

Catalytic Hydrodeoxygenation of Bio-oil and Model Compounds

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Declaration of Originality

I hereby declare that this thesis is the result of my own work and the thesis was entirely written by me in accordance with the academic rules of Imperial College London. Any ideas or quotations from the work of other people, published or otherwise, are appropriately referenced.

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Abstract

The upgrading of the Norwegian spruce derived bio-oil was carried out in a batch reactor with conditions of 50 bar H_2 (cold) and 3 to 13 hr of batch time at 175 to 250 °C. The emphasis was given on the effect of operating conditions on the hydrodeoxygenation (HDO) performance of unsupported NiMo nano sulphide catalysts. It is found that the degree of deoxygenation of the bio-oil increases and that of hydrogenation of the upgraded products declines with increasing the reaction temperature. The addition of sulphur to prevent the nanosulphide catalyst leaching problem is not essential. Extending the batch time produces more saturated products with less oxygen content, but it can be optimised as the deoxygenation reaction rate decreases along the time. As for HDO solvent, dodecane is preferred comparing with tetralin.

The HDO of p-cresol over Co/Al_2O_3 and Ni/Al_2O_3 catalysts at 250 to 375 °C and 50 bar of H_2 (hot) in a batch reactor gives 4-methylcyclohexanol, methylcyclohexane and toluene as the major products. Both catalysts are active leading to almost complete conversion ($\geq 98\%$) of p-cresol at all temperatures. The degree of deoxygenation and the product distribution of toluene increases with temperature. Toluene can be produced by the direct deoxygenation of p-cresol and by the disproportionation of methylcyclohexenes at high temperature (i.e. 375 °C). Sulphur suppresses the HDO of p-cresol. It deactivates the hydrogenation sites but does not appear to be a poison for the hydrogenolysis sites.

Same conditions were used for the HDO of guaiacol, except the H_2 pressure being used was 40 bar (cold). Dominant products are cyclohexanol, methoxycyclohexanols and cyclohexane at 300 °C and below and those at 325 °C and above are cyclohexane, benzene and ring contraction products (i.e. cyclopentane and methylcyclopentane). High temperatures facilitate deoxygenation and benzene production. As the temperature increases, the methoxyl group is firstly removed and then the hydroxyl group. At 350 °C, reducing the pressure from 40 bar (cold) to 20 bar (cold) increases the benzene product distribution from 2 wt% to 40 wt%. Sulphur has a detrimental effect on the HDO of guaiacol. Catechol is the main product from guaiacol in the presence of sulphur.

1 INTRODUCTION

Energy is essential for a functioning society. However, emerging economical, political and environmental concerns exert great pressure on existing energy sources. It is expected that the world energy consumption will be doubled before 2050 [1]. Considering the depletion of fossil fuels and the increasing demand for energy, it is imperative to develop alternative sources. On the other hand, CO₂, a major contributor to the climate change, is produced mainly by the burning and the thermal oxidation of fossil fuels [2]. Countries have engaged with the Copenhagen Accord. For the year 2020, EU aims to reduce the emission by 20 to 30% comparing with 1990 and US by 17% comparing with 2005. China has to reduce its carbon intensity by 40 to 45% from the 2005 level. Recommended by the UK Committee on Climate Change, the UK should support a target to reduce greenhouse gas emissions by at least 35% in 2020 and 80% by 2050, compared with that in 1990. Accordingly, the development of reliable and cleaner energy supplies is of special significance. For the coming post-fossil fuel era, the substitutes should be able to meet the power demand of the society and, especially, to accelerate the transition to a low carbon economy. With this respect, the research of biomass and its derivatives has aroused great attention and interests.

1.1 BIOMASS

Biomass is a renewable energy source that can be used for the production of fuels and various chemicals. Therefore, biomass and its derivatives have the potential to diversify energy resources and mitigate the environmental impacts [3]. They have received considerable attention in the chemistry, chemical engineering and agriculture. Essential information about biomass and bio-oil, as a biomass derivative, is extracted from the literature and reviewed in this chapter and the following one to set a background for the present study. However, terms need to be specified first. By definition, biomass is biological material derived from living or recently living organisms. From energy point of view, it often refers to plant based material [4]. Biofuel is a renewable energy source produced from biomass and it converts solid, liquid or gaseous fuels [5]. Pyrolysis of a hydrocarbon compound is incomplete thermal degradation in the absence or with low oxygen, which generates a liquid product known as bio-oil [6, 7].

There exist mainly two approaches to understand the development of biomass. Biomass, which is abundant, has the ability to fulfil the basic requirements of performance as the substitute of fossil fuels. Also, from ecological and sustainable points of view, the burning of fossil resources releases a wide variety of undesirable emissions which cause

negative environmental impacts and require expensive mitigation processes whereas biomass has negligible content of sulphur and nitrogen and thus, the emissions of SO_x and NO_x are substantially reduced. Furthermore, zero net CO_2 emission from biomass utilization can be achieved due to plant photosynthesis [6, 8].

1.1.1 Biomass composition

Typical sources of biomass include, but are not limited to, lignin, plant parts, fruits, vegetables, wood chips, chaff, grain, grasses, corn and any cellulose containing biological material or material of biological origin [7]. In contrast to fossil fuels, biomass would be used as a sustainable and renewable energy source due to its contribution for the mitigation of carbon dioxide from the atmosphere through cycles of regrowth and combustion (Figure 1.1.1).

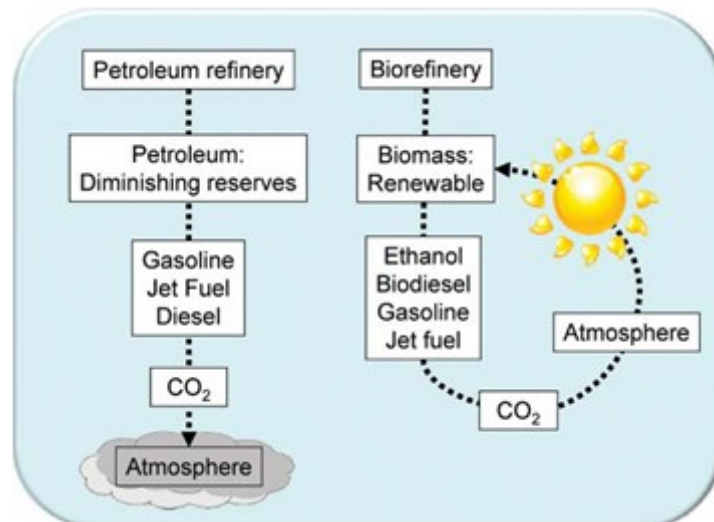


Figure 1.1.1 CO_2 cycles for petroleum and biomass-derived fuels [9]

The feedstocks derived from biomass can be classified as starchy, triglyceride and lignocellulosic feedstocks. Lignocellulosic biomass, from which bio-oil is mainly produced, consists of three principle biopolymers, e.g. cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%) [9], which are illustrated in Figure 1.1.2. This kind of biomass (i.e. lignocellulosic biomass) will be mainly discussed, since this thesis is concerned with bio-oil conversion processes.

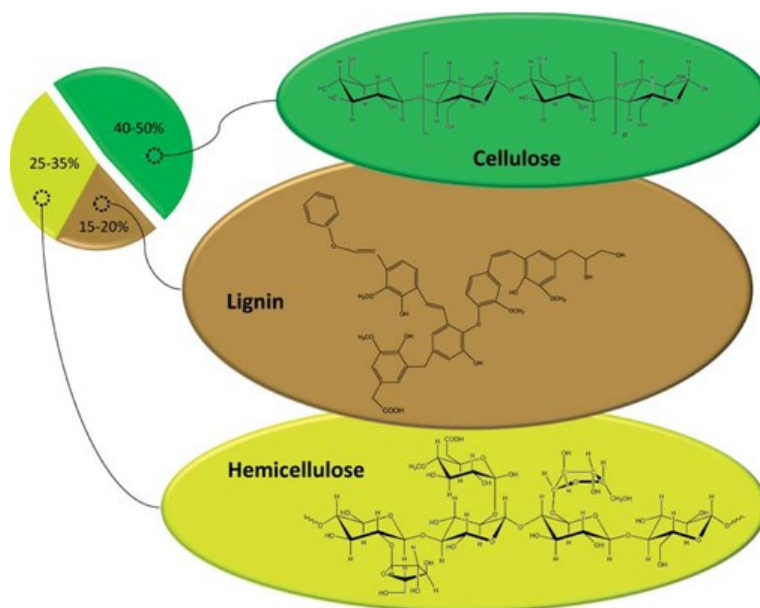


Figure 1.1.2 Lignocellulose composition [9]

1.1.2 Conversion of biomass to liquid fuels

It has been a long history since biomass derived fuels were used as liquid energy sources. Due to the diminishing supply of petroleum, bio-derived fuels and the conversion technologies for their production have received more attention than ever before.

Biofuels being used currently mainly consist of alcohols (bioethanol or biobutanol) and oils (biodiesel). During many years of development, the processes to obtain them have reached industrial maturity. In general, the aims of the conversion of biomass into liquid hydrocarbon fuels are to remove the oxygen with the least H_2 consumption and to form C-C bonds in order to control the molecular weight of the final products. Strategies adopted for biomass conversion include phase change of solid biomass into a gaseous or liquid chemical platform involving partial removal of oxygen. The liquid platform can be catalytic upgraded to biofuel by the C-C coupling reactions and by the deep removal of remaining oxygen. The gas platform can be further processed by Fischer-Tropsch synthesis.

Figure 1.1.3 details the various strategies of the two most frequently used approaches for biomass conversion. The production of biofuels by thermochemical approach requires the processing of whole lignocellulose at high temperature and/or pressures. As for the approach of hydrolysis, sugars and lignin are isolated from lignocellulosic feedstock and processed either by biological method or by chemical method. However, due to the

nature of the present work, this review will only focus on the discussion of bio-oil production through the thermochemical pathway via the pyrolysis route.

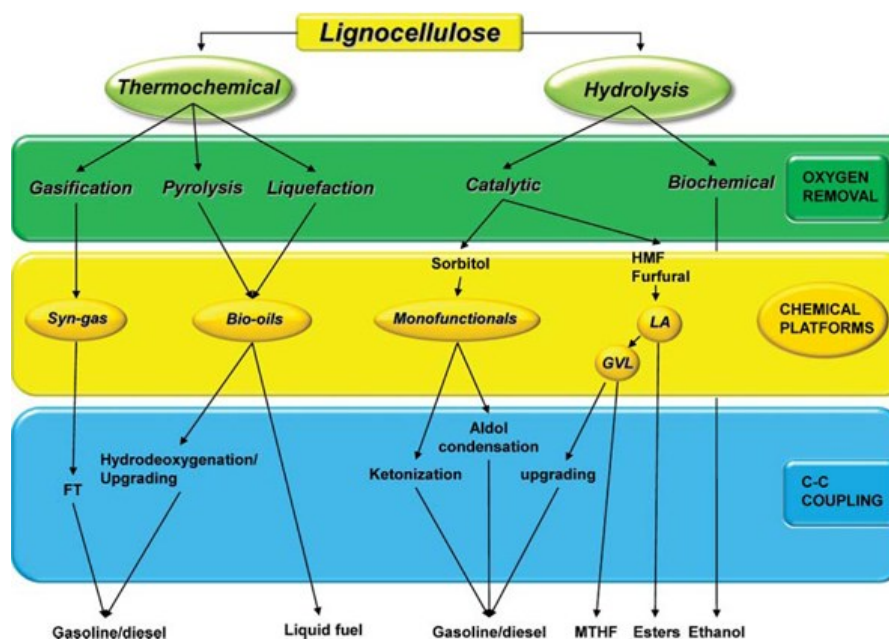


Figure 1.1.3 Strategies for the conversion of biomass [9]

As introduced at the beginning of this section, pyrolysis is a thermal process which enables the anaerobic decomposition of biomass at elevated temperatures. Pyrolysis of biomass produces a mixture of different molecules (e.g. alcohols, acids, ketones, esters and aromatic compounds) known as “bio-oil”. Synonyms for bio-oil include pyrolysis oil, wood oil, wood liquid and biofuel oil.

The biomass pyrolysis process has been reviewed many times, e.g. [10]. It is subdivided into slow pyrolysis and fast pyrolysis. Slow pyrolysis, also known as carbonisation, occurs at low temperatures and long residence time and its target product is charcoal that can be used to generate energy by combustion. Fast pyrolysis requires the biomass being processed at high temperatures (500 to 700 °C) and high heating rates (e.g. 300 °C/min) with a short residence time (only a few seconds) leading to the production of bio-oils. Normally, the moisture content of biomass should be reduced to 10% before fast pyrolysis [11]. Other than being converted to bio-oil, fast pyrolysis also yields aromatic compounds which are important intermediates for the production of chemicals [9]. Figure 1.1.4 presents the process schematic of biomass pyrolysis.

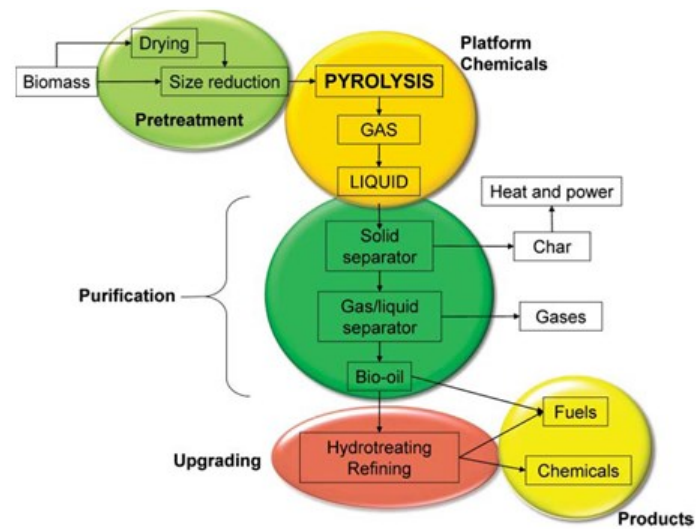


Figure 1.1.4 Process schematic: biomass pyrolysis and upgrading [9]

1.2 BIO-OIL AND MODEL COMPOUNDS

The production of energy from biomass has increased during recent decades. Bio-oils, which are produced from biomass by pyrolysis, are promising alternatives due to their potential similarity to the currently preferred fuel sources. Based on this unique feature, the modifications of the current transportation infrastructure and the internal combustion engine can be minimised in order to be adapted to take bio-oils [9].

