Hydrodeoxygenation of lignin-derived phenol compound isoeugenol over nickel- and cobalt-based catalysts

Master’s Thesis

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Abstract

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Carried out under supervision of Professor Dmitry Yu. Murzin and Associate Professor Päivi Mäki-Arvela at the Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, Åbo Akademi University, Turku/Åbo, Finland

Keywords

Isoeugenol, hydrodeoxygenation, catalyst characterization, cobalt, nickel, alumina, graphite, silica, batch reactor

Lignocellulose-derived bio-oils have become of high interest in recent research for producing renewable fuels, but face challenges due to their complex structure and high oxygen content. In this work, the catalytic hydrodeoxygenation (HDO) of isoeugenol over non-noble metal catalysts based on cobalt and nickel with hexadecane as a solvent was studied. The catalyst supports had low or no acidity (graphite, SBA-15 and SiO₂) as well as Lewis acidity for TiO₂ and Al₂O₃. A broad range of catalyst characterization methods was used for both spent and fresh catalysts to further explain molar concentrations of reactants and products, as well as selectivity and yields. All catalysts used in this work showed a complete conversion of isoeugenol as well as formation of the desired product propylcyclohexane at 300 °C and 30 bar, while no propylcyclohexane was formed at 200 °C and 30 bar on any of the catalysts. Cobalt-based catalysts with non-acidic supports and lower metal loading showed higher formation of propylcyclohexane than their counterparts on mildly acidic supports. Cobalt-based catalysts with high metal loading showed an enormous increase in gaseous products, especially methane, and therefore a low sum of the reactants and products in the liquid phase analysis (GCLPA) was obtained. Nickel-based catalysts with a high metal content and a high dispersion showed a higher formation of propylcyclohexane. Moreover, nickel-based catalysts showed a high GCLPA and formed less gaseous products than cobalt-based ones. Seventy-five percent conversion of isoeugenol was obtained in the trickle-bed reactor, revealing catalyst deactivation, compared to 100% conversion of isoeugenol in the batch reactor.
Preface

This thesis comprised catalyst characterization and investigation of reaction kinetics, therefore cooperation with many colleagues was needed. In particular, I would like to thank my supervisors Professor Dmitry Yu. Murzin and Associate Professor Päivi Mäki-Arvela for their patience, trust and guiding through this incredibly interesting, albeit difficult, work.

Other staff members at the Laboratory of Industrial Chemistry and Reaction Engineering are also humbly acknowledged for their positive attitude, especially Dr. Kari Eränen and Dr. Atte Aho for helping me with the equipment and chemicals in the experimental work. Also, I would like to express my appreciation to Professor Petriina Paturi and Dr. Markus Peurla at the University of Turku for helping me with catalyst characterization in their respective fields.

The research team at Neste is acknowledged. Especially I wish to thank Ms. Andrea Perez Nebreda, Dr. Marina Lindblad, Dr. Marja Tiitta and Mr. Sören Sundblom for their feedback and open-minded attitude during the work.

Tack, Kiitos, Thank you!

Christoffer
Abbreviations

n/d not defined
a.u. arbitrary unit
CHNS Carbon, Hydrogen, Nitrogen and Sulfur combustion analysis
FID Flame Ionization Detector
FTIR Fourier Transform Infrared Spectroscopy
GC-MS Gas Chromatography – Mass Spectrometry
GC-FID Gas Chromatography – Flame Ionization Detector
HDO Hydrodeoxygenation
ICP-MS Inductively Coupled Plasma – Mass Spectrometry
SEC Size-Exclusion Chromatography
SEM Scanning Electron Microscopy
TCD Thermal Conductivity Detector
TEM Transmission Electron Microscopy
TGA Thermogravimetric Analysis
TPR Temperature Programmed Reduction
XRD X-ray Powder Diffraction
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1. Introduction

Renewable resources supplied by solar power, geothermal energy, hydropower, wind power and especially biomass are expected to increase in the near future, due to the desired reduction of fossil fuels [1]. Of the above-mentioned renewable resources, biomass is still the only option for liquid fuel production and can also be used for chemical and energy production [2]. The importance of biofuels has not gone unnoticed, with the United States and the European Union both setting targets of 20% of transportation fuels to be obtained from biomass by 2030 and 2020, respectively [3, 4].

Biomass refers to materials produced in the natural life cycle. The most common of these materials are agricultural crops, wood, industrial waste, municipal waste and food waste. Biomass is seen as a renewable resource compared to fossil fuels, due to the differences in time of recovering carbon. Carbon originating from the natural life cycle has a maximum of ten years recycling period, whereas fossil carbon has a recycling period of thousands of years. Because of these differences in timespans, biomass utilization does not affect the carbon cycle [5, 6].

The main building blocks of biomass can be divided into four groups, mainly due to their molecular structures. These groups are carbohydrates (cellulose, hemicellulose and starch), lignin, lipids and proteins [7, 8]. Together, cellulose, hemicellulose and lignin form lignocellulosic biomass. Of these three, lignin has received the least attention in research for production of biofuels, even though it is regarded as the aromatic resource of the bio-based economy [3].
1.1 Structural units of lignocellulosic biomass

It is important to understand the chemical properties and compositions of the lignocellulosic biomass units at process conditions to further understand reaction patterns. The following sub-chapters present the compositions of the structural units of lignocellulosic biomass.

1.1.1 Cellulose

Cellulose is a polymer consisting of 500-10 000 glucose units linked together with beta 1,4-glycosidic bonds, shown in Figure 1.1. Special arrangement of these links, enabling intermolecular and intramolecular hydrogen bonds, makes cellulose insoluble in water. Glucose monomers can, however, be produced from cellulose by hydrolysis at near critical conditions for water. High temperatures in hydrothermal reactions are proven to increase the cellulose decomposition, which can be used for biofuel production [7,8].

![Figure 1.1 – The molecular structure of cellulose [9].](image-url)
1.1.2 Hemicellulose

Hemicelluloses are branched polymers, compared to the unbranched cellulose, with a polymersation degree between 500 and 3000. They consist of different sugars such as galactose, glucose, mannose and xylose connected to each other with beta 1,4-glycosidic bonds. The random structure of hemicellulose leads to a less crystalline and resistant form of polymer, consisting of different sugar monomers linked together, thus preventing formation of strong hydrogen bonds. Random structure of different hemicelluloses leads to easier decomposition and hydrolysis than for cellulose under hydrothermal conditions. [7, 10] The structure of hemicellulose can be seen in Figure 1.2.

Figure 1.2 – Structure of hemicellulose [10].
1.1.3 Lignin

Lignin is an aromatic polymer with high molecular weight being regarded as the building block of the lignocellulosic biomass, in which it takes 30% of the total weight. It has an amorphous yet complex structure and is believed to consist of three primary monomers, seen in Figure 1.3 [3]. The primary monomers are connected with C-C or ether bonds. The benzene ring of the primary monomers is stable under hydrothermal conditions and even though it degrades to methoxy phenols, its ring structure is not affected, making it a unique source of obtaining aromatic compounds [3, 7, 8]. A reaction pathway for lignin under hydrothermal conditions is presented in Figure 1.4.

**Figure 1.3** – Three main monomers of lignin, 1 – p-coumaryl alcohol, 2 – coniferyl alcohol and 3 – sinapyl alcohol [3].

**Figure 1.4** – Reaction steps in hydrothermal processes for lignin [11].
1.2 Bio-oils

Bio-oils are obtained by depolymerization and fragmentation of the lignocellulosic components mentioned in Section 1.1. High percentages of bio-oils can be obtained from wood (85 wt.%), while even higher weight percentages may be obtained from biological masses (95 wt.%) [12]. To be able to upgrade these organic mixtures to transportation fuels, hydrothermal liquefaction (HTL) and pyrolysis are considered to be the best option due to their simplicity and cost efficiency [13].

Even though bio-oils possess certain benefits with their insignificant sulfur content and small production of NOx gases compared to fossil oil, some common drawbacks exist [14]. Not only are bio-oils highly viscous, have poor volatility but they also have a high water as well as oxygen content of up to 40% and therefore low heating values compared to fossil fuels [15].

1.2.1 Model compounds of bio-oil

The complex structure of bio-oil has led to an increase in application of lower molecular weight model compounds in research. By using bio-oil model compounds one faces fewer analytical challenges and can gain an insight into the bio-oil as a whole [3]. Bio-oils from wood pyrolysis consist of water, oxygenates, sugars, furans, hydrocarbons and phenolics.

Of these, oxygenates can be divided into two groups: simple oxygenates and mixed oxygenates. Simple oxygenates consist of acids, alcohols, esters, ketones and aldehydes and are mostly originating from sugars, whereas mixed oxygenates, such as glycolaldehyde, originate from the lignocellulosic components cellulose and hemicellulose together with sugars and furans [13].

Anisoles, catechols, guaiacols, syringols and phenols all originate from lignin. In this work isoeugenol, which is a part of the guaiacol family, was selected as a model phenolic compound. Phenolics also produce oligomers and trimers visible in bio-oil [13].


1.3 Catalytic upgrading of lignocellulose-derived bio-oils

Catalytic hydrocracking is a well-known method of obtaining phenolic compounds from lignin, apart from HTL and fast pyrolysis mention in Section 1.2. Hydrocracking catalysts are frequently used in petroleum refineries to convert longer hydrocarbon chains into shorter and more valuable hydrocarbons by cracking the C-C bond [16]. The catalysts used in hydrocracking are mostly bifunctional, combining a metal with an active support for the hydrogenation reaction. The metals used are often nickel, cobalt or palladium on silica or zeolite supports [16]. By using similar hydrocracking catalysts as for petroleum based, the cleavage of the unstable C-C and β-O-4 bond are possible for lignin.

The resulting aromatic compounds can then be further converted to valuable aromatic products. Much research has been done in catalysis of phenolic compounds. According to previous studies, active metal sites are needed for hydrogenation and hydrolysis, whereas isomerization and dehydration happen on acid sites [17]. Even though acidity is required for hydrodeoxygenation, it is also known to promote coking, thereby leading to catalyst deactivation. This can be avoided by applying non-acidic supports such as carbon resulting in higher deoxygenation [17].
1.3.1 HDO of lignin-derived model compound eugenol

Eugenol is closely related to one of the main monomers found in lignin, coniferyl alcohol, and has been of great interest in recent research of lignin-derived model compounds. Non-catalytic and catalytic hydrodeoxygenation of eugenol under different temperatures and pressures has been tested in previous studies. A reaction network for catalytic hydrodeoxygenation of eugenol is presented in Figure 1.5, in which isomerization of eugenol (1) forms isoeugenol (2) while hydrogenation of eugenol (1) gives dihydroeugenol (3). Products with cleaved methoxy and hydroxyl groups are hydrogenolysed.

![Reaction scheme for catalytic hydrodeoxygenation of eugenol](image)

**Figure 1.5** – Reaction scheme for catalytic hydrodeoxygenation of eugenol (1 – eugenol, 2 – isoeugenol, 3 – dihydroeugenol, 4 – 2-methoxy-4-propylcyclohexanol, 5 – 3-propylmethoxycyclohexane, 6 – 4-methyl-2-methoxyphenol, 7 – 4-propylphenol, 8 – 4-propylcyclohexanol and 9 – propylcyclohexane) [18].

Deepa and Dhepe [18] did both catalytic and non-catalytic hydrodeoxygenation of eugenol experiments, with hexadecane as a solvent at 250 °C and 30 bar. They obtained no products in non-catalytic hydrodeoxygenation of eugenol after one hour, whereas different products were obtained in catalytic HDO using noble metal catalysts supported on carbon and mildly acidic Al₂O₃. The noble metals used were ruthenium, platinum and palladium, with the metal loading of 2 to 3.5 wt.%. All catalytic HDO experiments resulted in complete conversion of eugenol with dihydroeugenol as the most selective product. Yields of 20% and 10% propylcyclohexane were achieved on Pd/SiO₂-Al₂O₃ and Pd/Al₂O₃, respectively, with the yield of complete HDO related to the acidity of the supported Pd-catalysts [18].
Moreover, they also tested carbon-supported noble metal catalysts. Pt/C and Pd/C catalysts yielded in 89% and 95% of 1-hydroxy-2-methoxy-propylcyclohexane, whereas Ru/C mainly yielded in dihydroeugenol (77%).

Bjelic et al. [19] also tested ruthenium supported on carbon with a higher metal loading (4 wt.%). The authors performed four HDO experiments, lasting three hours at 275 °C and 40-70 bar. The products obtained were dihydroeugenol, propylcyclohexanol and propylcyclohexane. Interestingly, increasing yields of dihydroeugenol and propylcyclohexane could be observed between 40 and 60 bar, whereas a decrease in the yield of propylcyclohexane was observed at 70 bar. This indicates that high hydrogen pressure leads to a rapid hydrogenation and ineffective deoxygenation [19].

