh reaction conditions, a large extent on sulfidation and optimal performance of catalysts is required. Within this thesis, a micro scale reactor was used which was run at milder conditions than industrial systems. The same degree of sulfidation, as is suggested in the literature, has not been possible. No characterization, which is necessary to determine the catalyst structure-based performance, was done. Therefore, in the discussion, when comparing results gathered in this thesis with literature, a qualitative rather than quantitative approach has been taken.

Sulfidation

The catalysts were sulfided at a $\text{H}_2\text{S}/\text{H}_2$ ratio of 0.1 %, at 400 °C for 4 h or 6 h. In the sulfidation methods encountered in literature, the temperature and duration corresponded to this, but the $\text{H}_2\text{S}/\text{H}_2$ ratio was 10-15 % in different attempts. Despite the difference in activity exhibited by the NiMo catalysts with the different sulfidation times, the effect of more extensive sulfidation was not investigated in this thesis due to the health hazards of H_2S .

Characterization

For further development of the prepared catalysts, characterization would be necessary. In addition of the BET-analysis that was performed on the non-impregnated alumina, it would be essential to characterize the catalysts also after preparation, after sulfidation and after using them in the reactor. After the preparation, x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) characterization would render information about the crystal structure and identify the outermost atoms on the surface. This would indicate if the impregnation was successful and would also be helpful for optimizing the sulfidation step. After the sulfidation, a new XPS and XRD analysis would give valuable information about the amount and dispersion of the active phase. After using the catalyst in the reactor system a second BET-analysis could be done to see if any sintering has occurred. And, again, XPS and XRD would give information on, e.g., the amount of chemisorption on the catalyst surface.

Gradients

The gradients mentioned in the report, namely concentration and temperature could have negative effects on the reactor system. Though, it is only believed that there was a concentration gradient, in the axial dimension, since this is inevitable if there is any conversion of the reactants. All other gradients have been disregarded.

As for the concentration gradient in the radial dimension, that arises from the radial dispersion of reactants in the catalyst bed, it was neglected since the system is pressurized. The laminar flow profile of the gas, before reaching the catalyst bed, entails a higher flow rate in the centre of the pipe. Therefore, the “centre of the flow” is more affected by the pressure drop in the catalyst bed, leading to a turbulent flow profile through the catalyst bed.

The reactor was inserted into an isolated vessel with a heater surrounding the reactor. This oven-like set-up and the fact that the temperature was allowed to stabilize before any tests were run leads to the conclusion that the temperature was constant throughout the system, most importantly in the catalyst bed. The risk of a temperature gradient arising from exothermic or

endothermic reactions was disregarded due to the fact that the hydrotreating reaction for thiophene and DBT are only slightly exothermic, as reported in the literature study, and the whole system was considered to run isothermally. Also, the amount of sulfur was low contributing to that the exothermic reactions should not have affected.

The concentration gradient between the catalyst surface and the bulk, that depends on mass transfer limitations, was neglected assumed no liquid film was formed on the catalyst. The activation energy was calculated for the catalysts, and exceeded 20 kJ/mol for both, indicating that some diffusion could have inhibited the reaction rates.

Sulfur compounds

Two different sulfur compounds were tested separately: thiophene and DBT mixed with either dodecane or paraffin. Jet A1 as a fuel was tested and contained thiols, sulfides, thiophenes, BT and alkylated BT's. Thiophene and DBT were chosen based on their difference in reactivity, with thiophene being easily reacted in HDS and DBT being much more refractory. Alkyl substituted DBT's, were chosen not to be evaluated since they demand harsh reactor conditions and the micro scale set-up might not be enough to remove these compounds. Moreover, DBT and the substituted DBT's are not very common in Jet A1. Another factor favouring thiophene and DBT is that they have been widely used in previous research on the activity of HDS-catalysts. Jet A1 was chosen since this is the fuel on which the reactor is meant to run on when instead in the complete FC-application system.