Technologies have been developed in harvesting bio-oils in the forms of fuels and fuel blending components. However, the high oxygen content of bio-oils results in negative properties (e.g. low heating value, incompatibility with conventional fuels, solids contents, high viscosity, incomplete volatility and chemical instability) [12]. The removal of oxygen, therefore, is essential if they are going to be used as alternatives to fossil fuels.

Bio-oils are composed of numerous compounds including aldehydes, alcohols, furfurals, ketones, carboxylic acids, carbohydrates and guaiacols [13]. The compositions of these compounds depend on the bio-oil feedstocks. As a result, the understanding of the mechanisms of bio-oil deoxygenation is extremely complicated. A current strategy to study bio-oils is to use model compounds. The merits of using model compounds are that they are able to provide more precise chemical information and avoid thermal polymerisation reactions [14]. One can control the selectivity of certain products and probe the bio-oil upgrading towards fuels with desired qualities with the knowledge of the chemistry and mechanisms of model compounds [13].

1.3 AIMS AND OBJECTIVES

The jet and diesel fuel range hydrocarbons (with boiling point ranging from 175 to 375 °C and the carbon number from about C₈ to C₂₄) are valuable products and they are desirable targets from biomass and bio-oils. In order to provide knowledge to maximise the production of these engine fuels from wood derived pyrolysis oils, this research focuses on the catalytic upgrading of bio-oils and typical model compounds presented in bio-oils, specifically on HDO.

HDO is a common upgrading approach to reduce the oxygen levels in bio-oils and the method was originally inspired by the hydrotreating in the petroleum industry. However, the oxygen content of bio-oils is an order of magnitude larger than that of petroleum. A single-step direct deoxygenation, in this case, can lead to excess coke formation and catalyst deactivation. To overcome the problems, a two-step HDO has been proposed [15, 16] in which the bio-oil is first stabilised in a low temperature reactor and then a deep deoxygenation is accomplished in the second step at elevated temperatures. The study concerns only the first-step mild treatment, targeting to remove at least 20 wt% of the organo-oxygen of the bio-oil.

p-Cresol and guaiacol are basic branched phenols, common oxygenates from pyrolysis bio-oil. Nevertheless, they are important intermediates of the HDO of complex oxygen-containing aromatics. The study of these model compounds can provide essential information on the upgrading of bio-oils. Accordingly, emphasis in this research was given to the study of deoxygenation of p-cresol, guaiacol and a commercial bio-oil provided by Future Blends Ltd., UK.

Catalysts are necessary for HDO. Alumina supported Co and Ni mono-metallic catalysts are known for the selective hydrogenation of pyrolysis gasoline. Moreover, they also have the ability to remove oxygen, which has been demonstrated in a previous work. As a carry on study, Ni/Al₂O₃ and Co/Al₂O₃ are used to conduct a detailed HDO study on model compounds in the present work.

The objectives are to reveal the reaction pathways and to investigate the impacts of operating conditions (temperature, pressure, reaction time, sulphur level and etc.) on the HDO of the crude pyrolysis bio-oil and selected model compounds.

1.4 STRUCTURE OF THE THESIS

In Chapter 2, the catalytic upgrading of the bio-oil to liquid fuels and the HDO of model compounds are reviewed to set the background of the study. After a general introduction of bio-oil, its upgrading strategies and processes are explained. Emphasis is then given to the HDO of model compounds, especially p-cresol and guaiacol and their reaction mechanisms. Besides, catalysts, which are commonly used in the HDO research, are briefly reported with the potentials of using selective hydrogenation catalysts in HDO being addressed. Finally, the impact of sulphur on the performance of the catalysts is discussed.

The experimental procedures and analytical methods of the work in each of the following chapters are not always the same. Therefore, they are described in details in each chapter separately.

Chapter 3 presents the study of bio-oil upgrading over a wide range of catalysts under different conditions.

Chapter 4 and 5 deal with the HDO of model compounds over $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. A very brief background, relevant to the purposes of the study, is given at the beginning of Chapter 4. The HDO work of p-cresol is presented in Chapter 4 while that of guaiacol is given in Chapter 5. The results are presented and discussed.

The overall conclusions are summarised in Chapter 6 with the recommendations for future work.

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2 LITERATURE REVIEW

Energy crisis and environmental pollutions are worldwide problems. Nations have worked together to secure a better future of mankind. As is emphasised [1]:

“To deliver energy security and accelerate the transition to a low carbon economy requires urgent and ambitious action at home and abroad.

We need to:

- save energy;
- develop cleaner energy supplies; and
- secure reliable energy supplies at prices set in competitive markets.”

Improving existing energy supply and demand systems and developing renewable energy are of vital importance to build a low carbon society.

The developing of biomass technology is one of the promising approaches to accomplish the above objectives. This chapter discusses the open literature in various aspects regarding the catalytic upgrading of bio-oils and model compounds.

2.1 BIO-OIL AND BIO-OIL UPGRADING

2.1.1 Bio-oil

Bio-oil production by fast pyrolysis of biomass with high liquid yield is a reasonable and promising technique for the coming post-fossil fuel era [2]. However, due to the short residence time and rapid cooling or quenching from elevated temperatures during fast pyrolysis, bio-oil is not produced under the conditions of thermodynamic equilibrium. Consequently, the chemical composition of the condensate (i.e. bio-oil) might change towards thermodynamic equilibrium at storage temperatures [3].

The composition and the properties in terms of oxygen content, viscosity and acidity of bio-oils are crucial criteria to evaluate their potential of being co-processed in the refinery to diesel, gasoline and aviation fuel. Unlike conventional fuels, bio-oils are derived from depolymerisation and fragmentation of biomass feedstock by pyrolysis. The composition of bio-oil and petroleum based fuel, therefore, is different. Table 2.1.1 summarises the intrinsic properties of bio-oil and petroleum derived oil.

Table 2.1.1 Typical properties of wood pyrolysis bio-oil and heavy fuel oil [4-9]

	Pyrolysis liquids from different feedstocks							Heavy fuel oil
	Birch	Pine	Poplar	Switch-grass	Alfalfa-early bud	Alfalfa-full flower	Various	
Physical property								
Water (wt%)	18.9	17	18.9				15-30	0.1
pH	2.5	2.4	2.8				2.0-3.7	-
Density (10 ³ kg/m ³)	1.25	1.24	1.2				1.1-1.3	0.98
Viscosity at 50 °C (cSt)	28	28	13.5				13-80	200
LHV (MJ/kg)	16.5	17.2	17.4				13-18	30
Flash point (°C)	62	95	64				50-100	90-180
Element (wt%)								
C	44	45.7	46.5	47.53	44.3	45.97	32-49	85
H	6.9	7	7.2	6.81	5.43	5.52	6.9-8.6	11
N	<0.1	<0.1	0.15	0.51	2.52	1.6	0-0.2	0.3
S	0	0.02	0.02	0	0.22	0.088	0.00-0.05	0.5-3.0
O	49	47	46.1	42.54	38.2	40.58	44-60	1

As shown in Table 2.1.1, the oxygen content of bio-oils approaches almost 40 wt%. Moreover, oxygen is widely distributed in more than 300 compounds of bio-oils, depending on the type of biomass feedstock and the severity of the process (e.g. temperature, residence time and heating rate) [6]. The differences between bio-oils and hydrocarbon fuels are mainly derived from their high oxygen content, which has a detrimental effect on the utilisation of bio-oils. Some of the O-compounds in feed are

prone to polymerise. The fuel, therefore, is not stable and might have a poor performance during the combustion. These compounds may also cause a rapid catalyst deactivation during hydroprocessing [10]. The high oxygen content reduces the energy density of bio-oil respect to that of the conventional fuel by 50% and increases the immiscibility with hydrocarbon fuels [3].

Similar to the distribution of oxygen-compounds, the viscosities of bio-oils are also determined by the resources of biomass and the pyrolytic processes. However, they can be reduced by increasing the water content and decreasing the water insoluble components. Meanwhile, the addition of alcohols (e.g. methanol and ethanol) has the same effect on the reducing of the viscosities [11].

Bio-oils contain significant amount of carboxylic acids, including acetic and formic acids. Normally, the total acid number (TAN) of bio-oils ranges from 50 to 200 [12, 13]. The high acidity results in an increased corrosiveness of the fuel and will have a more severe effect at high temperatures [3].

These undesirable characteristics of bio-oils (e.g. viscosity, thermal instability, corrosiveness and immiscibility with conventional fuels) limit their application. Consequently, an upgrading process, especially reducing the oxygen content, is of a necessity before they can be processed in the refinery streams.

2.1.1.1 Compositions of bio-oil

Bio-oils can be derived from various sources and their compositions are diverse. Only typical studies are selected and presented here to provide a general idea on bio-oil compositions.

Bio-oils mainly consist of three elements, i.e. carbon, hydrogen and oxygen. However, they are complex mixtures that involve almost all kinds of oxygenated organic compounds including acids, alcohols, aldehydes, esters, ethers, ketones, sugars, phenols and furans. In general, the compounds identified in bio-oil can be classified into five groups: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids and phenolic compounds [4]. To facilitate the analysis of both bio-oils and upgraded bio-oil products, the method of using solvent fractionation to determine product groups has been proposed and reviewed by Oasmaa and Elliott [14-16]. It separates the bio-oil into water-soluble and water-insoluble phases at a moderate temperature. The water-soluble fraction can be subdivided into four main groups, i.e. water (feedstock moisture and

water formed during pyrolysis), acid (mainly acetic and formic acids), carbonyl compounds (aldehydes and ketones) and "sugars" (one to three ring anhydrosugars and hydroxy acids, oligomers, sugar acids and etc.). The water-insoluble fraction can be divided by dichloromethane extraction into low-molecular-mass and high-molar-mass fractions.

According to the work conducted by Wang et al. [17], furfural, dimethyl phenol, 2-methoxy-4-methyl phenol, eugenol, cedrol, furanone and etc. are the main compounds of the bio-oils. In addition, most of the components identified are phenols with ketones and aldehydes attached and the existence of oxygen can be found in almost all of the functional groups. Furthermore, it has been proved by the study that, due to aldehydes and ketones, bio-oils exhibit hydrophilicities and they are highly hydrated. Consequently, water is difficult to be removed from the feed.

Table 2.1.2 is from a study conducted by Luo et al. [18] and it shows the relative content of main compounds of a wood based bio-oil derived from *Pterocarpus indicus*. The main components displayed in the table agree with those obtained by Adam et al. from *Barkfree spruce wood* [19]. Table 2.1.3 lists the major components of bio-oils that derived from switchgrass and alfalfa. Table 2.1.4 categorises the components of an *aspen poplar wood* derived bio-oil according to functional group. The bio-oil was distilled at 200 °C under a vacuum of 172 Pa to separate the compounds.

Richard et al. [20] conducted research on hydrothermal deoxygenation of bio-oil derived from Norwegian spruce. ^{31}P NMR was used to analyse the oil and to monitor the compositional changes of the bio-oil. The characterisation results of the crude bio-oil are presented in Table 2.1.5. This NMR analytical technique was developed by Argyropoulos et al. [21, 22]. ^{31}P nucleus is naturally abundant and it is ideal for the qualitative and quantitative analysis of phosphitylated hydroxy groups by NMR [20]. However, it should be noted that some oxygenate species such as ethers are ^{31}P NMR silent, and therefore, their conversion and production during the bio-oil upgrading cannot be followed using this this technique. Recently, the use of ^{31}P NMR in biomass characterisation has been reviewed [23].

Table 2.1.2 Content of main compounds in *Pterocarpus indicus* derived bio-oil [18]

Compound	Relative content (%)
Furfural	9.06
Acetoxyacetone, 1-hydroxyl	1.21
Furfural, 5-methyl	1.82
Phenol	2.55
2-Cyclopentane-1-one, 3-methyl	1.58
Benzaldehyde, 2-hydroxyl	2.70
Phenol, 2-methyl	5.04
Phenol, 4-methyl	0.51
Phenol, 2-methoxyl	0.27
Phenol, 2,4-dimethyl	9.62
Phenol, 4-ethyl	2.18
Phenol, 2-methoxy-5-methyl	4.15
Phenol, 2-methoxy-4-methyl	0.55
Benzene, 1,2,4-trimethoxyl	3.80
Phenol, 2,6-dimethyl-4-(1-propenyl)	4.25
1,2-Benzenedicarboxylic acid, diisooctyl ester	1.80
2-Furanone	5.70
Levoglucozan	6.75
Phenol, 2,6-dimethoxy-4-propenyl	3.14
Furanone, 5-methyl	0.49
Acetophenone, 1-(4-hydroxy-3-methoxy)	2.94
Vanillin	6.35
Benzaldehyde, 3,5-dimethyl-4-hydroxyl	4.54
Cinnamic aldehyde, 3,5-demethoxy-4-hydroxyl	2.19

Table 2.1.3 Quantification of some bio-oil components (wt%) [5]

Compound	Group	Switch-grass	Alfalfa, early bud	Alfalfa, full flower	Typical wood
Cellulose/Hemicellulose derived compounds (wt%)					
acetic acid	acids	2.94	2.26	3.49	0.5-12
glyoxal	aldehyde	trace	0.35	1.05	
furfural	furan	0.62			0.1-1.1
furfuryl alcohol	furan		0.18	0.20	0.1-5.2
2-methyl-2-cyclopenten-1-one	ketone	0.16	0.27	0.26	
3-methyl-2-cyclopenten-1-one	ketone	0.34	0.46	0.44	
hydroxyacetaldehyde	oxygenates	2.40			0.9-13
4-hydroxy-4-methyl-2-pentanone	oxygenates	0.05	0.24	0.04	
acetol	oxygenates	2.75	0.78	2.35	0.7-7.4
levoglucosan	sugar	6.38	0.14	0.37	4.8-5.4
Lignin derived compounds (wt%)					
guaiacol	phenol	0.18	0.51	0.46	0.1-1.1
2-methoxy-4-methylphenol	phenol	0.07	0.21	0.16	0.1-1.9
isoeugenol	phenol	0.45	0.70	0.73	0.1-7.2
2,6-dimethoxyphenol	phenol	0.20	0.37	0.43	0.7-4.8
phenol	phenol	0.66	1.14	0.95	0.1-3.8
o-cresol	phenol	0.19	0.30	0.24	0.1-0.6
p-cresol	phenol	0.27	0.44	0.33	0.1-0.5
m-cresol	phenol	0.20	0.47	0.34	0.1-0.4
2,5-dimethylphenol	phenol	0.01	0.08	0.07	
2,4-dimethylphenol	phenol	0.10	0.17	0.14	0.1-0.3
3,5-dimethylphenol	phenol	0.05	0.12	0.08	
4-ethylphenol	phenol	0.22	0.17	0.15	
3-ethylphenol	phenol	0.04	0.06	0.06	
2-ethylphenol	phenol	0.03	0.07	0.04	0.1-1.3
Protein derived compounds (wt%)					
benzyl nitrile	nitrogen	trace	0.10	0.06	
indole	nitrogen		0.15	0.01	

