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*Thesis for the degree of Doctor of Technology to be presented with due permission of the School of Chemical Technology for public examination and criticism in Auditorium KE2 at Aalto University School of Chemical Technology (Espoo, Finland) on the 24th of April, 2015, at 12.00.*

# Preface

The experimental work described in this thesis was performed at VTT Technical Research Centre of Finland between May 2010 and April 2014. The financial support was provided by Stora Enso Oy and by VTT Graduate School. I would like to place my deepest gratitude to my funders in the first, for providing the most demanding support for conducting research in an interesting and highly applied field. I also thank them for supporting my trips to scientific conferences, and work visits to SIN-TEF, Norway and Ghent University, Belgium.

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# Academic dissertation

# List of publications

This thesis is based on the following original publications which are referred to in the text as I–V. The publications are reproduced with kind permission from the publishers.

I  Anthonykutty, J. M., Van Geem, K. M., Bruycker, R. D., Linnekoski, J., Laitinen, A., Räsänen, J., Harlin, A., Lehtonen, J. 2013. Value Added Hydrocarbons from Distilled Tall Oil via Hydrotreating over a Commercial NiMo Catalyst. Ind. Eng. Chem. Res. 52 (30), 10114–10125.

II  Anthonykutty, J. M., Linnekoski, J., Harlin, A., Laitinen, A., Lehtonen, J. Catalytic upgrading of crude tall oil into a paraffin-rich liquid. Biomass Conv. Bioref. DOI 10.1007/s13399-014-0132-8.

III  Anthonykutty, J. M., Linnekoski, J., Harlin, A., Lehtonen, J. Hydrotreating reactions of tall oils over commercial NiMo catalyst (Accepted for publication in Energy Science & Engineering)

IV  Pyl, S. P., Dijkmans, T., Antonykutty, J. M., Reyniers, M-F., Harlin, A., Van Geem, K. M., Marin.G. B. 2012. Wood-derived olefins by steam cracking of hydrodeoxygenated tall oils. Bioresour. Technol. 126, 48–55.

V  Bruycker, R. D., Anthonykutty, J. M., Linnekoski, J., Harlin, A., Lehtonen, J.,Van Geem, K. M., Räsänen, J., Marin, G. B. 2014. Assessing the potential of crude tall oil for the production of green base-chemicals: an experimental and kinetic modeling study. Ind. Eng. Chem. Res., 53 (48), 18430–18442.

# Author's contributions

I. The author planned and carried out the experiments, except the steam cracking modeling of hydrodeoxygenated distilled tall oil. The author interpreted the results and wrote the article together with the co-authors.

II. The author planned and carried out the experiments. The author interpreted the results and wrote the article.

III. The author planned and carried out the experiments. The author interpreted the results and wrote the article.

IV. The author planned the hydrodeoxygenation experiment with Dr. Reetta Kaila and SINTEF (Norway) researchers. The author interpreted the results from hydrode-oxygenation experiment with Dr. Reetta Kaila and wrote the experimental and re-sults section in the article related to the hydrodeoxygenation experiment together with the co-authors

V. The author planned the hydrodeoxygentaion and steam cracking experiments with Dr. Juha Linnekoski and Ruben De Bruycker (University of Ghent, Belgium) and carried out the long-run hydrodeoxygenation experiment. The author assisted Ru-ben De Bruycker in steam cracking experiments at University of Ghent, Belgium. The author interpreted the results from hydrodeoxygenation experiment and wrote the article together with the co-authors.

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**Papers I–V**

**Abstract**

# Abbreviations

AGO, Atmospheric Gas Oil

ASTM, American Society for Testing and Materials

COP, Coil Outlet Pressure

COT, Coil Outlet Temperature

CTO, Crude Tall Oil

CUS, Coordinatively Unsaturated Sites

DFT, Density Functional Theory

DHA, Detailed Hydrocarbon Analyzer

DMDS, Dimethyl disulfide

DOD, Degree of Deoxygenation

DTO, Distilled Tall Oil

FID, Flame Ionization Detector

FT-IR, Fourier Transform-Infrared Spectroscopy

GC×GC, Comprehensive two dimensional gas chromatograph

GC-MS, Gas Chromatography-Mass Spectrometric

GHG, Green House Gas

HAAD-STEM, High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy

HDN, Hydrodenitrogenation

HDO, Hydrodeoxygenation

HDO-CTO, Hydrodeoxygenated Crude Tall Oil

HDO-DTO, Hydrodeoxygenated Distilled Tall Oil

HDO-TOFA, Hydrodeoxygenated Tall Oil Fatty Acid

HDT, Hydrotreatment

KF, Karl Fischer

LGO, Light Gas Oil

LHSV, Liquid Hourly Space Velocity ($h^{-1}$)

MPa, Mega Pascal

NGC, Natural Gas Condensate

RGA, Refinery Gas Analyzer

STM, Scanning Tunneling Microscopy

TAN, Total Acid Number

TOFA, Tall Oil Fatty Acid

ToF-MS, Time-of-Flight Mass Spectrometer

TMPAH, Trimethylphenylammonium hydroxide

WHSV, Weight Hourly Space Velocity ($h^{-1}$)

# 1. Introduction

Biomass is a key resource for renewable carbon, which could be used as an alternative to existing fossil-based raw materials, as well as a new building block for chemicals.[1] At present, the bio-refinery concept is well recognized for producing biofuels and chemicals through sustainable routes from biomass. Particularly, the production of biofuels has attained significant research attention because of the potential of these bio-based fuels to act as a feasible alternative to fossil-based fuels.[2] The demand for biofuels is increasing, however, strict environmental policies associated with the production of biofuels is often a major bottleneck to producing these fuels as per the demand. Reducing carbon emissions or greenhouse gas (GHG) emissions, the principal regulatory incentive set by policy makers, is one of the key factors which drive the biofuel market.[3] EU fuel quality directive for biofuels states that, the mandatory requirement for GHG emissions reduction from the use of biofuels is at least by 35%.[4] Therefore, in an environmental perspective, the production of biofuels seems to be very challenging. Furthermore, the utilization of agro-based raw materials for biofuel production is disputed due to the interference with the food chain.[5] In this aspect, the production of value-added chemicals and materials from biomass through thermochemical routes appear a much more sensible route than the production of biofuels.[6]

The market for these bio-based products is apparently driven by the pressure from customers and consumers rather than regulations.[7] Consequently, it is anticipated that the development of a commodity chemical through sustainable routes will attract the interest of a customer to purchase the product under the label 'green'. An increased process cost in a bio-refinery in comparison with the conventional petrochemical routes can be met by acquiring the green premium for the sustainably developed bio-based product.[8] Nowadays, sustainable development in chemical industries is a comprehensively used approach especially in the United States with an objective to meet the vision 2020 program for US chemical industry by means of employing renewable feedstocks for the production of valuable chemicals.[9] In addition, the technology road map prepared for new process chemistry recommends renewable feedstocks as a source for valuable chemicals and suggests that, the use of these feedstocks should increase by 13% until 2020.[10] In Europe, the platform for sustainable chemistry established by Cefic (The European Chemical Industry Council) also demands that renewable raw materials should

be used more with an intention of making 30% of the chemicals through bio-chemical or thermo-chemical routes by 2025.[10] Importantly, it is generally accepted in these visions or perspectives that thermo-catalytic (heterogeneous catalysis) methods can be good options to achieve sustainable developments in chemical industries.[10]

## 1.1 Base-chemicals for the chemical industry

Ethylene, propylene, 1,3 butadiene and benzene are regarded as platform chemicals for the production of, for example, solvents, adhesives, plastics, rubbers and, pharmaceuticals.[11] Among the aforementioned platform chemicals, ethylene is the largest bulk chemical (in volume) produced world-wide.[12] Ethylene is mainly used for the production of plastics such as polyethylene, polystyrene (PS), polyethylene terephthalate (PET) and poly vinyl chlorides (PVC) as well as performance chemicals like ethylene oxide, glycol, ethanol, etc. The applications of these platform chemicals vary from technical chemicals to packaging uses, and to textile industries.[13] Presently, the production of ethylene is mainly based on steam cracking process which uses fossil-based materials such as naphtha, ethane, gas oil and condensate as feedstocks.[14] In Europe, steam cracking of naphtha is the principal route for the production of ethylene. It was reported in 2013 that over 143 million tons per year of ethylene is produced globally solely from fossil-based feedstocks.[15] The demand for ethylene is expected to increase and it is forecasted that in the next 10 years, the global ethylene demand will grow by 3.3% per year, on average.[16]

## 1.2 Production of olefins in a bio-refinery

In order to meet the global demand for base-chemicals, mainly for olefins through sustainable routes, several technologies have been developed for the production of olefins from bio-based raw materials as shown in Figure 1.1. Bio-ethylene production from sugar and starch based biomass via hydrolysis-fermentation-dehydration route is a commercialized technology in Brazil and the US.[18] The well-developed infrastructure for bio-ethanol production from feedstocks such as sugarcane and corn makes bio-ethylene production cost-competitive in Brazil and the US through bio-chemical routes, in comparison with petroleum derived ethylene.[18] Nevertheless, the production of bio-ethylene via bio-chemical routes does not fall under the scope of this study, therefore, excluded from further consideration.

Lignocellulosic biomass originating from forest (woody biomass) is a promising bio-resource especially in a European context. Woody biomass can be thermo-catalytically converted into olefins through various bio-refinery steps as represented in Figure 1.1. Production of chemicals from lignocellulosic biomass has been studied extensively in the literature.[13,19-20] An important intermediate for the production of chemicals in a bio-refinery which rely on woody biomass has been identified to be bio-oil. Bio-oil, produced by the fast pyrolysis of woody biomass,

can be gasified into syngas (CO/$H_2$). Syngas can also be prepared by direct gasification of woody biomass.[21] However, direct gasification methods are still at a stage of development. Moreover, the costs associated with gasification of solid biomass could be higher than gasification of bo-oil.[21] Syngas can be used to produce ethylene using the widely available techniques such as the cracking of syngas-derived methanol into ethylene over zeolite catalysts and the dehydration of ethanol derived from syngas (syngas-methanol-ethanol).[22-24] Methanol is produced with high selectivity from syngas using a catalyst which contains a mixture of copper, zinc oxide and alumina.[23] Ethanol is produced from syngas-derived methanol by further reaction with additional syngas.[23] Syngas can also be converted to paraffinic hydrocarbons by means of Fischer-Tropsch synthesis.[22] These paraffinic hydrocarbons can then be further converted into olefins by steam cracking or catalytic cracking reactions. In general, there are several possible ways of producing olefins in a lignocellulosic bio-refinery. The major problem observed in a bio-refinery based upon lignocellulose is that expensive catalysts and advanced separation technologies are normally needed for the selective production of major products.[25]
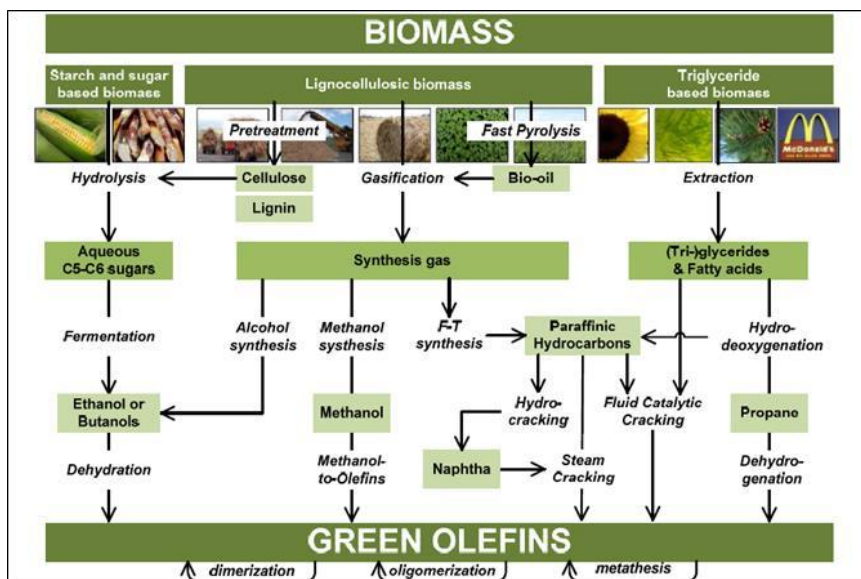


Figure 1.1. Biomass to olefins: currently investigated routes for producing green olefins [8,17] (reprinted with permission)

### 1.2.1 Cracking of renewable feedstocks

According to Huber et al., the production of bio-based chemicals and fuels in an existing petro-refinery set-up would be interesting as extra cost for building new

production facilities can be avoided in this option.[20] In this regard, bio-oil could be employed in a catalytic cracking facility for the production of olefins.[26] The literature reports on catalytic cracking of bio-oils to olefins is relatively scarce due to the disadvantage associated with the direct use of bio-oil for olefin production. Bio-oil possesses a high oxygen content (40–50 wt%).[27] A catalytic hydrodeoxygenation (HDO) step reduces the high oxygen content from bio-oils.[28, 29] However, the cost for this process is reported to be high due to the need of deep hydrotreatment conditions which requires hydrogen pressures up to 20 MPa.[29] In conventional petrochemical plants, steam cracking is preferred over catalytic cracking for the selective production of ethylene from naphtha. Vegetable oils or triglyceride based biomass can be alternatives to naphtha by fitting directly into a steam cracking process.[30] The oxygen content of vegetable oils is typically lower compared to bio-oils, and therefore, only a mild HDO step is needed with vegetable oils in order to make a diesel range hydrocarbon feed for steam cracking, as represented in Figure 1.1. Based on this approach, Syntroleum Corporation, a US based company, recently patented a process called bio-synfining for the production of hydrocarbon feeds from triglyceride based feedstocks such as waste fats/greases and vegetable oils.[31] The diesel range hydrocarbon feed produced from this process undergoes further steam cracking step in a conventional steam cracker to produce olefins.[32] Neste oil, the Finnish petrochemical company, uses the hydrotreating (HDO) technology and produces renewable hydrocarbon products (NExBTL, Neste Biomass to Liquid ) from plant based oils as well as waste animal fats and fish oils, suitable for the production of bio-plastics.[33] Catalytic hydrotreating technology is also employed by many companies worldwide such as UPM, Dynamic Fuels and ConocoPhillips, albeit, mainly for the production of bio-fuels.[3,34-35] The importance of hydrotreating technology for producing bio-based feedstocks or products continues to increase, however, the major feedstock widely used in this process, vegetable oils, are still food chain affecting feedstocks, which can no longer be regarded as a sustainable feedstock in a bio-refinery. As sustainability is of primary importance in a bio-refinery concept, the need for a non-food chain affecting, abundant and low cost feedstock remains still high in a bio-refinery.

