

Hydrodeoxygenation of methyl heptanoate and phenol over sulphided supported NiMo and CoMo catalysts

Eeva-Maija Turpeinen

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Aalto University
School of Chemical Technology
Department of Biotechnology and Chemical Technology
Industrial Chemistry

Supervisor

Prof. Outi Krause

Instructor

Prof. Outi Krause

Preliminary examiners

Dr. Christophe Geantet

Institute de recherches sur la catalyse et l'environnement de Lyon
France

Dr. Jostein Gabrielsen

Haldor Topsøe A/S
Denmark

Opponents

Prof. Erik Heeres

University of Groningen
the Netherlands

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Eeva-Maija Turpeinen

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Abstract

Biomass-based energy sources are under intensive study for replacing fossil fuels with environmentally friendly alternatives. Bio-oils, intended for use as such or mixed with fossil fuels, need to be upgraded by hydrodeoxygenation (HDO) due to the high oxygen-content of the molecules, which causes unwanted fuel properties. This thesis describes oxygen removal reactions of methyl heptanoate and phenol over sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. These two components were chosen as representative model reactants of the complex bio-oils.

Reaction schemes for the HDO of methyl heptanoate and phenol are presented. Reaction steps were justified with acid-catalysed reactions (hydrolysis, dehydration, esterification), reductive reactions and decarbonylation. Reactivity of the reactants individually and as a mixture and their product distributions were explored with and without a sulphur additive as sulphur is needed to keep the catalyst in the sulphided form. Sulphur-containing components were formed during the HDO reactions even without sulphur addition during the experiments. The source of the sulphur is the sulphur species attached to the catalyst surface. Possible active sites are also discussed. Reduction reactions were proposed to occur on coordinatively unsaturated sites (CUS), whereas acid-catalysed reactions and decarbonylation need sulphur-saturated sites.

The vapour-liquid equilibrium (VLE) of methyl heptanoate and solvent, in this case *m*-xylene, was measured to improve composition analysis of the multi-phase system. The Predictive Soave-Redlich-Kwong (PSRK) model was shown to be a good tool for simulation of the gas phase of a non-ideal system with polar components.

The findings give new insights into the HDO reactions by describing the reaction pathways of two different types of model components and how the sulphur species affect those pathways. Moreover, the performance of the sulphided catalyst and simulation of a non-ideal system are presented.

Keywords hydrodeoxygenation (HDO), methyl heptanoate, phenol, active sites, vapour-liquid equilibrium (VLE)

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Tekijä

Eeva-Maija Turpeinen

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Metyyliheptanoaatin ja fenolin hapenpoistoreaktiot rikitetyillä NiMo- ja CoMo-katalyyteillä

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Biotekniikan ja kemian tekniikan laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 78/2011**Tutkimusala** Teknillinen kemia**Käsikirjoituksen pvm** 02.03.2011**Korjatun käsikirjoituksen pvm** 10.08.2011**Väitöspäivä** 18.11.2011**Kieli** Englanti **Monografia** **Yhdistelmäväitöskirja (yhteenvedo-osa + erillisartikkelit)****Tiivistelmä**

Biomassapohjaisia energialähteitä tutkitaan laajasti, jotta fossiiliset polttoaineet voitaisiin korvata ympäristöystävällisemmällä vaihtoehdoilla. Bioöljyt sisältävät runsaasti happipitoisia molekyyliä, mikä tekee niistä ominaisuuksiltaan heikompia kuin fossiiliset öljyt. Metyyliheptanoaatin ja fenolin hapenpoistoreaktioita (HDO) tutkittiin rikitetyillä NiMo/ γ -Al₂O₃- ja CoMo/ γ -Al₂O₃-katalyyteillä. Bioöljyt ovat kymmenien erilaisten molekyylien seoksia, ja nämä kaksi mainittua reagenssia valittiin malliaineiksi.

Tässä työssä esitellään metyyliheptanoaatin ja fenolin hapenpoistoreaktiokaaviot. Reaktiovaiheina olivat happokatalysoidut reaktiot (hydrolyysi, dehydratointi ja esteröinti), pelkistysreaktiot ja dekarbonylointi. Malliaineita tutkittiin sekä yksin että seoksena. Osassa kokeista reaktioseokseen lisättiin myös rikkiä, sillä katalyytin tulisi pysyä rikitettynä. HDO-reaktioissa syntyy rikkipitoisia tuotteita myös ilman reaktion aikaista rikkilisäystä. Pelkistysreaktiot tapahtunevat koordinatiivisesti tyydyttymättömillä paikoilla (CUS), kun taas happokatalysoidut reaktiot ja dekarbonylointi tapahtunevat rikkityydytetyillä paikoilla.

Metyyliheptanoaatin ja liuottimen, tässä tapauksessa *m*-ksyleenin, kaasu-neste -tasapaino mitattiin, jotta voitiin kehittää monifaasisysteemin koostumusanalyysiä. Ennustavan Soave-Redlich-Kwong -mallin (PSRK) avulla voidaan simuloida kaasufaasipitoisuuksia epäideaalisissa systeemeissä, jossa on polaarisia komponentteja.

Työssä esitellään kahden erityyppisen malliaineen hapenpoistoreaktioreitit ja se, miten rikki vaikuttaa niihin. Tämän ohella tarkastellaan rikitetyn katalyytin rakennetta ja epäideaalisen monifaasisysteemin simulointia.

Avainsanat hapenpoisto (HDO), metyyliheptanoaatti, fenoli, aktiiviset pintapaikat, kaasu-neste -tasapaino

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PREFACE

The experimental part of this thesis and the main part of the writing process have been carried out at the Laboratory of Industrial Chemistry, Aalto University (formerly Helsinki University of Technology), during the period of January 2005 and February 2009. After this period, the thesis has been finished during the leisure time until February 2011. The primary funding was achieved from the Graduate School of Chemical Engineering, which is gratefully acknowledged.

I would like to express my sincerest gratitude to my supervisor Prof. Outi Krause for her advice and expertise in the field of catalysis. I am indebted to my co-authors Dr. Ilke Şenol, Dr. Erlin Sapei, Dr. Petri Uusi-Kyyny and Dr. Kari Keskinen for valuable advices. In addition, Dr. Maija Honkela and Dr. Tuula-Riitta Viljava deserve special mentioning being as co-authors and even more, supporting and pushing me forward. Prof. Reija Jokela is thanked for help in organic chemistry. I also show appreciation to the colleagues at the Laboratory of Industrial Chemistry for providing a pleasant working atmosphere. All the experimental work done by undergraduate students and summer trainees over the years is also appreciated. I am grateful to the specialists in English language, Kathleen Ahonen and Mary Metzler, for revising the manuscripts and the thesis.

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Ylöjärvi, September 2011

Eeva-Maija Turpeinen

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LIST OF PUBLICATIONS

This thesis is based on the following appended publications, which are referred to in the text by their Roman numerals:

I Turpeinen, E.-M., Sapei, E., Uusi-Kyyny, P., Keskinen, K.I., Krause, A.O.I., Finding a Suitable Thermodynamic Model and Phase Equilibria for Hydrodeoxygenation Reactions of Methyl Heptanoate, *Fuel*, 90 (2011) 3315-3322.

II Şenol, O.İ., Ryymin, E.-M., Viljava, T.-R., Krause, A.O.I., Reactions of Methyl Heptanoate Hydrodeoxygenation on Sulphided Catalysts, *Journal of Molecular Catalysis A: Chemical*, 268 (2007) 1-8.

III Ryymin, E.-M., Honkela, M.L., Viljava, T.-R., Krause, A.O.I., Insight to Sulfur Species in the Hydrodeoxygenation of Aliphatic Esters over Sulfided NiMo/ γ -Al₂O₃ Catalyst, *Applied Catalysis A: General*, 358 (2009) 42-48.

IV Şenol, O.İ., Ryymin, E.-M., Viljava, T.-R., Krause, A.O.I., Effect of Hydrogen Sulphide on the Hydrodeoxygenation of Aromatic and Aliphatic Oxygenates on Sulphided Catalysts, *Journal of Molecular Catalysis A: Chemical*, 277 (2007) 107-112.

V Ryymin, E.-M., Honkela, M.L., Viljava, T.-R., Krause, A.O.I., Competitive Reactions and Mechanisms in the Simultaneous HDO of Phenol and Methyl Heptanoate over Sulphided NiMo/ γ -Al₂O₃, *Applied Catalysis A: General*, 389 (2010) 114-121.

CONTRIBUTIONS

The author's contributions to the appended papers are as follows:

- I She planned the research with the co-authors and carried out the experiments except for the vapour-liquid equilibrium measurements. She participated in the interpretation of the results and wrote the manuscript, assisted by co-authors.
- II She planned, carried out and interpreted the results of batch reactor experiments. She contributed to the writing of the manuscript.
- III She planned the research and carried out the experiments. She interpreted the results and wrote the manuscript together with the co-authors.
- IV She planned, carried out part and supervised part of the batch reactor experiments and interpreted those results. She contributed to the writing of the manuscript.
- V She planned the research and carried out part and supervised part of the experiments. She interpreted the results and was the main contributor to the writing of the manuscript.

1. INTRODUCTION

1.1 From biomass to oil

The production of biomass-based transportation fuels has attracted special attention because of diminishing fossil fuel reserves, the rising price of crude oil and environmental problems associated with the greenhouse effect. Fossil fuels could be replaced partially or even totally with biomass-based fuels. The cycle for biomass-based fuels from carbon to CO₂ and back to carbon is much faster than that for conventional fuels. Fossil fuels are formed from material already existing under-ground whereas the biomass needed for biomass-based fuels continuously consumes CO₂ via photosynthesis [1, 2].

The final products of biomass conversion can be divided into three main groups: power/heat generation, transportation fuels and chemical materials. Conversion is generally achieved by some type of thermo-chemical, mechanical or biological process, as outlined in Figure 1 [3].

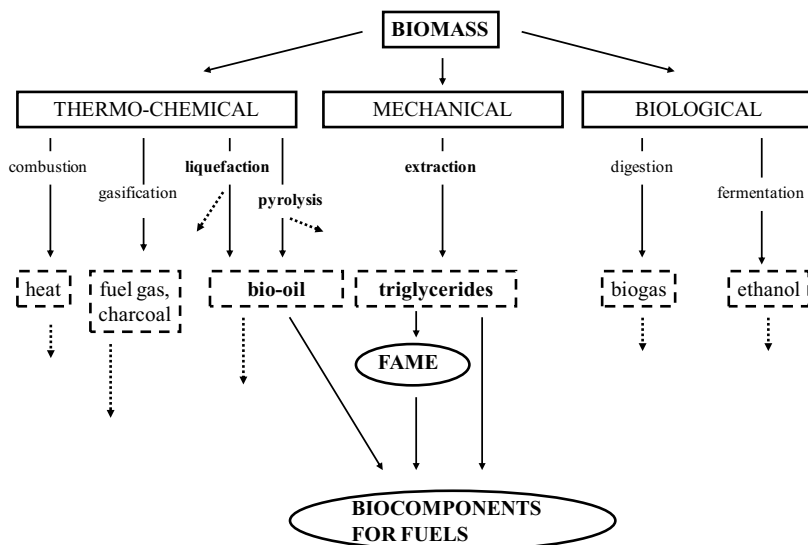


Figure 1. Biomass conversion methods for various energy products: primary products (dashed boxes) and secondary products (circles) [3].