Reactor systems

Two reactor systems were used for testing: a semi-batch system and a PFR system. The semi-batch system was introduced because of its easy handling in test runs. Though, with the semi-batch system, the test results from the analysis were unreliable. The problem with the reactor system was that when the reactor was heated, and the fuel started to boil some of the thiophene exited through the H₂S-drain, Figure 4.2. It was, therefore, hard to determine if the sulfur detected by the GC were only H₂S, resulting from the HDS reaction, or separated by boiling thiophene. The boiling point for thiophene is a lot lower and could have started separating early on during attempts.

Another disadvantage with the semi-batch system was that temperature and pressure could not be altered independently, and their individual impact on the activity could not be investigated.

These reasons motivated the introduction of the PFR system. In the PFR system, the catalyst activity was investigated based on thiophene or DBT-conversion, instead of H₂S-formation, as was the case for the semi-batch system. This removed the issue of having any unreacted organosulfur compound intervening with the analysis.

The PFR also enabled for more detailed testing regarding optimum reactor settings, since temperature and pressure could be altered separately. In the PFR system, a high-pressure pump was necessary to inject the fuel. This meant that one more component was involved in the system, implicating a larger risk for failure in operation.

Screening tests

The noble metal catalysts exhibited large differences in catalytic activity in the screening test. The commercial catalyst PPt-47 was the best catalyst with a thiophene conversion of 98.81 % while the PtPd catalyst, manufactured within this thesis work, had a thiophene conversion of 74.27 %, which was worse than all other catalysts. The poor activity of the PtPd catalyst might be a result of a too high sulfur level in the fuel. As reported by Sarrazin et al. [4, p. 2715], this type of catalyst is more suitable for pretreated fuels, with low sulfur levels. The PPt-47 has a high level of active metal on the very surface of the alumina pellets. As for the PtPd catalyst, some amount of the active metals may have been absorbed by the pellet leading to a reduced activity.

There was a slight difference in activity for the NiMo and CoMo catalysts sulfided for 4 h, and those sulfided for 6 h. Only 1.33 % and 0.48 % better conversion for NiMo and CoMo respectively. Although the differences in activity corresponded to the trends suggested by the literature, it is hard to assign them to the altered sulfidation time.

The NiMoW catalyst gave a slightly lower sulfur conversion than the CoMo catalyst and the NiMo catalysts without the added tungsten, differing from what Thomazeau et al. [25] suggested. This may be due to a complicated preparation process for this catalyst. After adding the pH-adjusting ammonia to the impregnation solution, its volume greatly exceeded that of the alumina pores. Also, two phases emerged in the solution, and it is possible that some of the active phases remained in the precipitated phase.

The CoMo-CA catalyst, prepared with citric acid present in the impregnation step, gave a sulfur conversion negligibly higher than the CoMo catalyst prepared in a conventional way. Stanislaus et al. [9] suggested that an important effect of the chelating agent was to increase the sulfidation temperature of the promoter metals, and since the extent of sulfidation for the catalysts in this thesis work is significantly less than what literature proposes, the effect of the chelating agent might not assert itself.

Detailed tests

When increasing the pressure, or decreasing the LHSV in the reactor system, the literature suggests, that the sulfur conversion should increase. These trends are evident in the detailed attempts run on PPt-47 and CoMo-CA, presented in Table 5.2 and Table 5.3 respectively.

According to literature HDS activity should increase when reactor temperature is increased, within reasonable limits. This pattern is seen for both catalysts, with the exception of the conversion at the SOP which exceeds the conversion reached at 450 °C. The expected values have been calculated through linear regression and were found to be 90.22 % for PPt-47 and 95.05 % for CoMo-CA, instead of 84.39 % and 88.47 %, which was the result of the analysis. By-products, similar to thiophene could have been formed at the high temperature, contributing to an apparent lower sulfur conversion than was expected. Another explanation could be that the thiophene, adsorbed on the catalyst at lower temperature testing, was fully desorbed at 450 °C, leading to an increased sulfur concentration in the product gas.