Table 2.1.4 Amount of distillate and residue and the composition of the organic distillate fraction of *aspen poplar wood* derived bio-oil [24]

Distillate (wt% of bio-oil)		62.3
Residue (wt% of bio-oil)		37.7
Organic distillate composition (wt% of organic distillate fraction)		
Acids and esters		2.5
Alcohols		6.6
Aldehydes and ketones		7.8
Aliphatic hydrocarbons		5.5
Aromatic hydrocarbons		21.6
Ethers		2.5
Furans		3.4
Phenols		28.1
Unidentified fraction		21.9
Total		100
Main components of the organic distillate fraction		
Acids and esters	Acetic acid, methyl ester-	0.1
	3-Propanoic acid	0.8
Alcohols	Cyclopentanol, 2-methyl-	0.9
	Cyclohexanol, 4-methyl-	1.9
Aldehydes and ketones	Cyclopentanone, 2-methyl-	3.1
	Hexanal, 4-methyl-	1.2
	Cyclohexanone	2.5
Aliphatic hydrocarbons	3-Octyne, 5-methyl-	1.1
	Cyclopentane, 2-ethyl-	3.5
Aromatic hydrocarbons	Benzene, cyclopropyl-	1.7
	Phenanthrene, methyl-	1.2
Ethers	Benzene, 1-methoxy-	0.7
	Benzene, 1-ethoxy-	2.5
Phenols	Phenol	1.9
	Phenol, 4-methyl-	1.6
	Phenol, 2-methoxy-4-(2-propenyl)-	23.6

Table 2.1.5 The overall oxygen content in the Norwegian spruce derived bio-oil vs. the content of different hydroxyl groups [20]

	Elemental analysis for oxygen (wt%)	³¹ P NMR analysis for OH (wt%)
Aliphatic alcohols		14.71
Condensed phenolic		3.39
Phenolic OH		1.08
Guaiacolic OH		4.32
Acidic OH		0.05
Overall content	28.05	23.55

2.1.2 Bio-oil upgrading and hydrodeoxygenation

As aforementioned undesirable characteristics of bio-oils, it must be upgraded if they are to be used in the current transportation system. There exist mainly three pathways for the upgrading of bio-oils to transportation fuels: (1) HDO with typical hydrotreating

catalysts, (2) zeolite upgrading and (3) steam reforming (combined with Fischer-Tropsch synthesis) or forming emulsions with diesel fuels [25]. Among them, HDO appears to be a promising route because the process is effective [26] and it has less impact on the existing aromatics in the feedstock [27]. It was originally inspired by hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN) of coal liquids and petroleum gas oils due to their similarities, as they all target to remove heteroatoms under analogous conditions.

HDO of bio-oils operates under moderate temperatures (300-600 °C) and pressurised conditions of H₂ in presence of heterogeneous catalysts [25]. Catalysts involved are mainly industrial hydrotreating catalysts for the removal of sulphur, oxygen and nitrogen from petrochemical feedstocks such as Co-Mo and Ni-Mo catalysts. Basic principle of HDO is that the oxygen in bio-oils reacts with H₂ to form water and saturated C-C bonds and thus, it is removed. However, the hydrogenation of aromatic components should be minimized otherwise it would lead to the reduction of octane number and the increasing of H₂ consumption. During hydroprocessing, both of the energy content and the stability of the fuel are substantially increased (Table 2.1.6). However, the unique feature of bio-oil HDO increases the process complexity. The oxygen content of bio-oils is an order of magnitude larger than that of fossil fuels. A single-step direct deoxygenation, in this case, can lead to excess coke formation and catalyst deactivation. Review articles are available to detail the bio-oil HDO process (e.g. kinetics and mechanisms) and catalysts involved (e.g. activities, selectivities and stabilities) [25, 28-30]. Still, certain original research articles are discussed here.

Table 2.1.6 Properties of bio-oils and upgraded bio-oils [31]

	High pressure liquefaction	Flash pyrolysis	Hydrodeoxygenated bio-oils
Elemental analysis			
Carbon (wt%)	72.6	43.5	85.3-89.2
Hydrogen (wt%)	8	7.3	10.5-14.1
Oxygen (wt%)	16.3	49.2	0.0-0.7
Sulphur (wt%)	<45	29	0.005
H/C atom ratio (dry)	1.21	1.23	1.40-1.97
Density (g/ml)	1.15	24.8	0.796-0.926
Moisture (wt%)	5.1	24.8	0.001-0.008
HHV (MJ/kg)	35.7	22.6	42.3-45.3
Viscosity (cP)	15000 (61 °C)	59 (40 °C)	1.0-4.6 (23 °C)
Aromatic/aliphatic carbon			38/62-22/78
RON			77
Distillation range (wt%)			
IBP-225 °C	8	44	97-36
225-350 °C	32	coked	0-41

To overcome some of the issues noted above, Elliott et al. [32, 33] suggested a two-step process for the HDO of pyrolysis bio-oils. The first step aims to hydrogenate the thermally unstable compounds with mild conditions (270 °C, 136 atm) to avoid their decomposition forming gums and coke leading to the plugging of the HDO reactor. The second step carries out the catalytic hydrogenation reactions with a higher temperature (400 °C, 136 atm). Either sulphided Co-Mo/Al₂O₃ or sulphided Ni-Mo/Al₂O₃ is used as the catalyst throughout the whole process. With a yield of 0.4 L_{refined-oil}/L_{bio-oil-feed}, the oxygen content of the refined oil is reduced to less than 1 wt%. The major reason that reduces the yield is the conversion of carbon (20-30%) in the bio-oil into gas phase carbon (e.g. CO₂). Process uncertainties include catalyst stability and gum formation within the system. Table 2.1.6 compares the properties of upgraded bio-oils with those of untreated crude bio-oils.

Zhang et al. [34] separated the pyrolysis oil into water phase and oil phase. The water phase which contains valuable chemicals such as acetic acid and hydroxyacetone is recovered for further process. Meanwhile, the oil phase is catalytic hydrotreated with Co-Mo-P/Al₂O₃ in an autoclave under the conditions of 360 °C, 30 min reaction time and 2 MPa cold H₂ pressure. Tetralin, as a H₂ donor solvent, is used. It acts as a H₂ vehicle which can transfer the gas phase H₂ in active form to radical fragments for their stabilisation. The oxygen content is reduced from 41.8% of the crude oil to 3% of the upgraded one.

McCall and Brandvold [35] claimed a process for the production of hydrocarbons (e.g. naphtha, aviation and or diesel fuel, blending components and etc.) from biomass with high yields. The pyrolysis oil is first treated in a partial deoxygenation zone with mild conditions to remove the water, gases and light ends. The partial deoxygenation zone is operated with the pressure ranging from 34 to 140 bar and the temperature ranging from 200 to 400 °C. Then, the partially deoxygenated stream is introduced into a full deoxygenation zone with severe conditions to generate a fully deoxygenated product. The full deoxygenation zone conditions have a pressure of 69 to 138 bar and a temperature of 300 to 500 °C. The partial deoxygenation zone can be considered as a hydrotreating zone with any hydrogenation and hydrotreating catalysts that such as Ni or Ni-Mo on high surface area support. Other catalysts claimed as suitable include one (Pt) or more noble metal (Pt and Pd) dispersed on high surface area support (gamma-alumina or activated carbon). The most reactive and thermally unstable oxygenates are removed within this zone. As for the full deoxygenation zone, it can be regarded as a hydrocracking zone with any hydrocracking catalyst. Other available catalyst proposed is a combined zeolitic and amorphous silica-alumina with at least one metal element

selected from Ni, Cr, Mo, W, Co, Rh, Ir, Ru and Re deposited on the support. The catalyst employed has higher activity than the one in partial deoxygenation zone because it aims to catalyse the deoxygenation of less reactive oxygenates. Table 2.1.7 is the summary of the major parameters of the process in one of their examples with the best results. Figure 2.1.1 is a detailed process flow scheme for the embodiment of the invention.

Table 2.1.7 Example of specified conditions for partial and full deoxygenation zones [35]

Zone		Partial deoxygenation (Hydrotreating)	Full deoxygenation (Hydrocracking)
Catalyst		Unspecified hydrotreating catalyst	Sulfided NiMo/Al ₂ O ₃ produced by UOP
Pressure (psig)		1950	1525
Temperature (°C)		340	407
LHSV (h ⁻¹)		0.2	0.19
H ₂ /oil (scf/bbl)		14000	13700
Oil yield (vol%)		79%	85%
Effluent properties	O (wt%)	12.8%	0.4%
	H ₂ O	3.2 wt%	450 ppm
	TAN (mg KOH/g oil)	47	1.6

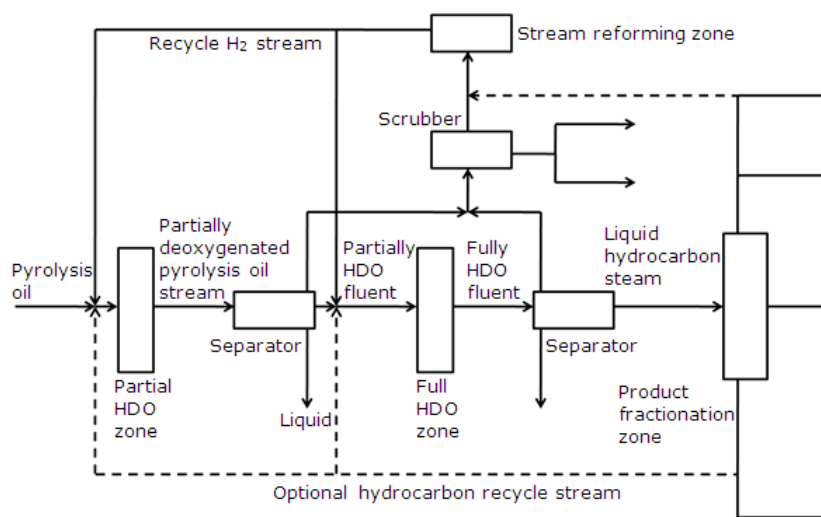


Figure 2.1.1 Process schematic [35]

Bauer and Boldingh [36] filed a patent application on the methods for the hydroconversion of biorenewable feedstocks using insoluble dispersed sulphided metal catalysts. In the process, a metal containing compound reacts with a sulphur containing compound at elevated temperature and pressure to form an insoluble particulate sulphided metal catalyst, and then the catalyst is added to at least one biorenewable feed to form a combined feed. After that, the combined feed enters a hydroconversion reaction zone for reaction. The product is then collected from the reactor. The active component of the catalyst is selected from Mo, Co, Fe, Ni, Ru, Sn, Cu and combinations thereof. Meanwhile, the catalyst is promoted by Ni and/or Co. The merit of using this

unsupported catalyst in a slurry reactor is that it enables the process to operate under more severe conditions. Therefore, a better heteroatom removal rate and a higher conversion of biorenewable feedstock into usable fuels can be achieved. Though no examples are given in the patent application, hypothetical preferred conditions of a pressure of 1500 to 2000 psig and a temperature of 420 °C of the HDO reactor loaded with unsupported sulphided molybdenum catalyst are proposed. In a similar patent [37], inventors described the process involved in the former one in details for the use of slurry hydroconversion of biorenewable feedstocks. The process, in which a low value petroleum derived hydrocarbon is combined with a biorenewable feedstock, enables the products to have a better yields or properties in comparison to those from pure feed of either feed components.

It is worth noting that the dispersed sulphided catalysts are recorded in the above patents, but no details on their performance are provided. Despite the fact that they are being used in the HDO research [38], Ruddy et al. [39] made no mention of these catalysts in their recent review.

2.2 MODEL COMPOUND

There exist mainly four aspects for the accurate modeling of a catalytic process: the development of reaction pathways consistent with the observed product distributions; prediction of an algebraic rate-law; estimation of kinetic parameter and discrimination of the model; and derivation of mathematical model or equation for the design of the catalytic reactor [24]. These approaches are essential for the optimisation the bio-oil upgrading process and the maximisation of the yields.

The identification of major reaction pathways (i.e. the first aspect) of bio-oil upgrading is one of the targets of the present study. However, the mechanisms of their upgrading are complex. In this case, model compounds are recommended for the understanding and identifying the reactions involved [24]. In addition, they can be used to determine the optimum reaction conditions. Moreover, they can give more precise chemical information and enable long time and complicated analysis to be processed [40].

Bio-oils contain various oxygen-containing compounds including dihydroxyphenols, alkyl-arylethers, ketones, carboxylic acids, esters and alcohols. He and Wang [41] grouped the typical model compounds that were widely studied. The model compounds and catalysts used are given in Table 2.2.1 and general routes of each group are available from the reference [41].

Table 2.2.1 Typical model compounds reviewed by He and Wang [41]

Group	Typical model compound	Catalyst
Carboxylic acids	Propanoic acid	Ru/C, Ru/ZrO ₂ and Ru/Al ₂ O ₃
	Acetic acid	Pt supported on transition metal oxides
	Oleic acid	Mo ₂ N, WN and VN supported on Al ₂ O ₃
Ketones and aldehydes	Benzaldehyde	Pd supported on zeolites and actived carbon
	Non-functional aryl aldehydes	
	Functional aldehydes	Pd(OAc) ₂
	Heterocyclic aldehydes	
	Alkenylaldehydes	
	Propanal (DFT calculation)	MoS ₂ and NiMoS active phases
Alcohols	Glycerol and 1- and 2-propanol, 1,2- and 1,3-propanediol	Pt/Al ₂ O ₃
Carbohydrates	Xylose	Zr-P, SiO ₂ -Al ₂ O ₃ , WO ₃ /ZrO ₂ , γ-Al ₂ O ₃
Phenols	Guaiacol	Sulfided CoMo and NiMo, nobel metals and etc.
	Phenol	Sulfided CoMo/Al ₂ O ₃ , nobel metals and etc.