1.3.2 HDO of lignin-derived model compound isoeugenol

Catalytic hydrodeoxygenation of isoeugenol has become of great interest since Bomont et al. [20] obtained propylcyclohexane with selectivity of 89% at 200 °C and 30 bar using Pt/H-beta-300 catalyst and dodecane as a solvent. HDO of isoeugenol has been reported more recently, with many experiments performed with bimetallic catalysts. Alda-Onggar et al. [21] used alumina-supported iridium, platinum and rhenium catalysts, with dodecane as a solvent, under 30 bar pressure in the temperature range of 200 °C – 250 °C. The results are presented in Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Conversion of isoeugenol, %</th>
<th>Duration of reaction, temperature and pressure</th>
<th>Yield of main product (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ir/Al₂O₃</td>
<td>Dodecane</td>
<td>100</td>
<td>4 hours, 200 °C and 30 bar</td>
<td>Dihydroeugenol (69)</td>
<td>[21]</td>
</tr>
<tr>
<td>2</td>
<td>Re/Al₂O₃</td>
<td>Dodecane</td>
<td>100</td>
<td>4 hours, 200 °C and 30 bar</td>
<td>Dihydroeugenol (84)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Re/Al₂O₃</td>
<td>Dodecane</td>
<td>100</td>
<td>4 hours, 250 °C and 30 bar</td>
<td>Dihydroeugenol (50)</td>
<td></td>
</tr>
</tbody>
</table>
All catalyst presented in Table 1 showed a rapid conversion of isoeugenol at 250 °C and 30 bar, which is in line with previous research [19]. From the results demonstrated in Table 1, it is clear that higher temperatures and pressures favor formation of propylcyclohexane and lead to better hydrodeoxygenation in the case of bimetallic catalysts. The IrRe/Al₂O₃ catalyst shown in entries 6 – 12 was prepared with three different methods, therefore giving different results.

Since hydrodeoxygenation of isoeugenol over bimetallic catalysts forms propylcyclohexane it is of significant interest to find possible hydrodeoxygenation conditions to achieve similar or higher yields of propylcyclohexane using cheaper non-noble catalyst based on cobalt and nickel.
1.4 Scope

The objective of this work was to perform hydrodeoxygenation (HDO) of the lignin-derived phenolic compound isoeugenol in a batch reactor. The catalysts used in HDO reaction were cobalt- and nickel-based, all with different metal loadings, on different supports. Namely graphite, SBA-15, TiO$_2$, Al$_2$O$_3$ and SiO$_2$. Moreover, the following tasks were set to get an overall understanding of isoeugenol hydrodeoxygenation:

1. Catalyst characterization of both fresh and spent catalysts used in hydrodeoxygenation of isoeugenol to determine reduction temperatures and evaluate metal particle distribution, coke formation etc.
2. Determine the optimal reaction temperature for production of propylcyclohexane under 30 bar pressure.
3. Perform recyclability and repeatability test of catalysts at 300 °C and 30 bar.
4. Identify gaseous products formed in the reaction with GC-FID.
5. Perform hydrodeoxygenation experiments in a trickle-bed reactor with a commercial catalyst.
2. Experimental

Chapter two is divided into four subsections and will present chemicals and gases used, catalyst pretreatment and reactor setup (Section 2.1). Section 2.2 explains the catalyst characterization methods followed by details of analysis for both liquid and gas phases (Section 2.3). Finally, formulae and definitions are explained in Section 2.4.

2.1 Chemicals and catalysts

2.1.1 Chemicals and gases utilized

Commercial chemicals used in this work are listed in Table 2 along with their respective purity and manufacturer.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity (%)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoeugenol (cis + trans)</td>
<td>≥98</td>
<td>Fluka</td>
</tr>
<tr>
<td>Isoeugenol (cis + trans)</td>
<td>98</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Dodecane</td>
<td>≥99</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>≥99</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Dihydroeugenol</td>
<td>≥99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>2-propanol</td>
<td>≥99.8</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Benzene</td>
<td>≥99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Hexane</td>
<td>≥99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>99</td>
<td>Lab Scan</td>
</tr>
<tr>
<td>Heptane</td>
<td>≥99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>2-hexanol</td>
<td>99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Octane</td>
<td>≥99</td>
<td>Fluka</td>
</tr>
<tr>
<td>Methoxycyclohexane</td>
<td>99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Propylcyclohexane</td>
<td>99</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>≥99.9</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>4-propylphenol</td>
<td>99</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1-decanol</td>
<td>97</td>
<td>Merck-Schuchardt</td>
</tr>
</tbody>
</table>
The commercial calibration gas mixtures that were used to identify gaseous products in HDO of isoeugenol can be seen in Table 3 along with their respective volume percentages.

**Table 3 – Calibration gas mixtures**

<table>
<thead>
<tr>
<th>Gas Mixture</th>
<th>Content, vol-%</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1.020</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.099</td>
<td>AGA</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.972</td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>The rest</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>1.000</td>
<td>AGA</td>
</tr>
<tr>
<td>Propane</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Iso-Butane</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>N-Butane</td>
<td>1.000</td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 Catalyst preparation methods

Seven catalysts applied in this work were supplied from different sources. 10 wt.% Co/SBA-15, 15 wt.% Co/TiO₂ and 15 wt.% Co/Al₂O₃ catalysts were prepared by Dr. David Kubicka from University of Chemistry and Technology, Prague, Czech Republic, whereas 11 wt.% Co/SiO₂ and 11 wt.% Ni/SiO₂ catalysts were prepared by Dr. Irina Simakova from Boreskov Institute of Catalysis (BIC), Novosibirsk, Russia. 20 wt.% Ni/graphite was synthesized by the late Dr. N. Kul’kova from Karpov Institute of Physical Chemistry, Moscow, Russia. Commercial 10 wt.% Ni/SiO₂ pellets was procured from Riogen. The preparation methods for these catalysts are not available.

2.1.2.1 Preparation of cobalt catalyst supported on Al₂O₃, SBA-15 and TiO₂

SBA-15, TiO₂ and Al₂O₃ were synthesized applying hexahydrate of cobalt nitrate as a precursor. The amount of Co(NO₃)₂·6H₂O was calculated based on the target cobalt concentration and then dissolved in 100 ml of distilled water, whereafter it was transferred to a round flask containing the prepared support. The resulting mixture was then stirred for 60 minutes at 25 °C using a horizontal shaker, after which the surplus water was evaporated under vacuum conditions using a rotator-evaporator. The wet support containing cobalt nitrate was then dried at 100 °C for two hours.
To decompose the precursor, the dried samples were heated to 150 °C to initiate a slow decomposition of the nitrate. The temperature was increased to 200 °C with a temperature ramp of 10 °C/h, whereafter the temperature was held at 200 °C for two hours. The samples were then calcined at 400 °C with a temperature ramp of 0.5 °C/min.

2.1.2.2 Preparation of cobalt and nickel catalyst supported on SiO₂

After calcination of SiO₂ at 550 °C for three hours, impregnation was performed with aqueous solutions of Ni(NO₃)₂·6H₂O or Co(NO₃)₂·6H₂O. The impregnated samples were then dried at 106 – 107 °C for 12 hours, being thereafter calcined in air at 550 °C for three hours. By measuring the pH value of outcoming gases, by a litmus indicator, decomposition of nickel and cobalt nitrates was monitored.

2.1.3 Reduction of catalysts

All catalysts analyzed in this work were reduced ex-situ prior to HDO of isoeugenol. The only catalyst reduced both ex-situ and in-situ was the commercial 10 wt.% Co/SiO₂ pellets, which was crushed to < 93 μm prior to reduction ex-situ and reduced as whole pellets in-situ.

The amount of catalyst to be reduced ex-situ was 50 mg. The catalyst was first flushed with argon for 10 minutes, hereafter the gas flow was changed to hydrogen and the temperature ramp was set. After the reduction program had been accomplished and the catalyst was cooled to 50 °C, the catalyst was again flushed with argon for 10 minutes. After that 10 ml of hexadecane was added and kept overnight. Reduction of 1 g of the commercial 10 wt.% Co/SiO₂ catalyst, which had a shape of pellets, under hydrogen, thereafter the catalyst was kept inside the trickle-bed reactor, at 1 bar, overnight.

Since the catalysts used in HDO of isoeugenol have different metals and metal loadings, their reduction programs slightly differed from each other. The reduction programs used prior to HDO of isoeugenol can be seen in Table 4.
Table 4 – Ex-situ and in-situ reduction programs for catalysts used in this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>T/°C</th>
<th>Ramp 1 °C/min</th>
<th>Hold 1 min</th>
<th>T/°C</th>
<th>Ramp 2 °C/min</th>
<th>Hold 2 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 wt.% Ni/Graphite</td>
<td>350</td>
<td>10</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10 wt.% Co/SBA-15</td>
<td>450</td>
<td>10</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15 wt.% Co/TiO₂</td>
<td>450</td>
<td>10</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>15 wt.% Co/Al₂O₃</td>
<td>450</td>
<td>10</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5A</td>
<td>11 wt.% Co/SiO₂</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>415</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>5B</td>
<td>11 wt.% Co/SiO₂</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>550</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>11 wt.% Ni/SiO₂</td>
<td>100</td>
<td>2</td>
<td>1</td>
<td>415</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>10 wt.% Co/SiO₂</td>
<td>415</td>
<td>5</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**IN-SITU**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>T/°C</th>
<th>Ramp</th>
<th>Hold</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>10 wt.% Co/SiO₂</td>
<td>415</td>
<td>5</td>
<td>120</td>
</tr>
</tbody>
</table>

2.1.4 Regeneration of catalyst

A reproducibility test of 11 wt.% Co/SiO₂ catalyst was performed by calcination of the spent catalyst in HDO of isoeugenol at 300 °C and 30 bar. Prior to calcination, the spent catalyst was washed with acetone and dried in air. The calcination program for the spent 11 wt.% Co/SiO₂ catalyst is shown in Table 5.

Table 5 – Calcination program for 11 wt.% Co/SiO₂ catalyst

<table>
<thead>
<tr>
<th>Ramp °C/min</th>
<th>T/°C</th>
<th>Hold min</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>415</td>
<td>120</td>
</tr>
</tbody>
</table>
2.1.5 Reactor setup

Hydrodeoxygenation experiments of isoeugenol were carried out in both batch as well as a trickle bed reactors. Schemes of the reactor systems are shown in Appendix A (Figures A.1 – A.4).

2.1.5.1 Batch reactor

The HDO experiments were carried out in a 300 ml batch reactor system (PARR Instruments). The reactor was equipped with a mechanical stirrer and a stirring speed of 900 rpm was used during the experiments. The samples were obtained through a sampling line, always cleaning the line before the samples were taken. A heating mantle was put on the reactor and the temperature was increased with 10 °C/min, using a temperature control system, until the desired temperature was reached.

For all HDO experiments, 50 mg of the reduced catalyst was added to the reactor system together with 50 ml of hexadecane and 100 mg of the reactant isoeugenol. One liquid sample was taken prior to the reaction and eight liquid samples during the four-hour experiment, all analyzed by GC. After the experiment was finished, and the reactor was cooled down to 40 °C, a gas sample was taken and analyzed in GC-FID.

2.1.5.2 Trickle-bed reactor

The commercial 10 wt.% Co/SiO₂ pellet catalyst was used for HDO of isoeugenol in a three-phase reactor system, to get information of time-on-stream behavior as well as on catalyst deactivation. The three-phase reactor system was equipped with six trickle-bed reactors, each with the length of 120 mm and an inner diameter of 12.5 mm, a pressure pump as well as pressure-, gas- and temperature regulators. The pressure and temperature were increased to 30 bar and 300 °C, using a control system. The samples were obtained through a sampling line, with six samples taken during the four-hour experiment.

1 g of catalyst and 18 g of quartz sand was added to the trickle-bed reactors in this HDO of isoeugenol experiment. A reaction mixture consisting of 100 ml 1-decanol and 200 mg isoeugenol was pumped with a flowrate of 0.1 ml/min together with 50 ml/min hydrogen flow. Since the liquid products obtained from the HDO experiment were in two phases due to hydrogenolysis of the solvent 1-decanol, they had to be separated and analyzed by GC.
2.2 Catalyst characterization methods

2.2.1 Liquid nitrogen physisorption

Liquid nitrogen physisorption was applied to determine the specific surface areas (SSA) of the catalysts, using the Brunauer – Emmett – Teller (BET) theory [22]. The measurements were done with a Carlo Erba Soptomatic 1900 apparatus by placing 0.2 g of catalyst in an already outgassed burette, with a known weight. The burette, with the catalyst inside, was then outgassed for three hours at 150 °C, thereafter the outgassed burette was placed in liquid nitrogen.