One of the well-known thermal processes for upgrading biomass to biocomponents for fuel applications is pyrolysis in which organic material is heated in the absence of air at temperatures between 450 and 650 °C. The product, biomass pyrolysis liquid, is also called pyrolysis oil, bio-oil or biocrude. Pyrolysis is not very selective and a wide range of compounds is usually obtained. In wood-based bio-oil the single most abundant compound is water. Aldehydes, ketones, acids, esters, alcohols, sugars and aromatic structures such as phenols and guaiacols with different substituents can also be detected in this type of fuel [1, 4].

Vegetable oil production is based on a mechanical process. Seeds of various biomass crops are extracted to obtain vegetable oil, i.e., triglyceride structure. Transesterification of triglycerides with methanol in the presence of catalyst produces fatty acid methyl esters (FAME) and glycerol [3].

A variety of terms is used when biomass-based oils are discussed. By definition in the European Union, biodiesel is a methyl ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel [5]. European Committee for Standardisation also states that biodiesel consists of fatty acid mono-alkyl esters [6]. Knothe [7] has recently suggested a term, renewable diesel, for a petrodiesel-like fuel derived from renewable resources. This term is needed as biodiesel covers only FAME and there are also other types of biomass-based molecules that can be used as biocomponents for fuels.

1.2 Hydrodeoxygenation (HDO)

Wood-based bio-oils, vegetable oils and FAME are highly oxygenated. Wood-based bio-oil is 35-40 wt% oxygen [1] and vegetable oil is about 11 wt% [8]. Oxygen confers unwanted properties on biomass-based oils, e.g. low energy density (50% of that of conventional fuels), high viscosity, immiscibility with hydrocarbon fuels and chemical instability [1, 4, 7]. Thus, the oil is generally upgraded using methods such as hydrodeoxygenation (HDO). HDO belongs to a group of hydrotreating reactions and it means removal of oxygen from an oxygen-containing compound under hydrogen pressure at high temperatures with the help of catalyst. After HDO, the oil can be blended with conventional fuels without the need for engine or infrastructure modifications. Other hydrotreating techniques similar to HDO are hydrodesulphurisation (HDS, removal of sulphur) [9] and hydrodenitrogenation (HDN, removal of nitrogen) [10].

Hydrotreating is carried out industrially under high H₂ pressure (between 7.0 to 20.0 MPa) and high temperature (between 350 to 400 °C) over

sulphided catalysts. The high hydrogen requirement makes the process economically unfavourable. In addition, the hydrogen often originates from steam reforming of natural gas although hydrogen can also be obtained from renewable sources [7, 11]. Hydrocarbons and water are formed as the main reaction products. The main focus in the literature has been on research dealing with HDS, as sulphur poisons various types of metal catalysts, which are needed for further upgrading. In addition, specifications for sulphur content of diesel fuel have been tightening year by year [12]. More recently, studies on HDO and HDN have attracted special attention, too.

1.3 Structure of HDO catalyst

The most commonly-used catalysts for HDO are sulphided molybdenum catalysts on alumina supports with nickel or cobalt as a promoter metal [13]. In addition, the catalysts often contain modifier elements such as phosphorous, boron, fluorine or chloride. The concentration of the metals is usually 1-4 wt% for Ni and Co and 8-16 wt% for Mo [14]. Other types of catalysts such as Rh/Al₂O₃, Pd/SiO₂, Pd/C and Pt/C are, however, continuously studied in attempts to avoid the use of sulphur because of the problem caused by traces of sulphur in the end products [7]. Experiments in this thesis were carried out using sulphided NiMo and CoMo catalysts and therefore, these catalysts will be presented in more detail.

Sulphidation is a pretreatment step performed in situ or ex situ for oxidic catalyst precursors with sulphur-containing compounds, e.g. gaseous H₂S or liquid organosulphides, to obtain Mo and Ni/Co metals as sulphides. The addition of a sulphur-containing compound induces the formation of water, indicating an oxygen-sulphur exchange reaction. The sulphidation procedure has a significant influence on HDO activity and stability of the catalyst [15, 16]. Arnoldy et al. [17] reported over twenty years ago that lower sulphidation temperatures can be used with increasing Mo content. A few years later Prada Silvy et al. [18] observed that the activity of CoMo catalyst was dependent on the pretreatment temperature and that the optimum temperature varied according to the sulphiding agent. Texier et al. [19, 20] have more recently investigated the pretreatment step with H₂S and organosulphides over unpromoted and Ni/Co promoted Mo catalysts. According to their study, using organosulphides may improve the structure of the active species formed. They also noticed that comparisons of the hydrotreating results are often done using results obtained under various

conditions and using different test components, which makes comparisons complicated.

In the literature a variety of different models describing the structure of the sulphided, promoted MoS₂ catalyst and the active sites can be found. Eijsbouts [21] has expressed in her review dealing with the active phase in hydrotreatment catalysts as follows: "Those, who are seeking for a single well-defined active phase acting according to a specific reaction mechanism, may not be satisfied for the overview." Co and Ni may be present as a stable but inactive Ni₃S₂/Co₉S₈ phase over the support, inserted in the alumina lattice or adsorbed on the edge of MoS₂ as a Ni/Co-Mo-S phase. The activity of Mo-based catalyst with Ni/Co as a promoter is higher than the activity of either Mo, Ni or Co sulphides alone [22]. Nowadays it is generally accepted that the Ni/Co-Mo-S model describes the structure of the catalyst well. It is suggested that the promoter atom can donate electrons to Mo which leads to a weakening of the metal-sulphur bond. As the sulphur atom leaves the structure, a sulphur anion vacancy, i.e., a coordinatively unsaturated site (CUS) is formed. In addition, the dissociation of hydrogen and H₂S occurs on CUS-S pairs, forming hydrides, sulfhydryl groups and protons. Recently, it has been suggested, on the basis of the density functional theory (DFT), that unpromoted and promoted MoS₂ catalysts may have specific metallic edge sites that give rise to bright brims in scanning tunneling microscopy (STM) [23].

Al atoms of the γ -alumina support are Lewis acid sites whereas the O atoms are basic sites [24]. It has been reported that H₂S may react with Al atoms but the oxygen sites are not adsorption sites for H₂S. Alumina is preferred as a support because of strong interactions with MoS₂ clusters. Over alumina, these clusters have high dispersion which is important for the formation of the active Ni/Co-Mo-S structure. Other support materials such as carbon and silica have also been studied but their structures have been determined to be less stable than that of alumina [14].

One should be careful when comparing experimental data produced using different catalyst activation procedures. It is also difficult to draw conclusions regarding catalyst structure and the active sites, as reported studies have been carried out using different kinds of catalysts such as unpromoted or promoted, with Ni or Co as a promoter metal, and nonsupported or supported. Moreover, conclusions on the basis of HDS or HDN reactions may not be valid for HDO reactions.

1.4 Role of hydrogen in HDO

Spectroscopic studies have revealed that hydrogen may be adsorbed on Mo and Ni/Co forming several types of hydrogen bonds, e.g. Mo-SH, Mo-H and Ni/Co-H [25]. In addition, OH⁻ groups may be present that originate from the alumina support, because of incomplete sulphidation of metals or as a result of the formation of water during the HDO. On one hand, the reaction of hydrogen with the MoS₂ phase is desired as it is necessary for the HDO reactions to occur and on the other hand, the adsorption of hydrogen may result in unwanted gradual removal of sulphur.

As the presence of hydrogen is crucial, the role of promoters in hydrogen activation has been studied [25]. The promoter atoms may contribute to the initial rate of hydrogen activation but most likely not the total amount of hydrogen adsorbed. An increase in hydrogen pressure was also observed to mostly have an effect on the initial rate of the reaction.

1.5 Vapour-liquid equilibrium (VLE)

To perform reaction kinetic studies, complete material balance is needed. Once the kinetic model is obtained it can be used as the basis for scale-up or design of different types of reactors. Several authors have reported inaccuracies in material balances of HDO systems. Hurff and Klein [26] have studied HDO of guaiacol and reported a material balance closure of 90% at 250 °C. In addition, increasing temperature led to a weaker deficiency. Laurent and Delmon [27] also performed experiments with guaiacol and reported material balance errors between 15 and 30%. In their studies, Viljava and Krause [28] simulated the vapour phase composition of phenol in HDO on the basis of the liquid phase compositions and thus they were able to improve material balances. However, the literature on VLE of HDO systems is very limited.

The presence of oxygen-containing compounds nearly always means that the system is thermodynamically non-ideal. Thus, liquid phase activity coefficients should be used in reaction kinetic models. However, due to the high amount of hydrogen, which is in the supercritical state in HDO applications, this approach is difficult. In addition, Henry's law constants for the gaseous components would be needed, and for real bio-oil they would be difficult to determine because of the large number of components involved. It could be possible to use an equation of state (EOS), which is used for predicting the state of gases and liquids, but it is not recommended to be used alone for mixtures containing polar compounds [29]. An EOS

could be improved with binary interaction parameters but the large number of binary pairs in HDO systems makes the model unusable. However, activity coefficient models combined with EOS, such as Huron-Vidal, MHV1, MHV2, Wong-Sandler and Predictive Soave-Redlich-Kwong (PSRK) [30] do not need binary interaction parameters for the EOS. All the others except MHV2 and PSRK must be excluded as the activity coefficients still need binary interaction parameters. PSRK could be suitable thermodynamic model to model reaction kinetics for complex mixtures as when compared to MHV2, the UNIFAC table for PSRK is wider.

1.6 Scope of the research

The aim of this work was to deepen understanding of HDO of aliphatic and aromatic components. As presented in the review of Furimsky [31] HDO studies of oxygen-containing compounds are mostly carried out using aromatic compounds, as they are the most abundant components of wood-based bio-oil. Together with vegetable oils, which could also be processed for use with conventional fuels, the liquids consist of components with several types of functional groups. Thus, it was necessary to study aliphatic components, too. Methyl heptanoate and phenol were chosen as representative model aliphatic and aromatic compounds, respectively. Reaction pathway studies, the role of the catalyst and the effect of the addition of sulphur on product distribution were the main concerns of the work presented here.

The VLE of the reactant, methyl heptanoate, with the solvent, *m*-xylene, was measured [Paper I] for validation of an appropriate thermodynamic model for a non-ideal system at high pressure and temperature. The preferred thermodynamic model was applied to the data acquired from liquid samples of the product of HDO of methyl heptanoate to simulate the composition of the vapour phase.

The reaction scheme for the HDO of methyl heptanoate was proposed on the basis of batch and flow reactor experiments [Paper II]. Methyl heptanoate and its intermediates were studied separately to confirm the routes to hydrocarbon end products. Possible reaction mechanisms and active sites were discussed. Reactions of methyl heptanoate were studied over a reduced catalyst to elucidate the effect of sulphur species of sulphided catalyst [Paper III]. The participation of surface OH⁻ and SH⁻ groups in the various reaction steps and the stability of the surface sulphur were discussed.

Progress of the HDO of methyl heptanoate and phenol were compared in the batch and flow reactor experiments with and without sulphur addition [Paper IV]. Methyl heptanoate and phenol were examined individually. Studies of the HDO of one component systems were continued by examining the simultaneous HDO of methyl heptanoate and phenol [Paper V]. These studies included experiments with and without sulphur addition, too. Active sites for different types of reaction steps were proposed.