As mentioned earlier, certain oxygen-containing compounds are prone to polymerise, and therefore a stabilisation process between 150 and 300 °C may be needed. Judging

from the temperatures being used, most of the HDO studies focused on this stabilisation process [42-44], in which phenols were the major oxygen-containing products. Under the circumstances, the HDO of stabilised bio-oil products can be generally described in terms of that of phenols [10]. Thus, the emphasis of the literature review of model compound HDO is given to phenols.

2.2.1 Hydrodeoxygenation of Phenols

Phenols form a significant proportion of bio-oils [10, 24, 45]. They are stable components and their upgrading requires a high catalytic reactivity and severe conditions [10, 46]. Furthermore, the formation of phenols is a critical path through which the HDO of oxygenated aromatics undergoes [47]. Consequently, the study of phenolic group can provide a moderate estimation of deoxygenation of bio-oils and it is of special importance. Generally, the HDO of phenols involves two routes [40, 42, 48]. One is the hydrogenation of the aromatic ring, which produces corresponding alicyclic alcohol as an intermediate. The intermediate is then deoxygenated. The other route is the direct elimination of oxygen by hydrogenolysis.

2.2.1.1 Cresol and phenol

Based on the work of HDO of cresols over sulphided CoMo/Al₂O₃ catalysts, Gevert et al. [42] suggested that there were two kinds of active sites involved, namely hydrogenation sites producing cycloalkanes and hydrogenolysis sites yielding parent aromatics. The adsorption which occurred between the aromatic ring and catalyst surface (pi-bonding system) would lead to the hydrogenated product whereas the adsorption through the hydroxyl group (sigma-bonding system) would result in aromatic product. They also pointed out that the relative positions of hydroxyl and methyl groups would affect activity due to steric hindrance. Odebunmi and Ollis [46] studied the HDO of cresols over the sulphided CoO-MoO₃/γ-Al₂O₃ catalyst. The relative reactivities of the cresols were found to be m-cresol ≥ p-cresol > o-cresol. The low reactivity of o-cresol was probably caused by the steric influence. The general HDO reaction scheme of cresols was proposed (Figure 2.2.1). Shin and Keane [49] established the same order of reactivities of cresols based on Ni/SiO₂ catalyst. Romero et al. [50] examined the performance of sulphided NiMo, CoMo and Mo catalysts over the HDO of 2-ethylphenol and reported that Ni promoted catalyst selectively favoured hydrogenation products whereas the CoMo and Mo catalysts led mainly to hydrogenolysis products. Wang et al. [51] prepared MoS₂ catalyst by hydrothermal method and tested the catalyst using p-cresol. According to their results, a low pH is preferred for the synthesis of MoS₂ with narrow bimodal peak

distribution and large specific surface area. High pressure would accelerate the aggregation of MoS₂ particles and further reduce the surface area. The catalyst demonstrated favourable activities of deoxygenation and aromatics production. The degree of deoxygenation and the ratio of hydrogenation to direct deoxygenation at 300 °C were 99.9% and 0.51, respectively. They explained the relationship between the product distribution and the microstructure of the catalyst by the Rim-Edge model of the molybdenum sulphide catalysts, which is originated from HDS [52]. The p-cresol molecule was adsorbed on the rim site via co-planar position whereas it was adsorbed on the edge site via perpendicular position. Hence, the selectivity towards direct deoxygenation increased with the degree of stacking. Table 2.2.2 is a summary of the original research reviewed in this section.

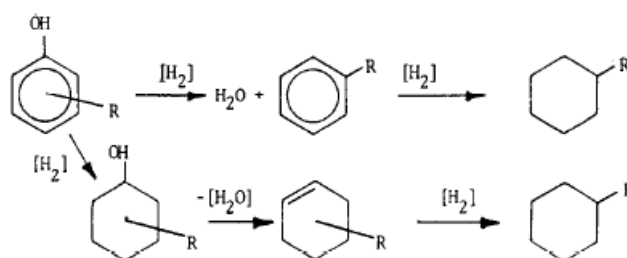


Figure 2.2.1 HDO Reaction pathways of cresols [46]

Table 2.2.2 Summary of original research reviewed for cresol and phenol HDO

Model compound	Temperature (°C) Reactor	Catalyst	Ref
Mono- and dimethyl substituted phenols	300 Batch	Sulphided CoMo	[42]
Phenol, m-, p- and o-cresol	150-300 Continuous	Ni/SiO ₂	[49]
2-Ethylphenol	340 Continuous	Promoted Mo/A ₂ O ₃	[50]
P-cresol	275-325 Batch	MoS ₂ nanosheets	[51]

2.2.1.2 Guaiacol

Bio oils, especially lignin-derived ones, have considerable amount of guaiacol and substituted guaiacols (up to 3 wt%) and they are thermally unstable [43, 53]. Guaiacol contains 3 different types of C-O bonds, i.e., C_{AR}-OH, C_{AR}-OCH₃ and C_{AR}O-CH₃ (Figure 2.2.2). Consequently, guaiacol and its derivatives are widely used as model compounds to understand the HDO behaviours of lignin-derived bio-oils.

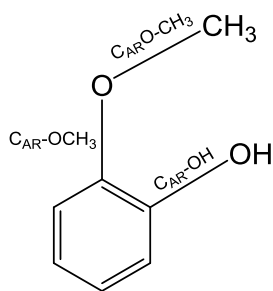


Figure 2.2.2 The chemical structure of guaiacol

A wide range of catalysts have been studied, such as noble and transition metal sulphide (TMS) catalysts. Lin et al. [54] compared classical sulphided CoMo and NiMo catalysts with mono- and bimetallic Rh-based catalysts on the HDO of guaiacol. Runs were operated in a batch reactor under a H_2 pressure of 50 bar at temperatures between 300 and 400 °C. They found that Rh catalysts were more active than CoMo and NiMo in terms of HDO. The mechanism of guaiacol HDO based on Rh catalysts involved two consecutive steps: guaiacol ring hydrogenation followed by demethoxylation and dehydroxylation of oxygenates. Correspondingly, one disadvantage is that they tended to over saturate valuable benzene rings. As for sulphided CoMo and NiMo/ Al_2O_3 , which showed potential in making aromatics, the HDO started with demethylation, demethoxylation and deoxygenation, followed by benzene ring saturation. Gutierrez et al. [43] tested the HDO of guaiacol over ZrO_2 supported noble metal catalysts in the presence of H_2 at 100 and 300 °C. Unlike conventional sulphided CoMo/ Al_2O_3 catalyst, the contamination of products by sulphur and the deactivation of catalysts due to carbon deposition were avoided with ZrO_2 -supported noble metal catalysts. In addition, the H/C molar ratios obtained on ZrO_2 -supported Rh and RhPt catalysts were similar to that of gasoline and diesel. HDO of guaiacol only occurred at high temperature, namely 300 °C. The desired low O/C ratios were achieved with Rh and RhPd catalysts (Figure 2.2.3). Though Rh is expensive, Rh-containing catalysts, are recommended by the authors in the upgrading of wood-derived bio-oils due to their high activities in the HDO and hydrogenation of guaiacol. Nimmanwudipong et al. [55] studied the HDO of guaiacol on Pt/MgO and Pt/ γ - Al_2O_3 catalysts with a flow reactor at 300 °C under 1.4 bar of H_2 . Phenol, catechol and cyclopentanone were main products. Results show that Pt/MgO has a better selectivity towards deoxygenated products and it deactivates less rapidly than Pt/ γ - Al_2O_3 . They also pointed out that, due to the acidity of the γ - Al_2O_3 support, Pt/ γ - Al_2O_3 also catalysed transalkylation reactions. Kong et al. [56] investigated the HDO of guaiacol on nickel over different bimetal oxides (i.e. Al_2O_3 - SiO_2 , Al_2O_3 - TiO_2 , TiO_2 - SiO_2 and TiO_2 - ZrO_2). Under the conditions of 300 °C, 40 bar of H_2 and 8 hr of batch time, complete conversion of guaiacol was reached over Ni/ TiO_2 - ZrO_2 with a selectivity to cyclohexane as high as 86% in decalin solvent. They pointed out that a stronger acidity of the

catalyst would give a better conversion but a higher selectivity to phenol, as methoxyl group adsorbed on the acid sites under the catalytic conditions and then its C-O bonds cleaved to form catechol and further to phenol in sequence. According to the study, decalin can facilitate the HDO process as a H₂ donor. Elliott and Hart [57] conducted their study using Ru/C and Pd/C catalysts over a temperature range from 150 to 300 °C under the operating pressure of 138 bar H₂. The hydrogenation route guaiacol over Ru/C mainly passes through methoxycyclohexanols (*cis* and *trans*) to cyclohexanediols at low temperatures (i.e. 150 and 200 °C). As the temperature continues to increase, cyclohexanol prevails. In addition, phenol is a major early product at medium temperature, yet it can be hydrogenated to cyclohexanone and cyclohexanol. At 300 °C, phenol is the primary recoverable product with cresols and benzene as byproducts. It is noteworthy that the liquid/vapour equilibriums begin to affect the liquid sample concentrations, and also the gasification reactions become important at 250 °C and above. In the case of Pd/C, guaiacol produces methoxycyclohexanone first at 150 °C and then methoxycyclohexanols at 200 °C with minor cyclohexanediol. For 250 to 300 °C, the product slate is shifted from cyclohexanol and cyclohexane to cyclohexane. There are also significant volatile hydrocarbons (e.g. methanol) being produced along with cyclohexane at 300 °C. Phenol is also observed and its role is more important at higher temperatures than that at lower temperatures, as is over Ru/C. Zhao et al. [53] examined the behaviours of transition metal phosphides (i.e. Ni₂P/SiO₂, Fe₂P/SiO₂, MoP/SiO₂, Co₂P/SiO₂ and WP/SiO₂) during the gas phase HDO of guaiacol in the temperature range of 200 to 300 °C at atmospheric pressure. Major products were benzene and phenol, with a small amount of methoxybenzene. Catechol and cresol were intermediates and formed at short contact times. Reaction network is proposed in Figure 2.2.4. Compared with the commercial catalysts (i.e. Pd/Al₂O₃ and CoMoS/Al₂O₃), transition metal phosphides show potential for the upgrading of bio-derived feedstocks. Table 2.2.3 is a summary of the original research reviewed in this section.

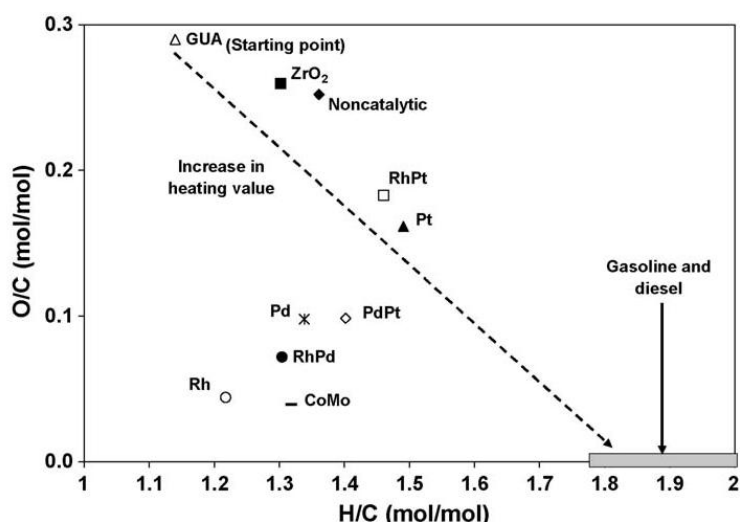


Figure 2.2.3 O/C and H/C molar ratios of guaiacol products (ZrO_2 , ZrO_2 -supported noble metal catalysts and a conventional HDO catalysts at 300 °C, 8 MPa and 3 hours) [43]

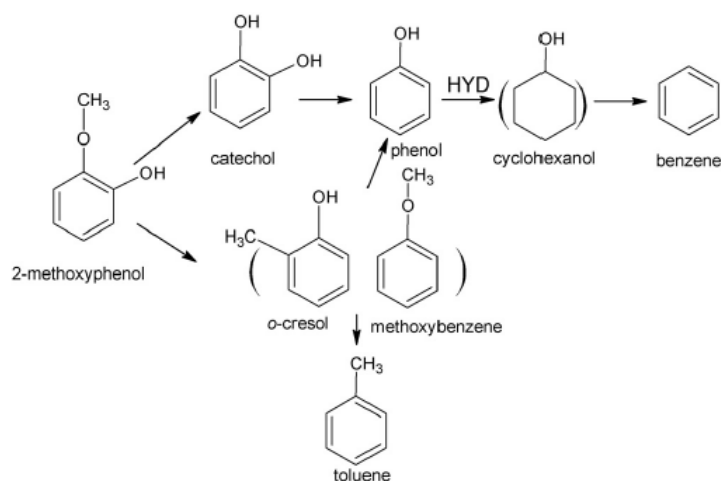


Figure 2.2.4 Reaction network for the HDO of guaiacol [53]

Table 2.2.3 Summary of original research reviewed for guaiacol HDO

Temperature (°C)	Catalyst	Ref
Reactor		
300-400 Batch	Rh based catalysts and sulphided CoMo and NiMo catalysts	[54]
100 and 300 Batch	ZrO_2 supported noble metals	[43]
300 Continuous	Pt/MgO and Pt/ $\gamma\text{-Al}_2\text{O}_3$	[55]
300 Batch	Nickel over bimetal oxides	[56]
150-300 Batch	Ru/C and Pd/C	[57]
200-300 Continuous	Transition metal phosphides	[53]

2.2.2 Furanics, aldehydes and acids

Besides phenols, furanics, aldehydes, acids and etc. are major oxygen containing groups presented in bio-oils. Though literature is widely available, some studies are summarised here with emphasis on the model compounds and the catalysts used (Table 2.2.4).