2.2.2 Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to measure Brønsted and Lewis acidity of the solid catalyst surfaces with pyridine as a probe molecule [23]. The equipment used to measure Brønsted and Lewis acidity was an infrared spectroscopy (ATI Mattson FTIR). The procedure was done by pressing a thin wafer of the catalyst with as mass of 10 – 30 mg that then was put into the FTIR cell. The cell was removed and the temperature was increased to 450 °C and held for one hour, followed by a decrease in temperature to 100 °C and recording of the background spectra of the sample. At the temperature of 100 °C pyridine was adsorbed on the sample for 30 minutes followed by desorption at 250, 350 and 450 °C for one hour. The spectra of the samples were recorded between all three temperature ramps. Scanning was performed under vacuum conditions at 100 °C and spectral bands at 1545 cm⁻¹ and 1450 cm⁻¹ were used to identify the Brønsted and Lewis acid sites. The amount of the acid sites was calculated according to the Emeis constants [24].

2.2.3 Temperature Programmed Reduction (TPR)

Temperature programmed reduction of hydrogen (H₂-TPR) was used to find the most suitable reduction conditions for the catalysts used in HDO of isoeugenol [25]. The analysis was done by gradually heating the sample at the desired rate and flushed it with an inert gas, argon in this case, followed by addition of hydrogen. The composition of the gas mixture used for the analysis in this work consisted of 5 vol.% hydrogen and 95 vol. % argon. When reduction takes place, hydrogen is consumed, which is recorded by a thermal conductivity detector (TCD). The instrument used for the H₂-TPR analysis was Micrometrics AutoChem 2910. For all experiments 0.100 g of the catalyst was used and the reduction program itself is presented in Appendix B.
2.2.4 Transmission Electron Microscopy (TEM)

A transmission electron microscope (JEM-1400) located in the Laboratory of Electron Microscopy, University of Turku, was used to analyze the metal particle distribution, metal particle size and structure of the fresh and the spent catalysts.

2.2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is used to follow the weight change of a catalyst by increasing the temperature in either air or nitrogen atmosphere [26]. TGA was done for both the fresh and the spent samples using a SDT Q600 V20.9 Build 20 instrument. The analysis was done in both nitrogen and air and the samples were heated to 1000 °C with a temperature ramp of 10 °C/min and a gas flowrate of 100 ml/min.

2.2.6 CHNS

CHNS analysis was applied to establish content of carbon, hydrogen, nitrogen and sulfur in the solid catalysts [27]. CHNS analysis was only done for the spent samples to identify the carbon content as well as hydrogen-to-carbon mole ratio using a Thermo Fischer Scientific Flash 2000 Combustion CHNS/O apparatus.

2.2.7 X-Ray Diffraction (XRD)

X-ray diffraction measurements were done at University of Turku using a Philips Empyrean diffractometer, Cu Kα radiation, Bragg-Brentano HD incident beam monochromator and a PiXcel 3D-Medipix 3 detector. The samples were first ground to powder using a zero background silicon sample holder. Every measurement scanned the 2θ range from 5 to 100 (°) with a stepsize of 0.0135 (°) and a 40 second integration time per step. Different phases were identified using the HighScore program and Crystallography Open Database (COD). The particle sizes were determined using the Maud Rietveld refinement program [28].

2.2.8 Size-Exclusion Chromatography (SEC)

SEC analysis was performed to investigate oligomers and polymers formation on the spent catalysts surface [29]. 20 mg of spent catalysts was added to a round flask together with 20 ml of the solvent heptane and a condenser. The flask was placed in an oil bath and heated to 98 °C, thereafter extraction occurred for four hours with a stirring rate of 400 rpm. The flowrate of the inert gas, consisting of 5 % Ar in 95 % N₂, was set to 100 ml/min. The solution obtained after the four-hour extraction was then kept at
40 °C until complete evaporation of heptane. The resulting residue was then dissolved in 10 ml of tetrahydrofuran, thereafter it was filtered for analysis. The resulting concentration of the residue was 2 mg/ml.

The apparatus used for SEC analysis was a SEC-HPLC equipped with two columns, a Guard column with the dimensions of 50 mm x 7.8 mm and a Jordi Gel DVB 500A column with the dimensions of 300 mm x 7.8 mm.

2.2.9 Scanning Electron Microscopy (SEM)

An apparatus consisting of a Zeiss Leo Gemini 1530 microscope together with detectors for backscattered and secondary electrons was used to identify the morphology of the catalysts [30].

2.2.10 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Liquid samples obtained at the end of HDO of isoeugenol were analyzed with ICP-MS at Neste, Kilpilahti to check if leaching of the catalyst occurred during the experiments [31].

2.3 Analysis of reaction mixture

The liquid phase of all HDO of isoeugenol experiments was analyzed with GC while the gas phase was analyzed with GC-FID.

2.3.1 Analysis of products in the liquid phase

For every HDO of isoeugenol experiment eight liquid samples were obtained at different times and analyzed with gas chromatography (GC). The capillary column used for GC analysis was a DB-1, Agilent 122-103e with the following dimensions: 30 m x 250 μm x 0.5 μm. The temperature program used for GC analysis can be seen in Table 6 and the retention times of the reactants and products are shown in Table 7.

<table>
<thead>
<tr>
<th>Ramp °C/min</th>
<th>T/°C</th>
<th>Hold min</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>135</td>
<td>15</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6 – GC program for liquid phase samples
Table 7 – Retention times of compounds present in the liquid phase in HDO of isoeugenol

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>1.4</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>2.1</td>
</tr>
<tr>
<td>Heptane</td>
<td>3.1</td>
</tr>
<tr>
<td>Octane</td>
<td>5.3</td>
</tr>
<tr>
<td>Nonane</td>
<td>9.2</td>
</tr>
<tr>
<td>Propylcyclohexane</td>
<td>10.5</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>11.2</td>
</tr>
<tr>
<td>Decane</td>
<td>14.2</td>
</tr>
<tr>
<td>Undecane</td>
<td>19.4</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>20.9</td>
</tr>
<tr>
<td>3 and 4 propylcyclohexene</td>
<td>21.0</td>
</tr>
<tr>
<td>Propylcyclohexanone</td>
<td>21.2</td>
</tr>
<tr>
<td>Dodecane</td>
<td>24.5</td>
</tr>
<tr>
<td>Tridecane</td>
<td>29.4</td>
</tr>
<tr>
<td>Dihydroeugenol</td>
<td>31.0</td>
</tr>
<tr>
<td>Trans-isoeugenol</td>
<td>32.1</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>32.6</td>
</tr>
<tr>
<td>Isoeugenol</td>
<td>33.1</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>34.5</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>35.8</td>
</tr>
</tbody>
</table>
2.3.2 Analysis of products in the gas phase

One gas sample of 0.5 ml was taken at 40 °C in the end of all HDO of isoeugenol experiments, using an Agilent 6890N-GC apparatus, with a GS-Q capillary column of the following dimensions: 30 m x 530 μm x 40 μm. The detection was done by a Flame Ionization Detector (FID) at 300 °C to identify light hydrocarbon gases and a Thermal Conductivity Detector (TCD) at 250 °C to identify gases containing oxygen, such as carbon dioxide. The temperature program used can be seen in Table 8 while the identified gas compounds and their respective retention times are shown in Table 9.

Table 8 – GC-FID program for gas phase samples

<table>
<thead>
<tr>
<th>Ramp °C/min</th>
<th>Hold T/°C</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>230</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 9 – Retention times for gas phase compounds present in gas samples in HDO of isoeugenol

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (FID)</td>
<td>5.1</td>
</tr>
<tr>
<td>CO₂ (TCD)</td>
<td>6.8</td>
</tr>
<tr>
<td>Ethylene (FID)</td>
<td>9.5</td>
</tr>
<tr>
<td>Ethane (FID)</td>
<td>10.9</td>
</tr>
<tr>
<td>Propane (FID)</td>
<td>15.9</td>
</tr>
<tr>
<td>N-Butane (FID)</td>
<td>18.7</td>
</tr>
<tr>
<td>Iso-Butane (FID)</td>
<td>19.5</td>
</tr>
</tbody>
</table>
2.4 Formulae and definitions

To follow the conversion of the reactant during HDO of isoeugenol, the following formula was used:

\[ X_t (\%) = \frac{C_0 - C_t}{C_0} \times 100 \%, \]  

(1)

where \( X_t \) is conversion at time \( t \), \( C_0 \) initial molar concentration (mol/l) of isoeugenol and \( C_t \) molar concentration of isoeugenol at time \( t \).

The sum of liquid phase compounds visible in GC was calculated with the following formula:

\[ GCLPA (\%) = \frac{GCLPA_t}{GCLPA_0} \times 100 \%, \]  

(2)

with \( GCLPA_t \) being the sum of reactants and products obtained in GC at time \( t \) and \( GCLPA_0 \) the sum of reactants and products at time 0. The formula excludes gas phase products and compounds adsorbed on the catalyst surface, meaning that the GCLPA does not reflect the full mass balance of the reaction.

Selectivity of products obtained during the reaction was calculated with the following formula:

\[ S_{a,t} (\%) = \frac{C_{a,t}}{\Sigma C_{a+b+c+...+w,t}} \times 100 \%, \]  

(3)

where \( S_{a,t} \) is selectivity of the product \( a \) at time \( t \), \( C_{a,t} \) molar concentration (mol/l) of product \( a \) at time \( t \) and \( \Sigma C_{a+b+c+...+w,t} \) molar concentration (mol/l) sum of all products at time \( t \).

Hydrodeoxygenation degree, also given in percentages, was calculated to follow up the oxygen content in the products of isoeugenol HDO. The formula used is shown below:

\[ HDO (\%) = \frac{n_a^0 - n_a^t - \Sigma n_b \times m_o}{n_a^0 - n_a^t} \times 100 \%, \]  

(4)

where \( n_a^0 \) is the initial amount of moles of isoeugenol, \( n_a^t \) moles of isoeugenol at time \( t \), \( n_b \) moles of product \( b \) in the liquid phase and \( m_o \) amount of oxygen atoms in product \( b \).
3. Results and Discussion

Chapter three is divided into two parts with catalyst characterization results explained in Section 3.1 followed by HDO of isoeugenol results in Section 3.2.

3.1 Catalyst characterization results

Numerous characterization methods were used for the reduced (fresh) as well as the spent catalysts in HDO of isoeugenol, mainly to gain an improved understanding of catalyst properties to further explain kinetic data and product distribution described in Section 3.2. Non-reduced catalysts were analyzed using liquid nitrogen physisorption, FTIR, TPR whereas the reduced catalysts were analyzed with SEM, TEM, TGA and XRD. The spent catalysts were analyzed with TEM, TGA, CHNS, SEC and XRD. The liquid samples were analyzed with ICP-MS at Neste, Kilpilahti. Sample 7, in Table 10, was the only sample analyzed with SEM, with the results shown in Appendix C.

3.1.1 Liquid nitrogen physisorption

The measured specific surface areas (SSA) of the catalysts used in this work are presented in Table 10 together with their respective pore volumes (V_p).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>SSA (m²/g)</th>
<th>V_p (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 wt.% Ni/graphite</td>
<td>204</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>10 wt.% Co/SBA-15</td>
<td>471</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>15 wt.% Co/TiO₂</td>
<td>94</td>
<td>0.19</td>
</tr>
<tr>
<td>4</td>
<td>15 wt.% Co/Al₂O₃</td>
<td>203</td>
<td>0.55</td>
</tr>
<tr>
<td>5</td>
<td>11 wt.% Co/SiO₂</td>
<td>220</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>11 wt.% Ni/SiO₂</td>
<td>244</td>
<td>0.51</td>
</tr>
<tr>
<td>7</td>
<td>10 wt.% Co/SiO₂ pellets</td>
<td>n/d</td>
<td>n/d</td>
</tr>
</tbody>
</table>

The measured specific surface areas differ from 94-471 m²/g for the catalysts used in HDO of isoeugenol. The highest SSA area belongs to Sample 2 and is in line with previous measurements [32]. It should be mentioned that the original surface area of the support, SiO₂, used to prepare Samples 5 and
6 was 378 m$^2$/g. Furthermore, the SSA is affected by the preparation method and impregnation of Co and Ni decreases the specific surface area [33].