## 1.3 Tall oil: a sustainable and cost-competitive feedstock for a bio-refinery

Tall oil is the major by-product obtained from Kraft-pulping process along with crude sulfur turpentine. The term 'tall oil' is derived as a Swedish product name associated with Kraft-pulping ('Tall': The Swedish word for pine).[36] During the Kraft-pulping process, the acidic components in wood chips (commonly pine) are converted into soaps by means of cooking in white liquor which consists of sodium hydroxide and sodium sulfide; the separated soap layer is then skimmed off from the black liquor resulted from cooking. In the next step, the skimmed soap is acidified with sulfuric acid, which gives rise to CTO.[37] CTO is mainly comprised of fatty acids, resin acids (rosin) and unsaponifiables or neutrals. The composition of

these components in tall oil is varied geographically as well as with the nature of wood species used for pulping. Table 1.1 shows geographical variation in the composition of crude tall oil, reported from the three major tall oil producing regions in the world.[38]

Table 1.1. Composition of crude tall oil (adapted from reference (38))

| Composition (wt.%) | South-eastern USA | Northern USA and Canada | Scandinavia |
|---|---|---|---|
| Resin acids | 35–45 | 25–35 | 20–30 |
| Fatty acids | 45–55 | 50–60 | 50–60 |
| Unsaponifiables | 7–10 | 12–18 | 18–24 |

Typically, the use of wood species other than pine wood for pulping process will lower the fraction of available fatty and resin acids in CTO.[36] Additionally, the yield of CTO from wood varies with seasonal and geographical changes. For instance, it is reported that the yield of tall oil is 40–50 kg/ton of pulp in southern Finland, and 60kg/ton of pulp in northern Finland.[39] In the southern parts of the US, the reported yield is 20–40 kg/ton of pulp.[37] Seasonal variations in tall oil yield are very significant in the US especially in the south-eastern states due to the faster biological degradation of wood during storage in summer months compared to winter months.[38] CTO is a dark brown, unpleasant smelling liquid due to the sulfur content (500–2500 ppm).[40] Sulfur is present in CTO as organic and inorganic sulfur compounds such as sulfate, sulfite, polysulfide, elemental sulfur, mercaptans, organic sulfides and organic sulfones and sulfonates.[40] In addition to the sulfur compounds, CTO also contains significant amount (50–100 ppm) of metal impurities such as alkali salts, alkaline earth metal salts and solubilized iron.[40] CTO is soluble in alcohols, esters, chlorinated solvents and mineral oil. The physical properties of CTO, especially viscosity and density, varies greatly with the chemical composition of CTO as well as temperature.[37] The physical properties of CTO are presented in Table 1.2.[36]

Table 1.2. Physical properties of tall oil (adapted from reference (36))

| | |
|---|---|
| Boiling range temperature (at 1.33 KPa) | 180–270$^{\circ}$C |
| Heat of vaporization | 290–330 KJ/kg |
| Specific heat | 2.1–2.9 J/g |
| Heat of combustion | - (33000–38000)KJ/Kg |
| Density (at 20$^{\circ}$C) | 950–1020 Kg/m$^3$ |
| Liquid viscosity (at 70$^{\circ}$C) | 25–40mm$^2$/s |

Traditionally, most of the CTO produced from Kraft-pulping is used for the production of different tall oil fractions.[37] CTO is distilled into tall oil fractions such as heads, TOFA, DTO, tall oil rosin (TOR) and tall oil pitch for a wide range of applications.[37] There are different scientifically designed fractional distillation methods available nowadays so as to produce tall oil fractions with high quality and purity. During the distillation of CTO under vacuum and at elevated temperature, the vaporization of high-boiling tall oil components is induced either in the presence of superheated steam (wet process) or without feeding any steam (dry process). Moreover, heat sensitive tall oil components are protected from degradation by ensuring functional security to the distillation apparatus adequate to meet the demand of steady running. Importantly, the quality of distilled tall oil products is influenced by the residence time of the product and the temperature differences between the product and the heating medium in different re-boilers involved in the distillation process. To achieve better distillation, a variable residence time from 5 seconds to 2 minutes is used at different stages of CTO fractional distillation.[36] In general, the yield and composition of the distilled products is widely found to be dependent on the employed distillation process as well as the quality of the CTO.

### 1.3.1    Fatty acids in tall oil

Fatty acids are long chain monocarboxylic acids which essentially make the main back bone of fats and oils.[41] The fatty acids in tall oil comprise primarily C$_{18}$ linear saturated and unsaturated chains. The major fatty acids present in tall oil are represented in Figure 1.2.
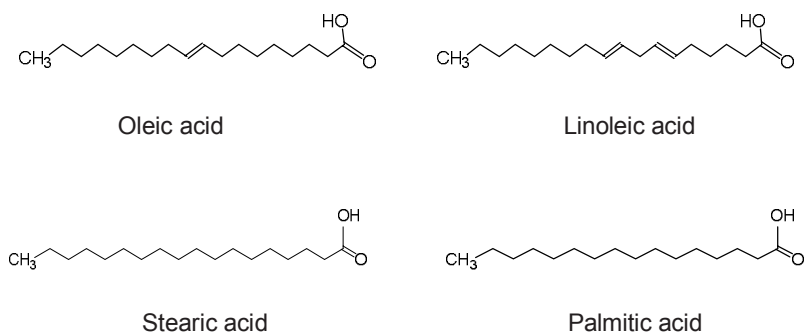
Figure 1.2. Major fatty acids present in tall oil

These fatty acids with a hydrophobic hydrocarbon chain and a hydrophilic polar group at one end can be used for number of industrial applications upon catalytic modification.[41] The reactivity of fatty acids is extensively discussed in the literature.[41] Unlike fatty acids in vegetable oils, tall oil fatty acids exist as free acids. Therefore, it is expected that the reaction chemistry of fatty acids in tall oil is slightly different than that of triglyceride based fatty acids in vegetable oils. The scope of different catalytic reaction routes from fatty acids in tall oil is well discussed in the review article published by Mäki-Arvela et al.[10]

### 1.3.2    Resin acids in tall oil

Resin acids are a mixture of organic acids which are derived from terpenes by means of oxidation and polymerization reactions.[42] In similarity with fatty acids, resin acids also contain carboxyl groups and double bonds as reactive centers. Resin acids in tall oil possess the same basic skeleton, a three ring fused system with empirical formula $C_{20}H_{30}O_2$.[37] The major resin acids present in tall oil are represented in Figure 1.3.

Abietic acid  Dehydroabietic acid  Neoabietic acid

Palustric acid  Pimaric acid  Isopimaric acid
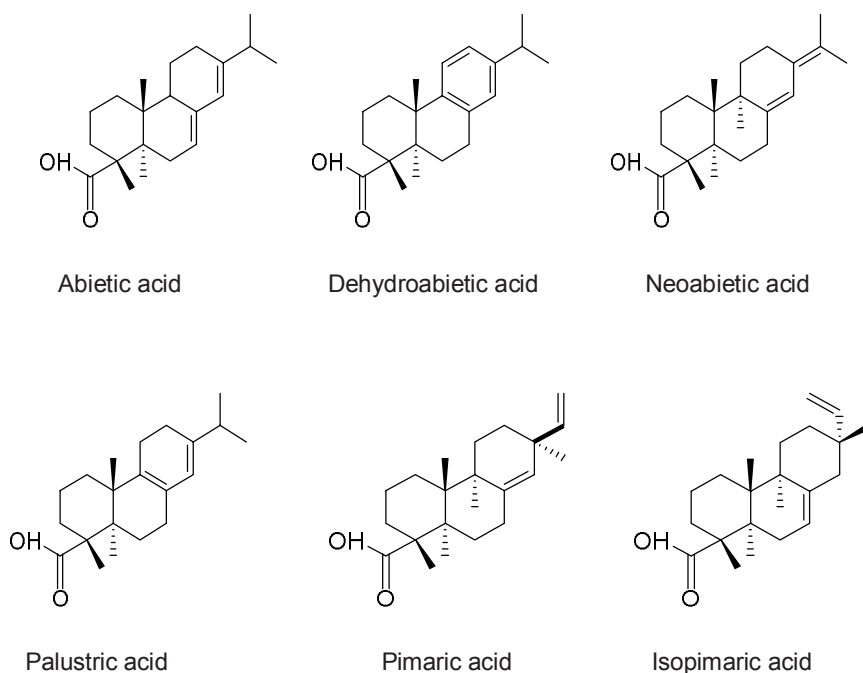
Figure 1.3. Major resin acids in tall oil

## 1.3.3 Neutral components in tall oil

Phytosterols and phytostanols are the major neutral components present in tall oil and termed as hydroxylated perhydro-1,2-cyclopentanophenanthrene deriva-tives.[43] These cyclic neutral components consist of 27–30 carbon atoms, and are characterized structurally by the presence of a phenanthrene ring system having an additional, fused five-membered ring. The two major phytosterols and phyto-stanols present in tall oil are β-sitosterol and β-sitostanol respectively, are pre-sented in Figure 1.4. In addition to sterols, the tall oil contains higher fatty alcohols such as policosanols (a mixture of long-chained primary alcohols composed main-ly of docosanol ($C_{22}$) and tetracosanol ($C_{24}$)).[44] Methylene derivative of cycloar-tenol, that is 24-methylenecycloartenol, is also present in considerable amount in tall oil. Importantly, a fraction of bonded (bound) acids, the sterol esters, are formed by the esterification of fatty and resin acids with sterols is also present in tall oil up to certain extent (3–5 wt%).

β-Sitosterol                              β-Sitostanol

Figure 1.4. Major sterols present in tall oil

## 1.4 Catalytic hydrodeoxygenation

HDO is one of the important hydrotreatment processes which use hydrogen to reduce the high oxygen content from feedstocks, both fossil-based and bio-based, in the presence of a suitable catalyst. In fossil-based feedstocks, the oxygen content is relatively low; therefore, HDO has not received much attention in conventional petro-refineries where hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the major hydrotreatment processes.[45] During an HDO process with a bio-based feed (bio-oil or vegetable oil), double bonds are saturated and oxygen is converted to $H_2O$ through a heterogeneous catalysis route.[45] In HDO, the severity of reaction conditions and the $H_2$ consumption required for achieving complete deoxygenation are mainly dependent on content and the type of oxygenates in the feed. In reality, HDO is a complex reaction that proceeds through a number of deoxygenation steps with the cleavage of several chemical bonds before the final elimination of oxygen.[45] The HDO mechanism of aliphatic and aromatic oxygenates is well documented in the literature.[45-47] HDO of aliphatic oxygenates (fatty acids) is usually carried out over conventional sulfided hydrotreating catalysts in a fixed bed reactor set-up under the conditions; temperature: 350–450$^{o}$C, $H_2$ partial pressure: 48–152 bar, LHSV: 0.5–5.0 h$^{-1}$.[20] The deoxygenation steps involved in the HDO of fatty acids are identified as reactions such as hydrodeoxygenation, decarboxylation and decarbonylation.[45] These catalytic routes are mainly influenced by the hydrogen pressure and flow, as well as the run temperature.[48] A higher $H_2$:oil ratio favors hydrodeoxygenation over decarboxylation; therefore, keeping on optimal partial pressure of hydrogen is vital in an HDO process. Importantly, selection of an active catalyst is the principal criteria for achieving high HDO conversions under industrial relevant conditions from complex bio-derived oils.

### 1.4.1 Selection of catalysts

It is widely accepted that the physical and chemical properties of the feed to be hydrotreated have a major influence on the selection process of the hydrotreating

catalyst. Selection of a hydrotreating catalyst for hydroprocessing reactions has been extensively reviewed in the literature.[49-50] All commercial catalysts developed for hydroprocessing are based on the elements from the groups VI and VIII of the periodic table.[49] Conventional hydrotreating catalysts such as cobalt (Co)- or nickel (Ni)-doped Molybdenum (Mo) on alumina ($Al_2O_3$) support in sulfide form are usually employed for HDO. The concentration of the metals on the support usually varies from 8 to 25% for the active metal (Mo) and from 1 to 4% for the promoter (Ni or Co).[51] It is believed that sulfidation with a sulfiding agent, such as $H_2S$ or a carbon containing sulfur compound, generate the active sites on a hydrotreating catalyst. Different theories have been proposed in the literature for characterizing the active sites on a sulfided CoMo or NiMo catalyst supported on alumina.[50] According to one model, it is identified that coordinatively unsaturated sites (CUS) and/or sulfur anion vacancies located at the slabs of $MoS_2$ crystallites are the active sites responsible for the reactions on a hydrotreating catalyst in the presence of hydrogen.[27,52-54] A Lewis acidic character is widely acknowledged to CUS site.[53, 55] It is proposed that these vacancies have an affinity with the hetero atom in the feed.[54] In agreement with this model (vacancy model), many researchers suggest that the sites responsible for hydrogenation are the same CUS sites located at the edges of $MoS_2$.[54] The increase in activity of the promoted (Co or Ni) hydrotreating catalyst has been attributed to the presence of Co (Ni)-Mo-S phase in which Mo-S bond is weaker than the unsupported $MoS_2$ phases.[56] It is believed that a weaker Mo-S bond will increase the concentration of CUS sites responsible for hydroprocessing reactions on the catalyst surface. There is criticism against the recognition of CUS sites for hydrogenation reaction. Topsoe et al. has proposed a brim sites model in order to understand the hydrogenation mechanism in a better way.[54] According to this model, brim sites, assigned by advanced characterization methods (STM, DFT and HAAD-STEM) are identified as catalytically active edge with metallic character responsible for hydrogenation reactions at the MoS2, Co-Mo-S and Ni-Mo-S nano-clusters. It is also identified that brim sites are not CUS. Nevertheless, "brim sites" model is not yet validated with complex molecules. Additionally, the presence of groups such as $S^{2-}$, $H^+$ and $SH^-$ are also identified on the surface of a sulfided catalyst. $H^+$ and $SH^-$ are assigned as Bronsted acid sites which provide hydrogen for hydroprocessing reactions.[51] It is also proposed that $SH^-$ groups can act as catalytic sites for acid catalyzed reactions which take place on a sulfided catalyst under favorable conditions.[57]

Support interactions are inevitable in the hydrotreating mechanism. It has been proposed that alumina is the preferable support for hydrotreating catalysts as the dispersion of $MoS_2$ edges can be high with this support due to the formation of small stable nanoclusters. A high dispersion of $MoS_2$ edges is presumably increases the amount of Co (Ni) accommodated at the Co (Ni)-Mo-S phase.[58]

Importantly, it has to be understood in the case of heavy feeds that the interaction of reactants with active sites on the catalyst can be different from the aforementioned proposals made for model compounds correlating the structure and activity of the catalyst. The properties of the hydrotreating catalysts are also greatly influenced by pre-treatment and sulfidation stages. Moreover, hydrogen solubili-

ty and diffusivity of reactants, both as a function of reactor temperature will have an influence on catalytic activity. In the aspect of diffusion of reactants into the catalyst pores, the selection of the right shape and size of the catalyst is important especially in the case of heavy feeds.[48]

As supported CoMo and NiMo catalysts are widely used for hydrotreating, the selection between these two should be made by considering the fact that NiMo catalyst has better hydrogenation activity than the CoMo catalyst.[58] NiMo catalysts promote more hydrocracking than CoMo catalyst. NiMo catalyst is reported to have better HDO activity than CoMo catalyst especially for aliphatic oxygenates.[51] In the literature, NiMo catalysts have often been used for the HDO of unsaturated acids such as fatty acids and resin acids.[59-60] The activity of conventional hydrotreating catalysts for HDO can be arranged in the decreasing order as: NiMo > CoMo > NiW > CoW.[50] Even though sulfided NiMo and CoMo catalysts are efficient catalysts for hydrotreating, the use of these catalysts for the HDO of most bio-based oils is not ideal, due to the necessity to co-feed sulfur compounds ($H_2S$ or DMDS) in order to keep the catalyst in sulfide form during the course of HDO reaction. Therefore, non-sulfur containing catalysts are preferred nowadays for the hydrotreating of sulfur free bio-oils and model bio-oil compounds. However, non-sulfur noble metal catalysts tend to face severe deactivation in HDO and therefore they have not entered into commercial use so far.[49,50] Furthermore, in the case of tall oils such as CTO, the use of sulfided catalysts for hydrotreating is justifiable because of the presence of sulfur compounds in the feed. It is expected that the sulfur compounds in tall oils will react with the hydrogen in the reaction medium and produce $H_2S$.[51,57] This formed $H_2S$ will most likely be beneficial for preserving the catalyst in its sulfided state.