In the detailed attempts, the sulfur conversion was lower than in the screening when comparing the SOP results. In the screening tests, samples were taken after ca 8 minutes, instead of after 30 minutes as in the detailed attempts. The reason for the difference can be explained by an

adsorption of the sulfur compounds to the catalyst pellets, contributing to a lower sulfur content in the outlet stream, at an early stage of the attempt. At steady state, when the sulfur compounds have broken through the catalyst bed, and the sulfur levels are dependent only on the catalyst activity, the measured sulfur levels are higher. Thiophene is rather easily reacted and should not take very long time to reach steady-state, though steady-state was not reached during the screening tests.

When desulfurizing the more refractory DBT's, literature proposes more severe reactor conditions, why the tests were conducted at a pressure of 8 bar and a temperature of 450 °C, and the only process parameter altered was the fuel flow. In accordance with the literature, the conversion for both CoMo-CA and PPt-47 was higher at a LHSV 1 than for LHSV 2.

Comparing the sample taken after of 1 h with the sample taken after 5 h of operation (at 8 bar, 450 °C, LHSV 1), the 1 h sample shows a higher conversion. This is evident for both catalysts and can be seen in Table 5.4 and Table 5.5. This indicates the absorption of sulfur compounds to the catalyst, as previously described. Also, when comparing the SOP values for PPt-47 and CoMo-CA on DBT and thiophene, a lower conversion of sulfur is expected for DBT. However, the results are the opposite, which again indicates that there is an absorption and that the effect is more prominent for DBT than for thiophene.

Jet A1-attempts

For the CoMo-CA catalyst, the sulfur conversion increases as the LHSV decreases. This trend is expected and is coherent both with literature and with previous investigations on the effect of LHSV conducted in the detailed attempts. Although a lower sulfur conversion was expected, since Jet A1 contains rather refractory sulfur compounds such as BT and substituted BT's. This can be explained by the diversity of sulfur compounds present in the Jet A1. Compounds such as thiols and thiophenes are easily reacted and indicate a high total sulfur conversion, even if the more refractory compounds remain unreacted. This effect is more prominent for high LHSV's.

The result, in sulfur conversion, for PPt-47 at LHSV 4 (89.48 %) was higher than the result for LHSV 2 (88.78 %). The former value is higher than anticipated. It could not be concluded if this was an error in the analysis or the sample was taken earlier on than it should, contributing to a higher sulfur conversion.

7 Conclusion

Using a microscale catalytic reactor system, the primary goal was to reduce the sulfur level of the Jet A1 to a level below 10 ppm, thereby making it feasible for use in FC applications. A level of 13.3 ppm was achieved and several factors may have inhibited the performance of the system; the micro scale set-up, the level of sulfidation and the structure of the manufactured catalysts.

PPt-47 and CoMo-CA exhibited the highest conversion in the catalyst screening tests. These catalysts were used in the detailed attempts, run on thiophene and DBT, and the effects of pressure, temperature and LHSV, in the interval of 260-400 °C, were in accordance with previous research. At the highest temperature, 450 °C, the conversion was lower than expected, and these results are regarded as a consequence of adsorption of the sulfur compounds to the catalyst pellets. As for their individual activity, the CoMo-CA has consistently been the better performing catalyst.

The results for Jet A1 follow the same trends as the detailed attempts, with CoMo-CA outperforming the PPt-47. Though, the overall conversion of the Jet A1 attempts was higher than what the detailed attempts suggest, and this is believed to be a result of a complete conversion of the least refractory compounds, while some of the substituted BT's remained unreacted.

As for gradients in the system, the activation energy indicates that mass transport limitations have been present in the catalyst pores. This did not affect the catalyst screening test but likely suppressed the overall activity of the system.