### 3.1.2 Fourier Transform Infrared (FTIR) Spectroscopy

Samples 2 – 6 were analyzed with the procedure mentioned in Section 2.2.2, whereas the pH of Sample 1 was measured to be 7. No acidity was measured for Sample 7. The measured Brønsted and Lewis acidity of Samples 1 – 7 are presented in Table 11.

#### Table 11 – Quantification of Brønsted and Lewis acid sites for Samples 1-7

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>Brønsted acid sites (μmol/g)</th>
<th>Lewis acid sites (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>250 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td>1</td>
<td>20 wt.% Ni/Graphite</td>
<td>n/d</td>
<td>n/d</td>
</tr>
<tr>
<td>2</td>
<td>10 wt.% Co/SBA-15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>15 wt.% Co/TiO$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>15 wt.% Co/Al$_2$O$_3$</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>11 wt.% Co/SiO$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>11 wt.% Ni/SiO$_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>10 wt.% Co/SiO$_2$</td>
<td>n/d</td>
<td>n/d</td>
</tr>
</tbody>
</table>

The FTIR results show that only Sample 4 has weak Brønsted acid sites (3 μmol/g). From earlier studies it is known that the support of Sample 4, alumina, has at least two types of Lewis acid sites that differ in acidity. This is also the case in this study, as Sample 4 has both weak and medium Lewis acid sites (25 and 3 μmol/g). [34] The other samples showing weak Lewis acid sites are Sample 2 and 3, with Sample 3 showing most acid sites of all samples (123 μmol/g). Samples 5 and 6 did not exhibit any adsorption of pyridine at the bands of 1545 cm$^{-1}$ and 1450 cm$^{-1}$; however, some Lewis acid sites could be found at different spectral bands [35].

### 3.1.3 Temperature Programmed Reduction

H$_2$-TPR analysis was done for Samples 2, 4, 5A, 5B, 6 and 7 by using the same reduction programs as presented in Section 2.1.3, Table 4. The H$_2$-TPR results are presented in Figures 3.1 – 3.6, where the reduction program (in black) and the hydrogen consumption (in blue) are visible.
Figure 3.1 – H$_2$-TPR spectra of 10 wt.% Co/SBA-15 (Sample 2).

Figure 3.2 – H$_2$-TPR spectra of 15 wt.% Co/Al$_2$O$_3$ (Sample 4).

Figure 3.1 shows a small hydrogen consumption peak at approximately 20 minutes, corresponding to a temperature of 150 °C, which most likely reflects the beginning of the first reduction step of Co$_3$O$_4$ to CoO. This step is followed by reduction of CoO to metallic Co at 400 °C [36]. Figure 3.2, in contrast, shows a large, narrow peak at 40 minutes corresponding to a temperature of 400 °C. This is most likely due to reduction of Co$_3$O$_4$ to CoO and CoO to metallic Co happening simultaneously, due to strong interactions with the support and cobalt oxides [37]. Figure 3.1 has a relative surface area of 1.6 compared to Figure 3.2.
Figure 3.3 – H₂-TPR spectra of 11 wt.% Co/SiO₂ at 415 °C (Sample 5A).

Figure 3.4 – H₂-TPR spectra of 11 wt.% Co/SiO₂ at 550 °C (Sample 5B).

Figure 3.3 and 3.4 show the same catalyst reduced at different temperatures. The reduction of Sample 5A shows a broad peak split in two parts in the interval of 350 °C – 415 °C. The broadness can be explained by the slow reduction step of CoO due to weak interactions between the support and CoO. By comparison, Figure 3.4 shows a remarkably small hydrogen consumption for Sample 5B. This is most likely due to unreduced CoO because of weak interactions between the support and CoO [38].
Figure 3.5 – $\text{H}_2$-TPR spectra of 11 wt.% Ni/SiO$_2$ (Sample 6).

Figure 3.5 clearly shows a peak at approximately 350 °C, corresponding to reduction of NiO to Ni$^0$, in agreement with previous studies [39]. The integrated area was 52.0.

Figure 3.6 – $\text{H}_2$-TPR spectra of 10 wt.% Co/SiO$_2$ (Sample 7).

The narrow reduction peak occurring at 220 °C for Sample 7 is assigned to reduction of Co$_3$O$_4$ to CoO, whereas reduction of CoO to Co$^0$ occurs at 415 °C [38].
From the \( H_2 \)-TPR graphs obtained in this work and according to the literature, it can be concluded that \( \text{Co}_3\text{O}_4 \) reduction to \( \text{Co}^0 \) proceeds in the following two steps [40]:

1. \[ \text{Co}_3\text{O}_4 + H_2 \rightarrow 3\text{CoO} + H_2O \]

2. \[ 3\text{CoO} + 3H_2 \rightarrow 3\text{Co} + 3H_2O \]

Furthermore, it should be mentioned that the reducibility of metal oxides depends on the interaction between the metal oxide and the support, whereas the interaction depends on the preparation procedure and the particle size. Small pore size catalysts tend to shift the reduction peaks to higher temperatures compared to a catalyst with a larger pore size being more difficult to be reduced. As for the interactions between the support and \( \text{CoO} \), weaker interactions are considered to lead to broader reduction peaks, which was especially prominent for Sample 5A (Figure 3.3).

Moreover, the amount of hydrogen consumed during TPR decreases as follows: 11 wt.% \( \text{Co/SiO}_2 \) > 11 wt.% \( \text{Ni/SiO}_2 \) > 10 wt.% \( \text{Co/SBA-15} \) > 15 wt.% \( \text{Co/Al}_2\text{O}_3 \), which means that less cobalt on \( \text{Al}_2\text{O}_3 \) is reduced due to strong interaction with support and the high reduction temperature. The particle size distribution is also related to the hydrogen consumption, with larger particles for 11 wt.% \( \text{Co/SiO}_2 \) and 11 wt.% \( \text{Ni/SiO}_2 \) showing relative surface areas of 5.4 and 4.7 compared to 15 wt.% \( \text{Co/Al}_2\text{O}_3 \). In contrast, hydrogen consumption for 10 wt.% \( \text{Co/SBA-15} \) and for 11 wt.% \( \text{Co/SiO}_2 \) starts already at a relatively low temperature. These values are not correlated with metal dispersion, since in TEM, nickel and cobalt oxides are not visible.
3.1.4 Transmission Electron Microscopy

TEM images and histograms are shown for Samples 1, 2, 3, 4, 5A, 5B and 6, in Figures 3.7 – 3.12. Additional TEM images are presented in Appendix D. TEM results of Sample 1, both fresh (A) and spent (B), as well as their respective histograms are given in Figure 3.7 in 200 nm scale.

Figure 3.7 – TEM images and histograms of the fresh (A) and the spent (B) 20 wt.% Ni/Graphite (Sample 1) in HDO of isoeugenol.

Large clusters can be seen in Figure 3.7 (A), reading values above 50 nm in diameter. The average metal particle size diameter of the fresh Sample 1 (A) was calculated to be 6.1 nm as is shown in the histogram. Nevertheless, some particles are above 15 nm in diameter, indicating a considerable spread in the metal particle size distribution. The histogram of the spent Sample 1 (B) shows a minor increase in average metal particle diameter (7.8 nm) after HDO of isoeugenol; indicating that no sintering occurs during the reaction.
Figure 3.8 – TEM images and histograms of the fresh (A) and the spent (B) 10 wt.% Co/SBA-15 (Sample 2) in HDO of isoeugenol.

The porous structure of Sample 2 is visible as clear channels in Figure 3.8 in 200 nm scale. The channels have a diameter of 10 nm, which is comparable to the literature [41]. Large metal particles can be seen, not only for the fresh Sample 2 (A), but also for the spent Sample 2 (B), varying from 50 to above 150 nm. The average metal particle size diameter of the fresh Sample 2 (A) is low, being 3.7 nm. A slight increase of the metal particle diameter occurred in HDO of isoeugenol (4.6 nm), as can be seen from the histogram of Sample 2 (B).
Figure 3.9 – TEM images and histograms of the fresh (A) and the spent (B) 15 wt.% Co/TiO$_2$ (Sample 3) in HDO of isoeugenol.

The histograms of Figure 3.9 show a narrow spread in the average metal particle size, ranging from 1 to 8 nm for the fresh Sample 3 (A). The average metal particle size diameter increased to 3.1 nm for the spent Sample 3 (B) compared to 2.6 nm for the fresh Sample 3 (A).
In Figure 3.10 (A) larger agglomerates can be seen, appearing as smaller particles close to each other. The support is visible as branches in both fresh (A) and spent (B) Sample 4, with darkened branches visible for the spent Sample 4 (B). The histograms of Sample 4 show a minimal increase in the average metal particle diameter, indicating absence or negligible sintering. The reason for this can be strong interactions between cobalt and the support [42].
Figure 3.11 – TEM images and histograms of the fresh (A) and the spent (B) 11 wt.% Co/SiO$_2$ (Sample 5A), reduced at 415 °C, in HDO of isoeugenol.

The porous structure of the support is clearly visible for Sample 5A in Figure 3.11, with metal particles located close to each other in larger agglomerates. The metal particle size varies from smaller particles of 3 nm to larger ones of the size 100 nm, as can be seen in Figure 3.11 (A). The TEM image of the spent Sample 5A (B) shows a large dark area in the bottom left corner that can be identified as coke.
Figure 3.12 – TEM images and histograms of the fresh (A) and the spent (B) 11 wt.% Co/SiO₂ (Sample 5B), reduced at 550 °C, in HDO of isoeugenol.

Fresh Sample 5B (A) shows five larger groups of smaller particles, whereas the spent Sample 5B (B) displays a large dark area as coke formation. The spread of the average metal particle diameter varies significantly, ranging from just 2 nm up to 50 nm. Furthermore, some sintering occurs for Sample 5B (B) in HDO of isoeugenol due to weak interactions between the metal and the support giving an increase in the particle size from 5.9 nm (A) to 7.8 nm (B) [43].
Figure 3.13 – TEM images and histograms of the fresh (A) and the spent (B) 11 wt.% Ni/SiO₂ (Sample 6) in HDO of isoeugenol.

TEM images of the fresh and the spent Sample 6 (Figure 3.13 A & B), both in 500 nm scale, show a good spread in the metal particle location on the support. The spread in the size of the metal particles however, ranges from 10 to 50 nm, with the average metal particle diameter being 9.7 nm for the fresh catalyst (A) and 10.1 nm for the spent one (B).
Furthermore, the metal dispersion of the catalyst was calculated for the fresh Samples 1, 2, 3, 4, 5A, 5B and 6. The results are shown in Table 12 along with the average metal particle diameter for the fresh and the spent samples. The dispersion of the fresh Samples was calculated using the following formula:

\[
\frac{1 \text{ nm}}{\text{Avg. d (nm)}} \times 100 = D(\%) \tag{5}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>Avg. diameter (nm)</th>
<th>TEM Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fresh</td>
<td>Spent</td>
</tr>
<tr>
<td>1</td>
<td>20 wt.% Ni/graphite</td>
<td>6.1</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>10 wt.% Co/SBA-15</td>
<td>3.7</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>15 wt.% Co/TiO₂</td>
<td>2.8</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>15 wt.% Co/Al₂O₃</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>5A</td>
<td>11 w.% Co/SiO₂</td>
<td>6.2</td>
<td>7.3</td>
</tr>
<tr>
<td>5B</td>
<td>11 w.% Co/SiO₂</td>
<td>5.9</td>
<td>7.8</td>
</tr>
<tr>
<td>6</td>
<td>11 w.% Ni/SiO₂</td>
<td>9.7</td>
<td>n/d</td>
</tr>
</tbody>
</table>

Table 12 shows that the metal dispersion was the highest for Sample 3 and the lowest for Sample 6, being 38.4 % and 10.3 % respectively, with Sample 3 also having the lowest average metal particle diameter (2.6 nm). As earlier mentioned, the increase in metal particle size is the largest for Sample 5B, increasing from 5.9 nm to 7.8 nm.
3.1.5 Thermogravimetric Analysis

The spent samples were obtained from HDO of isoeugenol at 300 °C and 30 bar experiments to get a better understanding of GCLPA (Section 3.2). By excluding water at 100 °C and comparing the weight losses of both the fresh and the spent samples, it can be concluded that coking is the highest for Sample 6 (25 wt.%) and the lowest for Sample 4 (12.1 wt.%), which is interesting considering that Sample 4 is the only acidic one (Section 3.1.2, Table 11) analyzed by TGA and should therefore, according to the literature, show a higher coke formation [44]. The low organic coke percentage for Sample 4 leads to larger formation of gases, as can be seen in Section 3.2.1.1, Figure 3.22. Coke formation on the samples is presented in Table 13, whereas a comparison of the mass losses in fresh and the spent Samples 1, 4, 5A and 6 is shown in Figures 3.14 – 3.17.