2. EXPERIMENTAL

The experimental procedures are described in detail in Papers I to V and only a short summary is given here.

2.1 Catalysts and chemicals

Commercial NiMo/ γ -Al₂O₃ [I-V] and CoMo/ γ -Al₂O₃ [II, IV] catalysts were crushed and sieved to produce particles 0.59-0.75 mm in size. Catalyst was dried at 100 °C for 5 h before measuring the amount of loading, which was typically 0.5 g. The activity of the catalyst support, γ -alumina, was also tested [V].

The main oxygen-containing reactants were methyl heptanoate [I-V] and phenol [IV, V]. In addition, intermediates of these compounds formed during the HDO reactions were extensively tested as reactants. Methyl heptanoate [I-V] and phenol [IV, V] were tested alone and as a mixture [V]. For justifying the methyl heptanoate product distribution and reaction pathways ethyl heptanoate was also used in some tests [III]. Reactants were diluted in *m*-xylene [I, II, IV] or in *n*-dodecane [III, V] in order to get initial concentrations between 1 and 5 wt%. In the batch reactor experiments, *n*-decane as an internal standard, was also added to the reaction mixture. In the flow reactor, cumene [II, IV] was used as an external standard for gas chromatographic analyses and in the batch reactor, *n*-dodecane [I, II, IV] or *n*-tetradecane [III, V] were used as external standards. All gases and chemicals used are listed in Table 1.

Table 1. Gases and chemicals used in the studies of HDO of methyl heptanoate and phenol.

Gases and chemicals	Use	Supplier	Purity	Paper
H ₂	reactant	Aga	99.999%	I-V
N ₂	inert	Aga	99.999%	I-V
5 mol% H ₂ S/H ₂	additive	Aga	99.999%	I-V
dimethyl disulphide (DMDS) ^a	additive	Fluka	≥98%	V
<i>m</i> -xylene	solvent	Merck	>99%	I, II, IV
<i>n</i> -dodecane ^a	solvent	Merck	≥99%	III, V
toluene	solvent	Sigma Aldrich	99.98%	I
<i>n</i> -dodecane ^a	external standard	Merck	≥99%	I, II, IV
<i>n</i> -tetradecane ^a	external standard	Merck	>99%	III, V
cumene ^b	external standard	Fluka	>98%	II, IV
<i>n</i> -decane ^a	internal standard	Sigma and Merck	>99% and >98%	I-V
methyl heptanoate	reactant	Fluka and Merck	>99% and >98%	I-V
ethyl heptanoate ^a	reactant	Aldrich	99 %	III
1-heptanoic acid	reactant	Aldrich and Merck	99% and ≥ 99%	II, III
1-heptanal ^a	reactant	Fluka	≥ 95%	III
1-heptanol	reactant	Aldrich and Merck	98% and ≥ 99%	II, III
1-heptene ^a	reactant	Merck	≥ 99%	III
phenol	reactant	J.T. Baker and Fluka	lab. grade and ≥99%	IV, V
benzene ^a	reactant	Fluka	>99.5%	IV, V
cyclohexanol	reactant	Aldrich and Fluka	99% and ≥99.0%	IV, V
cyclohexanone ^b	reactant	Fluka	>99%	IV
cyclohexene ^a	reactant	Aldrich	99 %	V
NiMo/Al ₂ O ₃	catalyst	Commercial		I-V
CoMo/Al ₂ O ₃	catalyst	Commercial		II, IV
γ-Al ₂ O ₃ ^a	catalyst	Akzo		V

^a used only in the batch reactor experiments

^b used only in the flow reactor experiments

2.2 Batch reactor experiments

2.2.1 Equipment

HDO experiments were mostly carried out in liquid phase in a 50 ml batch reactor delivered by Autoclave Engineers. Catalyst was loaded into a Robinson Mahoney type catalyst basket. Tests with mixing speeds between 1000 and 1750 rpm showed that the mixing speed did not affect product distribution or conversion values and therefore, 1000 rpm was chosen as the mixing speed.

2.2.2 Catalyst pretreatment

A batch of catalyst was sulphided [I-V] or reduced [III] in situ before addition of reactants. The reactor was heated up over the course of 1 h to a

final temperature of 350 °C under N₂ flow (6 l/h). For the sulphidation, after reaching the pretreatment temperature, the catalyst was subjected to a drying period of 2 h under N₂ flow (6 l/h) and a sulphidation period of 2 h under H₂S/H₂ flow (5 mol%, 3 l/h). In the reduction pretreatment, H₂S/H₂ was replaced by H₂ (3 l/h). Finally, the reactor was cooled down to the experimental temperature over 30 min under N₂ flow in order to flush the reactor free of pretreatment gases.

2.2.3 Experimental procedure

All the experiments presented in this summary were carried out at 250 °C and 7.5 MPa [I-V]. In most cases, a hydrogen atmosphere was used [I-V] but the use of nitrogen atmosphere was also examined [III]. Some of the experiments were carried out in the presence of sulphur additive. The amount of H₂S varied, up to a maximum of 2000 ppm, and the amount of dimethyl disulphide (DMDS) went up to a maximum of 0.8 wt%. Liquid phase occupied 1/3 of the reactor volume. Reaction times varied between 5 min and 5 h depending on the aim of the test. About 200 mg of waste liquid was removed before the liquid sample of about 100 mg was taken. The number of samples was limited to five in each test in order to avoid significant liquid-to-vapour ratio changes.

2.3 Flow reactor experiments

2.3.1 Equipment

Some of the experiments were carried out in vapour phase in a tubular flow reactor with an inside diameter of 10 mm and a length of 380 mm. The catalyst was packed between two layers of silicon carbide.

2.3.2 Catalyst pretreatment

A batch of catalyst (0.5 g) was pretreated in situ. A drying step of 2 h at 400 °C under N₂ flow (2.5 l/h) was firstly carried out and was followed by a sulphidation period of 4 h at 400 °C under H₂S/H₂ flow (5 mol%, 2.5 l/h). After pretreatment, the reactor was briefly flushed with hydrogen and the temperature was decreased to the reaction temperature.

2.3.3 Experimental procedure

Experiments were carried out at 250 °C and 1.5 MPa. The liquid feed was preheated and merged upstream of the reactor at a rate of 10 g/h and the

hydrogen flow was 2.0 l/h. Stabilisation took 2 h, after which the first liquid sample was taken. A standard run continued for 6.5 h with a sampling frequency of 30 min. In the flow reactor, some of the experiments were also carried out in the presence of sulphur additive. The amount of H₂S in the feed varied between 0 and 24 000 ppm.

2.4 VLE measurements

The VLE measurements were carried out with a circulation still of the Yerazunis-type [32] with minor modifications to the original design [33]. Approximately 80 ml of reactant was needed to run the apparatus. At first, pure component 1 was fed into the circulation still, and its vapour pressure was measured at several temperatures. Then component 2 was introduced into the still. It took 15 to 30 min to achieve constant temperature. The temperature was held constant for 30 to 45 min before sampling. After equilibration, the pressure was measured, and then vapour and liquid samples were withdrawn. Temperature and pressure were carefully measured and the uncertainties for the systems were estimated to be ± 0.05 °C and ± 0.17 kPa, respectively.

2.5 Analyses

Liquid samples from reactor experiments were analysed off-line with a gas chromatograph (GC) equipped with a capillary column (HP-1, 60 m x 0.25 mm x 1 μ m) and a flame ionisation detector (FID) [I-V]. The products were quantified by the internal standard method. In addition, qualitative analysis was facilitated by a mass sensitive detector. During a few flow reactor experiments, on-line GC (HP-PLOT/U, 30 m x 0.32 mm x 10 μ m) with a thermal conductivity detector was used for vapour phase analysis [II, IV]. Calibration was performed every fourth month. In the case of the batch reactor, the vapour phase was qualitatively probed for CO, CO₂ and H₂S with Dräger tubes [II, III]. Repeated experiments showed that conversion values varied within ± 2 percentage units.

Catalysts were collected after experiments [II-IV]. The sulphur and carbon contents of the catalysts were determined by a LECO SC-444 series analyser. Margin of error was ± 0.3 percentage units. The catalyst samples were dried in a separate oven in air for 24 h at 100 °C before analysis.

2.6 Definitions

The following definitions are used in Papers I to V.

Conversion is calculated as the ratio of amount of consumed reactant to amount of initial reactant for both batch and flow reactor experiments. Thus, complete conversion is achieved when no reactant is detected in a reaction mixture. Selectivity is calculated in flow experiments as the ratio of amount of product to amount of consumed reactant. In batch experiments the molar concentration of the product is given. That is the ratio of the number of moles of product to the total number of moles, including unreacted reactant and products.

Complete deoxygenation is achieved when no compounds containing hetero atoms are left in the reaction mixture, i.e., only hydrocarbons are present. Alkenes and alkanes are summed together when discussing the amount of hydrocarbon products.

In the presentation of the results of the simultaneous HDO of methyl heptanoate and phenol, the amounts of aliphatic products of methyl heptanoate and cyclic products of phenol are calculated separately. From this, the sum of final products of methyl heptanoate is 100 mol% and the sum of final products of phenol is also 100 mol%.

3. VAPOUR-LIQUID EQUILIBRIUM

3.1 Thermodynamic models for methyl heptanoate and *m*-xylene

Batch reactor experiments were carried out in liquid phase with hydrogen as a reactive gas. To evaluate the vapour phase composition due to mass transfer between gas and liquid phase and vice versa, and to validate the thermodynamic model for simulation, VLE calculations for the system of methyl heptanoate and *m*-xylene were performed [I].

Methyl heptanoate and *m*-xylene vapour pressures were measured [I, Figure 1]. To compare the experimental vapour pressures measured in this work, the average deviations were calculated for pressures obtained from literature and from published correlation. For *m*-xylene, the absolute average deviation of pressure between measured values and a published correlation [34] was 0.2 kPa and between measured values and those measured by Rodrigues et al. [35] was 0.4 kPa. For methyl heptanoate, the absolute average deviation of pressure between measured values and a published correlation [36] was 0.7 kPa and between our measured values and those measured by Postigo et al. [37] was 6 kPa.

VLE measurements (P , x_i , y_i) for the system of methyl heptanoate and *m*-xylene were done isothermally at temperatures of 125 °C and 135 °C and the results are displayed in Figures 2a and 2b, respectively [I]. In addition to the measured values, the corresponding equilibrium was predicted using four thermodynamic models, i.e., original UNIFAC, UNIFAC-Dortmund, SRK and PSRK with the VLEFIT program [38]. These thermodynamic models can be used for solutions containing several non-ideal polar components as is the case in a real bio-oil mixture.