8 Future work

Since the activity of the catalysts increased using longer sulfidation time, or higher H₂S/H₂ ratio, it would be interesting to further evaluate the effect of the extent of sulfidation on the sulfur conversion. On the same subject, it would be useful to optimize the sulfidation method, and for this optimization characterization of the catalyst surface would be necessary. Characterization would also give information about possible sintering of the catalyst pellets.

Investigating the time it takes to reach steady-state for both thiophene and DBT would be interesting in order to determine the sulfur conversion based on the actual HDS-activity of the catalysts rather than on chemisorption.

The experimental values obtained throughout the thesis work can be used in order to model the correlation between temperature, pressure and LHSV expressed in conversion (x), and can

be seen in the equation below: $x = 1 - e^{-k_0 \cdot P \cdot e^{\frac{E_a}{R \cdot T}} \cdot \frac{W}{F}}$, $\frac{W}{F} = \frac{1}{LHSV}$

This correlation can be set up as a 3D-model to overview how the sulfur conversion is affected by all of the parameters. The model gives the opportunity to see how the system performs even at reactor settings that were not tested.

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10 Appendices

Appendix I: Catalyst recipes

Appendix II: List of chemicals for catalyst manufacture

Appendix III: Results from analysis

Appendix IV: PPt-47 – Product Data Sheet

Appendix V: Bet Summary Report

Appendix VI: Expected sulfur conversion at 450 °C

Appendix I

CoMo/Alumina & NiMo/Alumina

1. Alumina pellets are grinded into desired size (~3.5 mm diameter)
2. A solution with enough ammonium molybdate to equal 8 wt% elemental molybdenum, when deposited on the alumina, is prepared. The alumina is impregnated using incipient wetness method.
3. The catalyst is dried in air at ambient temperature for 4 h, then in an oven at 120 °C for 15 h, then finally calcined at 500 °C for 4 h.
4. A solution with enough cobalt or nickel nitrate to equal 3-3.5 wt% elemental cobalt or nickel, when deposited on the alumina, is prepared. The catalyst is again impregnated using incipient wetness method.
5. Repeat step 3.

Pt-Pd/Alumina

1. Alumina pellets are grinded into desired size (~3.5 mm diameter)
2. Prior to impregnation, the supports are dried in air at 120 °C for 4 h and calcined at 500 °C for 4 h.
3. A solution with enough Pt and Pd to equal 0.25 and 0.22 wt% respectively when deposited on the alumina, is prepared. The catalyst is impregnated using incipient wetness method.
4. After impregnation the catalysts are dried overnight in air at ambient temperature, then 4 h at 120 °C, and finally calcined at 500 °C for 4 h.

NiMoW/Alumina

1. Alumina pellets are grinded into desired size (~3.5 mm diameter)
2. A solution with enough ammonium molybdate, ammonium metatungstate and nickel nitrate to equal 8 wt% elemental molybdenum, 0.22 wt% tungsten and 3.5 wt% nickel, when deposited on the alumina, is prepared. The solution is adjusted to a pH of 9.5 using diluted ammonia in water. The alumina is impregnated using incipient wetness method.
3. After co-impregnation and maturation, the catalyst is oven-dried overnight at 120 °C. Then calcined in air at 500 °C for 2 h.

Preparation of Titania-Alumina support

1. Aluminum isopropoxide is dissolved in n-propanol at room temperature, under vigorous stirring. 150 ml n-propanol per gram of isopropoxide.
2. Titanium isopropoxide is added to the solution to give $(\text{Ti}/(\text{Al}+\text{Ti}))$ equal to ratio 0.95. To achieve co-precipitation, the solution is put in an open flask to which demineralized water is added. The amount of water should be 30 times the stoichiometric value.
3. The precipitate is left for slow agitation for 24 hours.
4. The precipitate is filtered and washed five times. 250 ml of demineralized water per gram of precipitate for each wash.
5. The support is dried at 110 °C for 24 h. Then calcined at 550 °C for 4 h, with a temperature gradient of 2 °C/min.
6. Next step: Follow CoMo- or NiMo/Alumina recipe seen above.