## 1.5    Catalytic upgrading of tall oils

Catalytic upgrading of CTO and tall oil fractions (TOFA and DTO) has been studied over the past years with significant research attention, especially in industry. Table 1.3 lists the major studies reported in literature for upgrading CTO, tall oil fractions and tall oil model compounds.

Table 1.3. Major studies reported for tall oil upgrading

| | Conditions | Reference |
|---|---|---|
| Catalytic conversion of crude tall oil to fuels and chemicals over HZSM-5: Effect of co-feeding steam | Catalyst: HZSM-5<br>T= 370,380,390 and 405$^o$C<br>WHSV= 2.5 and 3.6h$^{-1}$ | (61) |
| Catalytic conversion of tall oil to chemicals and gasoline range hydrocarbons | Catalyst: HZSM-5<br>T= 350–520$^o$C  WHSV= 2.6–5.8h$^{-1}$ | (62) |
| Upgrading of tall oil to fuels and chemicals over HZSM-5 catalyst using various diluents | Catalyst: HZSM-5<br>T= 370–440$^o$C | (63) |
| Catalytic transformation of tall oil into biocomponent of diesel fuel | Catalysts: NiMo/Al$_2$O$_3$ and NiW/Al$_2$O$_3$-zeoloite<br>T= 360–380$^o$C H$_2$ Pr.= 5.5 MPa | (64) |
| Method and apparatus for preparing fuel components from crude tall oil | Catalyst: Commercial CoMo or NiMo for HDO<br>Pt or Pd supported on SAPO/ZSM-23 for isomerization T= 280–400$^o$C, H$_2$ Pr.= 3–10 MPa | (65) |
| Conversion of crude tall oil to renewable feedstock for diesel range fuel compositions | Catalyst: Conventional hydrotreating catalyst T= 320–450$^o$C | (40) |
| Hydrogen treatment of impure tall oil for the production of aromatic monomers | Catalysts: NiMo for HDO and ZSM-5 for cracking T= 330–450$^o$C<br>H$_2$ Pr.= 5–10 MPa | (66) |

Table 1.3. (Continued)

| | Conditions | Reference |
|---|---|---|
| Production of diesel fuel from crude tall oil | Catalyst: Commercial NiMo T= 200–400$^{o}$C H2 Pr.= 1.3–4.8 MPa | (67) |
| Process and apparatus for producing hydrocarbons from feedstocks comprising tall oil and terpene-compounds | Catalyst: NiW supported on $Al_2O_3$,zeolite, zeolite-$Al_2O_3$ T= 280–500$^{o}$C H2 Pr.= 3–10 MPa | (68) |
| Hydroprocessing biomass feedstock of tall oil, converting to hydrocarbons in diesel fuels, separation and fractionation | Catalyst: NiMo or CoMo T=370–450$^{o}$C $H_2$ Pr.= 4–15 MPa LHSV= 0.5–5h$^{-1}$ | (69) |
| catalytic cracking of rosin | Catalyst: Silica-zirconia-alumina T= 350–500$^{o}$C LHSV=0.4–1.2 ml/h | (70) |
| Hydrogenation/dehydrogenation reactions of rosin | Catalyst: NiMo/$Al_2O_3$, NiY-zeolite T= 350–450$^{o}$C $H_2$ Pr.= 7MPa | (59) |
| Conversion of the rosin acid fraction of crude tall oil into fuels and chemicals | Catalyst: Sulfided CoMo and NiMo $H_2$ Pr.= 3 MPa | (60) |
| Hydroprocessing of fatty acid methyl ester containing resin acids blended with gas oil | Catalyst: NiMo/alumina T= 300–370$^{o}$C $H_2$ Pr.= 5MPa | (71) |
| Catalytic deoxygenation of tall oil fatty acids over a palladium-mesoporous carbon catalyst: A new source of biofuels | Catalyst: Pd/C on a meso-porous carbon Sibunit T= 300–350$^{o}$C | (72) |
| Catalytic transformation of abietic acid to hydrocarbons | Catalyst: Pd/C T= 100–200$^{o}$C $H_2$ Pr.= 3MPa | (73) |

As noted from Table 1.3, in the literature most of the studies have been reported in the form of patents which investigate the potential of tall oil to produce fuel range hydrocarbons as an alternative to diesel fuel. Only a few studies are reported on the production of value-added chemicals from tall oil. In literature, tall oil upgrading has been carried out mainly based on two approaches: one is based on hydrogenation and HDO with sulfided NiMo or CoMo catalysts, and the other is based on zeolite catalysts at high temperatures. Tall oil upgrading using zeolites was studied by Sharma et al.[61,63] and Furrer et al.[62] These studies considered converting tall oil over a HZSM-5 catalyst to gasoline range of hydrocarbons and aromatics. Recently, Mikulec et al. investigated the hydrotreating of CTO with atmospheric gas oil (AGO) and reported that NiMo and NiW hydrotreating catalysts can be used for the production of a biocomponent for diesel fuel.[64] It has been suggested from this study that the reaction pathway of CTO under hydrotreating conditions involves hydrogenation of double bonds, decarboxylation, HDO, isomerization, and hydrocracking of alkane and cyclic structures. Most of the patents published related to tall oil upgrading [40, 65-69] disclose a methodology based on HDO using a commercial sulfided NiMo or CoMo catalyst. These patents also suggest that hydrotreating temperatures ranging from 300–450$^{\circ}$C and hydrogen partial pressures ranging from 3–10 MPa are the ideal hydrotreating (HDO) conditions with tall oil. The patent by Knuuttila et al.[65] demonstrates that the HDO catalyst can also be a catalyst with ring opening character, and in that case, a combined HDO and ring opening can be induced from cyclic oxygenates in tall oil. Harlin et al.[66] discloses a method for the production of aromatic monomers such as p-xylene, o-xylene and p-cymene through catalytic deoxygenation and cracking steps from tall oil. In addition to the listed patents, a number of patents are also available in literature, which proposes tall oil as a renewable feedstock to a bio-refinery. Myllyoja et al.[74] reveals that the specific sulfur content (2000–5000 w-ppm) in the feed is able to enhance the formation of $n$-alkanes through decarboxylation route in a hydrotreating process. Vermeiren and Gyseghem[75] disclose a method for the production of bio-naphtha from complex biomass derived oils. Furthermore, this patent demonstrates a method for steam cracking the bio-naphtha for the production of olefins.

Resin (rosin) acid fractions of tall oil have also been studied for catalytic conversion or upgrading processes. One of the major studies in this field was by Ira et al.[70] They have conducted the cracking reactions to convert rosin to lower molecular weight hydrocarbons, mainly aromatic hydrocarbons. A silica-zirconia-alumina catalyst was employed, and the experiments were carried out at different temperature and LHSV ranges. Essentially, it was identified from these cracking reactions with rosin that the rate of rosin feed had a less pronounced effect than the temperature upon the yield of aromatics. The details about the aromatization/cracking/isomerization reactions of rosin can also be found in the literature. Dutta et al.[59] describes the rosin hydrogenation under different conditions with NiMo/Al$_2$O$_3$, Ni-Y zeolite and ammonium tetramolybdate. Their studies suggest that, hydrocracking of the tricyclic compounds is the best route to produce good quality fuel range hydrocarbons. Moreover, these researchers also acknowledged

the hydrocracking activity of $NiMo/Al_2O_3$ catalyst under the tested conditions. Coll et al.[60] carried out a study of rosin fraction by using three commercial, sulfided NiMo and CoMo catalysts in a laboratory scale batch reactor. They considered different reaction mechanism for the hydrotreatment of rosin at high temperatures and pressures in the presence sulfided catalysts. The main consideration was based on the action of hydrogen on the carboxylic group as well as the unsaturated carbon-carbon bonds in resin acids. Based on this, a partial hydrogenation was proposed for the formation of oxygenated intermediates, and a complete hydrogenation was proposed for the formation of hydrocarbons. A deoxygenation route based on the thermal or catalytic cleavage of the carboxylic acid groups, which leads to the formation of $CO_2$, was also proposed by Coll et al.[60] Additionally, these researchers proposed catalytic cracking reactions at 400°C in the presence of NiMo catalyst and hydrogen. They estimated the cracking degree as the ratio of the elemental carbon present in the gaseous product to the elemental carbon present in the liquid product. Among the tested catalysts, NiMo catalyst (TK-555) was identified with highest cracking activity; with the degree of cracking achieved decreasing with an increase in hydrogen pressures and temperatures. In view of the achieved results, Coll et al.[60] concluded that further research is necessary to establish the better catalyst and operating conditions for the hydrotreatment of rosin.

Palanisamy et al.[71] studied the hydroprocessing of fatty acid methyl ester containing resin acids blended with gas oil. These researchers proposed a deoxygenation pathway for resin acids through hydrogenation, decarboxylation and decarbonylation routes. Importantly, this study identifies deoxygenation as the initial step and hydrogenation as the secondary step from resin acids during hydroprocessing. Catalytic conversion of a model compound of resin acids such as abietic acid is also reported in literature. In this study, Bernas et al.[73] investigated the transformation of abietic acid to hydrocarbons over a supported palladium catalysts under typical hydrogenation conditions. A successful conversion of abietic acid to tetrahydroabietic acid, a saturated resin acid, has been reported from this study. A thermal non-catalytic decarboxylation route for the formation of 18- norabieta- 8, 11, 13-triene from abietic acid was also identified from this study.

In recent years a new approach for upgrading bio-derived feedstocks has emerged, which is based on the deoxygenation reaction. The main advantage of this approach is that no hydrogen is required in the process compared to the hydrotreating process, thus, additional process costs can be eliminated. In line with this approach, a research study is reported from Rozmyslowicz et al.[72] for catalytically deoxygenationating TOFA over a palladium mesoporous carbon catalyst at temperatures between 300 and 350°C. This research work particularly demonstrates the selective formation of *n*-heptadecane ($C_{17}$) from $C_{18}$ fatty acids in TOFA in the absence of hydrogen.

## 1.6    Aim and scope

Tall oil is a widely identified, sustainable and cost-competitive feedstock for thermo-catalytic bio-refineries. Until now, a significant amount of research work has been carried out with tall oil and its fractions especially in a biofuel perspective. However, the potential of tall oil for petrochemical industries solely for the production of base-chemicals is not yet clearly understood or explored. Tall oil upon hydrotreating reduces its oxygen content, which can be further used in a conventional steam cracking process replacing the existing fossil-based feedstocks as well as the so called, renewable feedstocks such as vegetable oils and waste fats/greases. In this regard, understanding the whole process for the production base-chemicals from tall oil through hydrotreating and steam cracking is of great importance in association with the sustainable development in chemical industries.

Catalytic hydrotreating (hydrodeoxygenation) of biomass derived oils (e.g. vegetable oils) over a sulfided NiMo catalyst has been studied extensively.[48] An in-depth understanding about the structure-activity relationship of sulfided catalysts during HDO of oxygenates is known also from the studies with model compounds.[51,57] In the case of real feeds like tall oil which comprises oxygenates with different chemical nature, the hydrotreating chemistry can be complex. Therefore, an investigation of the hydrotreating mechanism of tall oil feedstocks such as TOFA, DTO and CTO under different process conditions is of particular importance.

The aims of this research work were:

- To study the effect of process conditions on distribution of products from tall oil (TOFA, DTO and CTO) in hydrotreating over a commercial, sulfided NiMo catalyst.
- To optimize the process conditions for hydrotreating in order to achieve maximum production of hydrocarbons together with high degree of deoxygenation from tall oils.
- To understand the hydrotreating chemistry of oxygenates in tall oil over a commercial, sulfided NiMo catalyst.
- To reveal the product distribution from steam cracking of hydrodeoxygenated tall oils.

# 2. Materials and methods

Catalytic hydrotreating experiments with tall oil feedstocks (TOFA, DTO and CTO) and steam cracking experiments with hydrotreated-tall oils were carried out in a continuous down flow, fixed bed reactor and a steam cracker set-up (pilot-scale and bench-scale) respectively. This chapter presents the details of materials and methodology applied in the experimental work.

## 2.1 Materials

A commercial alumina supported NiMo catalyst (1.3 Q, extrudates) was purchased and used for hydrotreating experiments in a trickle-bed reactor. The catalyst was dried and then sulfided prior to the experiments. Table 2.1 lists the feedstocks, chemicals and gases used in the experiments. Detailed chemical and elemental compositions of employed feedstocks (TOFA, DTO and CTO) can be found in Papers I, II, III and IV.

Table 2.1. Feedstocks, chemicals and gases used in the hydrotreating and steam cracking experiments

|  | Supplier | Purity | Paper |
|---|---|---|---|
| **Feedstocks** |  |  |  |
| TOFA | Arizona Chemical |  | III and IV |
| DTO | Arizona Chemical |  | I |
| CTO | Stora Enso |  | II and V |
| Naphtha | Confidential sample |  | IV and V |
| Natural gas condensate | Confidential sample |  | IV and V |
| **Chemicals** |  |  |  |
| *n*-Octadecane | Restek, Florida | 99% | I, II and III |
| *n*-Octatriacontane | Restek, Florida | 99% | I, II and III |
| TRPH standard ($C_8$–$C_{38}$) | Restek, Florida |  | I, II and III |
| trans-Decahydronaphthalene | Aldrich | 99% | I, II and III |
| 1,2,3,4-tetrahydronaphthalene | Fluka | 99.5% | I, II and III |
| 5-α-androstane solution | Supelco |  | I, II and III |
| Dichloromethane | Sigma-Aldrich | ≥99.8% | I, II and III |
| Hexane | Sigma-Aldrich | 95% | I, II and III |
| *Gases* |  |  |  |
| Hydrogen | AGA | ≥98.2% | I, II and III |
| Nitrogen | AGA | ≥99.5-% | I, II and III |
| Hydrogen sulfide | AGA | 99.99% | I, II and III |
| Argon | AGA |  | I, II and III |

## 2.2 Hydrotreating experiments

The bench-scale fixed bed reactor employed in hydrotreating experiments at VTT was 450 mm long, 15 mm internal diameter stainless steel tube, fixed coaxially in a furnace, as shown in Figure 2.1. The pilot-scale hydrodeoxygenation experiment for producing hydrodeoxygenated TOFA (HDO-TOFA) and hydrodeoxygenated DTO (HDO-DTO) for steam cracking experiments was carried out in a fixed bed reactor constructed of a 1 1/2" tube in 316 stainless steel (Fe, < 0.03% C, 16–18.5% Cr, 10–14% Ni, 2–3% Mo, < 2% Mn, < 1% Si, < 0.045% P, < 0.03% S) with an inner diameter of 38.5 mm at SINTEF Materials and Chemistry (Trondheim,

Norway) (Paper IV). The HDO experiment for producing hydrodeoxygenated crude tall oil (HDO-CTO) was carried out in the same bench-scale reactor set-up used for other hydrotreating experiments at VTT, however, with a reactor of different dimensions (500 mm long, 20 mm internal diameter stainless steel tube) (Paper V).
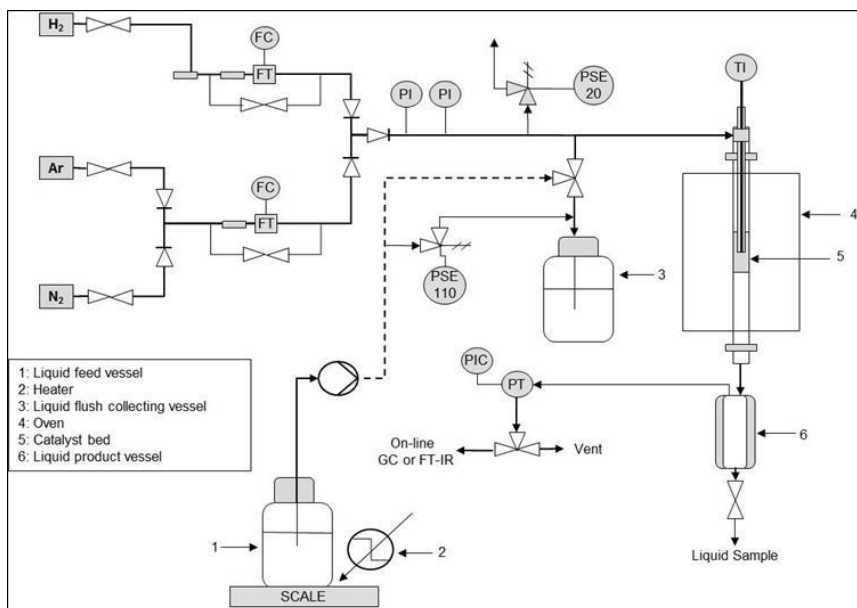


Figure 2.1. Bench-scale reactor set-up for the hydrotreating experiments

## 2.2.1 Catalyst pre-treatment

Catalyst pre-treatment for bench-scale hydrotreating experiments was carried out in the following procedure: the catalyst was dried at room temperature under nitrogen flow. The catalyst drying was continued for 2 hours until the catalyst bed temperature reached $400^{o}C$. After reaching $400^{o}C$, the reactor was kept isothermal for 30 minutes under nitrogen flow. Secondly, in-situ pre-sulfidation of the catalyst was carried out by feeding a mixture of $H_2S/H_2$ (5 vol%) to the reactor at $400^{o}C$ for 5 hours (Paper I). Catalyst pre-sulfidation for the pilot-scale HDO experiment was carried out by feeding light gas oil (LGO) spiked with 2 wt% DMDS (LHSV=2.0h$^{-1}$, soak period 3.5 hours) at $320^{o}C$ for 6 hours. After pre-sulfidation, the catalyst was stabilized with LGO at $250^{o}C$ for 1 day before switching to the tall oil feed (TOFA and DTO) (Paper IV).