Table 2.2.4 References on the HDO of model compounds

Furanics	Temperature (°C) Reactor	Catalyst	Ref
Tetrahydrofuran	330-430 Continuous	Co-Mo/Al ₂ O ₃	[58]
Furfural	210-290 Continuous	Cu, Pd and Ni supported on SiO ₂	[59]
Furfural	230-290 Continuous	Cu/SiO ₂	[60]
Aldehydes			
Benzaldehyde			
2-Phenylpropionaldehyde			
3-Phenylpropionaldehyde			
Propionaldehyde	30-130 Batch	Pd/C and Pd/ZSM-5	[61]
Cinnamaldehyde			
4-Isopropylbenzaldehyde			
Heptanal			
Carboxylic acids			
Acetic acid	150-300 Batch	Pd/C and Ru/C	[57]
Acetic acid			
Propanoic acid	150-210 Continuous	Ru/C, Ru/ZrO ₂ and Ru/Al ₂ O ₃	[62]
Butyric acid			
Isobutyric acid			
Stearic acid	300 Semi-batch	Pd/SBA-15	[63]
Stearic acid	350 Batch	Pd/Al ₂ O ₃	[64]
Stearic acid	260-290 Batch	Ni/SiO ₂ , Ni/Al ₂ O ₃ and Ni/HZSM-5	[65]
Stearic acid			
Oleic acid	300 Semi-batch	Pd/C	[66]
Linoleic acid			

2.3 CATALYST

Catalysts involved in the research of HDO include transition metal sulphides, noble metal catalysts (e.g. Ru, Rh, Pd and Pt) and metal carbides, nitrides, phosphide and borides. They can either be supported (e.g. on Al_2O_3 , SiO_2 , zeolites and carbons) or unsupported. Also, refinery type hydroprocessing catalysts based on nickel and/or molybdenum sulphides are being studied.

Because of the fact that the treatment of pyrolysis bio-oils and that of distillation products all require eliminating heteroatoms, conventional TMS catalysts (e.g. sulphided $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$), well known for the hydrorefining of petroleum based feedstocks (e.g. HDO, hydrodesulphurisation and hydrodenitrogenation) [67, 68], have been widely studied and reviewed extensively for this application [30, 39, 69-73]. Normally, Mo serves as the active component whereas Co or Ni act as a promoter and $\gamma\text{-Al}_2\text{O}_3$ is the most common support [41]. Generally, the coordinatively unsaturated sites (i.e. sulphur anion vacancies) associated with the MoS_2 phase, which are located at the edges of MoS_2 nanoclusters, are believed to be the active sites [10]. These sites exhibit Lewis acid character and can absorb atoms with unpaired electrons. Hence, the cleavage of the carbon-heteroatom bond can proceed [41]. The maintenance of the activity of TMS catalysts requires the presence of sulphur [74]. Different from petroleum distillates, bio-oils would lead to sulphur leaching of TMS catalysts and further result in catalyst deactivation because of the low sulphur content in the feedstocks [75]. Moreover, base metal catalysts require higher temperatures to be active for reactions, at which undesirable char formation is favoured [36].

Noble metal catalysts are believed to be particularly efficient in activating H_2 molecule, and hence, they are highly active for hydrogenation. According to the literature, Ru, Rh, Pd and Pt or bimetallic metals are widely studied for the purpose of HDO [26, 43, 63, 64]. However, considering the fact that maintaining a certain level of aromatics is of necessity for bio-oils towards success blending with diesel and jet fuels, it is reasonable to remove the oxygen with catalysts which have mild hydrogenation ability so that aromatics can be partially preserved and the consumption of H_2 , which is expensive, can be reduced. Other issues associate with noble catalysts are their sensitivity to poisons, cost and availability [41].

Alumina supported Ni and Co mono-metallic catalysts are known for the selective hydrogenation of pyrolysis gasoline [68, 76, 77]. Also they have the ability to remove heteroatoms [75, 78]. Furthermore, a sulphur environment is not necessary for these

catalysts to be active and they are economically viable. Particularly, this type of catalyst is active for the hydrogenation of diolefins as well as for the isomerisation of diolefins by the displacement of the double bond into internal olefins with a better octane number [68]. Considering these advantages, they can be promising candidates for the HDO work.

2.3.1 Nickel supported on alumina

Yakovlev et al. [75] have shown a deoxygenation degree of 95% over $\text{Ni}/\text{Al}_2\text{O}_3$ (containing 38 wt% of nickel) catalyst based on their work of HDO of anisole at 300 °C and 10 bar of H_2 . The catalyst was synthesised by wetness impregnation of the support with aqueous solutions of the nickel salt. They also tested bimetallic catalysts. $\text{Ni-Cu}/\text{Al}_2\text{O}_3$ is more active than $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst because Cu can facilitate the H_2 spillover process and therefore promote the reduction of nickel oxide. Yang et al. [79] investigated the HDO of acetic acid in a fix bed reactor over nickel based catalysts between 200 to 280 °C under 40 bar of H_2 . Over 80% of conversion can be achieved on $\text{Ni}/\text{Al}_2\text{O}_3$ at 280 °C with a yield of 75% to methane. The catalyst was prepared by wetness impregnation with a nickel content of 10 wt%. Mortensen et al. [80] tested four groups of catalysts for the HDO of phenol at 275 °C and 100 bar of H_2 in a batch reactor. Within the non-noble metals, Ni catalysts have been identified to have the best performance. According to the results, $\text{Ni}/\text{Al}_2\text{O}_3$ had a high activity towards hydrogenation and deoxygenation with a complete conversion and a 46% yield to cyclohexane. $\text{Ni}/\text{Al}_2\text{O}_3$ can also improve the carbon balance with less coking formation, comparing with Ni/SiO_2 , Ni/CeO_2 and etc. Ni/C had little activity for the HDO of phenol, whereas it was active for that of cyclohexanol. Based on these observations, they suggest that the activation of phenol before hydrogenation occurs on oxygen vacancy sites on the oxide support and the following deoxygenation may take place directly on the nickel crystallites. Therefore, a mechanism of HDO of phenol over nickel catalysts has been proposed (Figure 2.3.1).

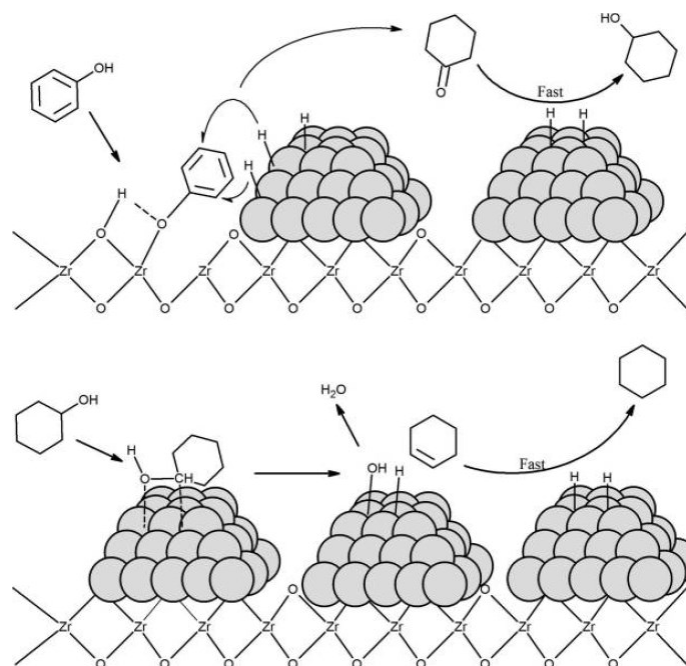


Figure 2.3.1 Reaction mechanism for the HDO of phenol over oxide-supported (Ni/ZrO₂) Ni catalyst (Grey spheres represent nickel atoms) [80]

2.3.2 Cobalt supported on alumina

Alumina supported cobalt catalysts are mostly developed in Fischer-Tropsch synthesis [81-83] and selective hydrogenation. Co is believed to be an agent with high selectivity and strong isomerising activity for the hydrogenation of diolefins and acetylenes [68]. Ando et al. [84] prepared a alumina-supported cobalt (0) catalyst for the selective hydrogenation of α,β -unsaturated aldehydes by reducing cobalt hydroxide precipitated from aqueous CoCl₂ solution on alumina with KOH. The catalyst is more active than conventional Co/Al₂O₃ by impregnation. The α,β -unsaturated aldehydes having the substituent at α - and/or β -position of acrolein were converted into corresponding α,β -unsaturated alcohols over the catalyst with good selectivity. In the respect of heteroatom removal, Co/Al₂O₃ is normally used for the purpose of HDS [85, 86] but less documented in the literature for the HDO purpose. Yakovlev et al. [75] examined the HDO activity of Co/SiO₂ with anisole at 300 °C and 10 bar H₂. It only converted 10% of the feed with a HDO degree of 6%. However, alumina supported cobalt catalyst was not tested.

2.4 SULPHIDE CATALYSTS

Typical hydrotreating catalysts (e.g. NiMo/Al₂O₃ and CoMo/Al₂O₃) are more active in sulphided form than in oxide form. However, bio-oil has negligible content of sulphur. Therefore, it is necessary to add sulphur agent in the feed to maintain the sulphidation level of the catalysts. Studies show that the effect of adding sulphur on HDO depends on the feed composition and process conditions. Generally, organosulphur compounds (e.g. benzothiophene) inhibit HDO [87].

Şenol et al. [88] compared the effects of H₂S on the HDO of aromatic (i.e. phenol) and aliphatic oxygenates (i.e. methyl heptanoate, ethyl heptanoate, heptanol and heptanoic acid) on sulphided NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃. Experiments were conducted at 250 °C under 75 bar H₂ pressure. They pointed out that the formation of benzene and alicyclic hydrocarbons involved two parallel reactions, namely hydrogenation and hydrogenolysis. Also, tests with cyclohexanol reveal that cyclohexane is formed from cyclohexanol deoxygenation via cyclohexene as intermediate. In both cases of with and without H₂S in the reactor, the main products of HDO of phenol were cyclohexane and benzene over NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃, respectively. The predominant formation of cyclohexane over the NiMo/γ-Al₂O₃ is because of the high hydrogenation activity of the catalyst. However, in the respect of HDO, CoMo/γ-Al₂O₃ demonstrates a higher activity than that of NiMo/γ-Al₂O₃. H₂S inhibits the HDO of phenol. The inhibiting effect can be explained by the competitive adsorption of phenol and H₂S on the catalytic sites. By evaluating the molar ratios of aromatic to alicyclic hydrocarbons, it shows that the degrees of inhibition of the routes to aromatic and alicyclics were about the same over NiMo catalyst whereas the inhibiting effect was stronger on the route to benzene than that to alicyclics over CoMo catalyst. They also discussed different deoxygenation mechanisms. The cleavage of C-O bond can occur by direct hydrogenolysis and dehydration reactions. Since the dehydration reaction, which is an acid-catalysed reaction, can only proceed if both α- and β-carbon atoms with respect to the oxygen atom are saturated, benzene could not be produced from phenol by the dehydration reaction. Interestingly, a promoting effect of H₂S on the HDO of aliphatic oxygenates was observed. Different reaction mechanisms were proposed to explain the opposite effects. The addition of H₂S could increase the catalyst acidity and therefore facilitate the acid-catalysed reactions of aliphatic oxygenates (e.g. dehydration and hydrolysis) while it suppressed the HDO of phenol by competitive adsorption.

Laurent and Delmon [40] reported the influence of oxygen-, nitrogen- and sulphur-containing compounds on the HDO of p-cresol over sulphided CoMo/ γ-Al₂O₃ catalysts.

They suggested two parallel reaction routes for the HDO of phenols, i.e. directly hydrogenolysis of the C-O bond and hydrogenation of the aromatic ring. The deoxygenation of 4-methylphenol is a first-order reaction at moderate conversion. Its reaction scheme is given by Figure 2.4.1. For typical runs, the final conversions of 4-methylphenol were between 80 and 100%. Toluene produced from the hydrogenolysis route and methylcyclohexane from hydrogenation of the aromatic ring were the main products. The conversion of phenol is inhibited by the involved molecules over both of the Co-Mo and Ni-Mo sulphided hydrotreating catalysts. The inhibiting strength follows the order of $\text{H}_2\text{O} < 2\text{-ethylphenol} < \text{H}_2\text{S} < \text{NH}_3$. In all cases, molecules exhibit a stronger inhibiting effect over the hydrogenolysis pathway, indicating that the associated active sites are more electrophilic. There exists a special case that H_2S slightly promotes the hydrogenation activity of CoMo catalyst. This might be explained by the interconversion between hydrogenolysis and hydrogenation active sites.

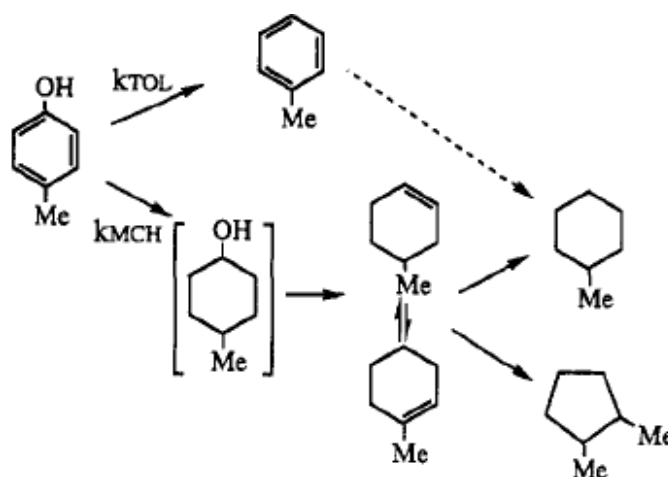


Figure 2.4.1 Reaction scheme of the conversion of p-cresol [40]

2.5 SUMMARY

Literature on the catalytic upgrading of the bio-oil to liquid fuels and model compounds HDO has been generally reviewed, emphasising four areas that may guide the research.

Biomass is a renewable energy source. Its major component, lignocellulose, from which bio-oil is produced, consists of cellulose, hemicellulose and lignin. The basic principles of the conversion of biomass into liquid hydrocarbon fuels are to remove the oxygen with the least H_2 consumption and to control the molecular weight of the final products. Fast pyrolysis, which requires the biomass being processed at elevated temperature and high heat rate over a short resident time, is a well-established method by which bio-oil can be obtained.

Bio-oils are complex mixtures which are highly oxygenated. In general, they contain all kinds of oxygenated organics including phenols, aldehydes, acids, alcohols, ketones, esters and ethers. Thus, there is bio-oil peculiarity in comparison to conventional fossil fuels: high oxygen content. This undesirable characteristic further introduces negative properties (e.g. low heating value, incompatibility with conventional fuels, solids contents, high viscosity, incomplete volatility and chemical instability). Therefore, upgrading of bio-oils is necessary. Bio-oils are treated either through a two-step process including one mild treatment to stabilise or partial deoxygenate the feed and one severe treatment to fully deoxygenate bio-oils or through a separation process followed by the HDO of oil phase.