CoMo/Alumina with citric acid (CA) impregnation

1. Alumina pellets are grinded into desired size (~3.5 mm diameter)
2. A solution with enough ammonium molybdate to equal 8 wt% elemental molybdenum, when deposited on the alumina, is prepared. The alumina is impregnated using incipient wetness method.
3. The catalyst is dried in air at ambient temperature for 4 h, then in an oven at 120 °C for 15 h, then finally calcined at 500 °C for 4 h.
4. A solution with enough cobalt or nickel nitrate to equal 3-3.5 wt% elemental cobalt or nickel, when deposited on the alumina, is prepared. Citric acid monohydrate at a molar ratio of 0.7 with respect to Co is added to the solution. The catalyst is again impregnated using incipient wetness method.
5. Repeat step 3.

Appendix II

Table A.1. List of chemicals for catalyst manufacture

	Specification (%)	Amount (g)	Cost (kr)	Link
DBT	≥ 99	5.0	1635	Sigma
BT	98	5.0	536	Sigma
Co(NO₃)₂·6H₂O	98	500	2375	Sigma
Ni(NO₃)₂·6H₂O	97/98.5	250/50	435/1017	Sigma
TiO₂	-	250	750	Alfa Aesar
(NH₄)₆H₂W₁₂O₄₀·xH₂O	99	100	728	Sigma
Citric acid	99	100	150	Sigma
ZnO	99	250	306	Sigma
H₂S (gas)				
Dodecane	99	2.5 LT	2900	FS
SiO₂				
γ-Al₂O₃				
Pt	99.99	250	1060	Sigma
Pd	10 wt% in H ₂ O	5 ml/25 ml	893/3265	Sigma
(NH₄)₆Mo₇O₂₄·4H₂O	99	100	806	Sigma
Al[OCH(CH₃)₂]₃	98	100	244	FS
Ti[OCH(CH₃)₂]₄	98+	250 ml	325	FS

Appendix III

Table A.2. Screening of the different catalysts, all with the same process parameters.

	PtPd	CoMo	NiMo	Ni-MoW	CoMo-CA	CoMo (6h)	NiMo (6h)	PPt-47	Ref. value
Area (Vs)	21.59	2.51	3.40	6.22	1.92	2.11	2.32	0.99	83.92
Sulfur conversion (%)	74.27	97.01	95.96	92.59	97.71	97.48	97.24	98.81	-

Table A.3. Detailed attempts on CoMo-CA with thiophene.

CoMo-CA										
Thiophene										
	8 bar	0.5 ml/min	2.0 ml/min	4 bar	2 bar	450 °C	350 °C	300 °C	260 °C	SOP
Area (Vs)	4.43	1.47	19.17	11.75	33.23	9.68	19.95	27.34	36.6	6.82
Sulfur conversion (%)	94.72	98.25	77.16	86.00	60.40	88.47	76.23	67.42	56.39	91.87

Table A.4. Detailed attempts on PPt-47 with thiophene.

PPt-47										
Thiophene										
	8 bar	0.5 ml/min	2.0 ml/min	4 bar	2 bar	450 °C	350 °C	300 °C	260 °C	SOP
Area (Vs)	8.63	4.56	28.34	27.43	39.99	13.10	30.47	36.60	41.54	9.91
Sulfur conversion (%)	89.72	94.57	66.23	67.31	52.35	84.39	63.69	56.39	50.50	88.19

Table A.5. Detailed attempts on CoMo-CA with DBT.

CoMo-CA				
DBT				
	8 bar 450 °C 1.0 ml/min	8 bar 450 °C 0.5 ml/min	8 bar 450 °C 0.5 ml/min (5h)	SOP
Counts	6,395	4,060	5,168	2,947
Sulfur conversion (%)	90.89	94.26	92.64	95.80

Table A.6. Detailed attempts on PPt-47 with DBT.