### 2.2.2    Catalytic experiments

Bench-scale hydrotreating experiments were carried out by loading 2, 3 and 6 g of catalyst in order to vary the volume of the catalyst bed and thus to study the effect of space time. The hydrotreating experiments were carried out in a 325–450$^{o}$C temperature range under 5 MPa hydrogen pressure. The catalyst bed was fixed with quartz wool on a supporting pin (stainless steel) in the middle of the reactor tube. The catalyst bed temperature was measured by a thermocouple (1×Typ K/1/-40/+1000, SAB BROCKSKES, Germany), which was monitored by a temperature controller (TTM-339 series). In addition, LabView support software (National Instruments LabView (2011)) was also employed for accurately collecting the data on catalyst bed temperature and reactor pressure. In a single hydrotreating run, the catalyst amount corresponds to the set weight hourly velocity (WHSV= 1-3h$^{-1}$) loaded in the reactor. The reactor was then placed in an oven (Oy Meyer Vastus). Feedstock with fixed feed rate (6g/h) was fed to the reactor using a pump (Lewa) along with hydrogen. The molar flow rate (62 mol/kg of feedstock) of hydrogen was chosen based on the rough theoretical calculation of the stoichiometric amount (in moles) of hydrogen needed to make complete hydrogenation and deoxygenation from tall oil feeds (Paper I). A consideration was also made for this calculation that excess hydrogen is required to remove the water formed during HDO and thereby prevent the catalyst from deactivation.[48] Typically, a hydrotreating experiment was carried out for 6 hours with sampling intervals at every 2 hours. After the experiment was stopped, the final liquid product was collected and fractionated into an organic and aqueous phase.

Pilot-scale HDO experiment at SINTEF was carried out by using the NiMo catalyst from the same batch as used in bench-scale experiments. The reactor was loaded with 180 ml catalyst diluted with SiC particles (size: 0.21–0.36 mm, 1:2 by volume). The experiment was conducted at 49.5 barg H$_2$ pressure, WHSV= 2.0 h$^{-1}$, Temperature = 310–350$^{o}$C. The experiment was carried out continuously for 12 days in order to produce 150 liters of hydrodeoxygenated product for further processing. (Paper IV).

Bench-scale HDO experiment for producing HDO-CTO for steam cracking experiments (Paper V) was carried out by using the same procedure used for bench-scale hydrotreating experiments with TOFA, DTO and CTO.

## 2.3    Steam cracking experiments

Pilot-scale steam cracking of HDO-TOFA and HDO-DTO were conducted in a steam cracker unit at University of Ghent (UGhent), Belgium, is made up of a gas fired furnace as the main part. The furnace is 4m long, 0.7m wide and 2.6m high, in which a tubular reactor is mounted where feedstock is evaporated, mixed with steam and subsequently cracked. Steam cracking of HDO-TOFA and HDO-DTO was studied at a coil outlet pressure (COP) of 1.7 bara, a dilution of 0.45 kg steam/Kg HDO-TOFA/HDO-DTO. Steam cracking experiments were conducted at

coil outlet temperature (COT) of 820, 850, and 880$^{o}$C for HDO-TOFA and at 820 and 850$^{o}$C for HDO-DTO (Paper IV). The experimental set-up used for the pilot scale steam cracking experiments is shown in Figure 2.2
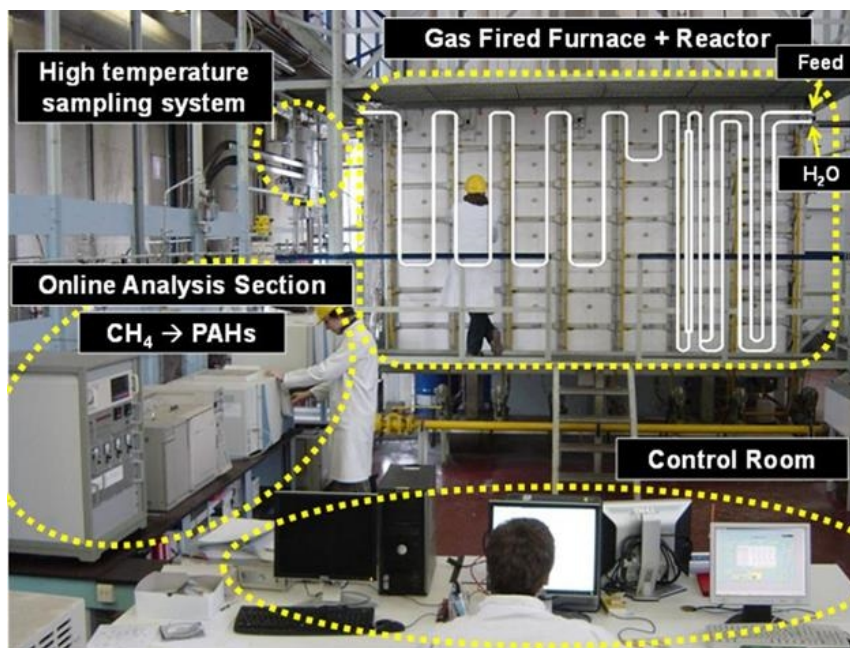


Figure 2.2. Pilot scale steam cracking experimental set-up

Steam cracking of HDO-CTO was conducted in a bench-scale steam cracker at UGhent, Belgium. The major part, the furnace/reactor, is 1.475m long and has an internal diameter of 6mm. HDO-CTO was fed to an evaporator at 400$^{o}$C prior to entering to the reactor, where it is evaporated and subsequently mixed with steam which formed in a similar way by the evaporation of water. Steam cracking of HDO-CTO was studied at a constant pressure of 0.17 MPa and a constant inlet flow rate of 0.1 kg hr$^{-1}$ hydrocarbon feedstock and 0.05 kg hr$^{-1}$ steam. COT was varied between 780 and 860$^{o}$C. Schematic overview of the experimental set-up for bench scale steam cracking is shown in Paper V (Figure 3). In both cases, pilot-scale steam cracking and bench-scale steam cracking, cracking experiments were also conducted with other feedstocks such as naphtha, NGC and blend of naphtha and hydrodeoxygenated tall oil (HDO-TOFA, HDO-DTO and HDO-CTO).

## 2.4    Analytical methods

Chemical composition of liquid phase samples from hydrotreating experiments were analyzed by various analytical techniques such as GC-MS, GCxGC-MS, GC×GC-FID/(ToF-MS) and GC-FID. In GC-MS analyses, samples were diluted with dichloromethane and analyzed using a HP-5 MS column (30m×0.25mm×0.25μm). GCxGC-MS set-up consisted of a combination of a one dimensional non-polar ZB-5 HT inferno column (30m×0.25mm×0.25μm) and a two dimensional semi-polar ZB-35 HT inferno column (15m×025mm×0.25 μm). GC×GC-FID/(ToF-MS) equipped with a combination of typical polar (Rtx-1 PONA, 50 m × 0.25 mm × 0.5μm)/medium-polar (BPX-50. 2m × 0.15mm × 0.15μm) column and cryogenic liquid $CO_2$ modulator. Two-dimensional gas chromatographic method was employed in this work in order to better identify and quantify the components in organic phase samples from hydrotreating. Experimental results from GC-MS are quantified based on the external calibration method, and presented in Paper I (Table 3), Paper II (Table 3) and Paper III (Table 3). Experimental result in Figure 7 in Paper I is presented based on the GC × GC-FID/(ToF-MS) analysis carried out at UGhent. Experimental results obtained from GC-MS quantification method was compared with the results obtained from GC ×GC-FID/ (ToF-MS). A quantification difference of ± 5 (wt%), on average, was identified to exist between two methods. The residual compositions of acid fractions and neutral fractions in organic phase samples was analyzed by GC-FID, by using a DB-23 (25–30m×0.25mm×0.20μm) column for acids and a Zebron ZB-1 column (30m×0.53mm×0.15μm) for sterols. The details of gas chromatographic techniques employed in this work and the method used for external calibration are discussed in Section 2.3 in Paper I. The elemental composition of organic phase samples were calculated by CHN equipment (Variomax) based on ASTM D 5291. Sulfur content in samples was determined by the ASTM D 4239 method. Water content in liquid phase samples was analyzed by Karl Fischer (KF) titration (Metrohm Karl Fischer 870 KF Titrino Plus) in accordance with ASTM E 203 method. Total acid number (TAN) from the feeds and some of the organic phase samples was calculated by means of standard ASTM D664 method. Analysis of gas phase products was carried out by a FT-IR instrument and also by a micro-GC at the later stages of this research work.

   The entire product stream from steam cracking experiments was analyzed by permanent gas analyzer (PGA), a refinery gas analyzer (RGA), a detailed hydrocarbon analyzer (DHA) and a GC × GC–FID/TOF-MS, as discussed in Section 2.2 in Paper IV as well as in Section 3 in Paper V.

## 2.5  Definitions

Conversion (%) of oxygenates in tall oil was calculated by the following equation

$$\text{Conversion X (\%)} = \frac{n_{A,\,Feed} - n_{A,\,OP}}{n_{A,\,Feed}} *100$$

Where $n_A$,Feed is the total mole of reactants (fatty acids/resin acids/sterols) present in the feed, $n_A$,OP is the total mole of residual reactants (fatty acids/resin acids/sterols) present in the organic phase.

Degree of deoxygenation (DOD) in hydrotreating of tall oil was calculated by the following equation:

$$\text{DOD (\%)} = \left[ 1 - \frac{\text{Mass of oxygen in OP}}{\text{Mass of oxygen in Feed}} \right] * 100$$

Product yield (%) of paraffins from fatty acid fraction in tall oil was calculated by

$$\text{Product yield (\%)} = \left[ \frac{\text{Total mol of paraffins in OP}}{\text{Total mol of fatty acids in Feed}} \right] * 100$$

# 3. Results and discussion

This section is divided into two parts: in the first part, catalytic hydrotreating of different tall oil feedstocks such as TOFA, DTO and CTO on a sulfided NiMo catalyst is discussed; the second part discusses the steam cracking of HDO-tall oil products (HDO-TOFA, HDO-DTO and HDO-CTO) in conventional steam cracker set-up.

## 3.1 Catalytic hydrotreating of tall oils

Catalytic hydrotreating of tall oils under the investigated conditions for 6 hours of time—on—stream (TOS) produced gas phase and liquid phase product streams. The highest yield (98%) of liquid products was obtained from TOFA hydrotreating at $325^oC$, and the highest yield (15.6%) of gas products was obtained from CTO hydrotreating at $450^oC$, WHSV=1h$^{-1}$. The gas phase was mainly composed of $CO_2$, CO, methane ethane, propane, ethylene, propylene and butane. The liquid phase product streams from tall oil hydrotreating consisted of aqueous and organic phases. During hydrotreating, water was formed from the HDO reaction as a by-product, and settled as a lower phase in a liquid product sample. Major products obtained in hydrotreating of TOFA, DTO and CTO under the tested conditions is listed in Table 3.1.

Table 3.1. Major products obtained in hydrotreating of TOFA, DTO and CTO

| Feedstock | Products | | |
|---|---|---|---|
| | Paraffins | Non-aromatics | Aromatics |
| TOFA | -$C_9$, $nC_{10}$-$C_{16}$ | Cyclohexane and Cyclohexyl derivatives | Benzene, Toluene, Xylene and Alkyl benzene |
| DTO | $nC_{17}$, $nC_{18}$, $nC_{19}$, $nC_{20}$, $nC_{20}$-$C_{24}$, $i$-$C_7$-$C_9$, $i$-$C_{10}$-$C_{16}$ $i$-$C_{17}$, $i$-$C_{18}$ | 18-Norabietane, Abietane, Cyclohexane, Cyclohexyl derivatives, Bicyclohexyl derivatives, Octadecene and Octadecanol | Benzene, Toluene, Xylene, Alkyl benzene, Tetralin, Norabietatrienes, Naphthalene, Anthracene and Phenanthrene |
| CTO | | 18-Norabietane, Abietane, Cyclohexane, Cyclohexyl derivatives, Bicyclohexyl derivatives, Octadecene, Octadecanol, Stigmastane, Cholestane and Ketonic derivatives of sterol | |

## 3.2 Product distribution in the organic phase obtained from the hydrotreating of tall oils

The product distribution (weight percentage yield (wt%)) in organic phases obtained from hydrotreating of TOFA, DTO and CTO was dependent on temperature and space time. The organic phase constituted approximately 90% and aqueous phase constituted 10% of the liquid products obtained in hydrotreating of tall oils. Remarkably, the organic phase yield was >70% of the feed (TOFA, DTO and CTO) in hydrotreating of tall oils. The effect of process conditions (space velocity and temperature) on product distribution during the hydrotreating of TOFA, DTO and CTO has been assessed in this study; shown in Tables in Papers III (Table 3), I (Table 3) and II (Table 3) respectively. It can be noted from these Tables that run temperature had a more pronounced effect than space time (inverse of space velocity) for producing a wide range of products. Also, a WHSV= $1h^{-1}$ was found to be the most favorable space time among the tested space velocities. Interestingly, the effect of process conditions (space time) on product distribution was found to be insignificant in the case of TOFA hydrotreating; therefore, not included in the present discussion.