Furthermore, it should be mentioned that both fresh and spent 20 wt.% Ni/graphite was analyzed in nitrogen due to an enormous weight loss for the fresh catalyst (72 wt.%) in air, which was caused by burning of the support. The curve for this is shown in Appendix E (Figure E.1) together with derivative temperature differences (DTD) for other catalysts (Figures E.2 – E.5).

### Table 13 – Total coke content of the catalysts used in HDO of isoeugenol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>Organic coke (N₂), %</th>
<th>Organic coke (air), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 wt.% Ni/graphite</td>
<td>22.4</td>
<td>n/d</td>
</tr>
<tr>
<td>4</td>
<td>15 wt.% Co/Al₂O₃</td>
<td>n/d</td>
<td>12.1</td>
</tr>
<tr>
<td>5A</td>
<td>11 wt.% Co/SiO₂</td>
<td>n/d</td>
<td>23.8</td>
</tr>
<tr>
<td>6</td>
<td>11 wt.% Ni/SiO₂</td>
<td>n/d</td>
<td>25.0</td>
</tr>
</tbody>
</table>
Figure 3.14 – TGA plot for the fresh versus the spent 20 wt.% Ni/graphite catalyst in nitrogen.

From Figure 3.14 a significant mass loss starting at 150 °C can be seen. This is most likely related to the removal of lighter hydrocarbons, whereas the mass loss starting at 400 °C can be identified as “hard coke” [45].

Figure 3.15 – TGA plot for the fresh versus the spent 15 wt.% Co/Al₂O₃ catalyst in air.
Figures 3.15 – 3.17 all show immense mass losses at around 150 – 200 °C for the spent catalysts, indicating deposition of soluble, soft coke. The weight loss between 200 – 550 °C for Sample 6 (Figure 3.17) indicates the transformation of soluble carbon to higher molecular mass derivatives [46]. Furthermore, the mass increase at 400 °C onwards for the fresh 11 wt.% Co/SiO₂ and 11 wt.% Ni/SiO₂ catalysts can be explained by formation of solid oxygenated compounds [47].
3.1.6 CHNS

The CHNS analysis was made for spent samples and can be seen in Figure 3.18, in which carbon content and hydrogen-to-carbon ratio are presented. The H/C ratio was calculated with the following formula:

$$\frac{\text{wt.} \%, H}{\text{Atomic weight}, H} \div \frac{\text{wt.} \%, C}{\text{Atomic weight}, C}$$

Figure 3.18 show that all samples analyzed with CHNS have a H/C ratio higher than 2, indicating that the coke present in the catalysts is not of aromatic nature [48]. The samples also contain a relatively high amount of carbon, ranging from 16 to 26 %, the highest being for Sample 6 and the lowest for Sample 7, which was used in the trickle-bed reactor. Interestingly, the reused Sample 5A (r) shows much lower carbon content than Sample 5A albeit similar H/C ratios. These results correspond well with the TGA results obtained in Section 3.1.5.

![Figure 3.18 – H/C ratio and carbon content in HDO of isoeugenol.](image-url)
3.1.7 XRD

The XRD results of fresh Samples 2, 3, 4, 5A, and 6 are presented in Figure 3.19 with spent XRD results given in Appendix F.

The peaks visible at 20° for Samples 2, 5A, and 6 can be identified as amorphous [49], whereas the peaks occurring at approximately 45° for Sample 2, 3, 4, and 5A are considered to be Co⁰, with Sample 4 showing a higher peak due to better reducibility of CoO to Co⁰. [50] Sample 3 shows peaks at approximately 22°, 30°, 38°, 50° and some smaller peaks between 60° and 90°. Sample 3 is considered to be poorly reduced exhibiting peaks of cobalt oxides species, with the peak at approximately 25° confirming the TiO₂ anatase structure [51]. The support of Sample 3 has a small specific surface area (Section 3.1.1, Table 10) and gives larger metal crystal sizes than other catalysts. Sample 4 shows its support in hexagonal form (corundum) at 40°. Sample 6 shows a large peak at 45° that can be identified metallic Ni (111) and three smaller peaks at 50°, 78°, and 95° [50]. The Ni particle size was calculated to be 11.6 nm according to the Rietveld refinement and corresponds quite well to the metal particle size presented in Section 3.1.3 (Table 11). It is worth to mention that no particle size calculations were done for Samples 2 and 5A due to small peaks, indicating that the Co particle size could be below 3 nm and thus lower than presented in Section 3.1.4 (Table 12).

![Figure 3.19 – XRD results of the fresh catalysts.](image-url)
3.1.8 Size-Exclusion Chromatography

SEC was used to analyze the spent Sample 4. The result is presented in Figure 3.20 with sitosterol as a standard compound and THF as a solvent. This figure shows that the spent Sample 4 (purple line) has a significantly higher molecular weight compared to sitosterol (415 g/mol).

![SEC analysis of the spent Sample 4 in HDO of isoeugenol at 300 °C and 30 bar.](image)

Figure 3.20 – SEC analysis of the spent Sample 4 in HDO of isoeugenol at 300 °C and 30 bar.

The spent Sample 4 was 0.5 mg/ml, whereas the concentrations of sitosterol were 0.1 and 0.033 mg/ml respectively. In Figure 3.30 two peaks occurring at 22 min belong to sitosterol and the large peak occurring at 14 min belongs to the spent Sample 4. Further information about the SEC results can be found in Appendix G.
3.1.9 ICP-MS

ICP-MS results for the liquid samples obtained in the end of HDO of isoeugenol experiments are presented in Table 14. They demonstrate no leaching, with only the experiment done with Sample 6 showing minor traces of silicon.

Table 14 – ICP-MS results obtained for liquid samples in HDO of isoeugenol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Aluminium (mg/kg)</th>
<th>Silicon (mg/kg)</th>
<th>Titanium (mg/kg)</th>
<th>Nickel (mg/kg)</th>
<th>Molybdenium (mg/kg)</th>
<th>Cobalt (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt.% Ni/Graphite</td>
<td>&lt; 0.10</td>
<td>n/d</td>
<td>n/d</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>15 wt.% Co/TiO₂</td>
<td>&lt; 0.10</td>
<td>n/d</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>15 wt.% Co/Al₂O₃</td>
<td>&lt; 0.10</td>
<td>n/d</td>
<td>n/d</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>11 wt.% Co/SiO₂</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>n/d</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>11 wt.% Ni/SiO₂</td>
<td>&lt; 0.10</td>
<td>18</td>
<td>n/d</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
<td>&lt; 0.10</td>
</tr>
</tbody>
</table>

3.2 Hydrodeoxygenation of isoeugenol

Seven different catalysts were tested in HDO of isoeugenol. The most interesting liquid- and gas phase results for cobalt and nickel based catalyst are explained hereafter, whereas a more detailed table of products and catalytic data is found in Appendix H.

3.2.1 Isoeugenol HDO on Co based catalysts

3.2.1.1 Co catalysts supported on SBA-15, TiO₂ and Al₂O₃

Figure 3.21 presents the GCLPA for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4) tested in HDO of isoeugenol at 300 °C and 30 bar, together with 10 wt.% Co/SBA-15 tested at 200 °C and 30 bar. This figure clearly shows that the GCLPA is the highest for 10 wt.% Co/SBA-15 at 200 °C, compared to the catalysts tested at 300 °C. Interestingly, experiments done at 300 °C resulted in an increase in GCLPA from 60 min onwards for Samples 2 and 4, which can be explained by an increase of lighter hydrocarbons formed in the liquid phase, such as hexane and heptane. The decline in GCLPA for 15 wt.% Co/TiO₂ can be explained by its low surface area (94 m²/g), high metal content (15 wt.%) and poor reduction, as can be seen in Section 3.1.8. All catalysts tested at
300 °C showed a complete conversion of the reactant after just one minute, whereas 10 wt.% Co/SBA-15 evaluated at 200 °C displayed a complete conversion of isoeugenol after 30 minutes. GCLPA percentages of 93.0% and 78.7% were obtained for 10 wt.% Co/SBA-15 at 200 °C and 300 °C, while lower GCLPA were obtained for Co supported on titania and alumina, being 38.3% and 56.2% respectively. The relatively low GCLPA obtained for 15 wt.% Co/Al₂O₃ can further be explained by a high H/C molar ratio of the spent catalyst (Section 3.1.6), indicating formation of gaseous products.

![GCLPA profiles for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4) in HDO of isoeugenol.](image)

A gas sample of 0.5 ml was taken at 40 °C for Co catalysts supported on SBA-15 and alumina (Sample 2 and 4) after finishing experiment on HDO of isoeugenol. The results are shown in Figure 3.22 as a staple diagram, with complete gas phase chromatograms found in Appendix I. Figure 3.22 shows a tremendous increase in gaseous products obtained in HDO at 300 °C compared to experiments done at 200 °C. Large amounts of methane were formed for 10 wt.% Co/SBA-15 and especially for 15 wt.% Co/Al₂O₃ which possess Lewis acidity. This is an explanation for a poor GCLPA percentage obtained for this catalyst (Figure 3.21). A high amount of gaseous products formed for Sample 4 can further be explained by its low GCLPA as well as by its low amount of organic coke (12.1%) obtained from TGA (Section 3.1.5). The latter observation is interesting, as acidic supports tend to form coke in HDO reactions, which is not the case here [44].
The concentration of dihydroeugenol versus time for Samples 2, 3 and 4 can be seen in Figure 3.23. Interestingly, 10 wt.% Co/SBA-15 (Sample 2) and 15 wt.% Co/Al₂O₃ (Sample 4) tested at 300 °C and 30 bar show no dihydroeugenol after the four-hour experiment, indicating better deoxygenation properties for these catalysts. As expected for a catalyst of low acidity, 10 wt.% Co/SBA-15 tested at 200 °C and 30 bar showed an increase in dihydroeugenol during the experiment, meaning that temperature is a crucial parameter in deoxygenation of isoeugenol for this catalyst. Moreover, a decrease in dihydroeugenol concentration is rapid for 10 wt.% Co/SBA-15 and 15 wt.% Co/Al₂O₃, showing 0.0043 and 0.0033 mol/l after just one minute of the reaction, whereas 15 wt.% Co/TiO₂ shows a steady decrease in dihydroeugenol concentration during the whole experiment giving a concentration of 0.0016 mol/l dihydroeugenol at the end of the experiment.

**Figure 3.22** – Gas products formed in HDO of isoeugenol for 10 wt.% Co/SBA-15 (Sample 2) and 15 wt.% Co/Al₂O₃ (Sample 4).
A high concentration of dihydroeugenol obtained for 10 wt.% Co/SBA-15 at 200 °C and 30 bar can further be related to absence of propylcyclohexane, shown in Figure 3.24. Experiments done at 300 °C and 30 bar all resulted in formation of propylcyclohexane, being 0.0077, 0.0033 and 0.0012 mol/l for Sample 2, 3 and 4 respectively. 10 wt.% Co/SBA-15 has a low Lewis acidity (Section 3.1.2, Table 11) and metal dispersion than other catalysts presented in this section (Section 3.1.4, Table 12), indicating that a high surface area and a lower metal content for 10 wt.% Co/SBA-15 are favorable for producing propylcyclohexane.

Figure 3.23 – Molar concentration of dihydroeugenol in HDO of isoeugenol for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4).

Figure 3.24 – Molar concentration of propylcyclohexane for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4) in HDO of isoeugenol.
Figure 3.25 further explains that the metal dispersion does not have an impact on formation of propylcyclohexane or the HDO degree for Samples 2, 3 and 4 tested at 300 °C.

![Graph](image1.png)  
![Graph](image2.png)

**Figure 3.25 –** Molar concentration of propylcyclohexane versus TEM dispersion (%) and HDO (%) for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4) in HDO of isoeugenol at 300 °C and 30 bar.