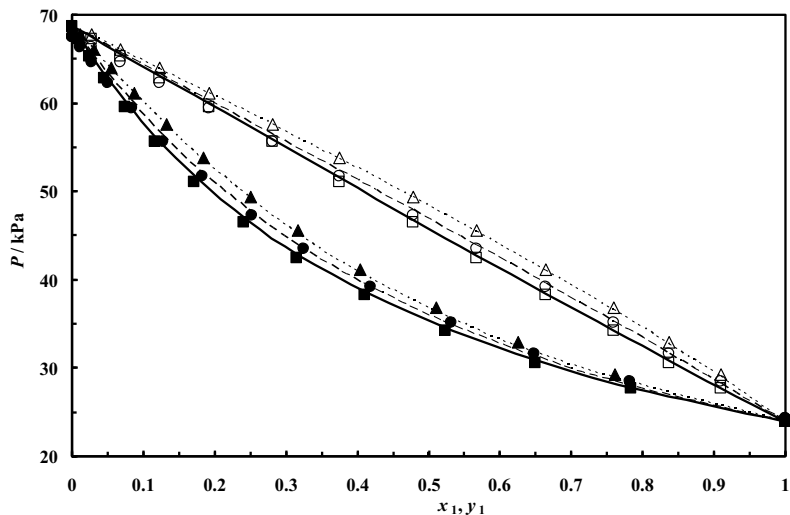


Figure 2a. VLE for the methyl heptanoate (1) + *m*-xylene system at 125 °C presented as a pressure-composition diagram: x_1 measured (\square), y_1 measured (\blacksquare), Wilson (—), original UNIFAC (---), UNIFAC-Dortmund (-.-), x_1 SRK (\circ), y_1 SRK (\bullet), x_1 PSRK (Δ), y_1 PSRK (\blacktriangle) [I].

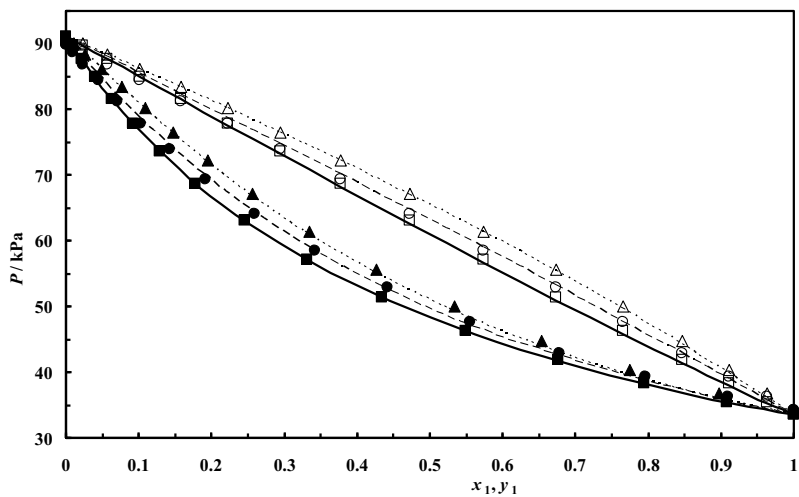


Figure 2b. VLE for the methyl heptanoate (1) + *m*-xylene system at 135 °C presented as a pressure-composition diagram: x_1 measured (\square), y_1 measured (\blacksquare), Wilson (—), original UNIFAC (---), UNIFAC-Dortmund (-.-), x_1 SRK (\circ), y_1 SRK (\bullet), x_1 PSRK (Δ), y_1 PSRK (\blacktriangle) [I].

PSRK gave results close to those of original UNIFAC while SRK results were close to those of UNIFAC-Dortmund. All VLE measurements passed point consistency tests [39], as the absolute average deviations between the measured and the calculated vapour phase mole fractions were smaller than 0.01 [I, Table 6]. All the models gave a good correlation with the

experimentally studied system. Although the mole fractions measured showed negative deviation from Raoult's law and all the thermodynamic models predicted positive deviation from Raoult's law, the ideal solution model was not appropriate. The large number of polar components involved in bio-oil makes the system non-ideal. Thus, PSRK was chosen for simulation of the HDO of methyl heptanoate as it does not require determination of binary parameters and the method is fully predictive. In addition, the extensive UNIFAC table needed for activity coefficient calculations, could be used.

3.2 Hydrogen and *m*-xylene

Good hydrogen solubility is essential for liquid phase reactions to occur. Estimations for hydrogen solubility in *m*-xylene were performed with the PSRK model using the FLOWBAT simulation program [40] at 229 °C and 269 °C [I]. These temperatures were chosen as test temperatures because the simulated results were compared with the experimental values of Simnick et al. [41], who had studied the system at the above mentioned temperatures. Simulation results were found to be in a good accordance with the experimental values [I, Figure 4].

Hydrogenation of *m*-xylene over sulphided NiMo catalyst has been described as consisting of the following consecutive reactions: *m*-xylene → dimethylcyclohexanes → trimethylcyclopentanes [42] of which small amounts of dimethylcyclohexanes were detected during the HDO of methyl heptanoate. Initial rates of *m*-xylene hydrogenation and methyl heptanoate decomposition were compared in order to estimate the consumption of hydrogen in unwanted reactions with *m*-xylene. A second order polynomial equation presenting the concentration of primary products versus time was differentiated and extrapolated to zero time. The reaction rates were as follows: *m*-xylene, $3.7 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ and methyl heptanoate, $2.2 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. The values of the initial rates were of different orders of magnitude and therefore it can be assumed that *m*-xylene hydrogenation was negligible under the studied conditions.

Good solubility of hydrogen and the use of hydrogen for the desired reactions, i.e., deoxygenation reactions, is an obvious requirement for obtaining high HDO rates. The predictive PSRK model was proven to be appropriate for simulating solubility data of non-ideal, polar systems and thus, the need for hydrogen could be estimated with high precision also for complex HDO systems.

3.3 VLE of HDO mixture

The PSRK model was used to estimate the VLE of the HDO of 5 wt% methyl heptanoate in *m*-xylene over sulphided NiMo at the initial conditions and at the end of the reaction [I]. The basis for the calculations at the end of the reaction was the amounts of heptane (85 mol%) and hexane (15 mol%) formed in the liquid phase [V]. These amounts were measured when no reactant or intermediates were left. Water-gas shift reactions have been ignored.

To perform the estimations, the amount of hydrogen was iterated to get the correct total mixture volume. The VLE of the system under the reactor conditions was calculated by estimating the amount of hydrogen using PSRK, which gives the phase compositions and their amounts. If the correct total reactor volume (50 ml) was not obtained the number of moles of hydrogen was re-estimated. The phase composition at the end of the batch was calculated with the help of initial and final product compositions. The overall reaction equations were used to complete the composition calculations and to observe the hydrogen consumption. A similar iteration method to that described above was used, but here the iterated variable was final pressure. In Table 2 the VLE values for the initial and end point conditions are presented.

Table 2. VLE values for HDO of methyl heptanoate at initial and end point conditions predicted based on the PSRK model.

	Initial conditions			At the end		
	Total reactor content	Vapour phase	Liquid phase	Total reactor content	Vapour phase	Liquid phase
<i>T</i> (K)	523.15	523.15	523.15	523.15	523.15	523.15
<i>P</i> (MPa)	7.5	7.5	7.5	6.78	6.78	6.78
<i>m</i> -xylene (g)	12.9961	0.7683	12.2278	12.9961	0.8581	12.1380
<i>n</i> -decane (g)	0.1420	0.0063	0.1357	0.1420	0.0070	0.1350
methyl heptanoate (g)	0.6911	0.0377	0.6534	not present	not present	not present
hydrogen (g)	0.0923	0.0699	0.0224	0.0566	0.0432	0.0134
water (g)	not present	not present	not present	0.1597	0.1327	0.0270
carbon monoxide (g)	not present	not present	not present	0.0201	0.0147	0.0054
heptane (g)	not present	not present	not present	0.4081	0.0539	0.3542
hexane (g)	not present	not present	not present	0.0620	0.0112	0.0508
methane (g)	not present	not present	not present	0.0768	0.0502	0.0266
<i>V</i> (cm ³)	50.0	25.1	24.9	50.0	25.5	24.5

The estimated values indicated that all the components are present in two phases. At the initial conditions, 6 mol% of the total amount of methyl heptanoate was vapourised. Moreover, at the end, 12 mol% of the total amount of heptane and 14 mol% of the total amount of hexane were in the vapour phase. Also, it must be noticed that due to the high temperature and pressure and the dissolution of hydrogen, densities of the compounds differ from ambient conditions. Thus, liquid volume increased up to 25 ml. Viljava and Krause [28] studied the HDO of phenol and showed the importance of considering simulation data together with the experimental data to make accurate kinetic models. Here, PSRK was shown to be a suitable thermodynamic model which allows estimation of data beyond conditions in which the measurements were made. This is important, for example, when estimating the formation of water, which deactivates the catalyst [43, 44], under non-expected reaction conditions.

The aim of Papers II to V was to explore reaction products and pathways for two different types of model components, methyl heptanoate and phenol. Liquid phase data depicts well systems which are studied using the same reactor type and the same reaction pressure and temperature, as is the case in this work where the aim is descriptive discussion. As determining the kinetic parameters and further modeling, was not a priority here, liquid phase analysis in batch reactor experiments was considered adequate for drawing conclusions about reactions of model components.

4. HDO OF METHYL HEPTANOATE

To determine the reaction products and pathways leading from methyl heptanoate to the end products, the following procedure was used. Initially, the main products of methyl heptanoate were identified from the liquid phase samples. After the main products were identified, they were used as reactants, as with methyl heptanoate. In this way, minor products were also detected. The reaction pathways were proposed with the help of product lists and concentration profiles drawn from the results for the liquid phase. Qualitative analysis of liquid reaction products improved over the course of the study. In the beginning only a flame ionisation detector was used, but later a mass sensitive detector was applied. Thus, the products reported in Papers II and III are not identical. Naturally, the main oxygen-containing product of the HDO, i.e. water, was formed but it is excluded from the results due to its problematic qualitative and quantitative analysis in hydrocarbon mixtures. The vapour phase was mainly probed qualitatively. In addition to above mentioned studies, the effect of sulphur addition on product formation and distribution was explored.

4.1 Methyl heptanoate

In the batch reactor, complete conversion of 5 wt% methyl heptanoate in *m*-xylene under H₂ atmosphere was reached in 2.5 h [II] with sulphided NiMo catalyst. However, it took 3 h for all of the formed intermediates to be consumed, as well. For 3 wt% methyl heptanoate in *n*-dodecane complete conversion was reached in 80 min [V] with the sulphided NiMo and nearly all the intermediates were consumed, too. In the flow reactor, total conversion of 3 wt% methyl heptanoate in *m*-xylene at steady state was about 78% for sulphided NiMo and 46% for sulphided CoMo catalyst.

The reactivity of the support, sulphided alumina, was tested in the batch reactor with methyl heptanoate using *n*-dodecane as a solvent in H₂ atmosphere [V]. Only heptanoic acid and methanol were detected at low concentrations. The same two products were detected in the flow reactor tests over the sulphided alumina [45].

Reaction products of the HDO of methyl heptanoate over the sulphided NiMo under H₂ and N₂ and over the reduced NiMo under H₂ are listed in Table 3 [III]. Gaseous products detected were H₂S, CO, CO₂ and CH₄. In the

flow reactor under H₂ using *m*-xylene as a solvent, NiMo catalyst was selective for saturated hydrocarbons (heptane) with a selectivity of 43%, and CoMo catalyst for unsaturated hydrocarbons (heptenes) with a selectivity of 35% [II].

Table 3. Reaction products of HDO of methyl heptanoate over reduced and sulphided NiMo/ γ -Al₂O₃ under H₂ and N₂ [III].