### 3.2.1 Effect of reaction conditions on product distribution in organic phase

The effect of reaction conditions on the distribution of products in organic phase was investigated from tall oils. As the distribution of products were found to be more dependent on run temperature, the product distribution data obtained from TOFA, DTO and CTO at WHSV= $1h^{-1}$ as a function of run temperature is represented in Figure 3.1.
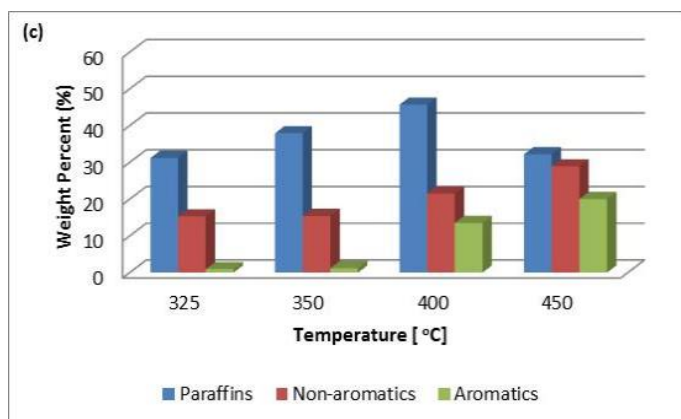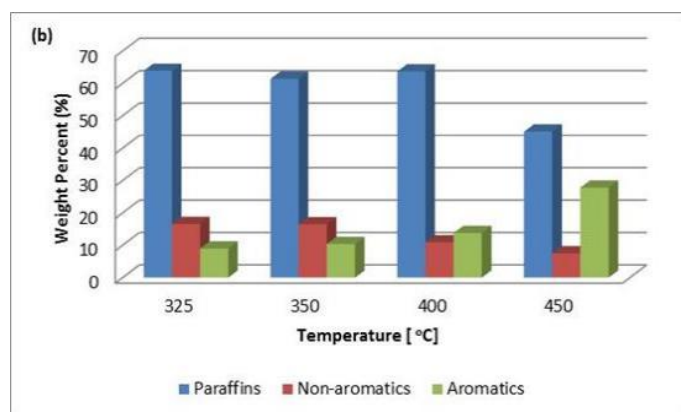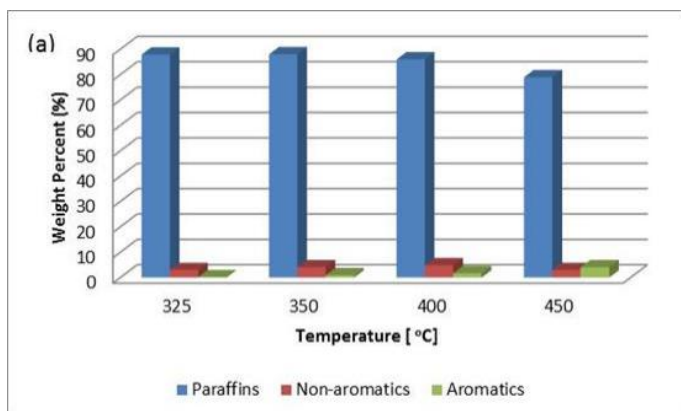
Figure 3.1. Product distribution in organic phase obtained from the hydrotreating of TOFA, DTO and CTO at WHSV=1h$^{-1}$, Temperature: 325–450$^{o}$C (a) TOFA, (b) DTO, (c) CTO. TOS = 6h

As demonstrated in Figure 3.1, the maximum production of paraffins is obtained up to 400°C with each tall oil feedstock after which there is a decline. It should be noted that non-aromatics in Figure 3.1 denote cycloalkanes (monocycloalkanes and polycycloalkanes), olefins and fatty alcohols. TOFA produced the maximum amount of *n*-octadecane and *n*-heptadecane among the tested tall oil feedstocks for hydrotreating. Therefore, an in-depth investigation on the distribution of these hydrocarbons obtained from the hydrotreating of TOFA at different process conditions was undertaken, and presented in Figure 3.2.
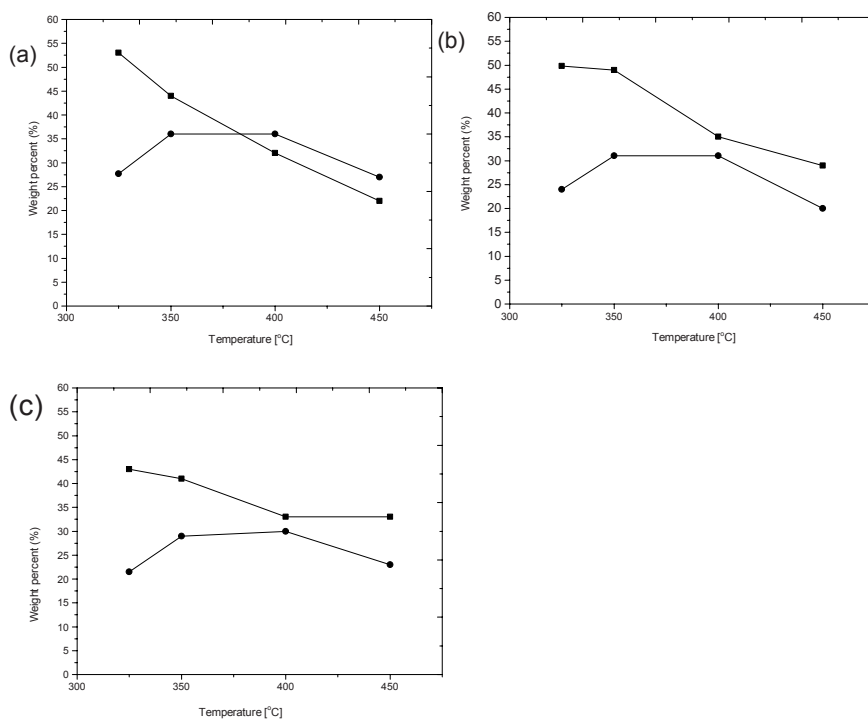


Figure 3.2. Product composition (wt%) of *n*-octadecane (■) and *n*-heptadecane (●) obtained from TOFA hydrotreating at various run temperatures (a) WHSV=1h⁻¹(b) WHSV=2h⁻¹ (c) WHSV=3h⁻¹

The distribution of the *n*-octadecane and *n*-heptadecane obtained from the hydrotreating of TOFA, DTO and CTO as a function of temperature at WHSV=1h⁻¹ is also presented in this section, shown in Figure 3.3.
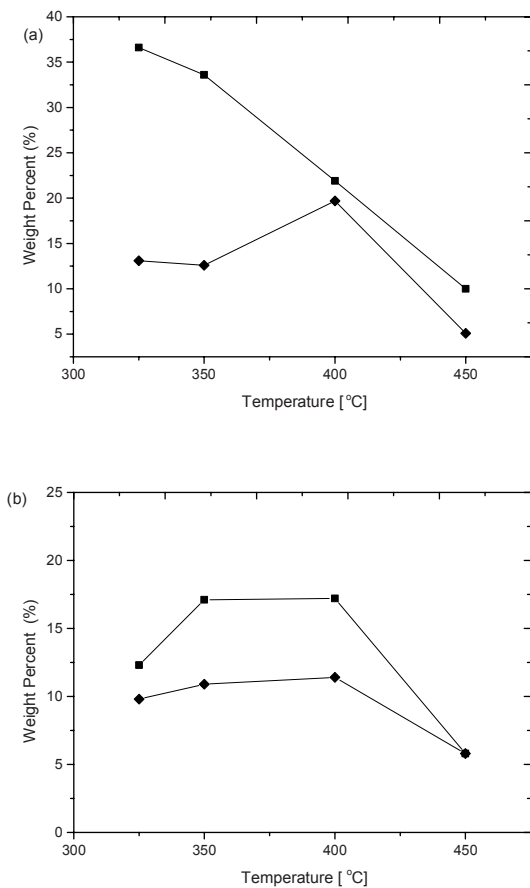
Figure 3.3. Product distribution (wt%) of *n*-octadecane (■) and *n*-heptadecane (♦) obtained in the hydrotreating of DTO (a) and CTO (b); Temperature: 325-450$^{o}$C, WHSV= 1h$^{-1}$, TOS = 6h.

These results (Figure 3.2 and Figure 3.3) show that low or intermediate temperatures for hydrotreating are more favorable for the formation of *n*-octadecane through a HDO reaction. The formation of *n*-heptadecane, the alkane which is assumed to be formed by the decarboxylation and decarbonylation reactions, was found to increase as the run temperature increases from 325$^{o}$C to 400$^{o}$C. At 450$^{o}$C, the formation of *n*-octadecane and *n*-heptadecane was sharply decreased especially in the case of DTO and CTO hydrotreating at WHSV= 1h$^{-1}$. This sharp decrease in weight percentage yield of $nC_{17}$+ $nC_{18}$ was resulted by the increase in

formation of lower alkanes ($nC_7$–$C_9$ and $nC_{10}$–$C_{16}$), cycloalkanes and aromatics at 450$^o$C. It is known in literature that decarboxylation route is promoted over HDO route on a NiMo catalyst as a function of increasing temperature.[76] In line with this report it is observed in this study that the decarboxylation route is promoted over the HDO route in TOFA hydrotreating at high temperatures (450$^o$C) (Figure 3.2). It is also observed that the promotion of decarboxylation route solely take place at longer space time (WHSV=1h$^{-1}$), and also only in TOFA hydrotreating.

The reaction course of HDO and decarboxylation was assessed in this research study by calculating the ratio of $C_{17}$/$C_{18}$ (wt%/wt%) hydrocarbons from the products obtained from the hydrotreating of tall oils. This ratio calculated in this work additionally gives an idea about how the distribution of $n$-octadecane and $n$-heptadecane occurs from tall oil hydrotreating at different WHSV's as a function of temperature (Figure 5, Paper III). In tall oil (TOFA, DTO and CTO) the hydrotreating $C_{17}$/$C_{18}$ ratio was obtained in a range of 0.2–1.3. The calculated $C_{17}$/$C_{18}$ ratio gives a clear picture that the distribution of $C_{17}$ and $C_{18}$ in DTO hydrotreating is well in agreement with the distribution of same compounds in TOFA hydrotreating. More specifically, the temperature dependence on $C_{17}$/$C_{18}$ ratio was found to be similar in both cases. In the case of CTO hydrotreating, a decrease in $C_{17}$/$C_{18}$ ratio was obtained from 325$^o$C to 400$^o$C a result dissimilar with other cases (TOFA and DTO hydrotreating). This difference in the distribution of $C_{17}$ and $C_{18}$ from CTO hydrotreating especially at low temperatures can only be assessed based on the complex composition of CTO feedstock. A detailed discussion in this aspect can be found in Section 3.3.1 of this thesis, and also in Paper III.

In addition to major $n$-alkanes, considerable amounts of $n$-hexadecane ($nC_{16}$), $n$-nonadecane ($nC_{19}$) and $n$-eicosane ($nC_{20}$) were formed from the hydrotreating of tall oils. These alkanes are presumably formed from the fatty acid fraction in tall oil by HDO, decarboxylation and decarbonylation reactions.[77] Distribution of these hydrocarbons from TOFA, DTO and CTO hydrotreating at different process conditions is represented in Paper III (Table 3), Paper I (Table 3) and Paper II (Table 3) respectively. The formation of $nC_{16}$, $nC_{19}$ and $nC_{20}$ hydrocarbons (as a function of temperature) in TOFA hydrotreating followed the same trend which is observed in the formation of these hydrocarbons in DTO and CTO hydrotreating. Furthermore, short chain alkanes and $i$-alkanes were found to be formed from fatty acid fraction with a variable product distribution. The residual compositions of fatty acids, resin acids and sterols obtained in hydrotreating of tall oils at different process conditions are shown in Appendix B.

Product distribution of non-aromatic cyclic structures and aromatic hydrocarbons was also investigated in this study. Paper I reports (Table 3) that the concentration of 18-norabietane, the major cyclic compound obtained in DTO hydrotreating, decreases with as increase of temperature. This trend was found to be more prominent at WHSV=1h$^{-1}$. The trends obtained with the product distribution of monocyclic ($C_7$–$C_{20}$ Hydrocarbons), polycyclic (18-norabietane, bicyclic $C_{18}$ and polycyclic $C_{20}$ hydrocarbons) and aromatic hydrocarbons (norabietatrienes, mono-aromatics (benzene, toluene and xylene) and polyaromatics) as a function of in-

creasing temperature at WHSV=1h$^{-1}$ in DTO hydrotreating is represented in this section in Figure 3.4.
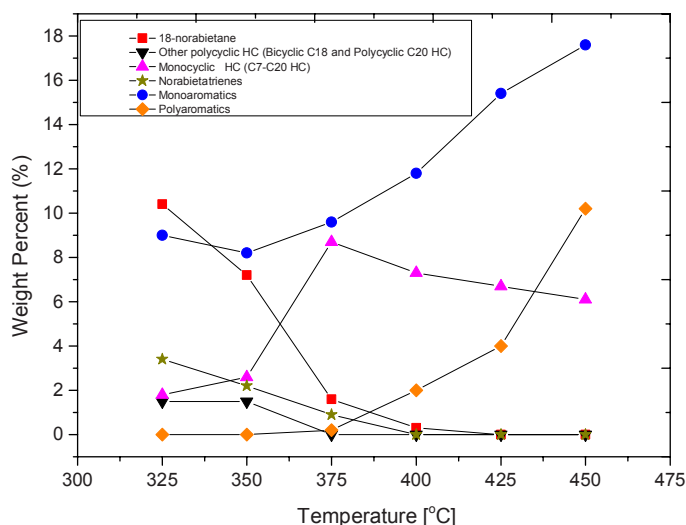


Figure 3.4. Distribution of monocyclic, polycyclic and aromatic hydrocarbons in DTO hydrotreating; Temperature: 325–450$^{\circ}$C, WHSV= 1h$^{-1}$, TOS = 6h.