PPt-47				
DBT				
	8 bar 450 °C 1.0 ml/min	8 bar 450 °C 0.5 ml/min	8 bar 450 °C 0.5 ml/min (5h)	SOP
Counts	9,119	4,591	8,961	6,332
Sulfur conversion (%)	87.07	93.46	87.23	90.98

Table A.7. Attempt on Jet A1.

	Jet A1						Ref. value
	CoMo-CA			PPt-47			
	LHSV 1	LHSV 2	LHSV 4	LHSV 1	LHSV 2	LHSV 4	
Sulfur amount	13.30	35.11	82.81	51.19	83.88	78.65	748.09
Sulfur conversion (%)	98.22	95.30	88.92	93.15	88.78	89.48	

Table A.8. Blind testing without a catalyst.

T (°C)	P (Bar (a))	F (ml/min)	Area (Vs)
375	6	1	54.92
250	2	1	83.92

Table A.9. Detailed attempts on PtPd with thiophene.

PtPd										
Thiophene										
	8 bar	0.5 ml/min	2.0 ml/min	4 bar	2 bar	450 °C	350 °C	300 °C	260 °C	SOP
Area (Vs)	12.44	8.85	17.76	35.28	59.45	42.65	60.40	71.85	82.31	21.59
Sulfur conversion (%)	85.18	89.45	78.84	57.96	29.16	49.18	28.03	14.38	0.02	74.27

Appendix IV



Product Data Sheet



VOC* Oxidation Catalyst PPt-47

The platinum catalyst PPt-47 is used for the catalytic incineration of volatile organic compounds (VOC) from industrial offgases.

1. Composition

Active component: Platinum
Support material: Alumina

2. Sales specification

Platinum content 0.1 % by weight
Spheres diameter min 95% within this range 4.0-6.7 mm
Tapped density 72-79 kg/m³
Crush strength: >90 N

3. Packing and storage

60 litres plastic drums, each containing 40kg of catalyst
We recommend to store the product in the closed drums under dry conditions. The catalyst shall be protected against contact to water (including humidity).

4. Safety

With each delivery of our products, a Material Safety Data Sheet will be sent. When using this product, the information and advice given in the Material Safety Data Sheet should be observed.

5. Used catalyst

Used catalyst may be returned to Stonemill AB for environmentally safe disposal.

The information contained in this publication are based on our current knowledge and experience. In view of the many factors that may affect processing and application of our product, the customer is not released from the obligation to conduct careful inspection and testing of incoming goods. Performance of the product described herein should be verified by testing, which should be carried out only by qualified experts in the sole responsibility of the customer.

Stonemill Ab
Box 70
Visiting address: kontorsg. 4
SE-260 39 Hasslarp
Sweden
Phone: +46 42 20 68 60
Fax: +46 42 20 68 65

Stonemill AB website: (www.stonemill.se)
Stonemill AB e-mail address: (info@stonemill.se)

Appendix V

y-Al₂O₃ BHD 27083 4M

ASAP 2400 V3.06

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SAMPLE DIRECTORY/NUMBER: BL141210/266
SAMPLE ID: exjobb Christian Niklas y-Al₂O₃ BDH
SUBMITTER: avg 150 C 24h
OPERATOR: BL
STATION NUMBER: 1 EQUIL INTERVAL: 20 sec

START 16:01:34 05/13/16
COMPL 09:52:21 05/16/16
REPRT 12:10:15 05/16/16
SAMPLE WT: 0.9200 g
FREE SPACE: 53.4217 cc

SUMMARY REPORT

AREA

BET SURFACE AREA:	300.1011	sq. m/g
LANGMUIR SURFACE AREA:	415.7103	sq. m/g
SINGLE POINT SURFACE AREA AT P/P ₀ 0.2065:	286.5156	sq. m/g
BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	206.2450	sq. m/g
BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	321.2202	sq. m/g
MICROPORE AREA:	-20.2982	sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN 3961.3535 A DIAMETER AT P/P ₀ 0.9951:	0.353802	cc/g
BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.258207	cc/g
BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.329142	cc/g
MICROPORE VOLUME:	-0.012639	cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):	47.1576	A
BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):	50.0776	A
BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):	40.9864	A