	Oxygen-containing products	Sulphur-containing products	Hydrocarbon products
Reduced NiMo under H ₂	1-heptanoic acid, 1-heptanal, 1-heptanol, methanol, dimethyl ether, heptyl heptanoate	not detected	<i>n</i> -hexane, <i>n</i> -heptane
Sulphided NiMo under N ₂	1-heptanoic acid, dimethyl ether	not detected	hexenes ^a
Sulphided NiMo under H ₂	1-heptanoic acid, 1-heptanal, 1-heptanol, methanol, dimethyl ether, heptyl heptanoate, 2-heptanone, 2-heptanol	1-methanethiol, 1-hexanethiol, 1-heptanethiol	hexenes ^a , heptenes ^b , <i>n</i> -hexane, <i>n</i> -heptane

^a isomers of hexenes: 1-hexene, *cis/trans*-2-hexene and, *cis/trans*-3-hexene

^b isomers of heptenes: 1-heptene, *cis/trans*-2-heptene and, *cis/trans*-3-heptene

Batch reactor tests with NiMo catalyst and methyl heptanoate as a reactant showed that hydrocarbons (hexenes, hexane, heptenes and heptane), methanol, heptanol, heptanoic acid, heptanal and heptyl heptanoate dominated. Other products were formed in trace amounts (max. 2 mol%). On the basis of the concentration profiles of the products it was concluded that hexane and heptane were the hydrocarbon end products while hexenes, heptenes, methanol, heptanol, heptanoic acid, heptanal and heptyl heptanoate were intermediates. Among the intermediates, heptanoic acid and heptanol were classified as primary products due to their high amounts at the beginning of the reaction.

4.2 Heptanoic acid and heptanol

Reaction products of the HDO of heptanoic acid and the HDO of heptanol in *n*-dodecane over reduced and sulphided NiMo are listed in Tables 4 and 5 [III]. Examination of the amounts of hydrocarbon products (Table 6) revealed clear differences between differently pretreated catalysts and reactive gases. Moreover, the H₂ atmosphere becomes important when acids, widely present in bio-oils, are treated as their deoxygenation reactions do not proceed under N₂.

Table 4. Reaction products of HDO of heptanoic acid over reduced and sulphided NiMo/ γ -Al₂O₃ under H₂ and N₂ [III].

	Oxygen-containing products	Sulphur-containing products	Hydrocarbon products
Reduced NiMo under H ₂	1-heptanal, 1-heptanol, heptyl heptanoate	not detected	<i>n</i> -hexane, <i>n</i> -heptane
Sulphided NiMo under N ₂	not detected	not detected	hexenes ^a , heptenes ^b , <i>n</i> -hexane, <i>n</i> -heptane
Sulphided NiMo under H ₂	1-heptanal, 1-heptanol, heptyl heptanoate	1-hexanethiol, 1-heptanethiol	hexenes ^a , heptenes ^b , <i>n</i> -hexane, <i>n</i> -heptane

^a isomers of hexenes: 1-hexene, *cis/trans*-2-hexene and, *cis/trans*-3-hexene

^b isomers of heptenes: 1-heptene, *cis/trans*-2-heptene and, *cis/trans*-3-heptene

Table 5. Reaction products of HDO of heptanol over reduced and sulphided NiMo/ γ -Al₂O₃ under H₂ and N₂ [III].

	Oxygen-containing products	Sulphur-containing products	Hydrocarbon products
Reduced NiMo under H ₂	diheptyl ether	not detected	heptenes ^a , <i>n</i> -heptane
Sulphided NiMo under N ₂	diheptyl ether	1-heptanethiol	heptenes ^a , <i>n</i> -heptane
Sulphided NiMo under H ₂	diheptyl ether	1-heptanethiol	heptenes ^a , <i>n</i> -heptane

^a isomers of heptenes: 1-heptene, *cis/trans*-2-heptene and, *cis/trans*-3-heptene

Table 6. Reactivity of heptanoic acid and heptanol over reduced and sulphided NiMo/ γ -Al₂O₃ catalyst under H₂ and N₂ [III].

	1-heptanoic acid		1-heptanol	
	Conversion (%)	Hydrocarbon products (mol%)	Conversion (%)	Hydrocarbon products (mol%)
Reduced NiMo under H ₂ ^a	56	3	94	74
Sulphided NiMo under N ₂ ^a	42	14	100	92
Sulphided NiMo under H ₂ ^b	100	97	100	98

^a at 90 min (heptanoic acid) or 60 min (heptanol)

^b at 30 min (both reactants)

4.3 Reaction scheme

On the basis of the detected liquid and gaseous products, a scheme for the HDO of methyl heptanoate was suggested [III]. The scheme is presented in Figure 3.

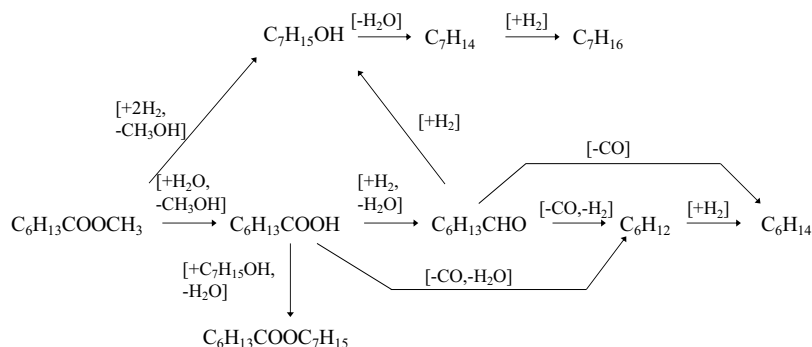


Figure 3. Proposed reaction scheme for HDO of methyl heptanoate over sulphided NiMo/ γ - Al_2O_3 [III].

4.3.1 Methyl heptanoate hydrolysis

The formation of heptanoic acid was explained by acid hydrolysis of methyl heptanoate. However, the question of the origin of the water needed for the first hydrolysis reaction was raised [II, III]. In Paper II it was proposed that the alumina support with its Lewis acid sites, could initiate the hydrolysis. After the formation of some heptanoic acid, reduction of heptanoic acid to heptanal would release water for acid hydrolysis. In addition to this explanation, other reasons for the formation of water were still sought in Paper III.

In alkaline hydrolysis, the carbonyl carbon of an ester is attacked by a good nucleophile, most commonly OH^- , without prior protonation of the ester [46]. Alkaline hydrolysis of esters irreversibly produces carboxylate ions and alcohol. When protons are available, the carboxylate ion forms acid. OH^- and SH^- groups are known to be good nucleophiles [46] and thus, SH^- groups could act similarly to OH^- groups, forming carboxylate ions. In Figure 4 the proposed reaction mechanism for the attack of an SH^- group on methyl heptanoate is presented [III].

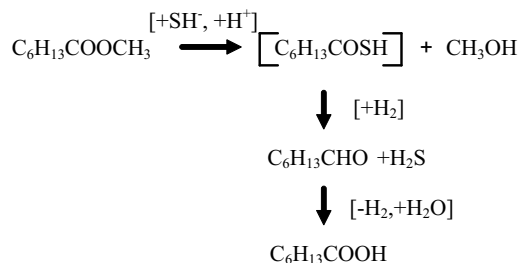


Figure 4. Proposed reaction mechanism for alkaline hydrolysis of methyl heptanoate [III].

The strong attraction of SH^- nucleophiles to the carbonyl carbon of methyl heptanoate could indicate the formation of thioheptanoic acid although it was not detected in the experiments. Through thioheptanoic acid and heptanal, heptanoic acid could have been formed. Formation of heptanoic acid from heptanal was shown to be possible with thermodynamic calculations at 250 °C with 10% equilibrium conversion. In addition, with heptanal as a reactant over sulphided NiMo under N_2 atmosphere, heptanoic acid was detected in the reaction mixture. Thus, decomposition of methyl heptanoate may proceed by acid and alkaline hydrolysis of which acid hydrolysis dominates.

On the basis of detection of methanol as an intermediate, it could also be concluded, that in order to form heptanoic acid, hydrolysis of methyl heptanoate occurs [II, III]. However, HDO studies carried out recently with triglyceride over the sulphided NiMo catalysts have not revealed the presence of glycerol, which is the alcohol in triglyceride HDO reactions that corresponds to methanol [47, 48]. Instead, in these reports it has been suggested that hydrogenolysis of triglyceride, yielding fatty acid and propane, would occur, which would mean heptanoic acid and methane in the case of methyl heptanoate. This would support a high rate of formation of acid without water molecules. If this were the pathway, another explanation for the production of methanol would be needed. In addition to hydrolysis, as described above, reduction of methyl heptanoate to heptanol produces methanol (Figure 3). However, the corresponding alcohol to methanol in the case of triglyceride is, again, glycerol. The formation of methanol as a reaction between CO or CO_2 and H_2 also cannot be ruled out. The ester molecule decomposes most preferably at the bond between the carbonyl carbon and adjacent oxygen, which allows hydrolysis to occur. In addition, it should be noted that the decomposition temperature of glycerol is 290 °C and a part of the studies on the HDO of triglyceride are performed at over 300 °C. Experiments in this study cannot completely resolve the

mechanism for the fast formation of heptanoic acid at the beginning of the HDO of methyl heptanoate.

4.3.2 Pathways for production of heptane

Two reaction pathways for formation of heptanol are presented [II, III]. Heptanoic acid can be converted via heptanal to heptanol. In addition, methyl heptanoate could be reduced to heptanol, although this reaction was not unambiguously proven. The amount of heptanol increased slower than the amount of heptanoic acid. Neither heptenes nor heptane were produced in the beginning, and thus heptanol does not react quickly to produce further components. These two findings together give support to a reaction path going through heptanal. In addition, as described in Paper V, methyl heptanoate reduction to heptanol and hydrolysis to heptanoic acid take place on different active sites and no competition would occur between these reaction types.

HDO of heptanol revealed the formation of heptenes and heptane [II, III] and thus, dehydration and hydrogenation were suggested to be consecutive reactions. The dehydration of alcohols is known to take place by the E_1 and E_2 elimination mechanisms [II, Scheme 2]. In the E_1 mechanism, the protonated alcohol should form an energetically unstable primary carbenium ion. Zhao and Prins [49] have reported that the acidity of the sulphided catalyst is not sufficient for this. Thus, the reaction of heptanol is preferably explained by the E_2 elimination mechanism.

The reaction of heptanol was studied under N_2 over sulphided catalyst [III] to determine whether heptane is formed by direct hydrogenolysis from heptanol or through a heptene intermediate. Trace amounts of heptane were formed when heptanol was tested. As the catalyst surface contains groups such as $-SH$, $-OH$ and $-H^+$, it was proposed that the hydrogenation could occur with the help of these surface species. From these findings, it appears that the main pathway to heptane is through a heptene intermediate under the conditions studied.

4.3.3 Pathways for production of hexane

Heptanoic acid was found to produce unsaturated and saturated hydrocarbons [II, III]. The experiments revealed the formation of hexenes and hexane in addition to the heptenes and heptane detected previously in heptanol experiments. Moreover, the HDO of heptanal proved the presence of these four hydrocarbon products. The pathways from heptanoic acid to hexenes and hexane could not be easily proved because of the many parallel and consecutive reactions (Figure 3). Snåre et al. [50] have reported that

stearic acid can be converted to saturated and unsaturated hydrocarbons by both decarbonylation (formation of CO) and decarboxylation (formation of CO₂). Using triglycerides as a reactant, Boda et al. [47] reported a fatty acid decarbonylation reaction and, conversely, Kubička et al. [48] deduced that decarboxylation occurs. Uncertainty about the direct cleavage of CO₂ from heptanoic acid presented in Paper II for methyl heptanoate HDO remains. The direct production of hexenes by decarbonylation of acid was supported in Paper III since both methyl heptanoate and heptanoic acid produced hexenes under N₂ while heptanal was not detected. A very low concentration of hexane was detected when heptanoic acid was used as a reactant under N₂ over sulphided NiMo. As in the case of heptanol, the formation of hexane was suggested to occur with the help of surface species. Thus, it was assumed that the decarboxylation of acid did not proceed at a discernible rate and the decarboxylation arrow presented in Paper II, Scheme 1 was omitted from further consideration.