Importantly, Figure 3.4 shows that the formation of monocyclic hydrocarbons increased with an increase in run temperature up to a certain extent at the expense of polycyclic hydrocarbons. In CTO hydrotreating, no clear trend for the distribution of individual cyclic structures and aromatic hydrocarbons was observed due to the complex nature of the product mixture especially in high temperature (>400$^{\circ}$C) experiments. However, general trends for the distribution of cyclics and aromatics as a function run temperature was observed to be in agreement with DTO hydrotreating, and are reported in Paper II. Based on the distribution of products obtained from the hydrotreating of tall oils (TOFA, DTO and CTO) under the tested reactor temperatures (325–450$^{\circ}$C), a reactivity scale is proposed for the formation of major products from each tall oil feeds as a function of temperature, as shown in Figure 3.5.

```
TOFA ──► n-alkanes ──► i-alkanes ──► Cycloalkanes ──► Aromatics
                                                        ( BTX)

DTO ──► Saturated tricyclics ──► Cycloalkanes ──► Polyaromatics
                                 (-mono,-di,-tri)

        Norabietatrienes

                                                 Aliphatic hydrocarbons

CTO ──► Steranes

        Ketonic derivatives
        of sterol          ──►  Cyclic oxygenates
```

Temperature [°C]
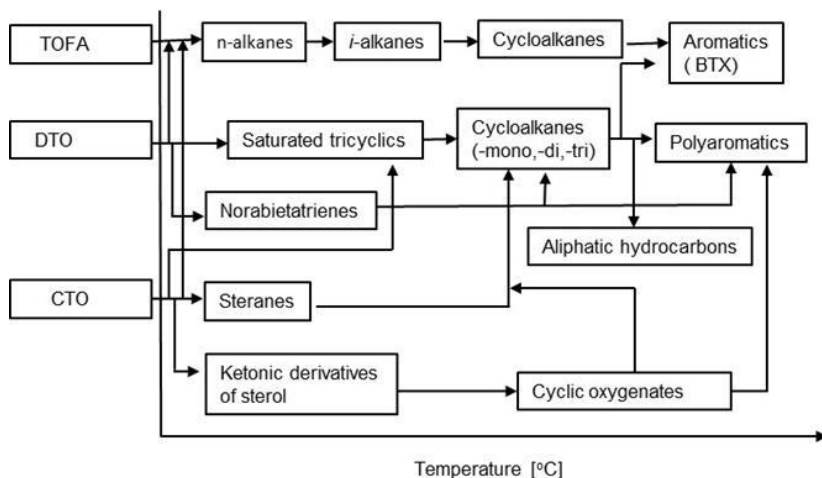
\* Reactivity scale excludes the possible thermal or catalytic cracking reactions directly from acid and neutral fractions in tall oil

Figure 3.5. Proposed reactivity scale for the formation of major products from tall oil feeds in hydrotreating (T= 325–450°C) (Paper III)

## 3.3 Hydrotreating chemistry of oxygenates in tall oil

### 3.3.1 Reactivity of fatty acids

The reaction mechanism of fatty acids under hydrotreating (HDO) conditions has been extensively studied in the literature over the past years.[48, 78-79] In vegetable oils, fatty acids exist as triglycerides, and it is reported that under hydrotreating conditions the double bonds in triglycerides are first hydrogenated before being converted to fatty acids via hydrogenolysis.[78] Different mechanisms have been assumed for the deoxygenation reaction from fatty acids.[48,79,80] One mechanism involves the simple HDO reaction which produces water, propane and normal alkanes with the same chain length as the fatty acid chain. Another mechanism considers the decarboxylation step, in which $CO_2$, propane and $n$-alkanes with one carbon atom less than the parent fatty acid chain are formed. Deoxygenation of fatty acids also occurs by decarbonylation reaction to produce CO, water, and $n$-alkanes (one carbon atom less than the parent fatty acid chain) in a hydrogen atmosphere. It has been considered that the HDO step proceeds through a complicated mechanism with a high hydrogen requirement in comparison with other

routes such as decarboxylation and decarbonylation. The hydrogen requirement for these routes is inferred to decrease as hydrodeoxygenation > decarbonylation > decarboxylation.[80] Hydrodeoxygenation, decarbonylation and decarboxylation reactions are represented by Equations (1), (2) and (3) respectively.

$$R\text{-}CH_2\text{-}COOH + 3H_2 \longrightarrow R\text{-}CH_2\text{-}CH_3 + 2H_2O \cdots\cdots\cdots\cdots(1)$$

$$R\text{-}CH_2\text{-}COOH + H_2 \longrightarrow R\text{-}CH_3 + CO + H_2O \cdots\cdots\cdots\cdots(2)$$

$$R\text{-}CH_2\text{-}COOH \longrightarrow R\text{-}CH_3 + CO_2 \cdots\cdots\cdots\cdots\cdots(3)$$
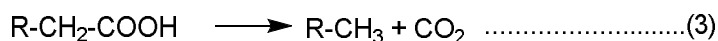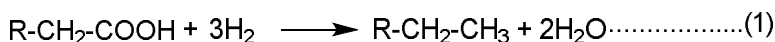
It is reported that in the HDO mechanism, the first step would be a hydrogenation, forming an aldehyde and alcohol as intermediates prior to the final formation of n-alkanes.[79] In tall oils, fatty acids exist as free acids, therefore, it has been accepted that the hydrotreating chemistry of fatty acids in tall oil are slightly different from than that of triglycerides in vegetables oils where the first step in deoxygenation is usually the hydrogenolysis of triglyceride backbone to produce fatty acids and propane. It is noteworthy that a minor fraction of fatty acids in tall oil especially in CTO feedstock exist as bonded acids. These bonded acids exist as steryl esters, formed by means of esterification reaction between a sterol molecule and a fatty acid. From free fatty acids in tall oil, it is identified in this work, as reported in Paper III, that the deoxygenation starts with an initial hydrogenation of double bonds in the free fatty acid chain, which produces a saturated fatty acid, that is, linoleic acid and oleic acid to stearic acid. The molar amount of stearic acid in tall oil feeds and hydrotreated products (organic phase) is represented in Figure 3.6. As noted from Figure 3.6, the molar concentration of this saturated fatty acid (stearic acid) was higher in TOFA hydrotreating at 325°C in comparison with the hydrotreating of DTO and CTO.
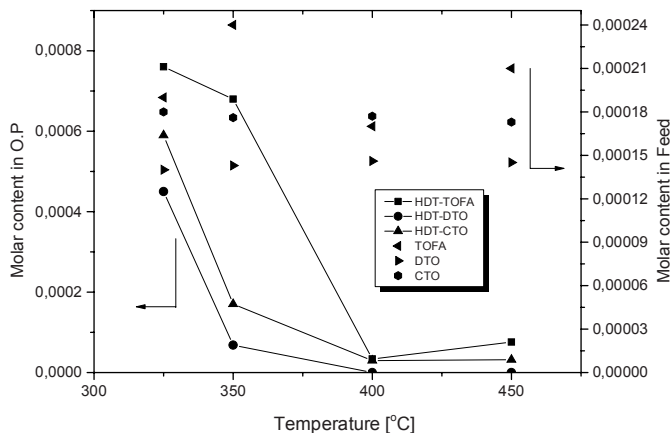
Figure 3.6. Concentration (molar content) of stearic acid in feeds and hydrotreated products at WHSV= 1h$^{-1}$, Temperature: 325–450$^{o}$C, TOS = 6h (Paper III)

The achieved distribution $n$-octadecane and $n$-heptadecane as the principal n-alkanes from tall oil hydrotreating especially at low temperatures investigated in this study confirms that the intermediate fatty acid, stearic acid, is deoxygenated through HDO, decarboxylation, and decarbonylation in the presence of hydrogen as proposed for the vegetable oils. The plausible reaction routes (adapted from the deoxygenation mechanism proposed for vegetable oils)[77,81] involved in the selective deoxygenation (HDO, decarboxylation and decarbonylation) of fatty acids (linoleic acid) in tall oil through an intermediate fatty acid (stearic acid) are shown in Scheme 3.1.
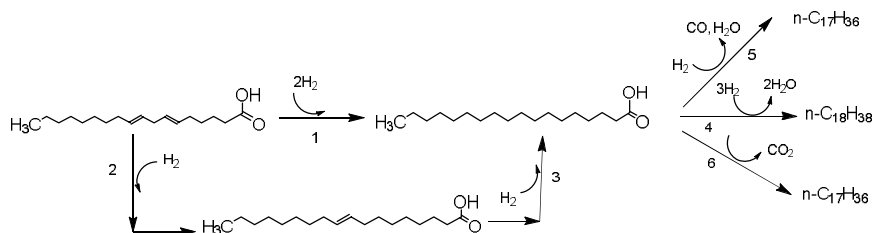


Scheme 3.1. Selective deoxygenation routes from fatty acids (linoleic acid) in tall oil under hydrotreating conditions.

In this study, hydrotreating of tall oils under the investigated conditions resulted fatty acid conversions at a high extent from both TOFA and DTO feedstocks (Figure 3(a) in Paper III). In CTO hydrotreating, a considerable drop in fatty acid conversion (at low temperatures) was observed, which can be attributed to the effect of sulfur content in the feed as explained in Paper III. It is reported that sulfur content in the feed ( TOFA, 53 ppm; DTO, 161 ppm; CTO, 1800 ppm) up to certain extent increases the decarboxylation reactions and decreases the hydrogenation and HDO reactions.[51,57] A detailed discussion of this aspect correlating with the achieved product distribution (weight percentage yield) of n-octadecane and n-heptadecane can be found in Paper III. The reactivity of individual fatty acids in tall oil is further discussed in detail in Paper III. Paper III (Figure 4) reports that, the conversion of linoleic acid decreased slightly with DTO and marginally with CTO at the lowest reactor temperature tested ($325^{\circ}$C) as function of decreasing space time. A similar trend with a more pronounced drop in reactivity was also observed with oleic acid (Figure 4 in Paper III) in DTO and CTO hydrotreating. As represented by route 2 in Scheme 3.1, oleic acid can be formed from linoleic acid by a partial hydrogenation reaction. Consequently, it is observed that at shorter space times (WHSV= 2 and 3 h$^{-1}$) partial hydrogenation resulted to give an increase in the concentration of oleic acid, which in turn resulted in a drop in the observed conversion (reactivity) of oleic acid in an indirect manner. Furthermore, intermediate structures such as fatty alcohols (e.g. n-octadecanol) and esters were found to be obtained in significant yields in CTO hydrotreating at low temperatures even at longer space times. This observation supports the earlier conclusions that fatty acids in tall oils are hydrodeoxygenated through intermediate structures as observed in the case of vegetable oils. Generally these intermediate compounds such as fatty alcohols and fatty acid esters were found to be highly reactive under favorable conditions (longer space time) especially with TOFA and DTO feedstock.

While selective deoxygenation reactions (HDO, decarboxylation and decarbonylation) are the major reactions which take place with fatty acids at lower or intermediate temperatures, the cracking (thermal or catalytic) reactions of fatty acids may exist especially at higher temperatures. These cracking reactions bring deoxygenation (non-selective) of fatty acids by the decomposition of the carboxylic group to produce n-alkanes and alkenes (long chain as well as short chain). Based on the residual composition of fatty acids obtained in TOFA and DTO hydrotreating, it is also identified that cracking at this stage produced oxygenates such as shorter chain fatty acids. Interestingly, the existence of a non-catalytic decarboxylation route was confirmed in this study by means of thermal reactions which were carried out with tall oils at $350^{\circ}$C and $450^{\circ}$C. Thermal reactions in a hydrogen atmosphere produced n-heptadecene and n-heptadecane from the fatty acid fraction in tall oil with the former as the major fraction and later as the minor fraction.

It is widely accepted that i-alkanes, cycloalkanes and monoaromatics (alkyl benzene) are formed from fatty acid fractions through intermediate alkanes by isomerization, cyclization and aromatization reactions respectively.[82] The ob-

served trend in this study (Tables (No. 3) in Paper I and II), is that a decrease in the weight percentage yield of $n$-alkanes as a function increasing temperature (> 400°C), signifies the existence of a reaction route from $n$-alkanes for the formation of the aforementioned hydrocarbons through a thermodynamically feasible cyclization and aromatization steps.[82] Furthermore, it is expected that the existence of a double bond in the parent compound will favor the formation of cycloalkanes and aromatics.[82] Therefore, as proposed by da Rocha Filho et al.,[82] the possible existence of direct cyclization and aromatization routes from the fatty acids in tall oils under high temperature (>400°C) experimental conditions are expected. In this route, firstly cyclic acids will be formed, which then undergo the deoxygenation step and produce cycloalkanes, cycloalkenes and aromatics as final products. It is noteworthy, especially from TOFA hydrotreating, that unlike cycloalkanes, cycloalkenes were not obtained in significant quantities at high temperatures. This finding signifies that a partial hydrogenation route is exists from fatty acids such as linoleic acid at high temperatures as the direct cyclization of linoleic acid would have mainly resulted in the formation of cycloalkenes. Based on these observations, a reaction scheme for the formation of cycloalkanes and aromatics (alkyl benzenes) from oleic acid (partially hydrogenated acid from linoleic acid) via direct cyclization-aromatization route as well as the indirect route through intermediate decarboxylated product (alkene) is proposed and shown in Scheme 3.2.
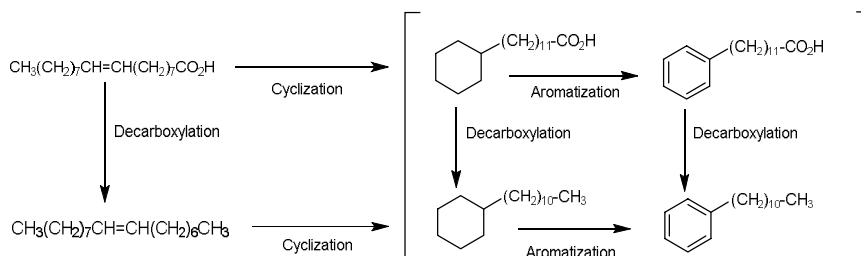


Scheme 3.2. Proposed reactions of fatty acids for high temperature hydrotreating (adapted from reference (82))

### 3.3.2    Reactivity of resin acids

In literature, it is stated that deoxygenation of carboxylic group in resin acids can occur by means of complete hydrogenation which produces hydrocarbons.[60] In addition, thermal or catalytic cleavage of the carboxylic group (decarboxylation) in resin acids also occurs to bring about deoxygenation.[59,60] Moreover, as suggested by Dutta et al. and Palanisamy et al., a dehydrogenation route is also proposed to exist with resin acids in low temperature hydrotreating experiments.[59,71] In this study, the obtained distribution of resin acid derived products (Table 3 in Paper I) reveal that hydrogenation and dehydrogenation routes exist under the tested hydrotreating conditions. The possible reasons for the existence of these routes in parallel in low temperature hydrotreating could be that the thermodynamics of

chemical equilibrium of these hydrogenation and dehydrogenation reactions are different or reactions are not limited by thermodynamics since the products of some of these reactions are immediately consumed further. The significant yield of 18-norabietane in comparison with the minor yield of abietane obtained from resin acids in this study implies that the major deoxygenation route was hydrogenation and decarboxylation or decarbonylation rather than HDO (hydrogenation and dehydration mechanism through intermediate structures) especially under low temperature hydrotreating conditions. Furthermore, the appearance of nora-bietatrienes (18-norabieta-8,11,13-triene) in the product streams of low tempera-ture hydrotreating runs revealed the existence of a dehydrogenation and decar-boxylation route from abietic-type resin acids.[59,71,83] Based on this observation, a reaction scheme for the low temperature hydrotreating of resin acids (abietic acid) has been proposed in this research work and is presented in Scheme 3.3.
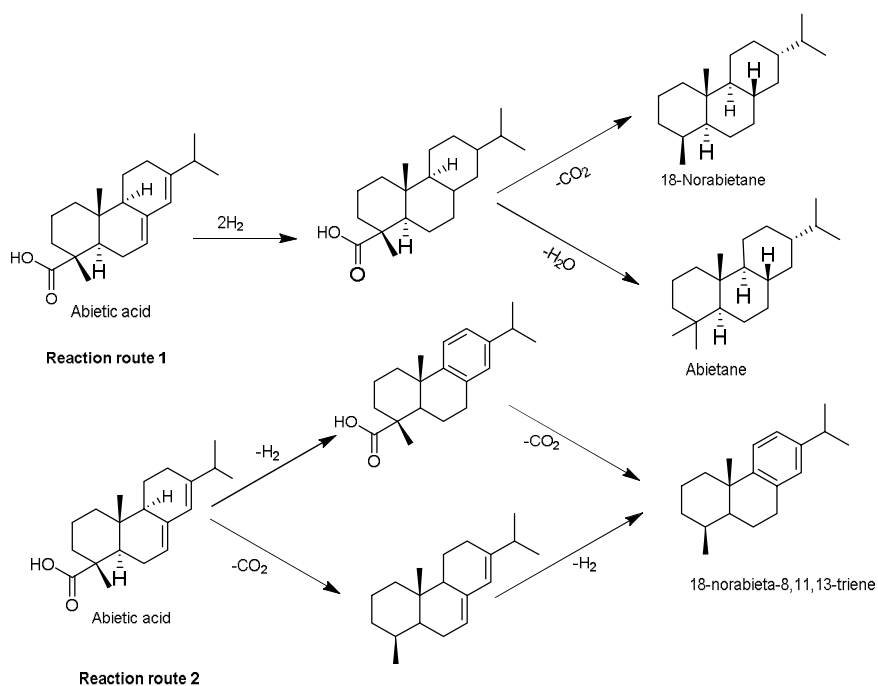


Scheme 3.3. Proposed reaction scheme for resin acids (abietic acid) under HDO conditions[59]

As shown by reaction route 1 in Scheme 3.3, for selective deoxygenation reac-tions (HDO, decarboxylation and decarbonylation), it can be proposed that these routes occur similarly with fatty acids, that is, starting with an initial hydrogenation which results in the formation of saturated resin acids (tertahydroabietic acid).[73] However, no such saturated structures were detected as intermediates in our GC-

FID analysis presumably due to the high reactivity of these intermediates under the tested hydrotreating conditions. It is suggested that the decarboxylation step involved in the above mentioned routes can be catalytic or non-catalytic. A non-catalytic route to the formation of norabietatrienes was confirmed in this study by thermal reactions. It is proposed based on our study that the dehydrogenation step involved in the formation of norabietatrienes from abietic acid (reaction route 2) can occur prior to or after deoxygenation, which would be in agreement with Dutta et al.[59] A route is also proposed for the formation of norabietatrienes through direct decarboxylation reaction from dehydroabietic acid. Additionally, a possible route for the formation of norabietatrienes from 18-norabietane via dehydrogenation can be proposed. However, it is assumed that severe reaction conditions such as high temperature (>400$^o$C) may be needed for the complete dehydrogenation of a saturated ring from 18-norabietane and thus, to produce norabietatrienes. Interestingly, norabietatrienes were observed in significant yield solely from low temperature hydrotreating (Figure 3.4 in Section 3.2.1 of this thesis). This observation indicates that the major route for the formation of norabietatienes is the dehydrogenation and decarboxylation of partially saturated resin acids (abietic acids) as well as the direct decarboxylation from dehydroabietic acid, and not the dehydrogenation of a completely saturated tricyclic structure such as 18-norabietane.