Yields of products obtained in the liquid phase differ considerably between experiments done at 200 °C and 300 °C, 30 bar, as can be seen from Figure 3.26. The yield of dihydroeugenol was 80.1% for 10 wt.% Co/SBA-15 tested at 200 °C while the yields of 2.0% and 6.0% were obtained for cyclohexene and 3- and 4-propylcyclohexene. The same catalyst tested at 300 °C displayed a high yield percentage of the desired product propylcyclohexane (63.3%), as well as minor yield percentages of 3 & 4 propylcyclohexene (1.0%) and propylcyclohexanone (2.2%). 15 wt.% Co/TiO₂ showed a quite similar yield percentage of propylcyclohexane (9.4%) and dihydroeugenol (12.9%) as well as a minor propylcyclohexanone percentage of 2.1%. Interestingly, 15 wt.% Co/Al₂O₃ only shows yields of propylcyclohexane (27.4%). High yields of hexane and heptane formed for these catalysts are worth to mention. 15 wt.% Co/Al₂O₃ showed the highest yield percentages of both hexane (41.2%) and heptane (22.2%), whereas 10 wt.% Co/SBA-15 tested at 200 °C gave only yields of 8.3% and 2.5% for hexane and heptane.
Figure 3.26 – Yield of products formed in the liquid phase for 10 wt.% Co/SBA-15 (Sample 2), 15 wt.% Co/TiO₂ (Sample 3) and 15 wt.% Co/Al₂O₃ (Sample 4).

3.2.1.2 Co catalysts supported on SiO₂

The GCLPA percentages for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B) tested in HDO of isoeugenol at 300 °C, 30 bar along with 11 wt.% Co/SiO₂ reduced at 415 °C tested at 200 °C and 30 bar, are presented in Figure 3.27. All catalysts showed a complete conversion of isoeugenol. Remarkably similar GCLPA (72.8% and 72.7%) were defined for 11 wt.% Co/SiO₂ independent on reduction temperature (415 °C and 550 °C, respectively). Furthermore, the GCLPA is highest for Sample 5A tested at 200 °C (86.6%) and a slight increase in GCLPA with time for Samples 5A and 5B can be identified as formation of hexane and heptane in the liquid phase.

Figure 3.27 – GCLPA profiles for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B) in HDO of isoeugenol.
Gas phase results for 11 wt.% Co/SiO₂ tested at 300 °C can be seen in Figure 3.28. Interestingly, when compared to similar GCLPA results obtained for these materials (Figure 3.27), the catalyst reduced at low temperature showed almost twofold of gas products formed compared to a higher reduction temperature. Again, a high amount of methane was formed for both cases, indicating that cobalt forms methane in HDO of isoeugenol at 300 °C. The causes for this can be many, with one possible explanation being the difference in H₂-TPR profiles (Section 3.1.3, Figures 3.3 and 3.4). The gas phase chromatograms of Sample 5A and 5B are presented in Appendix I.

Figure 3.28 – Areas of gas phase analysis of 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B) in HDO of isoeugenol.

A high molar concentration of dihydroeugenol 0.009 mol/l was obtained for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) tested at 200 °C and 30 bar, whereas lower molar concentrations of dihydroeugenol were obtained for Samples 5A and 5B tested at 300 °C, being 0.0004 mol/l and 0.0003 mol/l after the four-hour HDO experiment. This further explains the importance of reaction temperature in HDO of isoeugenol explained earlier.
Figure 3.29 – Molar concentration of dihydroeugenol for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B) in HDO of isoeugenol.

Figure 3.30 shows no formation of propylcyclohexane at 200 °C and 30 bar, whereas independent on reduction temperature exactly the same molar concentration of propylcyclohexane 0.006 mol/l was obtained. Furthermore, reduction of Co at a lower temperature shows a more rapid increase in propylcyclohexane concentration between 30 and 120 minutes compared to a higher reduction temperature with the latter catalyst again showing a more rapid increase from 120 minutes onwards. An explanation for this might be the different reduction profiles for these materials (Section 3.1.3, Figures 3.3 & 3.4) Interestingly, both tests at 300 °C show a linear increase of propylcyclohexane, indicating that even higher molar concentration of propylcyclohexane could be achieved at longer reaction times.

Figure 3.30 – Molar concentration of propylcyclohexane for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B) in HDO of isoeugenol.
A major difference in the yield of products obtained at 200 °C and 30 bar compared to HDO experiments performed at 300 °C and 30 bar, can be seen in Figure 3.31. A high yield percentage of dihydroeugenol (73.7%) can be observed for Sample 5A tested at 200 °C with lower yield percentages for cyclohexene and 3- and 4-propylcyclohexene, being 3.8% and 10.5% respectively. Samples 5A and 5B evaluated at 300 °C and 30 bar showed almost exactly the same yields for the products obtained, the only difference being a minor yield (0.82%) of propylbenzene obtained for 11 wt.% Co/SiO₂ reduced at 550 °C (Sample 5B). Even though the yield percentage of propylbenzene is small, it indicates that the phenyl ring is not hydrogenated and therefore the catalyst can deactivate. The obtained yield percentages of hexane and heptane for Sample 5A and 5B at 300 °C were the same, being 28.2% for hexane and 12.7% for heptane. Interestingly, Sample 5A tested at 200 °C does not show any hexane, only heptane (2.2%).

Figure 3.31 – Yield of products formed in the liquid phase for 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) and 550 °C (Sample 5B).
3.2.1.3 Recyclability tests of 11 wt.% Co/SiO₂

Recyclability tests of 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A) were performed in HDO of isoeugenol at 300 °C and 30 bar. The first reaction was performed with an initial isoeugenol concentration of 0.097 mol/l, with 0.4 g catalyst and 0.8 g isoeugenol, thereafter the spent Sample 5A was regenerated with the temperature program described in Section 2.1.4. The regenerated catalyst was reused in HDO of isoeugenol with an initial isoeugenol concentration of 0.012 mol/l, the catalyst mass of catalyst being 0.05 g and the mass of isoeugenol 0.1 g.

Figure 3.32 shows that the first experiment had a remarkably low molar concentration of propylcyclohexane (0.0052 mol/l) even though it had a high initial isoeugenol concentration. This result is interesting, since no isoeugenol was visible in the GC after the four-hour experiment and a low GCLPA percentage was obtained (48.5%). A minor molar concentration of propylbenzene at the end of the reaction can be a possible explanation for this, since it indicates catalyst deactivation. Hexane and heptane were also formed during the reaction, having concentration of 0.0013 mol/l and 0.0004 mol/l.

![Figure 3.32 - Molar concentration of products obtained versus time over the fresh 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A).](image-url)
The regenerated catalyst showed a high molar concentration of propylcyclohexane during the four-hour HDO experiment (0.0072 mol/l) compared to its initial isoeugenol concentration of 0.012 mol/l. Since the regenerated Sample 5A displayed a higher molar concentration of propylcyclohexane than the non-regenerated one (0.006 mol/l, Section 3.2.12, Figure 3.30), it is possible that an unknown amount of isoeugenol was still strongly adsorbed on the surface of the regenerated catalyst from the first experiment. Dihydroeugenol was not completely converted, with minor molar concentrations of 3- and 4-propylcyclohexene, propylcyclohexanone and cyclohexane visible in the end of the reaction. The regenerated Sample 5A had a high GCLPA (76.7%) and a low carbon content (18 wt.%). The regenerated Sample 5A formed 0.004 mol/l of hexane and 0.002 mol/l of heptane during the reaction.

Figure 3.33 – Molar concentration of products obtained versus time over the regenerated 11 wt.% Co/SiO₂ reduced at 415 °C (Sample 5A).
3.2.1.4 Comparison between batch and trickle-bed reactors

Commercial 10 wt.% Co/SiO$_2$ catalyst was used in HDO of isoeugenol in both batch and trickle-bed reactors, with the crushed pellets (< 93 $\mu$m) used in the batch reactor and pristine 3 mm pellets applied in the trickle-bed reactor. Both experiments were done at 300 °C and 30 bar. The GCLPA percentages show steady curves for both experiments, as can be seen in Figure 3.34. The trickle-bed experiment gave a GCLPA of 92.1% compared to 64.9% for the batch. The peak visible at 30 minutes for the trickle-bed experiment can be explained by a rather long time (30 min) needed to completely fill the reactor.

Figure 3.34 – GCLPA for 10 wt.% Co/SiO$_2$ (Sample 7) in batch and trickle-bed reactors.

Figure 3.35 shows that complete conversion of isoeugenol was achieved almost immediately for commercial 10 wt.% Co/SiO$_2$ in the batch reactor, whereas a decreasing conversion in the trickle-bed can be explained by catalyst deactivation.

Figure 3.35 – Isoeugenol conversion for 10 wt.% Co/SiO$_2$ (Sample 7) in batch and trickle-bed reactors.
The product yields were different in the two reactors. As visible from Figure 3.36, in the batch reactor mostly propylcyclohexane was formed (34.8 %) along with minor yields of propylbenzene (6.1%), 3- and 4-propylcyclohexene (3.9%) and propylcyclohexanone (3.6%). A decreasing molar concentration of dihydroeugenol was observed during the experiment, ending with a yield of 5.7%. Furthermore, large amounts of hexane (26.3%) and heptane (11.2%) were formed.

Different solvents used in the experiments, namely hexadecane for the batch and 1-decanol in the trickle-bed, certainly affected the product distribution. A relatively high yield of 3- and 4-propylcyclohexene (26.0%) can be observed. Moreover, there were substantial yields of products containing oxygen, in particular propylcyclohexanone and dihydroeugenol having yields of 19.1% and 13.7%. No hexane or heptane were formed for 10 wt.% Co/SiO₂ in the trickle-bed experiment. Furthermore, an extent of HDO was lower for the trickle-bed reactor (53.4%) compared to the batch experiment (85.0%), even if more hydrogen was used in the trickle-bed reactor (50 ml/min). Possible reasons for this might be hydrodeoxygenation of the solvent 1-decanol during the experiment as well as influence of mass transfer.

![Figure 3.36](image_url) – Yield of products formed in the liquid phase for commercial 10 wt.% Co/SiO₂ (Sample 7) in batch and trickle-bed reactor.
3.2.2 Isoeugenol HDO on Ni based catalysts

Data for GCLPA obtained for 20 wt.% Ni/graphite (Sample 1) and 11 wt.% Ni/SiO₂ (Sample 6) tested in HDO of isoeugenol at 300 °C and 30 bar together with the former catalyst tested at 200 °C and 30 bar are presented in Figure 3.37. The results show a GCLPA of 87% for the nickel on graphite when HDO was performed at 200 °C compared to GCLPA of 75% and 68% obtained for Samples 1 and 6 tested at 300 °C. In all cases, a complete conversion of isoeugenol after just one minute of the four-hour experiment was achieved. Differences in GCLPA can be explained by formation of the gaseous products at higher HDO temperatures, as can be seen in Figure 3.38. A slight increase in GCLPA for both nickel catalysts evaluated at 300 °C at 120 minutes of HDO can be explained by formation of lighter hydrocarbons such as hexane and heptane in the liquid phase. Without taking hexane and heptane into consideration, the GCLPA for 20 wt.% Ni/graphite and 11 wt.% Ni/SiO₂ tested at 300 °C would decrease to 52% and 45.7%. Furthermore, it is worth mentioning that no calibration was done for octane and nonane, whose concentrations increase during HDO at 300 °C. GCLPA for both nickel catalysts should be even higher than the values presented in Figure 3.37.

Figure 3.37 – GCLPA for 20 wt.% Ni/graphite (Sample 1) done at 200 °C and 300 °C as well as 11 wt.% Ni/SiO₂ (Sample 6) done at 300 °C.

Analysis of the gas phase results for both nickel catalysts tested at 300 °C is presented in Figure 3.38. Interestingly, when comparing GCLPA results for these catalysts (Figure 3.37), 20 wt.% Ni/graphite (Sample 1) showed a more than double amount of gas products formed compared to 11 wt.% Ni/SiO₂ (Sample 6). The reason for this behavior is a high metal loading for the former catalyst, as nickel is known to form more methane in hydrodeoxygenation of phenolic compounds [52].
Figure 3.38 - Gas products formed in HDO of isoeugenol for 20 wt.% Ni/graphite (Sample 1) and 11 wt.% Ni/SiO₂ (Sample 6).

The difference in nickel loading of the tested catalysts certainly affects the rate of dihydroeugenol conversion. This can be seen in Figure 3.39. Interestingly, both catalysts tested at 300 °C and 30 bar showed almost exactly the same molar concentration of dihydroeugenol, 0.0003 mol/l for 20 wt.% Ni/graphite (Sample 1) and 0.0002 mol/l for 11 wt.% Ni/SiO₂ (Sample 6), at the end of the experiment. At 0.5 min*g, however, 11 wt.% Ni/SiO₂ displayed a molar concentration of 0.002 mol/l compared to 0.004 mol/l for the other nickel-based catalyst. A high molar concentration of dihydroeugenol obtained for Sample 1 at 200 °C indicates, as anticipated, that the reaction temperature is a major factor also for nickel-based catalysts.