The great importance of study different model compounds is that it can provide the knowledge to understand the complex behaviours of different bio-oil components. Given the chemistry and reaction mechanisms, one can control the selectivity towards target products and further probe the upgrading of real bio-oils to usable fuels and chemicals. Pyrolysis bio-oils contain single-ring phenols, which are stable under hydrotreating conditions. Of particular concern in the HDO of phenols are the optimisation of the deoxygenation conditions, the prediction of the products and the elucidation of reaction networks. The products from the HDO of phenols can be roughly divided into two groups, i.e. alicyclics with/without functional group(s) from the hydrogenation of the phenolic ring and aromatics from the direct deoxygenation of the phenols. Aromatic products of which the selectivity rises with temperature should be preserved because they can increase the octane number of the fuels.

An active and stable catalyst is vital for the HDO process. Due to the nature of HDO, hydrotreating and hydrogenation catalysts are mostly being used with and without modifications. TMS catalysts are therefore adapted for the purpose of deoxygenation. Their sulphur vacancies are believed to be the active sites for catalysis but the maintenance of their activity relies on the presence of sulphur. Noble catalysts are efficient but the challenges such as their limited availability and high-cost exist. Alumina supported Co and Ni mono-metallic catalysts are known for the selective hydrogenation of pyrolysis gasoline, and also they have the ability to remove heteroatoms. Given their potential, they may be promising catalysts for the upgrading of bio-oils.

Conventional hydrotreating catalysts are normally in sulphide form and it is necessary to maintain their activities by adding sulphur into the system if they are being used to process bio-oils. Generally, organosulphur compounds inhibit HDO. As for H_2S , literature has been reported that it suppresses the HDO of phenolic compounds by competitive adsorption whereas it promotes that of aliphatic oxygenates by increasing the acidity of the catalysts. Considering the fact that added sulphur can alternate the activities of the catalysts, it is interesting to know its impact on the performance of the selective hydrogenation catalysts.

With the background being established, the following chapters present the research on bio-oil processing, cresol and guaiacol HDO over $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ selective hydrogenation catalysts with and without ambient sulphur.

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3 CATALYTIC HYDRODEOXYGENATION OF PYROLYSIS BIO-OIL

3.1 INTRODUCTION

With the Earth's temperature on the rise and the need for clean energy greater than ever before, the stakes for the utilisation of biomass and its derivatives as alternatives of conventional fuels could not be higher. Biomass based liquid fuels have the potential to deliver the energy demanded and yet mitigate the environmental crises. Efforts have been made to convert biomass into fuels by methods such as hydrothermal liquefaction, slow and fast pyrolysis, fermentation and gasification, [1]. Among which, fast pyrolysis is the leading method for producing liquid fuels [2]. The merits of fast pyrolysis include low production costs, high thermal efficiency, low fossil fuel input [3]. However, as demonstrated in the last chapter, products from fast pyrolysis, i.e. bio-oils, suffer from undesirable properties (e.g. high acidity, instability, low heating value and etc.) due to their high oxygen content. Bio-oil upgrading, therefore, is a necessity. Different from the petroleum industry, the upgrading of biomass derived materials normally concentrates on the HDO as they contain negligible amount of sulphur and nitrogen.

The high oxygen content of bio-oils can lead to excess coke formation and plug the reactors. In this respect, a two-stage HDO has been proposed [4], i.e. a pre-treatment process with mild conditions to stabilise the feed followed by a high temperature deep deoxygenation process. The study reported in this chapter concentrated on the first-stage treatment of the bio-oil.

In order to achieve efficient deoxygenation and aqueous phase separation in this mild stage treatment and to optimised the process, conditions, several parameters (temperature, catalyst loading, batch time and etc.) and catalysts (supported and unsupported) were investigated. Unsupported nanosulphide catalysts have a history (mainly in research and pilot studies) of being used in the hydrotreatment of heavy and residual oils [5-7]. The advantages of using unsupported catalysts are that they allow relatively small loadings and the active phase is highly dispersed. With these features, not only the mass transfer limitation is mitigated but also the undesired polymerisation is suppressed by the rapid hydrogenation of free radicals (i.e. coke precursors). In this research, NiMo nano-sulphides were selected to be studied due to the desirable performance of NiMo supported catalysts for HDO [8].

Among the supported catalysts tested in the present study, Ru/C produced an oil phase with least oxygen content but it consumed large amount of H₂. Ni/Al₂O₃, on the other

hand, presented a fairly good result while only using 1/3 amount of H_2 comparing with that of Ru/C. Pd/C had the same level of H_2 consumption as Ni/Al₂O₃ but the oxygen content in the oil phase was much higher than that of Ru/C and Ni/Al₂O₃. Co/Al₂O₃ was considered to be inactive as it barely consumed any H_2 .

The study on the effect of the reaction conditions was done over the unsupported NiMo nano-sulphide catalyst. Increasing the temperature and catalyst loading would benefit the deoxygenation of bio-oil and reduce the degree of hydrogenation of the products. The extra background sulphur only had a marginal effect on the catalyst performance. Extend the batch time reaction would lead to a higher degree of deoxygenation as well as hydrogenation. Dodecane is recommended to be used as HDO solvent. Based on the experimental results over the NiMo unsupported catalyst, a process model was proposed to maximise the fuel production. Also, in combination with hydrothermal process, an integrated H_2 self-sustained bio-oil upgrading system was also established.

3.2 EXPERIMENTAL METHODS

Standard methods to carry out the experiment are provided here. Details will be provided later in each section where necessary. Raw bio-oil samples (i.e. Oil-A, Oil-B, Oil-C, Oil-D and Oil-E) were supplied by Future Blends Ltd. All the oils were derived from Norwegian spruce (*Picea Abies*). Oil-E, which was a fresh batch from an updated pyrolysis process, was directly used in this study.

3.2.1 Bio-oil hydrodeoxygenation

Parr 100 mL stainless steel pressure vessel was used for the bio-oil upgrading research. Either commercial catalyst (e.g. Pd/C from Sigma-Aldrich) or home made one (i.e. unsupported NiMo nano-sulphide) was used and mixed with the feed to form a slurry phase. Catalyst sulphidation and runs with background sulphur (normally 100 ppm) were carried out using dibutyl disulphide (97%, Sigma-Aldrich).

The autoclave was charged with 21 g of the feed, containing 7 g of bio-oil and 14 g of solvent (tetralin, 99% Sigma-Aldrich, and/or dodecane, $\geq 99\%$ Sigma-Aldrich). Air was purged out by low pressure N_2 first and then H_2 . The reactor was pressured with H_2 to 50 bar (cold) afterwards. The temperature was raised while the stirring speed was gradually increased to 700 rpm to prevent external mass transfer limitation. The standard batch time of 3 hr was counted when the reactor reached the target temperature. Typically for the runs carried out at 300 °C, the hot pressure ranged from 64.6 to 67.0 bar.

3.2.2 Analysis

Karl Fischer titration of water content, elemental C and H analysis (EA), Gas Chromatography Mass Spectrometry (GC-MS), quantitative ^{31}P -Nuclear Magnetic Resonance (NMR) and Inductively Coupled Plasma (ICP) analysis were employed to provide detailed chemical information of the raw bio-oil and the upgraded products. The water content was determined by METTLER TOLEDO volumetric Karl Fischer compact titrator V20 with HYDRANAL-Coulomat A (Sigma-Aldrich) as reagent. Detailed Karl Fischer operation procedures and relevant calculations can be found in Appendix. The elemental C and H analysis was carried out by Sheffield University (SU) with the oxygen content obtained from the mass balance. The reliability of the oxygen content obtained from EA mass balance was checked by direct oxygen content determination carried out by Intertek Sunbury Technology Centre (ISTC) on Oil-A, Oil-B and Oil-C, as the agreement was satisfactory (Table 3.3.1). Qualitative and semi-quantitative analysis of

chemical compounds was obtained by a Hewlett Packard G1800C GCD chromatograph GC-MS equipped with a Zebron WAX plus column at King's College London. Detailed information and procedure for ^{31}P -NMR analysis were provided in the published work [9]. ICP analysis (Perkin Elmer Instruments, Optical Emission Spectrometer, Optima 2000 DV) was done by the analytical services of the Department of Chemical Engineering of Imperial College London. The total amount of H_2 being consumed was calculated (see Appendix for details) from the change of pressure during the run and the known reactor head space volume.

3.3 RESULTS AND DISCUSSION

This bio-oil upgrading study was conducted under moderate conditions to simulate the first stage treatment. It addressed a range of catalysts including the unsupported sulphide catalysts, i.e. NiMo nano sulphide.

3.3.1 Bio-oil feed

The elemental analysis of oils A-D was given in Table 3.3.1. The bio-oil in use, i.e. Oil-E (Figure 3.3.1), contains phenolic residues and aliphatic functionalities. The former species are typical lignin derivatives, which are essential structural components in woody based biomass. According to the analysis, the raw oil contains 33.6 wt% of free water with the C, H and O being 40.0, 8.2 and 51.8 wt%, respectively. Correspondingly, an organo-oxygen content of 33.0 and 21.9 wt% in dry and wet oil can be calculated. Properties of the oil are summarised in Table 3.3.2. ^{31}P -NMR was used to quantify the content of organic hydroxy oxygenates of the bio-oil. The spectrum is shown in Figure 3.3.2 and typical chemical shift ranges are given in Table 3.3.3. Detailed results on OH oxygen content are presented in Table 3.3.4. Results show that hydroxyl groups comprise 57.6% of organo-oxygen in dry oil. The dominant OH species are aliphatic alcohols which make up to 68.9% of the organo-OH.

Table 3.3.1 Elemental analysis (Oil-E)

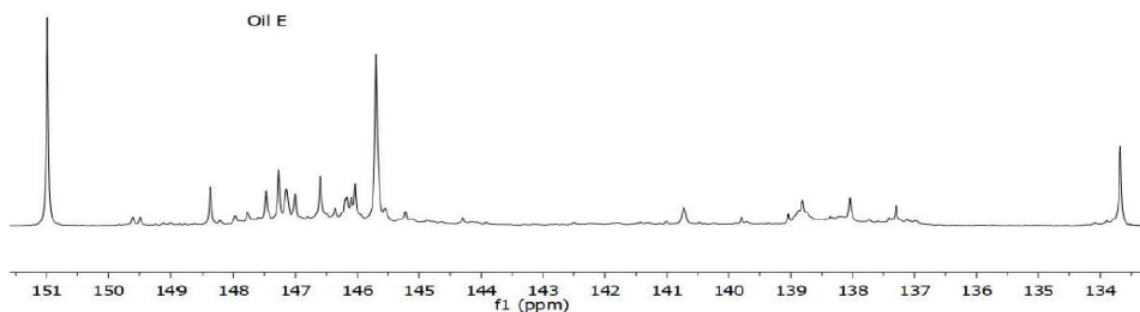
Element	Oil-A		Oil-B		Oil-C		Oil-D
	ISTC	SU	ISTC	SU	ISTC	SU	SU
C (wt%)	43.5	44.0	39.9	43.6	38.0	40.6	38.8
H (wt%)	7.5	7.5	7.6	7.1	8.4	8.4	8.0
O (wt%)	48.6	48.5	51.4	49.2	51.6	51.0	53.2



Figure 3.3.1 Oil-E (unprocessed raw oil)

Table 3.3.2 Properties of the raw bio-oil (Oil-E)

Elemental analysis (wt%)			Water content (wt%)	Organo-oxygen content dry base (wt%)
C	H	O		
40.0	8.2	51.8	33.6	33.0

Figure 3.3.2 ^{31}P -NMR spectrum of the raw bio-oil (peak at 151 ppm is the NMDI internal standard)Table 3.3.3 ^{31}P -NMR shift ranges of phosphitylated hydroxy compounds [9]

Type of hydroxy group	Chemical shift range/ppm	Representative structures in PO
Aliphatic	δ 150.0–145.5	
C5-Substituted Syringyl/ Condensed Phenolic	δ 144.7–140.2	
Guaiacyl/	δ 140.2–139	
p-phenolic/catecholic	δ 139–137.3	
Carboxylic	δ 136.3–133.3	
Water	δ 133.1–131.3, δ 16.9–15.1	H_2O

Table 3.3.4 OH oxygen content in the bio-oil (Oil-E) from quantitative ^{31}P -NMR

Groups	Content in dry oil (wt%)
Aliphatic alcohols	13.1
Condensed Phenolic	1.4
Phenolic OH	0.43
Guaiacolic OH	3.1
Acidic OH	1.0
Overall OH oxygen	19.0

3.3.2 HDO with supported catalysts

Elliott and Hart [10] have demonstrated favourable performance of Pd/C and Ru/C catalysts on the HDO model compounds. Huber et al. [11] also mentioned the use of Ru for the HDO of bio-oils. Therefore, Pd/C and Ru/C were selected, together with commercial Co/Al₂O₃ and Ni/Al₂O₃ catalysts, as examples of supported catalysts to be investigated in this section.

The commercial catalysts were reduced and the carbon supported catalysts were activated prior to the experiments. The reduction of Co/Al₂O₃ and Ni/Al₂O₃ catalysts was carried out ex-situ with 5% H₂/N₂ for 4 hr at 450 and 350 °C, respectively. With 1 g of reduced catalyst and 21 g of reaction mixture (consisting of 7 g of bio-oil and 14 g of tetralin) loaded in, the autoclave was sealed for the HDO experiment. Detailed reduction procedures of the two catalysts can be found in Chapter 4. Tetralin, as a H₂ donor solvent, was used in most of the runs. It acts as a H₂ vehicle which can transfer the gas phase H₂ in active form to radical fragments for their stabilisation [12]. For the experiment with 5% Pd/C or 5% Ru/C (purchased from Sigma-Aldrich), the autoclave was loaded with 1 g of the catalyst, and was purged by N₂ to displace air. The reduction gas of 5% of H₂/N₂ then passed through the autoclave at atmospheric pressure. The temperature was gradually raised to 200 °C and hold for 1 hr. After activation, the autoclave cooled down naturally to room temperature. The gas was switched from 5% H₂/N₂ back to N₂ to prevent the catalyst from contacting with air. Afterwards, the autoclave was opened and was quickly charged with 7 g of oil and 14 g of tetralin. All experiments were performed under standard conditions without added sulphur.