In high temperature hydrotreating experiments, based on the obtained product distribution (Table 3 in Paper I and Figure 3.4 in Section 3.2.1 of this thesis) it is assumed that resin acids are reacted through their primary deoxygenation products such as 18-norabietane and norabietatrienes, in agreement with our earlier statement that hydrogenation and dehydrogenation reactions are not thermodynamically limited with resin acids. However, a dominance of dehydrogenation and decarboxylation route (reaction route 2) over hydrogenation route (reaction route 1) should be expected as the hydrotreating temperature increases to beyond 375$^o$C.[71] Therefore, cycloalkanes or napthenes (mono and poly) and aromatics (mono and poly) obtained at these conditions predominantly result from the dehydrogenation, decarboxylation and cracking of resin acids. It is expected that at this stage selective ring opening occurs through the cleavage of C-C bond in the presence of hydrogen.[84] These so called hydrocracking reactions are the main route for the production of -mono and -di cyclic groups from resin acids.[71] The ring opening chemistry of cycloalkanes on a solid acid catalyst is well known.[84] Importantly, Palanisamy et al. proposed a ring opening route for the formation of alkanes and alkenes through intermediate cyclic structures from resin acids on a NiMo catalyst under HDO conditions.[71] The present study also suggests a similar ring opening route from resin acids under the investigated conditions. Nevertheless, no route for the formation of specific hydrocarbons (alkanes) through ring opening has been proposed in this study due to the complexity associated with the product mixture to identify resin acid derived alkanes.

Regarding the reaction chemistry of resin acids at high temperatures, cycloalkanes and aromatics are not necessarily formed through the intermediate saturated tricyclic structures. Deoxygenation at these high temperature conditions may occur through the non-selective deoxygenation of the carboxyl group (thermal

splitting), and in that case formation of cycloalkanes and aromatics will result as proposed in previous paragraph. However, a slight amount of cycloheaxnol (mono and bicyclo) derivative obtained in DTO hydrotreating at high temperatures denote that an equal chance of C-C splitting (thermal or catalytic) at the saturated ring of the resin acid exist prior to the removal of oxygen (non-selective deoxygenation). It can be learnt from the literature that this proposed C-C splitting from some resin acids, for example, diabietic and dehydroabietic acid, can be minimal before the removal of carboxylic group.[85] As reported in Paper I, these resin acids may remain partly intact during high temperature hydrotreating as deoxygenation can be minimal in this juncture due to the unfavorable selective deoxygenation route which is believed to be the major deoxygenation pathway responsible for complete deoxygenation. The C-C bond cleaved in resin acids at high temperature may undergo dehydrogenation or further cracking (thermal or hydrocracking) and produce aromatic oxygenates and cyclic oxygenates which may then further undergo deoxygenation (non-selective) and produce cycloalkanes and aromatics as final products. Interestingly, the present study detected small amounts of aromatic oxygenates (aromatic alcohols) and cyclic oxygenates in product streams from high temperature hydrotreating. This observation highlights that deoxygenation was not complete from resin acids even by means of a non-selective route under the investigated conditions in this study.

### 3.3.3    Reactivity of sterols

Hydrotreating chemistry of sterols is unknown in the literature. In literature, the HDO of phenols and alicyclic alcohols on sulfided NiMo catalyst has been reported.[51,86] Based on these reports, it is proposed that hydrogenation and rupture of C-O bond in sterols occur either with a direct hydrogenolysis reaction or a dehydration reaction. In view of the obtained distribution of sterol-derived products (Paper II), this study proposes a reaction scheme for the HDO of a major sterol compound, β-sitosterol, which is found in tall oils. The proposed reaction route is shown as Scheme 3.4.
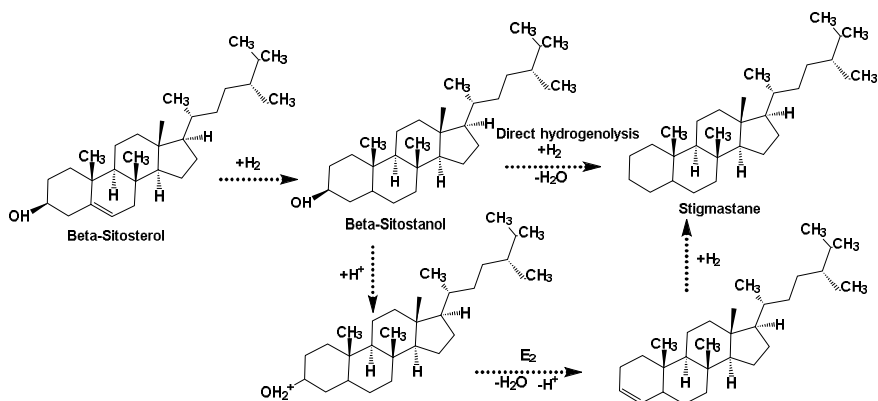
Scheme 3.4. Proposed reaction scheme for the HDO of sterols (beta-sitosterol) (Paper II)

The proposed reaction route (Scheme 3.4) predominantly occurs in low temperature hydrotreating with sterols. In addition to this reaction mechanism, dehydrogenation of sterol structures is also possible producing ketonic derivatives such as cholest-4-en-3-one and 4, 6-cholestadien-3-one, as observed during this study (Paper II). At high temperatures, the dehydrogenation reaction prevails over hydrogenation and occurs with cracking and non-selective deoxygenation reactions as observed with resin acids, producing cycloalkanes and aromatics from sterols. However, the significant amount of cyclic oxygenates, for example, epoxy derivatives of sterol obtained in these conditions reveal that non-selective deoxygenation of sterols was minimal unlike that of fatty acids and resin acids.

## 3.4    Nature of active sites on a sulfided NiMo catalyst for the hydrotreating of tall oils

A commercial NiMo catalyst was employed in this study. Therefore, making an in-depth investigation about the nature of active sites for tall oil hydrotreating has fallen outside the scope of this research work. Nevertheless, some general trends are depicted in this work relating to the active sites on the catalyst and the reactivity of oxygenates. Based on the widely accepted assumption regarding the active sites on a sulfided catalyst, it can be stated that in tall oil hydrotreating the adsorption of reactant acid molecules onto the edges of $MoS_2$ (sulfur vacancy) takes place through the oxygen of the carbonyl group (C=O).[87] Consequently, in DTO hydrotreating a competitive adsorption of fatty acids and resin acids can be expected although it is reasonable to assume that preferential adsorption modes may exist based on the steric hindrance associated with each group (fatty acid or resin acid). However, as discussed in Paper III most of the resin acids are found to be consumed through a decarboxylation or decarbonylation step without inducing much interaction with the active site responsible for HDO (CUS sites). The decar-

bonylation and decarboxylation reactions presumably take place on an active site other than CUS, likely to be a sulfur saturated site (SH⁻).[57] The similarity in reactivity of fatty acids and resin acids can be thus explained. In CTO hydrotreating, it is assigned that CUS sites are responsible for the HDO (C-O hydrogenolysis) of sterols.[51] Therefore, one reason for a drop in the reactivity of acid fractions in CTO hydrotreating can be identified as competitive adsorption of acid fractions and sterols on CUS sites where sterols may get dominance over acids. Another reason could be the adsorption of sulfur compounds present in CTO feedstock onto the catalyst surface, presumably to a CUS site.[57] It is reported that adsorption of a sulfur additive will increase the acidity of the catalyst by transforming a CUS to a sulfur saturated site.[54] The consequent decrease in the concentration of CUS sites will result in the drop of reactivity of acid fractions by means of a suppressed HDO reaction route.

## 3.5 Quality assessment of hydrotreated products from tall oils for further applications

Overall hydrotreating efficiency of the employed NiMo catalyst was investigated in this study based mainly on the quality of the obtained products of hydrotreatment. Quality assessment was focused on the evaluation of degree of removal of heteroatoms (O and S) from three tall oil feeds at different process conditions. Hydrotreating of TOFA and DTO at T= 400$^o$C, resulted in a maximum degree of deoxygenation, that is greater than 99%, whereas with CTO, a maximum degree of deoxygenation (91%) was achieved at a lower temperature (350$^o$C) when compared to TOFA and DTO under the same WHSV=1h$^{-1}$. As reported in Paper II, with CTO maximum degree of desulfurization (96.2%) was obtained from hydrotreating at 450$^o$C, WHSV = 2h$^{-1}$. Importantly, it was observed based on these assessments that keeping an optimum temperature condition which is in a range of 350–400$^o$C is needed in order to bring a synergy effect of different deoxygenation pathways such as selective and non-selective deoxygenations for attaining a complete DOD from tall oils with a NiMo catalyst. Generally, the quality of a hydrotreated product for further refinery processes is evaluated based on the achieved H/C ratio and O/C ratio.[88] Therefore, Van Krevelen diagrams has been plotted in this study in order to represent the obtained H/C and O/C ratios (molar) with each tall oil feedstock at different hydrotreating temperatures and space times, as shown by Figure 3.7. In comparison with tall oil feeds, a drastic decrease in the O/C ratio was observed with all hydrotreated products. Furthermore, a higher H/C ratio which signifies the severity of hydrogenation was observed for hydrotreated TOFA (HDT-TOFA) and hydrotreated DTO (HDT-DTO). With HDT-TOFA and HDT-DTO, an increase in H/C ratio can be observed when increasing temperature from 325$^o$C to 450$^o$C without compromising much with O/C ratio except in DTO hydrotreating at 450$^o$C. The increase in the H/C ratio at high temperature can also be attributed to the hydrocracking activity of the NiMo catalyst resulting in hydrogenation and cleavage (thermal or catalytic) of C-C bonds and carbox-

ylic group (non-selective deoxygenation). Cracking leads to the loss of elemental carbon from the liquid product stream and consequently to a higher H/C ratio. A lower H/C ratio obtained with the hydrotreated products from CTO indicates a lesser degree of hydrogenation. For evaluating the potential of hydrotreated tall oil products for further petrochemical processes such as steam cracking, one must consider that a hydrotreated product with lower O/C ratio would be more preferred over a product with higher H/C ratio. In this aspect, hydrotreated products from tall oils, especially from TOFA and DTO feeds remain as good quality feeds for steam cracking.
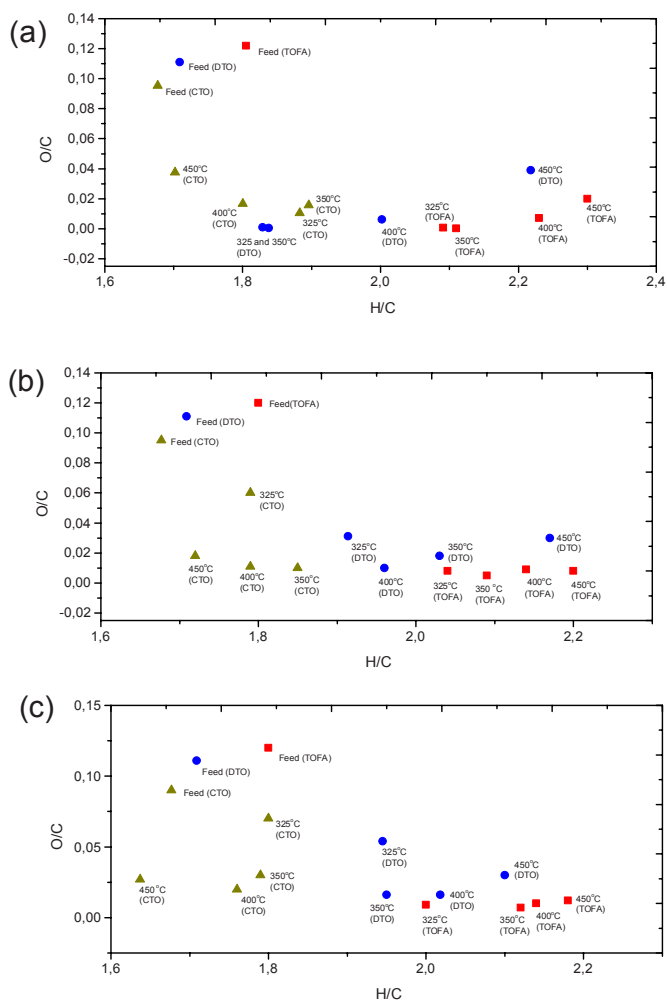
Figure 3.7. H/C and O/C ratio for tall oil feeds and hydrotreated tall oil products (Van Krevelen diagram)   (a) WHSV=1h$^{-1}$, (b) WHSV=2h$^{-1}$, (c) WHSV=3h$^{-1}$ (■: HDT-TOFA; ●:HDT- DTO; ▲: HDT-CTO), TOS = 6 h

## 3.6    Steam cracking of hydrodeoxygenated tall oil products

This section discusses the steam cracking of HDO-tall oil products such as HDO-TOFA, HDO-DTO and HDO-CTO which were obtained under optimized conditions from the bench-scale hydrotreating experiments with TOFA, DTO and CTO.