Figure 3.39 – Molar concentration of dihydroeugenol for 20 wt.% Ni/graphite (Sample 1) and 11 wt.% Ni/SiO₂ (Sample 6).
A high concentration of dihydroeugenol obtained at 200 °C and 30 bar is in line with the absence of propylcyclohexane obtained after four hours, as visible in Figure 3.40. Both catalysts tested at 300 °C and 30 bar gave propylcyclohexane, namely 0.0775 mol/l for 20 wt.% Ni/graphite (Sample 1) and 0.0054 mol/l for 11 wt.% Ni/SiO₂ (Sample 6) after the four-hour experiment. Interestingly, both catalysts displayed similar rates of propylcyclohexane formation considering differences in their metal loading. Since both of these catalysts have no acidity and similar coke content (Section 3.1.4, Table 13), metal dispersion (Section 3.1.3, Table 12) and metal loading are of interest. A high amount of propylcyclohexane formed for 20 wt.% Ni/graphite can be explained by its high nickel loading (20 wt.%) and a high metal dispersion (16.4%), characteristics that lead to more prominent hydrodeoxygenation [53].

![Figure 3.40](image)

**Figure 3.40** – Molar concentration of propylcyclohexane obtained for 20 wt.% Ni/graphite (Sample 1) and 11 wt.% Ni/SiO₂ (Sample 6).

Yields of products obtained in the liquid phase differ considerably between experiments done at 200 °C and 300 °C, as can be seen from Figure 3.41. Dihydroeugenol (82.6 %) yield was predominant at 200 °C for 20 wt.% Ni/graphite. In addition, minor yields of 1.5 % and 0.73 % for 3- and 4-propylcyclohexene and cyclohexene were obtained. Both catalysts tested at 300 °C exhibited high yields of the desired product propylcyclohexane, being 60.4% and 44.0% for graphite and silica-supported catalysts, respectively. The silica-supported catalyst also generated in 3- and 4-propylcyclohexene (5.8%) and propylcyclohexanone (3.4%). Both catalysts showed the same yields of dihydroeugenol, 2.4%. Formation of hexane and heptane occurred in the liquid phase for experiments performed at 300 °C, with 20 wt.% Ni/graphite showing yields of 29.3% hexane and 13.0% heptane compared to 28.3% and 12.1% for 11
wt.% Ni/SiO₂. Furthermore, the former catalyst (Sample 1) afforded the highest selectivity towards propylcyclohexane of all catalysts tested in this work (55.4%).

Figure 3.41 – Yield of products formed in the liquid phase for 20 wt.% Ni/graphite (Sample 1) and 11 wt.% Ni/SiO₂ (Sample 6).
4. Conclusions

The climate change has increased the need of renewable transportation fuels obtained from lignocellulosic biomass. Due to its high oxygen content and complex structure, catalytic hydrodeoxygenation (HDO) is needed to upgrade compounds derived from renewable resources for their efficient competition with fossil fuels. In this work, catalytic hydrodeoxygenation of lignin-derived phenolic compound – isoeugenol was investigated over cobalt- and nickel-based catalysts. The hydrodeoxygenation experiments were mostly performed in a batch reactor at 200 °C and 300 °C and 30 bar total pressure. A commercial cobalt catalyst in the form of pellets was applied in a trickle-bed reactor to follow time-on-stream behavior and catalyst deactivation. All experiments showed complete conversion of isoeugenol after just one minute at 200 °C, 300 °C and 30 bar.

HDO of isoeugenol over cobalt-based catalysts showed that 300 °C is required for formation of propylcyclohexane. Of the cobalt-based catalysts tested, 10 wt.% Co/SBA-15 catalyst gave the highest yield of propylcyclohexane (63.3%) in the liquid phase and had the highest gas chromatography-based sum of reactants and products in the liquid phase (GCLPA) of 78.7%. 15 wt.% Co/TiO2 and 15 wt.% Co/Al2O3 showed lower formation of propylcyclohexane and GCLPA. Of these two catalysts, 15 wt.% Co/Al2O3 yielded propylcyclohexane as the only product (27.4%) together with hexane and heptane. This result can be explained by a high methane formation, support acidity as well as adsorption of compounds on the catalyst surface, which was verified by SEC analysis.

HDO of isoeugenol, using 11 wt.% Co/SiO2 catalyst, revealed that the reduction temperature does not affect the GCLPA. Both reduction temperatures, 415 °C and 550 °C, allowed similar GCLPA of 72.7% and 72.8%, respectively. Lower reduction temperature gave a twofold amount of gaseous products compared to a higher reduction temperature. In the latter case, minor formation of propylbenzene was noticed, indicating that the catalyst is prone to deactivation.

11 wt.% Co/SiO2 was also used for stability and regeneration tests. An experiment with higher catalyst and isoeugenol amounts produced small amounts of propylcyclohexane, whereas the regenerated 11 wt.% Co/SiO2, tested at 0.012 mol/l, displayed a high concentration of propylcyclohexane 0.0072 mol/l and a high GCLPA, indicating that some isoeugenol from the first experiment in this series was still strongly adsorbed on the catalyst surface.
10 wt.% Co/SiO₂ catalyst was used in both batch and trickle-bed reactors, to follow time-on-stream behavior and catalyst deactivation. Crushed pellets (< 93μm) were used in the batch reactor while 3 mm pellets were applied in the trickle-bed reactor. Complete conversion of isoeugenol was achieved in the batch reactor, whereas only 75% conversion of isoeugenol was obtained in the trickle-bed reactor, revealing catalyst deactivation. Furthermore, HDO of isoeugenol in the batch reactor mainly yielded propylcyclohexane, whereas the experiment performed in the trickle-bed reactor showed relatively high yields of many different products, including propylcyclohexane. The reason for this besides the impact of mass transfer may be different solvents used in the experiments, namely hexadecane in the batch reactor and 1-decanol in the trickle-bed reactor, with possibilities of hydrodeoxygenation of the solvent 1-decanol taking place.

Furthermore, cobalt-based catalysts with a high metal loading on mildly acidic supports gave lower GCLPA and tend to form more gaseous products in hydrodeoxygenation of isoeugenol at 300 °C and 30 bar, whereas cobalt-based catalysts on supports with a high specific surface area generated less gaseous products and gave higher yields of propylcyclohexane.

HDO of isoeugenol over 20 wt.% Ni/graphite and 11 wt.% Ni/SiO₂ catalysts showed that the metal loading and dispersion are directly connected to the formation of propylcyclohexane at 300 °C and 30 bar. 20 wt.% Ni/graphite, with a dispersion of 16.4% based on TEM, showed a high GCLPA (75.2%) and a high amount of propylcyclohexane (0.0775 mol/l). 11 wt.% Ni/SiO₂, with a dispersion of 10.3% according to TEM, displayed a slightly lower GCLPA (68.8%) and less propylcyclohexane (0.0554 mol/l), with a TEM dispersion of 10.3%. Furthermore, 11 wt.% Ni/SiO₂ also resulted in the smallest formation of gaseous products of all catalysts tested.

Molar concentrations of hexane and heptane varied for different catalysts used, therefore affecting the GCLPA percentages obtained in HDO of isoeugenol at 300 °C and 30 bar. It is worth to mention that no calibration was done for octane and nonane, i.e. hydrocarbons present in all HDO experiments performed at 300 °C and 30 bar.

HDO of isoeugenol should be further investigated with different metal loadings on high specific surface area supports. A special focus should be on cobalt-based catalysts with silica as a support. Lighter hydrocarbons such as octane and nonane should be calibrated in GC to get an improved GCLPA. In continuous trickle-bed operation, further experiments should be done with varying temperatures and pressures using a non-alcoholic solvent to avoid formation of products in two phases.
Hydrodeoxygenering av den lignin härleda fenolföreningen isoeugenol på nickel- och koboltbaserade katalysatorer

Förnyelsebara resurser såsom solenergi, vindkraft och biomassa har ökat kraftigt det senaste årtiondet för att minska användningen av fossila bränslen. Av dessa är biomassa det enda alternativet för tillverkning av flytande bränsle, vilket lett till att både EU och USA satt som mål att 20% av alla transportbränslen ska härstamma från biomassa 2020 respektive 2030. Biomassa anses vara material som producerats i naturen som träd, samt diverse matrester och industriavfall. Den ses även som förnyelsebar då återvinningstiden är tio år, jämfört med fossila källor som olja, som har en återvinningsperiod på flera tusen år.


Katalytisk hydrodeoxygenering (HDO) av isoeugenol på koboltbaserade katalysatorer visade att en temperatur på 300 °C behövs för bildning av den önskade produkten propylcyklohexan. Av de koboltbaserade katalysatorerna visade Co/SBA-15-katalysatorn, med 10 viktprocent kobolt, högsta produktion av propylcyklohexan (63,3%) i vätskefasen och den högsta massbalansen baserat på reaktanter och produkter i vätskefasen (78,7%). Katalysatorerna Co/TiO2 och Co/Al2O3, med 15 viktprocent kobolt visade låg produktion av propylcyklohexan och låg massbalans i vätskefasen. Av dessa två producerade Co/Al2O3 endast propylcyklohexan bland sina produkter (27,4%). Detta kan
förklaras med denna katalysators höga produktion av gaskomponenter under experimentet, med den milda surheten hos bärarmaterialet och med adsorption av diverse komponenter på katalysatorytan.

Hydrodeoxygenering av isoeugenol med användning av en Co/SiO$_2$-katalysator med 11 viktprocent kobolt visade att reducierungstemperaturen inte har någon effekt på massbalansen i vätskefasen. Bägge reduktionstemperaturerna på 415 °C och 550 °C för katalysatorn ifråga visade nästan identiska massbalanser i vätskefasen, 72,7% och 72,8%. Den lilla skillnaden mellan dessa experiment var den dubbla mängden gaskomponenter som producerades vid en lägre reduktionstemperatur samt en mindre bildning av propylbensen för katalysatorn som reducerats vid 550 °C. Detta indikerar på deaktivering av katalysatorn.

Den enda katalysatorn som användes i både en satsreaktor och en kontinuerlig reaktor var Co/SiO$_2$ med 10 viktprocent kobolt. Krossade katalysatorpartiklar användes i satsreaktorn och hela pelletar i den kontinuerliga reaktorn. En fullständig reaktion av reaktanten isoeugenol uppnåddes i satsreaktorn medan endast 75% av isoeugenol kunde konverteras till andra produkter i den kontinuerliga reaktorn, vilket indikerar på deaktivering av katalysatorn. Vidare så skapade hydrodeoxygeningsexperimenten som utfördes i satsreaktorn för det mesta propylcyklohexan, medan experimentet som utfördes i den kontinuerliga reaktorn skapade många olika produkter, även propylcyklohexan. Orsakerna till detta kan vara de olika lösningsmedlen som användes i de två olika experimenten, där hexadekan användes i satsreaktorn och 1-dekanol i den kontinuerliga reaktorn. En möjlig deoxygeneringsreaktion av lösningsmedlet 1-dekanol i den kontinuerliga reaktorn är inte utesluten.

Det producerades en större mängd gaskomponenter och lägre massbalanser i vätskefasen för katalysatorerna med högre viktprocent kobolt på bärarmaterial med milt sura säten, medan koboltkatalysatorer med hög ytarea producerade mer propylcyklohexan och mindre mängd gaskomponenter vid HDO av reaktanten isoeugenol vid 300 °C och 30 bar.

Hydrodeoxygenering av isoeugenol med nickelbaserade katalysatorer som Ni/Grafit och Ni/SiO$_2$ visade att viktprocent nickel och dispersionen är direkt proportionell mot bildningen av propylcyklohexan vid 300 °C och 30 bar. Katalysatorn Ni/Grafit, med 20 viktprocent nickel och en dispersion på 16,4% resulterade i en massbalans på 75,2% i vätskefasen samt en hög koncentration (0,0775 mol/l) av den önskade produkten propylcyklohexan. Katalysatorn Ni/SiO$_2$, med 11 viktprocent nickel och en dispersion på 10,3% uppnådde en massbalans på 68,8% och en koncentration av propylcyklohexan på 0,0554 mol/l. Värt att notera är även att Ni/SiO$_2$-katalysatorn formade minst gasprodukter av alla katalysatorer i detta arbete.
De molära koncentrationerna av hexan och heptan varierade för de olika katalysatorerna som testades i detta arbete, vilket visade sig ha stor effekt på de uppnådda massbalanserna i vätskefasen för hydrodeoxygenering av isoeugenol vid 300 °C och 30 bar. Vårt att notera är även att ingen kalibrering utfördes för oktan och nonan, kolväten som bildades i alla HDO-experiment vid 300 °C samt 30 bar som inte är medräknade i massbalanserna.