4.4 Sulphur addition

4.4.1 Effect of sulphur on reactivity and product distribution

The effect of a sulphiding agent on the HDO of methyl heptanoate has been studied by Şenol et al. [51] over sulphided NiMo and CoMo catalysts in vapour phase in a flow reactor. The addition of sulphiding agent increased the conversion of methyl heptanoate over both catalysts. In the absence of H₂S the main end products were C₇ hydrocarbons. With H₂S the main product was shifted from C₇ to C₆. However, the effect of H₂S on hydrogenation reactions was not identical for both catalysts. H₂S inhibited hydrogenation over the sulphided NiMo and had no effect over the sulphided CoMo.

The changes observed in the study of Şenol et al. [51] and the demand for low sulphur content transportation fuels [12] gave rise to a need to explore the effects of sulphur addition. Studies were performed in the batch reactor mainly using heptanol as a model component as its reactions are simpler than those of methyl heptanoate. The experiments with 2 wt% heptanol over the sulphided NiMo clearly revealed the production of sulphur-containing product, heptanethiol [II, III]. The maximum molar concentrations of heptanethiol in the liquid phase ranged from 0.1 mol% with no H₂S addition to 0.4 mol% with 400 ppm of H₂S [III]. In the HDO of methyl heptanoate with a sulphur additive, in addition to heptanethiol, methanethiol, hexanethiol, dimethyl sulphide, diheptyl sulphide and H₂S were also detected [V].

The presence of sulphiding agent in the HDO of heptanol increased the formation of heptanethiol and heptenes and decreased the formation of heptane. Even without sulphiding agent, heptanethiol was detected. Whether heptanethiols are formed using 1-heptene as a reactant was also tested, and heptanethiols were identified in the reaction mixture, which is in accordance with the study of Mashkina [52], in which the reaction of alkene and H₂S is presented. It can be concluded that two types of reactants, alcohol and alkene, may produce alkanethiols with and without H₂S addition.

As stated in Section 4.3.2, the E₂ of mechanism was suggested for formation of heptenes from heptanol because the E₁ mechanism would require unstable carbenium ion. Thiols, on the other hand, can be produced by S_N1 or S_N2 nucleophilic substitution mechanisms, as presented in Paper II, Scheme 2. The end products differ as the former mechanism leads to 2-heptanethiol and the latter to 1-heptanethiol. As the formation of 2-heptanethiol was not observed and the S_N1 mechanism requires carbenium ion, it was concluded that the S_N1 mechanism does not occur.

In study of HDN of alkylamines with H₂S by Zhao and Prins [53] it was postulated that all alkenes and alkanes are formed indirectly by elimination and hydrolysis of alkanethiol intermediates. On the other hand, in the study of HDO of *n*-propanol and *n*-butanol with H₂S by Mashkina and Khairulina [54], it was concluded that alcohols react directly to give either alkanethiols or alkenes. HDO of heptanol over the reduced catalyst resulted in the formation of alkenes, although alkanethiol was not detected. This indicated that alkanethiols are not obligatory intermediates between alcohol and alkenes, in accordance with the conclusion of Mashkina and Khairulina [54].

4.4.2 Sulphur content of NiMo catalyst

The sulphur content of NiMo catalyst was measured for pretreated and for used catalysts. After sulphidation and nitrogen flushing in the batch reactor, the sulphur content was 5.7 ± 0.3 wt%. After a 60 min HDO experiment in the batch reactor with methyl heptanoate, the sulphur content was practically unchanged, being 5.6 ± 0.3 wt% [III]. Although the sulphur content remained almost unchanged, the detachment of sulphur species from the catalyst surface was studied to understand the origin of sulphur-containing intermediates. The H₂S concentration was measured from the vapour phase at the outlet of the batch reactor [III]. In this specific study the batch reactor was used like a flow reactor. After sulphidation and nitrogen flushing, no H₂S was detected in the vapour phase. After changing

the gas feed to H₂, the H₂S concentration increased noticeably, reaching concentration of 230 ppm. The concentration dropped to approximately 30 ppm when flushing was continued. In addition, after 180 min of H₂ flushing the sulphur content of the catalyst was 4.8 ± 0.3 wt%.

It appears that the addition of sulphiding agent during the experiment is essential to maintaining an active, unchanging MoS₂ structure. However, the addition of sulphiding agent initiates the formation of sulphur-containing compounds. In addition, the reaction of H₂ and surface sulphur may further initiate and enhance the formation of sulphur-containing compounds. Sulphided catalysts are used in industrial applications of HDS [55, 56] for the production of low sulphur content fuel and the same unit could be used for HDO. Because of tightening fuel quality requirements, the formation of sulphur-containing compounds in the course of hydrotreating reactions should be avoided.

5. HDO OF PHENOL

The aims of the studies of HDO of phenol were to explore the reaction products and to propose reaction pathways as well as to determine the effect of sulphur addition on products and their distribution. Initially, the main products of the HDO of phenol were identified and then, using the main products as reactants, minor products were detected. As was described for methyl heptanoate in Chapter 4, reaction pathways were proposed with the help of product lists and concentration profiles drawn from liquid phase results. The studies of methyl heptanoate with sulphur additive indicated the formation of sulphur-containing compounds. Thus, it was essential to perform the HDO experiments with phenol and a sulphur additive, too.

5.1 Phenol

In the batch reactor the complete conversion of 3 wt% phenol over sulphided NiMo was achieved in 150 min with *n*-dodecane as a solvent [V]. Conversion for phenol in *m*-xylene was not measured in Paper IV as the *m*-xylene experiments were mainly for qualitative detection of products. In the flow reactor in the vapour phase the conversion for sulphided NiMo was 19% and for sulphided CoMo 28% with *m*-xylene [IV].

The experimental method for determining the products of the HDO of phenol was similar to that described for methyl heptanoate in Chapter 4. Reaction products are presented in Table 7. Improved qualitative analysis with GC-MS in Paper V revealed the presence of cyclohexanol, cyclohexyl cyclohexane and 2- and 4- cyclohexyl phenol. Otherwise the detected products in Papers IV and V are the same.

Table 7. Reaction products of HDO of phenol over sulphided NiMo/ γ -Al₂O₃.

Oxygen-containing products	Sulphur-containing products	Hydrocarbon products
cyclohexanone	cyclohexanethiol	benzene
cyclohexanol		cyclohexene
2- and 4-cyclohexyl phenol		cyclohexane
		cyclohexyl cyclohexane

Concentration profiles of the components showed that cyclohexene, cyclohexanol, cyclohexanone and cyclohexyl phenols do not accumulate in the reaction mixture and thus, they are intermediates. Cyclohexane and cyclohexyl cyclohexane were classified as end products. The role of benzene remained unclear on the basis of concentration profiles and this will be discussed in Section 5.2. In vapour phase experiments in the flow reactor the main products of the HDO of phenol were cyclohexane over the NiMo and benzene over the CoMo.

5.2 Benzene, cyclohexanone and cyclohexanol

Although benzene does not contain any oxygen, the question was raised whether benzene would be hydrogenated in the system. The reactions of benzene were investigated over sulphided NiMo catalyst in the batch reactor in *m*-xylene [IV]. Cyclohexene and cyclohexane were detected in the liquid phase, which clearly indicated hydrogenation. Later, the reactions of benzene were studied in *n*-dodecane [V]. Cyclohexene and cyclohexane were again identified. In Paper IV a dashed arrow was drawn for the reaction between benzene and cyclohexene, but in Paper V it was presented as an equal reaction to the other ones. It appears that benzene is an intermediate.

HDO of cyclohexanone and cyclohexanol produced cyclohexene and cyclohexane. As no new products were detected at high reactant concentrations, it was clear that cyclohexanone and cyclohexanol are intermediates on the pathway towards deoxygenation.

5.3 Reaction scheme

Reaction tests with phenol and intermediates justified the suggestion of a reaction scheme for phenol [V]. This is presented in Figure 5.

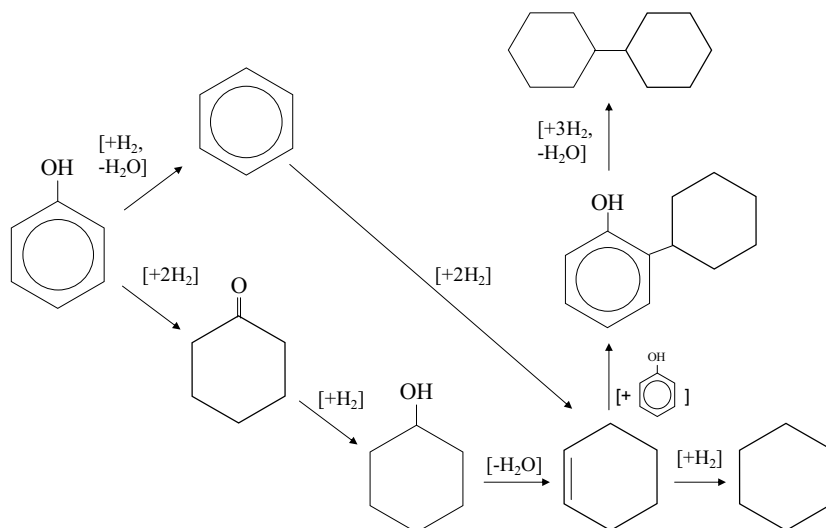


Figure 5. Proposed reaction scheme for HDO of phenol over sulphided NiMo/ γ -Al₂O₃ [V].

Benzene and cyclohexanone are formed by two parallel reactions of phenol. Both compounds are formed by the reductive reaction of phenol. In the formation of benzene the OH group is removed and the aromatic character of the compound is not altered. Cyclohexanone is, instead, formed by hydrogenation of the aromatic ring. Cyclohexanone contains a C=O π -bond and another hydrogenation step before rupture of the C-O σ -bond is to be expected. Hydrogenation of cyclohexanone produced cyclohexanol. Cyclohexene was formed by two parallel reactions, i.e., hydrogenation of benzene or dehydration of cyclohexanol. Finally, cyclohexene was hydrogenated to cyclohexane. In Paper V, Scheme 1, the arrow from benzene was accidentally drawn directly to cyclohexane although cyclohexene should have been shown as an intermediate, as presented in Paper IV, Scheme 1. This is corrected in Figure 5.

A reaction pathway leading to cyclohexyl cyclohexane was not evident without further experiments in the batch reactor, as various reaction pathways to produce cyclohexyl cyclohexane have been proposed in the literature, among which are reductive dehydration of alcohol [57], hydrogenation of cyclohexyl benzene [58] and alkylation of phenol with cyclohexanol [59]. In our experiments, cyclohexyl phenol as an intermediate and cyclohexyl cyclohexane as a final product were detected with phenol and cyclohexene as reactants [V], in agreement with the reaction pathways proposed by Yadav and Kumar [60]. After the formation of cyclohexyl phenol, hydrogenation and dehydration are needed to produce cyclohexyl cyclohexane.