HDO products were collected from the autoclave. Weight loss was inevitable due to the problems of retrieving high viscous species deposit on the liner, dip tube, stirrer, and condensed liquid on the head. Generally, 85-90 % of the reaction mixture could be recovered.

The post-run products were composed of three phases (Figure 3.3.3), namely oil phase (mainly organic solvent), water phase (mainly water) and residue (mainly heavy components, coke and spent catalysts). The post-run products were decanted first to separate the residue. Subsequently, liquids were centrifuged and then separated into water and oil layers in a separating funnel (Figure 3.3.4).

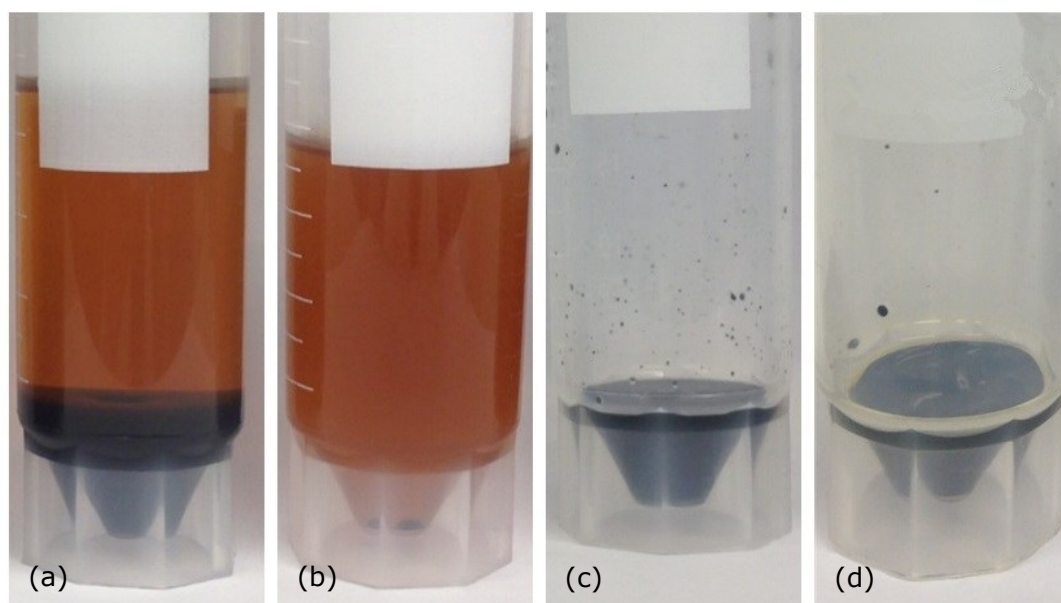


Figure 3.3.3 Bio-oil HDO products: (a) Original products collected from the autoclave, (b) separated oil phase, (c) separated water phase and (d) separated residue phase

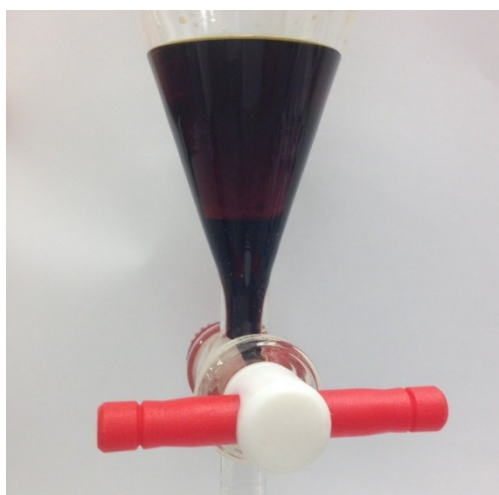


Figure 3.3.4 Phase separation

The H_2 consumption was calculated (see Appendix for details) and the EA was performed on the oil phase of each run. Data is presented in Table 3.3.5. The effect of solvent hydrogenation was negligible and therefore the EA of the oil phase should provide a reliable guide, except the case of Ru/C. Though the excess H_2 was consumed due to the hydrogenation of the tetralin solvent, Ru/C produced an oil phase which had the least oxygen content. Broadly speaking, Pd/C and Ni/ Al_2O_3 consumed the same amount of H_2 . However, Ni/ Al_2O_3 had a better activity than Pd/C in terms of deoxygenation and hydrogenation judging from the H and O content of the oil phase. The Co/ Al_2O_3 was not very active judging from the H_2 consumption, and therefore the EA analysis was not performed.

Table 3.3.5 HDO of bio-oil over selected supported catalysts

Catalyst	Temperature (°C)	H ₂ consumed (mol/g oil)	EA of oil phase (wt%)			Decalins yield (%)
			C	H	O	
Pd/C	175	0.0047	88.2	8.8	2.9	~1
Ru/C	175	0.0145	87.9	9.9	2.2	20
Co/Al ₂ O ₃	175	0.0009	-	-	-	~1
Ni/Al ₂ O ₃	175	0.0050	88.4	9.1	2.5	~1

3.3.3 HDO with NiMo nanosulphide catalysts

A previous study [13] investigated the HDS performance of Mo nanosulphide catalysts on dibenzothiophene (DBT) at 300 °C, 100 bar H₂ and 2 hr batch time. It was found that adding a small amount of Ni (within Ni/Mo molar ratio of 0.3 to 0.45) increased the DBT conversion (from 21% to 65%) and the ratio of direct desulphurisation to hydrogenation (from 1.4 to 3). It is suggested that adding Ni does not change the nature of active sites of the MoS₂ but it increases their numbers by increasing electron density on the sulphur atoms [14, 15]. Therefore, the conversion of DBT could be increased. Ni can also increase the number of MoS₂ layers, as the XRD analysis for NiMo catalysts showed exactly the same pattern of MoS₂ with high degree of stacking. Correspondingly, the direct desulphurisation path was enhanced more than the hydrogenation path according to the Rim-Edge model discussed in Chapter 2.

NiMo nanosulphide catalysts were made for the HDO of bio-oil based on the previous study [13]. The Ni/Mo molar ratio of 0.4 (corresponding to 2000 ppm/0.0420 g of element Mo and 490 ppm/0.0103 g of element Ni in 21 g of reaction feed) was used as a guidance to synthesise the catalyst. Molybdenum naphthenate 0.7 g (containing 6 wt% of element Mo, MP Biomedicals) and nickel naphthenate 0.086 g (containing 12 wt% of element Ni, Alfa Aesar) as precursors were mixed with 14 g of solvent (tetralin and/or dodecane) and 0.322 g of dibutyl disulphide (corresponding to 4 times amount of sulphur required to form 2000 ppm of MoS₂) in the autoclave. The autoclave was flushed in N₂ before H₂ was introduced to the desired pressure, i.e. 10 bar cold. The synthesis was carried out at 300 °C for 2 hr with 1000 rpm agitation. The catalyst was expected to have a particle size between 7 to 8 nm and a degree of stacking between 4 to 6 layers according to the above mentioned study. For the HDO experiment, 7 g of bio-oil feed was added into the autoclave containing the synthesised catalyst. Finally, 100 ppm of background sulphur was provided (by adding 5 wt% of dibutyl disulphide in dodecane) to improve the stability of the nanosulphide catalyst.

The parameters used in the following sections were defined before any discussion.

- The organo-oxygen removal and the total content of organo-oxygen in oil and water phases (dry base)

Considering the fact that the residue was separated from the other two phases by decantation at room temperature (20 to 25 °C), it is reasonable to assume its water content was negligible. ICP analysis of the selected water phase sample did not reveal any significant amount of Ni or Mo. It is therefore assumed that the spent catalyst remained in the residue. Even with the assumption, only minor amount of catalyst (ppm level) was used so the existence of catalyst was ignored. Hereby, the organo-oxygen removal is calculated by Equation (1). Total content of organo-oxygen in oil and water phases (dry base) is given by Equation (2).

$$\begin{aligned} & \text{Percentage of Organo oxygen removal} \\ &= \frac{\text{Organo oxygen in the feed} - \text{Sum of Organo oxygen in three phases}}{\text{Organo oxygen in the feed}} \% \end{aligned} \quad (1)$$

$$\begin{aligned} & \text{Total content of organo oxygen in oil and water phases (dry base)} \\ &= \frac{\text{Organo oxygen in oil phase} + \text{Organo oxygen in water phase}}{\text{Oil phase (dry base)} + \text{Water phase (dry base)}} \% \end{aligned} \quad (2)$$

As weight loss during the product recovery and phase separation was inevitable, therefore fitting the data (weight of each phase after separation) into Equation (1) and Equation (2) would only lead to a maximum value and a minimum one, respectively. Assumptions were made in order to provide a reasonable range of the two values for the purpose of comparison of the catalyst performance. The weight loss during phase separation was assumed to be the oil phase coated on the wall of the separating funnel and centrifuge tubes, and therefore this would give the minimum loss of the oil phase. While, the minimum loss of water can be obtained by subtracting the total amount of water detected in the separated two phases (i.e. oil and water phases) from the original amount of water that existed in the bio-oil. Accordingly, the deduction of the above two minimum values from the total weight loss could yield the maximum loss of the unidentified phase(s). Based on the EA and GC-MS analysis, the water phase had the highest organo-oxygen content of all three phases. Therefore, if the loss of the unidentified phase(s) was assumed all coming from the water phase, then the minimum value of the percentage of organo oxygen removal from Equation (1) and the maximum value of the total content of organo-

oxygen in oil and water phases from Equation (2) can be obtained using the corrected weight of each phase.

- Ratio of deoxygenation to hydrogenation

Generally, deoxygenation and hydrogenation were major reactions involved in the bio-oil HDO. A ratio of deoxygenation to hydrogenation (DEO/HYD) is necessary to evaluate the impact of operating conditions. Since naphthalene was not detected in the GC-MS analysis of the oil phase and decalins were typically less than 0.5% yield from tetralin, the ratio of DEO/HYD can be generally estimated by Equation (3).

$$\begin{aligned} & \text{Ratio of DEO/HYD} \\ &= \frac{H_2 \text{ consumed by t/he removal of organo oxygen}}{\text{Total } H_2 \text{ consumed} - H_2 \text{ consumed by t/he removal of organo oxygen}} \end{aligned} \quad (3)$$

3.3.3.1 Effect of temperature

HDO experiments were carried out at 200 and 250 °C to investigate the effect of temperature. Table 3.3.6 and Table 3.3.7 present the results. It is worth noting that the EA was not performed on the residue phase from the run at 200 °C. However, due to the similarity of the EA results on analysed residue phases, the elemental content of the residue phase from the run at 200 °C was assumed to be the same as that from 250 °C. It can be seen that the effect of deoxygenation was only marginal at 200 °C according to the degree of organo-oxygen removal. The H_2 consumed at this temperature was probably due to hydrogenation reactions. Though the pseudo chemical structure of the water phase at 250 °C had more oxygen than that of 200 °C, increasing the temperature would increase the degree of deoxygenation, judging from the total content of organo-oxygen in oil and water phases. It has been observed in the previous work [13] that increasing the reaction temperature would generally increase the degree of stacking of the Mo nanosulphide catalysts. Similarly, the number of active sites for deoxygenation on the edge of the NiMo catalyst might have increased at 250 °C. The temperature effect on deoxygenation is consistent with the model compound works (see later chapters). In order to achieve the target of maximum oxygen removal, following experiments were all conducted at 250 °C.

The chemical structures at 200 °C were more saturated than those at 250 °C indicating that there was relatively more hydrogenation, which is exothermic, at the lower temperature.

Table 3.3.6 Effect of temperature over NiMo nano-sulphide catalysts (analysis results)

Temperature (°C)	H ₂ consumed (mol/g oil)	water content (wt%)		Product weight/Product composition (g/wt%)			EA (wt%)								
							Oil phase			Water phase			Residue		
		Oil phase	Water phase	Oil phase	Water phase	Residue	C	H	O	C	H	O	C	H	O
200	0.0040	0.1	65.0	14.6/76.7	2.5/13.0	2.0/10.2	86.4	9.4	4.3	17.5	10.1	72.4	64.0	7.2	28.8
250	0.0061	0.1	74.4	15.0/79.6	2.4/12.5	1.5/7.9	88.2	9.5	2.3	13.0	9.9	77.1	64.0	7.2	28.8

2000 ppm Mo, 7 g of oil, 14 g of tetralin, 100 ppm of background sulphur, 3 hr batch time and 50 bar of H₂ cold

Table 3.3.7 Effect of temperature over NiMo nano-sulphide catalysts (derived results)

Temperature (°C)	Organo-oxygen removal (%)	DEO/HYD	Pseudo chemical structure of the organic in each phase		Total content of organo-oxygen in oil and water phases (dry base) (wt%)	Minimum loss of water (g)	Minimum loss of oil phase (g)	Maximum loss of unknown material (g)	Total weight loss (g)
			Oil phase	Water phase					
200	0.0-2.3	0.0-0.1	CH _{1.30} O _{0.036}	CH _{1.95} O _{0.626}	6.3-8.1	0.8	0.2	2.4	3.3
250	15.3-34.4	0.5-3.4	CH _{1.29} O _{0.019}	CH _{1.54} O _{0.636}	3.8-5.4	0.6	0.2	2.7	3.5

3.3.3.2 Effect of added sulphur

The NiMo nano-sulphide catalyst may have sulphur leaching problem. Therefore, 100 ppm of sulphur was added to the reaction mixture in order to maintain the catalyst activity. The impact of this operation on the catalyst performance was investigated. Under such circumstance, a control experiment without added sulphur was set forth to clarify the effect (Table 3.3.8 and Table 3.3.9). It is worth noting that the EA was not performed on the residue phase from the run without added sulphur. However, due to the similarity of the EA results on analysed residue phases, the elemental content of the residue phase from the run without added sulphur was assumed to be the same as that with 100 ppm added sulphur.