Hydrodeoxygenering av ligninderivatet isoeugenol bör undersökas vidare med katalysatorer på bärarmaterial med hög ytarea och olika viktprocent metall. Ur ett vetenskapligt perspektiv skulle ädelmetaller på bärarmaterialet SBA-15 vara av intresse för produktion av propylcyklohexan, medan industriföretag borde fokusera på koboltbaserade katalysatorer med silikon som bärarmaterial, då dessa är förmånligare lösningar. Lätta kolväten som oktan och nonan borde kalibreras med hjälp av gaskromatografi för att få en klarare bild av massbalansen i vätskefasen för samtliga katalysatorer i detta arbete. För den kontinuerliga reaktorn borde flera experiment utföras med olika tryck och temperatur. Även lösningsmedlet borde anpassas för reaktorsystemet för att undvika produkter i två faser.
References


42. Lucredio, A. F., Bellido, J. D. A., Zawadzki, A. and Assaf, E. M. Co catalysts supported on SiO\textsubscript{2} and y-Al\textsubscript{2}O\textsubscript{3} applied to ethanol steam reforming: Effect of solvent used in the catalyst preparation method. *Fuel* (2011), 90(4), 1424-1430.


Appendix A

Batch and trickle-bed reactors used in HDO of isoeugenol.

Figure A.1 – Scheme of the batch reactor system.

Figure A.2 – Batch reactor.
**Figure A.3** – Scheme of the trickle-bed reactor system.

**Figure A.4** – Trickle-bed reactor.
Appendix B

Temperature programmed reduction (H₂-TPR) program.

The H₂-TPR program was carried out using the following procedure:

1. Sample drying in argon for 5 minutes
2. Sample heating to 120 °C at a heating rate of 5 °C/min and holding at 120 °C for 60 minutes
3. Cool to ambient pressure
4. Applying cold trap
5. Change gas to (5 % H₂ – 95 % Argon)
6. Wait for baseline stability
7. Recording start with one measurement every 0.5 second
8. Sample heating to 100 °C at a heating rate of 5 °C/min
9. Sample heating to desired reduction temperature with a heating rate of 2 °C/min and holding at desired temperature for 120 minutes
10. Recording stop
11. Cool to ambient temperature
Appendix C

SEM images and data of the fresh Sample 7 pellets.

**Figure C.1** – SEM image of the fresh Sample 7 pellets in 100 µm scale.

| Table C.A – Weight percentage of the fresh Sample 7 pellets using SEM-EDX analysis |
|-----------------|---------------|---------------|---------------|---------------|---------------|
| **Pellet 250x (1) pt1** | O | 33.83 | Mg | 0.48 | Al | 45.85 | Si | 0.31 | Ca | 46.14 | Co | 19.54 |
| **Pellet 250x (1) pt2** | O | 37.57 | Mg | 0.27 | Al | 47.55 | Si | 12.01 | Ca | 46.14 | Co | 14.61 |
| **Pellet 250x (1) pt3** | O | 40.55 | Mg | 0.24 | Al | 47.20 | Si | 13.78 | Ca | 45.66 | Co | 13.38 |
| **Pellet 250x (1) pt4** | O | 39.87 | Mg | 0.16 | Al | 46.14 | Si | 12.01 | Ca | 47.27 | Co | 13.38 |
| **Pellet 250x (1) pt5** | O | 40.66 | Mg | 0.32 | Al | 45.56 | Si | 13.78 | Ca | 47.27 | Co | 13.38 |
| **Pellet 250x (1) pt6** | O | 39.35 | Mg |       | Al |       | Si |       | Ca |       | Co |     |
Appendix D

Fresh and spent TEM images of Samples 1 – 6 in HDO of isoeugenol.

Figure D.1 – TEM images of the fresh Sample 1.

Figure D.2 – TEM images of the spent Sample 1 in HDO of isoeugenol.
Figure D.3 – TEM images of the fresh Sample 2.

Figure D.4 – TEM images of the spent Sample 2 in HDO of isoeugenol.

Figure D.5 – TEM images of the spent Sample 3 in HDO of isoeugenol.
Figure D.6 – TEM images of the fresh Sample 4.

Figure D.7 – TEM images of the spent Sample 4 in HDO of isoeugenol.

Figure D.8 – TEM images of the fresh Sample 5A.
Figure D.9 – TEM images of the spent Sample 5A in HDO of isoeugenol.

Figure D.10 – TEM images of the fresh Sample 5B.

Figure D.11 – TEM images of the spent Sample 5B in HDO of isoeugenol.
Figure D.12 – TEM images of the fresh Sample 6.

Figure D.13 – TEM images of the spent Sample 6 in HDO of isoeugenol.
Appendix E

Thermogravimetric analysis plots of the fresh Sample 1 analyzed in air as well as derivative temperature differences (DTD) for the Samples presented in Section 3.1.5.

Figure E.1 – TGA plot for the fresh Sample 1 in air.

Figure E.2 – DTD plot for the fresh versus the spent Sample 1 in nitrogen.
Figure E.3 – DTD plot for the fresh versus the spent Sample 4 in air.

Figure E.4 – DTD plot for the fresh versus the spent Sample 5A in air.
Figure E.5 – DTD plot the fresh versus the spent Sample 6 in air.
Appendix F

XRD diffractograms of the spent Samples 2, 5A, 5B and 6 in HDO of isoeugenol at 300 °C and 30 bar.

**Figure F.1** – XRD diffractograms of the spent Samples 2, 5A, 5B and 6.
Appendix G

Size-exclusion chromatography data for the spent Sample 4.

Figure G.1 – SEC chromatogram for sitosterol with a concentration of 0.1 mg/ml.

Table G.A – Retention times and areas for sitosterol 0.1 mg/ml

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Figure G.2 – SEC chromatogram for sitosterol with a concentration of 0.033 mg/ml.
Table G.B – Retention times and areas for sitosterol 0.033 mg/ml

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Figure G.3 – SEC chromatogram for the spent Sample 4 in HDO of isoeugenol at 300 °C and 30 bar.

Table G.C – Retention times and areas for the spent Sample 4 in HDO of isoeugenol at 300 °C and 30 bar

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</table>
# Appendix H

Table H.A – List of experiments performed in HDO of isoeugenol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant mass (g) and reaction conditions</th>
<th>Conversion of isoeugenol and GCLPA, %</th>
<th>Molar selectivity of final products, %</th>
<th>Yield of final products, %</th>
<th>HDO, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt.% Ni/Graphite</td>
<td>(0.1 g), <strong>200 °C</strong>, 30 bar, 900 rpm</td>
<td>100 &amp; 86.5</td>
<td>Dihydroeugenol (95.0), 3 &amp; 4 Propylcyclohexene (1.7), Cyclohexene (0.8)</td>
<td>Dihydroeugenol (82.6), 3 &amp; 4 Propylcyclohexene (1.5), Cyclohexene (0.7)</td>
<td>n/d</td>
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<tr>
<td>20 wt.% Ni/Graphite</td>
<td>(0.1 g), <strong>300 °C</strong>, 30 bar, 900 rpm</td>
<td>100 &amp; 75.2</td>
<td>Propylcyclohexane (55), Dihydroeugenol (2), Propylcyclohexanone (2)</td>
<td>Propylcyclohexane (60), Dihydroeugenol (3), Propylcyclohexanone (2)</td>
<td>93</td>
</tr>
<tr>
<td>10 wt.% Co/SBA-15</td>
<td>(0.1 g), <strong>200 °C</strong>, 30 bar, 900 rpm</td>
<td>100 &amp; 93.0</td>
<td>Dihydroeugenol (80.9), 3 &amp; 4 Propylcyclohexene (6.1), Cyclohexene (2.1)</td>
<td>Dihydroeugenol (80.1), 3 &amp; 4 Propylcyclohexene (6.0), Cyclohexene (2.0)</td>
<td>n/d</td>
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<tr>
<td>10 wt.% Co/SBA-15</td>
<td>(0.1 g), <strong>300 °C</strong>, 30 bar, 900 rpm</td>
<td>100 &amp; 78.7</td>
<td>Propylcyclohexane (55), Propylcyclohexanone (2), Dihydroeugenol (0.3)</td>
<td>Propylcyclohexane (63), Propylcyclohexanone (2), Dihydroeugenol (0.35)</td>
<td>97</td>
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<tr>
<td>Co/Support</td>
<td>Conditions</td>
<td>Products</td>
<td>Yield (%)</td>
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<tr>
<td>Co/TiO₂</td>
<td>15 wt.%</td>
<td>Dihydroeugenol (24), Propylcyclohexane (18), Propylcyclohexanone (4)</td>
<td>72</td>
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<td></td>
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<tr>
<td>Co/Al₂O₃</td>
<td>15 wt.%</td>
<td>Propylcyclohexane (30)</td>
<td>100</td>
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<tr>
<td>Co/SiO₂,</td>
<td>11 wt.%</td>
<td>Dihydroeugenol (81.8), 3&amp;4 Propylcyclohexene (11.6), Cyclohexene (4.2)</td>
<td>n/d</td>
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<tr>
<td>Reduced at 415 °C</td>
<td>11 wt.%</td>
<td>Propylcyclohexane (48), 3&amp;4 Propylcyclohexene (5), Propylcyclohexanone (4), Dihydroeugenol (3)</td>
<td>90</td>
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<tr>
<td>Co/SiO₂,</td>
<td>11 wt.%</td>
<td>Propylcyclohexane (47), 3&amp;4 Propylcyclohexene (5), Propylcyclohexanone (3), Dihydroeugenol (2)</td>
<td>92</td>
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<tr>
<td>Reduced at 550 °C</td>
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<tr>
<td><strong>11 wt.% Co/SiO₂, Regenerated</strong></td>
<td>Propylcyclohexane (52.1), 3&amp;4 Propylcyclohexene (2.5), Propylcyclohexanone (2.3), Cyclohexene (1.2), Dihydroeugenol (0.6)</td>
<td>Propylcyclohexane (58.7), 3&amp;4 Propylcyclohexene (2.8), Propylcyclohexanone (2.6), Cyclohexene (1.3), Dihydroeugenol (0.7)</td>
<td>96</td>
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<tr>
<td>11 wt.% Ni/SiO₂</td>
<td>Propylcyclohexane (44.4), 3&amp;4 Propylcyclohexene (5.9), Propylcyclohexanone (3.4), Cyclohexene (3.0), Dihydroeugenol (2.4)</td>
<td>Propylcyclohexane (44.0), 3&amp;4 Propylcyclohexene (5.8), Propylcyclohexanone (3.4), Cyclohexene (3.0), Dihydroeugenol (2.4)</td>
<td>92</td>
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<tr>
<td><strong>10 wt.% Co/SiO₂, crushed pellets (&lt; 93 μm), Batch reactor with hexadecane as solvent</strong></td>
<td>Propylcyclohexane (37.3), Propylbenzene (6.5), Dihydroeugenol (6.1), 3&amp;4 Propylcyclohexene (4.2), Propylcyclohexanone (3.9), Cyclohexene (1.8)</td>
<td>Propylcyclohexane (34.8), Propylbenzene (6.1), Dihydroeugenol (5.7), 3&amp;4 Propylcyclohexene (3.9), Propylcyclohexanone (3.6), Cyclohexene (1.7)</td>
<td>85</td>
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<tr>
<td>10 wt.% Co/SiO₂, 3 mm pellets, trickle-bed reactor with 1-decanol as solvent (0.2 g), 300 °C, 30 bar, 0.1 ml/min (H₂ flowrate)</td>
<td>73.3 &amp; 92.1</td>
<td>3&amp;4 Propylcyclohexene (24.2), Propylcyclohexanone (17.8), Dihydroeugenol (12.7), Cyclohexene (11.7), Isoeugenol (10.8), Propylcyclohexane (10.0), Propylbenzene (2.7)</td>
<td>3&amp;4 Propylcyclohexene (26.0), Propylcyclohexanone (19.1), Dihydroeugenol (13.7), Cyclohexene (12.6), Isoeugenol (10.9), Propylcyclohexane (10.7), Propylbenzene (2.9)</td>
<td>53.5</td>
<td></td>
</tr>
</tbody>
</table>
Appendix I

Gas phase diffractograms of Samples 1 – 7 obtained in HDO of isoeugenol at both 200 °C and 300 °C and 30 bar in the trickle bed reactor.

Figure I.1 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 1.

Figure I.2 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 200 °C and 30 bar for Sample 2.
Figure I.3 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 2.

Figure I.4 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 4.
Figure I.5 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 5A.

Figure I.6 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 5B.
Figure I.7 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 2.

Figure I.8 – GC-FID chromatogram of gaseous products obtained in HDO of isoeugenol at 300 °C and 30 bar for Sample 7.