5.4 Sulphur addition

The sulphur-containing product detected in the HDO of phenol was cyclohexanethiol. In the experiments of Paper IV cyclohexanethiol was only detected when sulphiding agent was added to the reactor. Later, with the improved analysis method, its formation was also identified without sulphiding agent [Paper V].

HDO of phenol was studied in the presence of sulphiding agent in the flow reactor over sulphided NiMo and CoMo [IV]. Contrary to what was observed with methyl heptanoate [51], the HDO conversion of phenol decreased as a function of H₂S concentration over both catalysts. In addition, the yields of aromatic hydrocarbons (benzene) and monocyclics (cyclohexene and cyclohexane) decreased. In Paper IV, cyclohexyl cyclohexane was not yet detected. Comparison of molar ratios of aromatic hydrocarbons to monocyclics showed that with the CoMo catalyst the molar ratio dropped from 9.0 in the absence of H₂S to 1.0 in the presence of 24 000 ppm H₂S. The route to benzene was suppressed more than the route to monocyclics. With NiMo catalyst, the decrease was minor, indicating similar inhibition for the pathways from phenol to benzene and from phenol to monocyclics.

Changes in hydrogenation activity of NiMo and CoMo catalysts with and without H₂S addition were compared, too [IV, Figure 3]. The molar ratio of cyclohexane to cyclohexene decreased clearly from 9 (without H₂S) to below 2 (with 12 000 ppm H₂S) over the NiMo but over the CoMo the ratio was not notably affected.

6. SIMULTANEOUS HDO OF METHYL HEPTANOATE AND PHENOL

6.1 Methyl heptanoate versus phenol

Comparison of conversion values, which were 78% for methyl heptanoate and 19% for phenol, in the flow reactor studies over sulphided NiMo at 250 °C and 1.5 MPa revealed that the conversion levels under the same conditions clearly differed [IV]. Moreover, the addition of H₂S had opposite effects on the reactivity of methyl heptanoate and phenol, as the conversion of methyl heptanoate increased and that of phenol decreased. The effect of H₂S on hydrogenation activity was similar with both reactants. H₂S suppressed the hydrogenation over NiMo and did not have an effect over CoMo.

6.2 Simultaneous reaction

Methyl heptanoate and phenol showed different trends in conversion levels when H₂S was added to the gas feed in the flow reactor as described in Section 6.1. As the bio-oil is a mixture of several types of components, it was necessary to study the reactivity of two types of reactants simultaneously. In addition, no literature reports of the simultaneous HDO of aliphatic and aromatic components were found. Thus, the HDO of methyl heptanoate and phenol in a mixture was explored without sulphur additive and with either H₂S or DMDS in the batch reactor at 250 °C and 7.5 MPa over sulphided NiMo [V].

Practically complete conversion of the mixture of methyl heptanoate and phenol was achieved in 240 min. The conversion profiles for the components alone and in the mixture are shown in Figure 6 [V]. A decrease in conversions due to the presence of co-reactant was more pronounced for phenol than for methyl heptanoate. Similarly, when conversion of reactants in the mixture was compared with and without sulphur additive, a decrease in phenol conversion as a function of time was apparent [V, Figure 2] while the conversion of methyl heptanoate increased slightly.

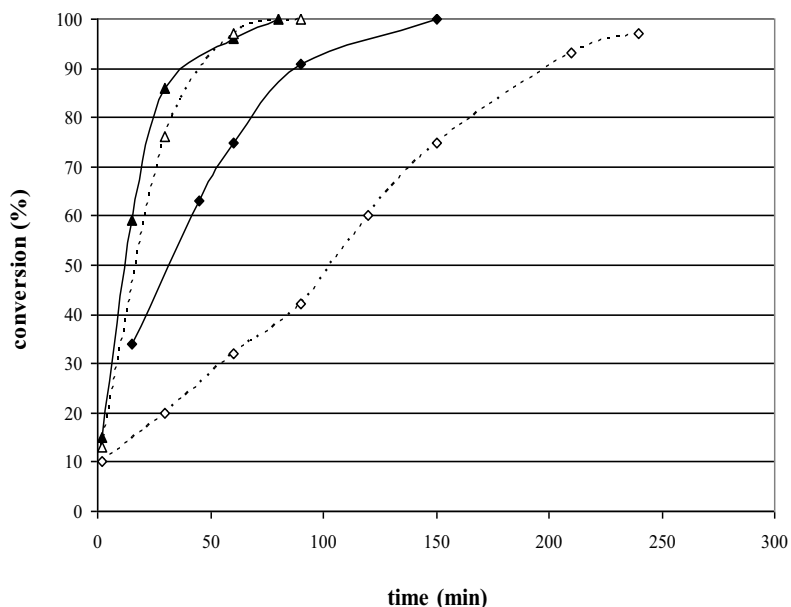


Figure 6. Conversion of phenol (♦), methyl heptanoate (▲), phenol in mixture (◇) and methyl heptanoate in mixture (Δ) [V].

In the experiments with the simultaneous HDO of methyl heptanoate and phenol a few new products were detected in addition to the products detected already in single reactant tests. Methyl cyclohexane, methoxy benzene, 2- and 3-methyl phenol, phenyl heptanoate, 4-heptyl phenol and 1- and 2-methyl thioheptane were identified and assumed to be the products because of reaction of two reactants. Their concentrations were low (<2 mol%), and on the basis of their concentration profiles all but methyl cyclohexane were deduced to be intermediates. Concentration profiles for the end products of the simultaneous HDO of phenol and methyl heptanoate are presented in Figures 7a and 7b [V]. Methyl cyclohexane was excluded as its molar concentration was only 2 mol% at complete deoxygenation.

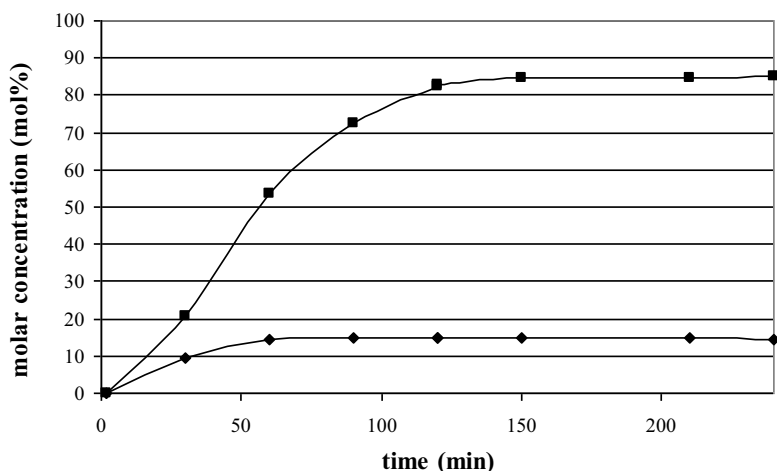


Figure 7a. Concentration profiles of heptane (■) and hexane (◆) in HDO of phenol and methyl heptanoate mixture [V].

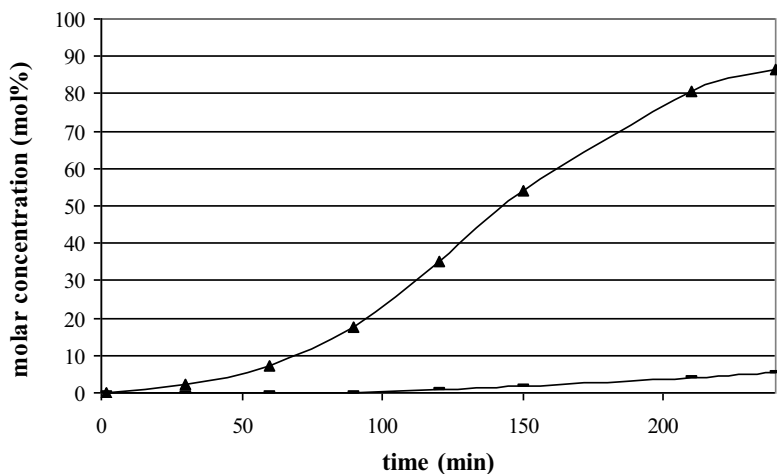


Figure 7b. Concentration profiles of cyclohexane (▲) and cyclohexyl cyclohexane (—) in HDO of phenol and methyl heptanoate mixture [V].

Reactivity and the effect of sulphur addition were shown to differ between methyl heptanoate and phenol. Variations were observed when the reactants were tested alone and in a mixture. Thus, it is evident that performance of the HDO reactions is dependent on the type of reactants, i.e., the type of bio-oil. Moreover, NiMo and CoMo catalysts were also demonstrated to have different effects on the HDO of methyl heptanoate and phenol. Reasons for the different behaviours were sought, and they are

presented in the next chapter from the point of view of the catalyst structure.

7. CATALYST SURFACE SITES

In this work, the widely accepted model for active sites of sulphided catalysts is used [14, 61-63]. The catalyst surface consists of two types of active centers: coordinatively unsaturated sites (CUS), i.e., sulphur anion vacancies, and surface groups such as S^{2-} , SH^- , OH^- and H^+ . It is proposed that sulphur vacancies are located adjacent to Ni/Co or Mo atoms and they may have Lewis acid character. Surface groups are proposed to be connected to Mo atoms and they may have Brønsted acid character [14, 53]. The importance of surface groups may be related making hydrogen available to the adsorbed compound [64]. In this work these surface group sites are called sulphur-saturated sites. Dissociative adsorption of H_2S may change CUS to sulphur-saturated sites as protonic SH^- groups are formed [14, 62]. The discussion on active sites is focused on the combined action of promoter atoms (Ni or Co) and Mo although the model itself does not indicate what the exact location of active site is.

Hydrotreating reactions, i.e., HDO, HDN and HDS, are often categorised more specifically into hydrogenolysis and hydrogenation reactions. The cleavage of a carbon-hetero atom bond under hydrogen is called hydrogenolysis. Also, the term direct hydrogenolysis is used to indicate that the cleavage and addition of hydrogen occur simultaneously. Saturation of the carbon-carbon double or triple bond with hydrogen is called hydrogenation. On the basis of this classification it is suggested that hydrogenolysis sites are Mo atoms with neighbouring surface groups and hydrogenation sites are sulphur anion vacancies [61, 62].

In Paper IV it was reported that the catalytic site for cleavage of the oxygen from aliphatic oxygenates are sulphur anion vacancies and further that in the case of phenol the formation of hydrocarbons by direct hydrogenolysis is related to the availability of the vacancy sites and hydrogen. It was concluded that the dissimilar trends in conversion of methyl heptanoate and phenol in the presence of sulphur additive were due to the different reaction mechanisms being influenced by the molecular and electronic structures of the respective aliphatic and aromatic oxygenates. In Paper V, the reactions of methyl heptanoate and phenol were examined stepwise taking into account the formation of intermediates and not only the reactivity of the original reactant. Looked at in this way, it can be seen that there is similar behaviour among the same kinds of reaction types and thus, the aliphatic or aromatic character of the compound was not the only

determining factor, as proposed in Paper IV. To explore the reactions in even more detail and to suggest active sites for the catalyst for each reaction type, a more detailed classification was created [V]. The proposed groups are:

- 1) reductive reactions, where
 - a. H_2 is added, i.e., hydrogenation (saturation of a double bond)
 - b. H_2 is added and simultaneously water or alcohol is released (hydrogen is added adjacent to a carbonyl carbon)
- 2) acid-catalysed reactions refer to esterification, hydrolysis, dehydration and alkylation (initiated with electrophilic proton transfer to a nucleophilic oxygen of the reacting molecule)
- 3) decarbonylation reactions (removal of carbon monoxide)

Schemes for the HDO of methyl heptanoate and phenol were presented previously in this work. In Figures 8a and 8b the same schemes are shown but the reactions are divided into reductive, acid-catalysed and decarbonylation reactions.