### 3.6.1    Steam cracking of HDO-TOFA

In this work, steam cracking of HDO-TOFA under the investigated conditions in a pilot-scale reactor produced a wide range of chemicals starting from light olefins and alkanes to pyrolysis gasoline (e.g. benzene, toluene and xylenes), and up to fuel oil (e.g. naphthalene, phenanthrene, heavy paraffins and olefins, and heavy naphthenes). A detailed comparison of the product distribution obtained from the steam cracking of HDO-TOFA, naphtha and natural gas condensate (NGC) at different coil outlet temperatures (COT) has been described in Paper IV (Table 3). To simplify this comparison, distribution of the main group products obtained from the cracking of the aforementioned feedstocks at $820^{\circ}C$ (COT) is represented in this section as Figure 3.8.
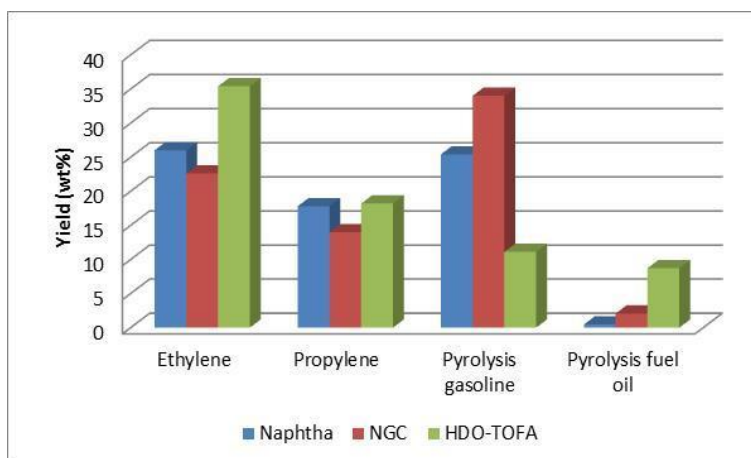


Figure 3.8. Product distribution obtained from steam cracking of naphtha, NGC and HDO-TOFA at $820^{\circ}C$ (COT) and same reactor conditions

As shown in Figure 3.8, a higher yield of olefins especially ethylene yields was obtained from HDO-TOFA cracking than naphtha or NGC cracking. The higher yield of ethylene from the cracking of HDO-TOFA is attributed to the high amount of *n*-alkanes in HDO-TOFA. It is suggested that during cracking, thermal decom-

position of long chain alkanes (e.g. *n*-octadecane and *n*-heptadecane) proceeds through a free radical mechanism, resulting in the production of ethylene molecules.[89-90] Higher amounts of pyrolysis gasoline obtained from NGC cracking , mainly because of the composition of NGC with significant amounts of cycloalkanes (naphthenes) and aromatics. Pyrolysis fuel oil, the heavy and low value product streams from a steam cracker, was obtained in higher yield from HDO-TOFA. It is expected that polycyclic aromatic (norabietatriene isomers) and non-aromatic (norabietane isomers) hydrocarbons present in HDO-TOFA undergo dehydrogenation reactions into aromatics under steam cracking conditions and produce naphthalene and poly aromatics (PAH). The absence of norabietane and norabietatriene isomers in naphtha and NGC resulted in a lower yield of PAH from cracking. Paper IV also discusses the effect of over-cracking during the steam cracking experiments. Apparently, over-cracking that is, cracking at too high temperatures enhanced the decomposition of ethylene molecules through secondary reactions and produced a low yield of ethylene. An optimal COT, which is in a range of 820–850$^{o}$C, was identified in this study with HDO-TOFA for better production of olefins in a steam cracker. Furthermore, in industrial perspectives, a desirable propylene to ethylene ratio (P/E-ratio) of 0.5 was achieved with HDO-TOFA at a COT of 820$^{o}$C. In comparison with other feedstocks investigated in this study, it was also identified that, the required heat input is lesser when cracking HDO-TOFA to obtain a desirable P/E ratio.

### 3.6.2    Co-cracking of HDO-TOFA/HDO-DTO with naphtha

Co-cracking of HDO-TOFA/HDO-DTO with naphtha produced slightly higher yields of light olefins in comparison with pure naphtha (Table 3 in Paper IV). However, HDO-TOFA/HDO-DTO mixtures with naphtha did not produce complete conversion during cracking process when compared with the cracking of pure HDO-TOFA. This incomplete conversion was apparent as residual feed components were present in the product stream, even at a COT of 850$^{o}$C. Furthermore, the influence of quantity of HDO-TOFA in co-cracking experiments was assessed by investigating the production of economically valuable products (ethylene, propylene, 1, 3 butadiene and ethane) as function of the amount of HDO-TOFA added to the naphtha. This assessment was performed by COILSIM 1D micro kinetic modeling.[91] These assessments result to demonstrate that co-cracking of naphtha and HDO-TOFA does not lead to significant positive or negative synergetic effects on the yields of base-chemicals from a steam cracker.

### 3.6.3    Steam cracking of HDO-CTO

Steam cracking of HDO-CTO under the investigated conditions in a bench-scale reactor produced more than 100 components as identified and quantified by online analysis. A summary of the obtained results is presented in Paper V (Table 1). As also observed in HDO-TOFA steam cracking, a higher yield of ethylene was ob-

served in the cracking of HDO-CTO in comparison with the cracking of naphtha and NGC under same reactor conditions. Among the tested COT's, a COT of 860oC was found to the most favorable temperature condition for producing a maximum yield of ethylene from HDO-CTO. The distribution of various product streams obtained from steam cracking of HDO-CTO, naphtha, NGC and HDO-CTO-naphtha blend at a COT of 860°C is shown in Figure 3.9.

Unlike other HDO-tall oil feedstocks, HDO-CTO comprises significant amount (42 wt%) of polycyclic hydrocarbons in addition to paraffins (n-alkanes and i-alkanes). Therefore, an additional investigation was carried out with the steam cracking of HDO-CTO in order to assess the thermal decomposition of polycyclic hydrocarbons (Paper V). As stated in Section 3.3.2 of this thesis, the thermal decomposition of polycyclic hydrocarbons leads to the formation of aromatics through intermediate saturated or unsaturated cyclic intermediates (ring-opened structures).
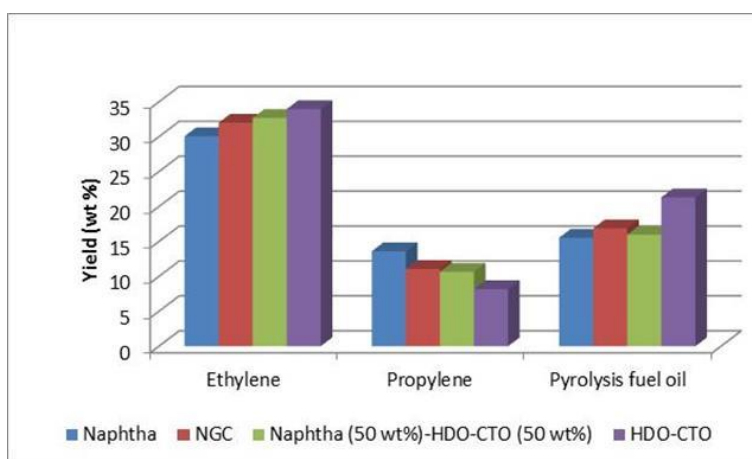


Figure 3.9. Product distribution obtained from steam cracking of naphtha, NGC, HDO-CTO-naphtha blend and HDO-CTO at 860°C (COT) and same reactor conditions.

# 4. Concluding remarks and future prospects

In this work, the catalytic hydrotreatment of tall oils on a sulfided NiMo catalyst and steam cracking of HDO-tall oils in conventional steam cracking set-up clearly validated the potential of tall oil as a renewable feedstock for the production of base-chemicals, especially olefins, as conceived in the thermo-chemical bio-refinery concept.

This work revealed the optimum operating conditions for the hydrotreatment of tall oils on a sulfided NiMo catalyst in order to produce a hydrocarbon feed for a steam cracking process with high degree of deoxygenation. Based on the achieved results, an industrial relevant space velocity in a range of $1–2 \, h^{-1}$ is suggested for hydrotreating of tall oil feeds such as TOFA and DTO. In the case of more complex tall oil feeds as CTO, a space velocity range as low as $0.5–1 \, h^{-1}$ is suggested for the complete deoxygenation. This work also demonstrates that at given partial pressure of 5 MPa of hydrogen, operating run temperatures below $300^{o}C$ would not be suitable with tall oil feeds for producing a paraffin-rich hydrocarbon fraction with high degree of deoxygenation. As it was evident from this study, an elevated temperature ($>400^{o}C$) and longer space time ($> WHSV \, 1h^{-1}$) will favor the formation of napthenoaromatics from tall oils during hydrotreating stage. These naphtenoaromatics will end up as low value products (pyrolysis fuel oil) in the subsequent steam cracking step. Therefore, an optimum temperature range, that is, $325–400^{o}C$, is suggested for the hydrotreating of tall oil feeds with the intention of obtaining maximum yield of hydrocarbons being precursors for olefin production in a succeeding HDO-tall oil steam cracking step.

The reactions of oxygenates were carefully assessed in this research study. The reactivity of fatty acids in tall oil follows the well-known deoxygenation routes which have been proposed for the hydrotreating of vegetable oils. Importantly, the trend obtained for the formation of *n*-octadecane and *n*-heptadecane in this study especially from TOFA feedstock is found to be in agreement with the behavior of sulfided NiMo catalyst reported in the literature for hydrotreating of vegetable oils. Fatty acids were converted in high extent in TOFA and DTO hydrotreating, whereas as in CTO hydrotreating, a decrease in reactivity of fatty acid was observed at low temperatures; which is attributed to the complex nature of CTO feedstock. Resin acids are proposed to deoxygenate mostly through decarboxylation/decarbonylation reactions in low temperature hydrotreating.

The catalyst stability test run carried out with DTO feedstock in this work proves that sulfided NiMo catalyst can be used for the hydrotreating of tall oils for a considerable period of time without any catalyst deactivation. This observation motivates the preferential use of sulfided catalysts over sulfur-free catalysts for the future hydrotreating studies of tall oils. Sulfur- free catalysts may offer better hydrogenation activity than sulfided catalysts, however, deactivate faster than the latter in the presence of sulfur impurities as well as coking.[92] Therefore, it is suggested that future catalyst developments for hydrotreating of tall oils should be based on tuning the surface properties of the sulfided NiMo catalyst so as to achieve better conversion of oxygenates to value-added hydrocarbons. A better control over undesirable reactions especially at elevated temperatures (> 400$^{o}$C) would also be needed. In this aspect of future catalyst development, identification and characterization of active sites responsible for dehydrogenation reactions would be desirable with the aid of in-situ characterization techniques.

Since the importance of employing renewable feedstocks for the production of base-chemicals through HDO and steam cracking is increasing, the investigated process conditions in this work can be applied to future industrial-scale hydrotreating experiments with tall oil feedstocks. The understanding on the product distribution from tall oil feedstocks as a function of hydrotreating temperature and space velocity is a major development achieved in this study, which in turn could be used in future research work to carefully tune the process conditions for producing desired products from tall oil through a HDO route. The reaction chemistry of oxygenates in tall oil at low hydrotreating temperatures was validated. However, a detailed know-how about the reactions of cyclic oxygenates in tall oil at elevated (>400$^{o}$C) hydrotreating temperatures is yet to achieve, therefore, it is suggested that future studies should be performed with model cyclic compounds in tall oil in order to assess the pathways for the formation of hydrocarbons (n-alkanes) through a ring-opening mechanism.

Nowadays, commercial steam crackers have a high flexibility regarding feedstock composition. Steam cracking of HDO-tall oil fractions carried out in this work emphasizes the possibility of using complex bio-based feedstocks for a steam cracking process. Furthermore, the knowledge acquired on the thermal decomposition of cyclic hydrocarbons in steam cracking can be essentially used for the optimal use of complex renewable feedstocks in a steam cracker.

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# Appendix A: Papers I–V

The author regrets for the following errors which occurred in the published articles.

Erratum:

1. Weight percentage (wt%) denoted in Table 2 in Paper I should be read as per centage yield (%)

2. The temperature range denoted in the caption of Figure 5 in Paper I should be read as 325–450$^o$C.

3. The temperature range denoted in the caption of Figure 6 in Paper I should be read as  325–450$^o$C.

# Appendix B: Residual fatty acid, resin acid and sterol compositions

## TOFA

| HDT temp (°C) | 325 | 350 | 400 | 450 | 325 | 350 | 400 | 450 | 325 | 350 | 400 | 450 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDT WHSV (h$^{-1}$) | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 |
| Residual composition (wt%) | | | | | | | | | | | | |
| Fatty acids | 7.1 | 5.8 | 1.6 | 0.5 | 11.8 | 4.9 | 2.1 | 1.1 | 11.7 | 4.7 | 2.5 | 0.8 |

## DTO

| HDT temp (°C) | 325 | 350 | 375 | 400 | 425 | 450 | 325 | 350 | 375 | 400 | 425 | 450 | 325 | 350 | 375 | 400 | 425 | 450 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDT WHSV (h$^{-1}$) | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 |
| Residual composition (wt%) | | | | | | | | | | | | | | | | | | |
| Fatty acids | 6.5 | 3.3 | 1.8 | 1.4 | 3.7 | 4.7 | 21.7 | 6.6 | 3.6 | 1.6 | 2.4 | 2.8 | 25.8 | 8.8 | 6.6 | 1.9 | 2.4 | 3.1 |
| Resin acids | 0.3 | 0.3 | 0 | 0.1 | 0.4 | 0.8 | 4.7 | 0.7 | 0.4 | 0.2 | 1.1 | 1.1 | 5.2 | 1.1 | 1 | 0.2 | 1.2 | 1 |

**CTO**

| HDT temp (°C) | 325 | 350 | 400 | 450 | 325 | 350 | 400 | 450 | 325 | 350 | 400 | 450 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HDT WHSV (h⁻¹) | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 3 |
| Residual composition (wt%) | | | | | | | | | | | | |
| Fatty acids | 8.7 | 5 | 3.3 | 5.2 | 22.7 | 7.4 | 3.5 | 5.4 | 24.2 | 11.7 | 7.2 | 7.8 |
| Resin acids | 3.3 | 1.8 | 1.1 | 2.6 | 13.9 | 3.4 | 1.8 | 2.3 | 14.2 | 7.6 | 2.2 | 3.8 |
| Sterols | 1.3 | 0.8 | 0.05 | 0.1 | 2 | 0.4 | 0.2 | 0.16 | 1.4 | 0.1 | 0.08 | 0.01 |

| Title | **Hydrotreating of tall oils on a sulfided NiMo catalyst for the production of base-chemicals in steam crackers** |
|---|---|
| Author(s) | Jinto Manjaly Anthonykutty |
| Abstract | Development of new and innovative products through efficient technologies is essential for the implementation of sustainable developments in highly competitive chemical industries. Based on this context, raw materials originating from biomass have been widely used for the production of chemicals and materials.<br><br>Steam cracking of bio-based or renewable feedstocks in a conventional steam cracking set-up is identified as a promising approach for the sustainable production of base-chemicals. In a two-step process for the production of base-chemicals, firstly, bio-derived feedstock is upgraded into a more suitable feedstock which comprises mainly paraffin range hydrocarbons with a lower oxygen content than the original feedstock; secondly, the upgraded feedstock is converted into base-chemicals by conventional steam cracking technology. This research work identifies wood-derived tall oil as a potential feedstock for the production of base-chemicals by catalytic upgrading and steam cracking methods.<br><br>The main aim of this work was to carry out the catalytic hydrotreating of tall oil feedstocks such as tall oil fatty acid (TOFA), distilled tall oil (DTO) and crude tall oil (CTO) on a commercial, sulfided NiMo catalyst at different process conditions. The effects of space time and process temperatures on the distribution of products from the hydrotreatment of different tall oil feeds were investigated. Hydrotreating chemistry of oxygenates in tall oil were assessed based on the achieved conversion of reactants and product distribution under the investigated conditions. Furthermore, the steam cracking of hydrodeoxygented tall oil (HDO-tall oil) feeds was carried out, and evaluation of the yield of olefins in comparison with conventional steam cracking feeds such as naphtha and natural gas condensate (NGC). |
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# Hydrotreating of tall oils on a sulfided NiMo catalyst for the production of base-chemicals in steam crackers

The technology development for the production of value-added chemicals from biomass through various thermo-chemical approaches is more demanding than ever. Renewable feedstocks appear as the best starting materials to achieve these developments in an industrial perspective. Tall oil, the by-product of kraft-pulping process is already well-known as a sustainable and low cost feedstock.

This research thesis validates the potential of tall oil as a renewable feedstock for the production of base-chemicals, especially olefins, as conceived in the thermo-chemical bio-refinery concept. The focus was on the use of hydrotreating and steam cracking technologies with different tall oil feedstocks. Particular advances were accomplished in terms of technology development for high yield of ethylene from a complex and challenging bio-feedstock, such as tall oil.

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