Appendix VI

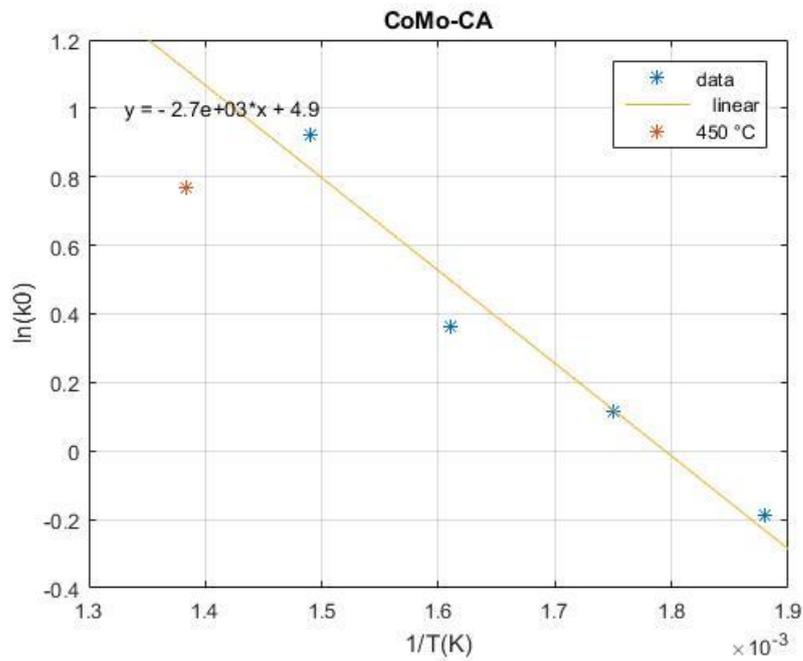


Figure A.1. Linear regression on CoMo-CA for expected conversion at 450 °C.

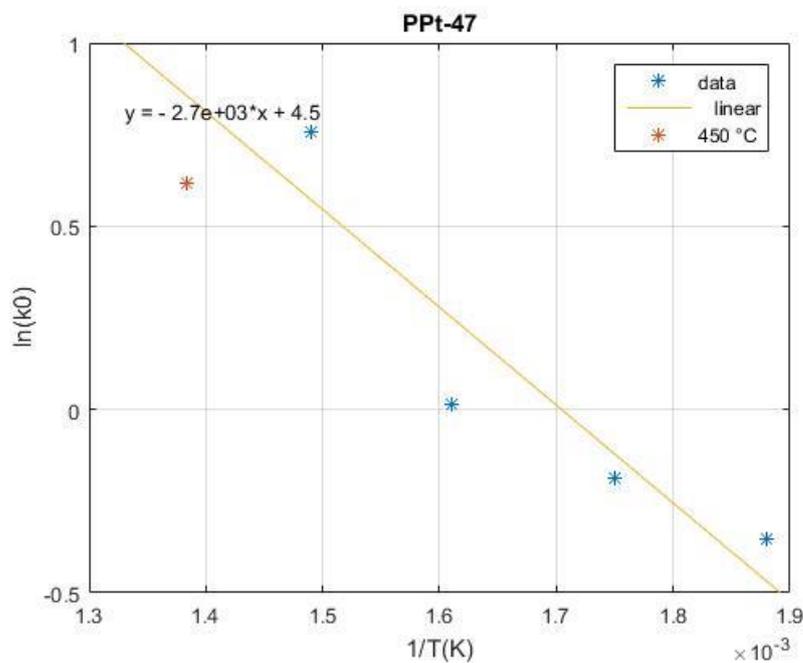


Figure A.2. Linear regression on PPt-47 for expected conversion at 450 °C.

$$k_0 = -\ln(1 - x), \quad x = \text{conversion}$$