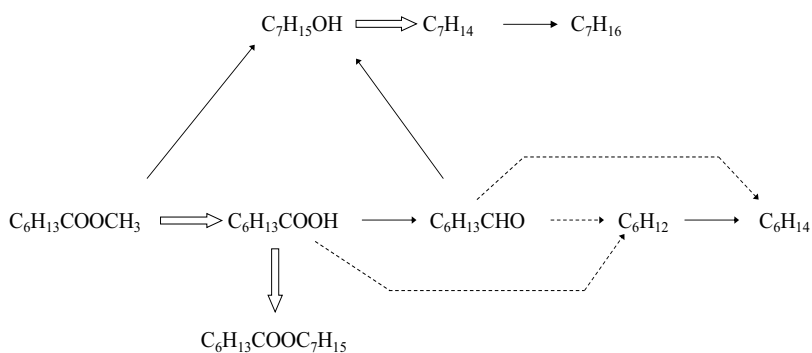


Figure 8a. Reaction pathways of HDO of methyl heptanoate classified as reductive (\longrightarrow), acid-catalysed (\rightleftharpoons) and decarbonylation steps ($-\text{--}\longrightarrow$).

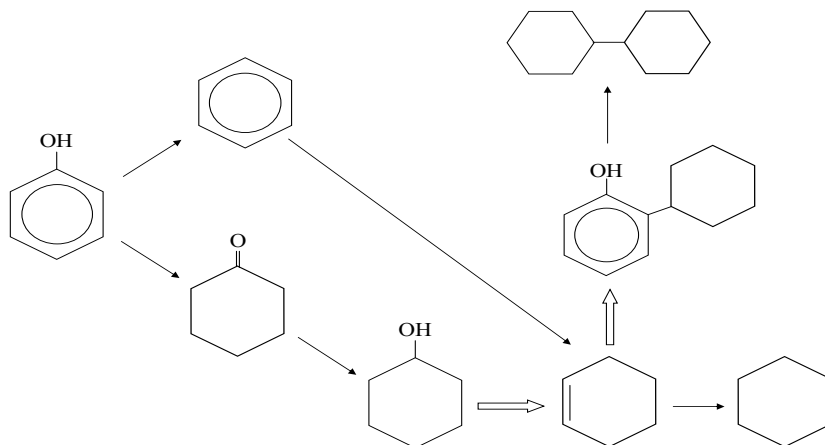


Figure 8b. Reaction pathways of HDO of phenol shown with reductive (\longrightarrow) and acid-catalysed (\rightleftharpoons) steps.

It was concluded that Brønsted acid sites, in other words sulphur-saturated sites, take part in acid-catalysed reactions, as the addition of sulphiding agent had an enhancing effect on these reactions [IV]. From this, it can be concluded that the methyl heptanoate hydrolysis would occur on sulphur-saturated sites. When conversions of methyl heptanoate and phenol with and without sulphiding agent were compared as a function of time [IV, V], it was noticed that the reactivity was affected dissimilarly. Thus, it was presumed that methyl heptanoate hydrolysis and phenol reduction occur on different active sites leading to the suggestion that the active site for phenol reduction is CUS [V].

Hydrogenation reactions of methyl heptanoate and phenol were affected similarly by H_2S in individual HDO reactions in the flow reactor [51, IV]. With both reactants, the addition of H_2S suppressed the hydrogenation reactions over sulphided NiMo while no effect over sulphided CoMo was observed. In batch reactor experiments using sulphided NiMo with phenol and methyl heptanoate alone and with the mixture, the decrease in hydrogenation activity was also observed [V, Figure 6a and 6b] and thus, it is evident that sulphur prevents hydrogenation. The inhibiting effect of H_2S on hydrogenation is in agreement with the results of Dos Santos et al. [65]. However, Dos Santos et al. carried out their tests using sulphided CoMo in a fixed-bed reactor and thus, the inhibiting effect is contrary to the observation [51, IV] that sulphur does not affect hydrogenation over CoMo. The different effect may have contributed, for example, to the lengths of time used for the experiments. The results of Dos Santos et al. [65] showed that stabilisation of the catalyst took around 100 h, whereas our tests needed only 2 h for stabilisation. On the basis of the presented data, it

cannot be explained why the stabilisation times differ markedly. As the reactivity of phenol and hydrogenation reactions were both suppressed in the presence of H₂S over NiMo, it was concluded that phenol reactions and hydrogenation need the same site, i.e., CUS, for the reactions to occur. Moreover, it was concluded that all the reduction reactions occur on CUS and compete with the adsorption of sulphur. The availability of sulphur vacancies determined the hydrogenation rate. On one hand, this competition might contribute to the diminished amount of CUS, as the adsorption of sulphur is known to change CUS to sulphur-saturated sites. The change to sulphur-saturated sites is in agreement with the previous result indicating enhanced conversion of methyl heptanoate (acid or alkaline hydrolysis) with H₂S. Competitive adsorption of aldehyde and sulphur species is postulated to suppress reduction of aldehyde [66]. This supports well the conclusions presented above.

Sulphur-saturated sites may act as sources of protons for the initiation of acid-catalysed reactions and as a source for SH⁻ or OH⁻ groups as nucleophilic species [63]. CUS, in contrast, provide vacancies for adsorption. Heptanoic acid may react by esterification (acid-catalysed reaction), reduction or decarbonylation. Thus, it is not possible to address the active site only on the basis of the functional group of the reacting component. The site for decarbonylation may be debated although it was proposed [V] that the reactions occur on sulphur-saturated sites. As the fraction of C₆ hydrocarbons increased in the presence of sulphur, acid/aldehyde reduction reactions towards C₇ hydrocarbons were suppressed. If decarbonylation had occurred on the same site as reduction, i.e., CUS, the formation of C₆ hydrocarbons would also have been suppressed or even blocked with sulphur.

Two options for reaction of cyclohexanol to cyclohexene were reported [IV]: direct hydrogenolysis and dehydration. A set of experiments was carried out with cyclohexanol in the absence and presence of sulphiding agent. Compared to the tests without sulphur, the conversion of cyclohexanol decreased 7 percentage units after a 60 min experiment with sulphur additive. It was concluded previously [51], that acid-catalysed reactions are enhanced by the addition of H₂S. On the basis of this, the reaction between cyclohexanol and cyclohexene was explained as occurring by direct hydrogenolysis. It must be noted that the experiments with cyclohexanol were performed over sulphided CoMo catalyst and with CS₂ as a sulphiding agent. Şenol et al. [51] have reported that liquid CS₂, which produces H₂S after decomposition and gaseous H₂S had divergent effects on the molar ratios of saturated and unsaturated hydrocarbons with increasing concentration of sulphiding agent. Considering this, the decrease in

conversion could rather be explained by carbon deposition due to CS_2 and therefore, dehydration on sulphur-saturated sites cannot be ruled out.

8. SUMMARY

The increasing level of CO₂ in the atmosphere and diminishing fossil fuel reserves are among the various reasons why production of biomass-based transportation fuels is of great interest. However, biomass-based fuels, for example wood-based bio-oil and vegetable oils, are highly oxygenated. These oxygen-containing mixtures need to be upgraded because high oxygen content leads to undesirable oil properties. Upgrading can be performed by catalytic hydrodeoxygenation (HDO). HDO is designed to produce hydrocarbon fractions that can be blended with fossil fuels or used as such.

Hydrodeoxygenation reactions (HDO) of methyl heptanoate and phenol were investigated at 250 °C and 7.5 MPa over sulphided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃. Methyl heptanoate and phenol were chosen as model components representing molecules with dissimilar functional groups that are present in biomass-based liquids. The aim of the work was to determine the HDO reaction routes and to show the effect of sulphur, when present over the catalyst or in liquid or vapour phases, on the reactions. The reactants were studied individually and as a mixture to demonstrate the interactions of reactants and their intermediates on the route to hydrocarbon end products. In addition, a predictive simulation method was sought to describe non-ideal multi-phase systems with polar components.

Isothermal vapour-liquid equilibrium (VLE) of methyl heptanoate and *m*-xylene was measured to determine the most suitable thermodynamic model to predict vapour phase compositions of HDO mixtures on the basis of the composition of the liquid phase. The preferred thermodynamic model was predictive Soave-Redlich-Kwong (PSRK). Simulation values for the HDO of methyl heptanoate were presented to show the distribution of components into vapour and liquid phases. The exact distribution of components in the two phases would be needed for determination of reaction kinetic parameters and for modeling the system for scale-up purpose.

Reaction schemes for methyl heptanoate and phenol were proposed on the basis of detailed analyses of reaction intermediates and end products. The main end products of methyl heptanoate were hexane and heptane and of phenol cyclohexane and cyclohexyl cyclohexane. The reaction steps were proposed to involve acid-catalysed reactions (hydrolysis, dehydration, esterification), reductive reactions and decarbonylation.

Conversions of the reactants individually and in a mixture in the presence and absence of sulphur were measured and the effects of sulphur on each reaction step were carefully examined under identical conditions. Phenol was more sensitive to the presence of methyl heptanoate than vice versa. Hydrocarbon product fractions were different for reactants in the mixture and the reactants tested separately, though in both cases heptane was the predominant product for methyl heptanoate and cyclohexane for phenol. The presence of sulphur suppressed the conversion of phenol but conversion of methyl heptanoate remained practically unchanged. It was also noticed that sulphur additive changed the product distribution of separate reactants more than that of the mixture.

Sulphur-containing intermediates were detected with and without sulphur addition using both reactants, and thus the participation of sulphur species in various steps was further explored. As sulphur-containing compounds are formed, the sulphidation level of the catalyst changes and moreover, hydrogen, as a reactant gas, reacts with surface sulphur and forms H_2S . The detected products, excluding sulphur-containing compounds, were found to be similar with non-sulphided and sulphided catalysts but the reactivity was notably enhanced over the sulphided catalyst. It was concluded that the OH^- and SH^- groups most likely act similarly but the action of OH^- groups is weaker than that of SH^- groups.

The studies of the HDO of methyl heptanoate and phenol indicated that reduction reactions occur on coordinatively unsaturated sites (CUS). Acid-catalysed reactions and decarbonylation reactions, in turn, require sulphur-saturated sites. Sulphur adsorption is suggested to take place on CUS and thus, competition between reduction reactions and sulphur occurs. It was noticed that the same type of reactions of methyl heptanoate and phenol, for example, all reductive reactions, compete with each other although the molecular structures of aliphatic and aromatic compounds differ.

As the activity of the catalyst alters over the course of the HDO reaction due to the detachment of sulphur species and there is competition between reactive components, finding the most favourable HDO conditions requires understanding of the reaction pathways of various reactants. Moreover, the role of sulphur in the pathways must be understood in order to produce desired end products. The work reported here provides an approach for resolving these questions using model components.

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