Table 3.3.8 Effect of sulphur over NiMo nano-sulphide catalysts (analysis results)

Sulphur (ppm)	H ₂ consumed (mol/g oil)	water content (wt%)		Product weight/Product composition (g/wt%)			EA (wt%)								
							Oil phase			Water phase			Residue		
		Oil phase	Water phase	Oil phase	Water phase	Residue	C	H	O	C	H	O	C	H	O
100	0.0055	0.0	80.2	14.3/76.2	1.8/9.5	2.7/14.3	85.7	12.1	2.3	12.0	10.7	77.4	64.2	7.1	28.7
0	0.0061	0.0	76.1	14.4/74.9	2.9/14.9	2.0/10.2	85.7	12.3	2.0	13.1	10.5	76.4	64.2	7.1	28.7

2000 ppm Mo, 7 g of oil, 7 g of tetralin and 7 g of dodecane, 250 °C, 3 hr batch time and 50 bar of H₂ cold

Table 3.3.9 Effect of sulphur over NiMo nano-sulphide catalysts (derived results)

Sulphur (ppm)	Organo-oxygen removal (%)	DEO/HYD	Pseudo chemical structure of the organic in each phase		Total content of organo-oxygen in oil and water phases (dry base) (wt%)	Minimum loss of water (g)	Minimum loss of oil phase (g)	Maximum loss of unknown material (g)	Total weight loss (g)
			Oil phase	Water phase					
100	12.2-22.0	0.4-1.2	CH _{1.69} O _{0.020}	CH _{1.74} O _{0.382}	3.0-3.8	0.9	0.3	2.4	3.6
0	13.8-28.3	0.5-1.8	CH _{1.72} O _{0.018}	CH _{1.90} O _{0.504}	3.6-4.8	0.2	0.3	2.5	2.9

Generally, the analysis results were similar. Pseudo chemical structures of the products with sulphur were less saturated than those without sulphur, indicating that added sulphur suppressed the hydrogenation reactions, as it may adsorb on hydrogenation sites as a poison. According to the total content of organo-oxygen in oil and water phases, the added sulphur provided a slightly better rate of deoxygenation. Nevertheless, it

produced much more residues. The organo-compounds presented in the water phase were analysed by GC-MS and major products are given in Table 3.3.10. The presence of acids, ethanol, 1,2-ethanediol indicated the occurrence of parallel hydrothermal treatment and hydrocracking reactions. It can be seen that oxygenates in the water phase followed a similar distribution. In general, the sulphur effect on the overall deoxygenation was found to be marginal and the addition 100 ppm of sulphur was not essential.

Table 3.3.10 Organo-oxygen compounds in water phase: effect of sulphur

Compound	Percentage of all O-containing compounds (wt%)	
	0 ppm of Sulphur	100 ppm of sulphur
Ethanol	15.5	15.8
Acetoin	2.9	2.3
Acetic acid	25.8	23.5
1,2-Ethanediol	2.2	1.7
Propionic acid	2.9	2.7
Butanoic acid & G4	14.7	16.8
Pentanoic acid derivatives	4.9	4.5

3.3.3.3 Effect of catalyst loading

One experiment with lower catalyst loading (i.e. 1000 ppm of Mo of same Ni/Mo molar ratio) was carried out. In Table 3.3.11 and Table 3.3.12, comparison is made to a case with a catalyst containing 2000 ppm of Mo. It is worth noting that the EA was not performed on the residue phase from the run with 1000 ppm of Mo loading. However, due to the similarity of the EA results on analysed residue phases, the elemental content of the residue phase from the run with 1000 ppm Mo loading was assumed to be the same as that with 2000 ppm Mo loading.

Table 3.3.11 Effect of catalyst loading over NiMo nano-sulphide catalysts (analysis results)

Catalyst Mo loading (ppm)	H ₂ consumed (mol/g oil)	water content (wt%)		Product weight/Product composition (g/wt%)			EA (wt%)								
		Oil phase	Water phase	Oil phase	Water phase	Residue	Oil phase			Water phase			Residue		
							C	H	O	C	H	O	C	H	O
2000	0.0055	0.0	80.2	14.3/76.2	1.8/9.5	2.7/14.3	85.7	12.1	2.3	12.0	10.7	77.4	64.2	7.1	28.7
1000	0.0039	0.0	76.2	14.2/73.2	2.9/14.8	2.3/12.0	86.1	12.3	1.6	12.6	10.6	76.7	64.2	7.1	28.7

100 ppm Sulphur, 7 g of oil, 7 g of tetralin and 7 g of dodecane, 250 °C, 3 hr batch time and 50 bar of H₂ cold

Table 3.3.12 Effect of catalyst loading over NiMo nano-sulphide catalysts (derived results)

Catalyst Mo loading (ppm)	Organo-oxygen removal (%)	DEO/HYD	Pseudo chemical structure of the organic in each phase		Total content of organo-oxygen in oil and water phases (dry base) (wt%)	Minimum loss of water (g)	Minimum loss of oil phase (g)	Maximum loss of unknown material (g)	Total weight loss (g)
			Oil phase	Water phase					
2000	12.2-22.0	0.4-1.2	CH _{1.69} O _{0.020}	CH _{1.74} O _{0.382}	3.0-3.8	0.9	0.3	2.4	3.6
1000	13.5-25.2	0.9-7.2	CH _{1.71} O _{0.014}	CH _{2.06} O _{0.535}	3.3-4.3	0.2	0.3	1.9	2.4

As expected, a lower Mo loading reduced the H₂ consumption. Interestingly, products of the run with 1000 ppm of Mo were more saturated than those with 2000 ppm Mo, indicating that there was relatively more hydrogenation with the low catalyst loading run. Also, the ratio of DEO/HYD suggested that the H₂ consumed in the case of 1000 ppm of Mo was mostly for deoxygenation rather than hydrogenation. The distribution of products in the water phase was relative insensitive to the increase of catalyst loading (Table 3.3.13). These observations, therefore, suggest that there may be scope for thriftiness of the catalyst.

Table 3.3.13 Organo-oxygen compounds in water phase: effect of catalyst loading

Compound	Percentage of all O-containing compounds (wt%)	
	1000 ppm of Mo	2000 ppm of Mo
Ethanol	12.8	15.8
Acetoin	6.2	2.3
Acetic acid	24.8	23.5
1,2-Ethandiol	1.5	1.7
Propionic acid	2.6	2.7
Butanoic acid & G4	13.7	16.8
Pentanoic acid derivatives	5.2	4.5

3.3.3.4 Effect of batch time

The effect of batch time was investigated with 2000 ppm of Mo (Ni/Mo molar ratio of 0.4). Results are tabulated in Table 3.3.14 and Table 3.3.15. It can be seen that extending the batch time would lead to a higher degree of deoxygenation. Also, it raised the H₂ consumption to conduct more hydrogenation as well according to the chemical structures. According to the ratio of DEO/HYD, the deoxygenation increased mostly with batch time instead of hydrogenation. This may be due to the increased degree of stacking of the catalyst at a longer reaction time [13]. Another possible reason is that initial hydrogenation may be needed before oxygen can be removed. Nevertheless, the increase of organo-oxygen removal was not in line with the increase of batch time indicating that the rate of deoxygenation reaction decreased with time.

Table 3.3.14 Effect of batch time over NiMo nano-sulphide catalysts (analysis results)

Batch time (hr)	H ₂ consumed (mol/g oil)	water content (wt%)		Product weight/Product composition (g/wt%)			EA (wt%)								
							Oil phase			Water phase			Residue		
		Oil phase	Water phase	Oil phase	Water phase	Residue	C	H	O	C	H	O	C	H	O
3	0.0055	0.0	80.2	14.3/76.2	1.8/9.5	2.7/14.3	85.7	12.1	2.3	12.0	10.7	77.4	64.2	7.1	28.7
13	0.0072	0.0	84.8	14.5/74.3	2.9/14.7	2.2/11.0	86.5	12.3	1.2	9.5	10.9	79.6	66.9	7.2	25.9

2000 ppm of Mo, 100 ppm Sulphur, 7 g of oil, 7 g of tetralin and 7 g of dodecane, 250 °C and 50 bar of H₂ cold

Table 3.3.15 Effect of batch time over NiMo nano-sulphide catalysts (derived results)

Batch time (hr)	Organo-oxygen removal (%)	DEO/HYD	Pseudo chemical structure of the organic in each phase		Total content of organo-oxygen in oil and water phases (dry base) (wt%)	Minimum loss of water (g)	Minimum loss of oil phase (g)	Maximum loss of unknown material (g)	Total weight loss (g)
			Oil phase	Water phase					
3	12.2-22.0	0.4-1.2	CH _{1.69} O _{0.020}	CH _{1.74} O _{0.382}	3.0-3.8	0.9	0.3	2.4	3.6
13	37.1-44.6	2.5-5.9	CH _{1.71} O _{0.011}	CH _{1.80} O _{0.333}	2.0-2.7	0.0	0.2	2.7	2.9

3.3.3.5 Effect of solvent

Pure tetralin, dodecane and a mix of tetralin and dodecane were used to investigate the impact of donor solvent. It must be recognised that the change of solvent may affect the intrinsic properties of the catalysts as they were synthesised under different conditions, i.e. solvents. Therefore, the deoxygenation performance may be not only affected by the solvent, but also by the catalyst. Results obtained (Table 3.3.16 and Table 3.3.17) in this section hereby can only provide general information on the selection of proper solvent.

Table 3.3.16 Effect of solvent over NiMo nano-sulphide catalysts (analysis results)

Solvent (g)		H ₂ consumed (mol/g oil)	water content (wt%)		Product weight/Product composition (g/wt%)			EA (wt%)								
			Oil phase	Water phase	Oil phase	Water phase	Residue	Oil phase			Water phase			Residue		
Dodecane	Tetralin							C	H	O	C	H	O	C	H	O
7	7	0.0055	0.0	80.2	14.3/76.2	1.8/9.5	2.7/14.3	85.7	12.1	2.3	12.0	10.7	77.4	64.2	7.1	28.7
0	14	0.0061	0.1	74.4	15.0/79.6	2.4/12.5	1.5/7.9	88.2	9.5	2.3	13.0	9.9	77.1	64.0	7.2	28.8
14	0	0.0050	0.0	79.1	14.4/76.6	2.0/10.8	2.4/12.6	83.4	14.9	1.7	11.3	10.4	78.3	65.3	7.1	27.6
2000 ppm of Mo. 100 ppm Sulphur. 7 g of oil. 3 hr of batch time. 250 °C and 50 bar of H ₂ cold																

2000 ppm of Mo, 100 ppm Sulphur, 7 g of oil, 3 hr of batch time, 250 °C and 50 bar of H₂ cold

Table 3.3.17 Effect of solvent over NiMo nano-sulphide catalysts (derived results)

Solvent (g)		Organo-oxygen removal (%)	DEO/HYD	Pseudo chemical structure of the organic in each phase		Total content of organo-oxygen in oil and water phases (dry base) (wt%)	Minimum loss of water (g)	Minimum loss of oil phase (g)	Maximum loss of unknown material (g)	Total weight loss (g)
Dodecane	Tetralin			Oil phase	Water phase					
7	7			12.2-22.0	0.4-1.2	CH _{1.69} O _{0.020}	CH _{1.74} O _{0.382}	3.0-3.8	0.9	0.3
0	14	15.3-34.4	0.5-3.4	CH _{1.29} O _{0.019}	CH _{1.54} O _{0.636}	3.8-5.4	0.6	0.2	2.7	3.5
14	0	20.0-31.5	1.2-6.2	CH _{2.14} O _{0.015}	CH _{1.71} O _{0.530}	2.7-3.8	0.7	0.3	2.2	3.2

It can be seen that pure tetralin case consumed the highest amount of hydrogen with the least amount of residue being produced, which may be attributed to the increased availability of H₂ in the solvent. With abundant H₂, catalyst is able to break heavy components into lighter ones. Also, coking problem can be mitigated in this circumstance. However, judging from the total content of organo-oxygen in oil and water phases as well as the oxygen content of the pseudo chemical structures of oil and water phases, pure dodecane solvent had a better performance than the pure tetralin solvent. Increase the dodecane content in the solvent would increase the degree of deoxygenation as shown by the ratio of DEO/HYD. In the case of using pure dodecane as solvent, deoxygenation was mainly the preferred reaction rather than hydrogenation. The GC-MS analysis of the water phase (Table 3.3.18) suggested a decrease in hydrothermally treated products with dodecane solvent, as shown by the decreasing acid content.

Quantitative GC-MS analysis of the oil phase was done only for the run with pure dodecane as solvent. Guaiacyl-propane (81 wt% of all O-containing compounds) and p-ethyl-guaiacol (12 wt% of all O-containing compounds) were the most significant compounds detected.

Generally speaking, the overall performance of dodecane was better than tetralin. Furthermore, since the use of a saturated hydrocarbon is preferred for the in-situ catalyst synthesis and it also can reduce the complexity of downstream separation, dodecane is recommended.

Table 3.3.18 Organo-oxygen compounds in water phase: effect of solvent

Compound	Percentage of all O-containing compounds (wt%)		
	Dodecane-Tetralin	Tetralin	Dodecane
Ethanol	15.8	11.7	12.4
Acetoin	2.3	3.2	28.7
Acetic acid	23.5	25.3	15.7
1,2-Ethanediol	1.7	2.3	0.8
Propionic acid	2.7	2.8	2.1
Butanoic acid & G4	16.8	16.0	11.5
Pentanoic acid derivatives	4.5	5.8	3.1

3.3.4 Application

Above results demonstrated the usefulness of the dispersed nano-sulphide catalysts. It is necessary to evaluate the potential of this kind of catalysts being used in a bio-refinery. This bio-oil upgrading project was in collaboration with Centre for Process Systems Engineering (CPSE) of Imperial College London. Only relevant modelling results were presented in this section. Detailed information can be found in the literature [16]. The simulation was done and credited to Dr. M. Sharifzadeh.

3.3.4.1 Bio-oil HDO

Based on the above mentioned laboratory results, a combined hydrotreating scheme of a low temperature stabilisation process with sulphide nano-catalysts and a more severe second stage deoxygenation is proposed (Figure 3.3.5). The catalyst is firstly synthesised using molybdenum naphthenate and nickel naphthenate as precursors with sulphur agent (dibutyl disulphide) in the solvent preparation vessel. Dodecane is used as hydrotreating solvent due to its advantages as previously discussed. Then, the catalyst containing solvent is mixed with the bio-oil at the solvent to oil ratio of 2:1 in the slurry reactor, which operates at 250 °C under 50 bar of H₂. After the mild treatment, the effluents are separated into 4 streams, i.e., gases, oil phase, water phase and residues. The water phase is then sent to a reformer followed by a low temperature gas-shift

reactor for H_2 production. Therefore, the whole process is partially H_2 self-sustained. Meanwhile, the oil phase (composed of dodecane solvent and water insoluble components) and residues flow to a high temperature hydrotreating reactor for deep deoxygenation. The upgraded bio-oil consists of solvent, gasoline boiling point range and diesel boiling point range components, which are sent for separation and further processing.

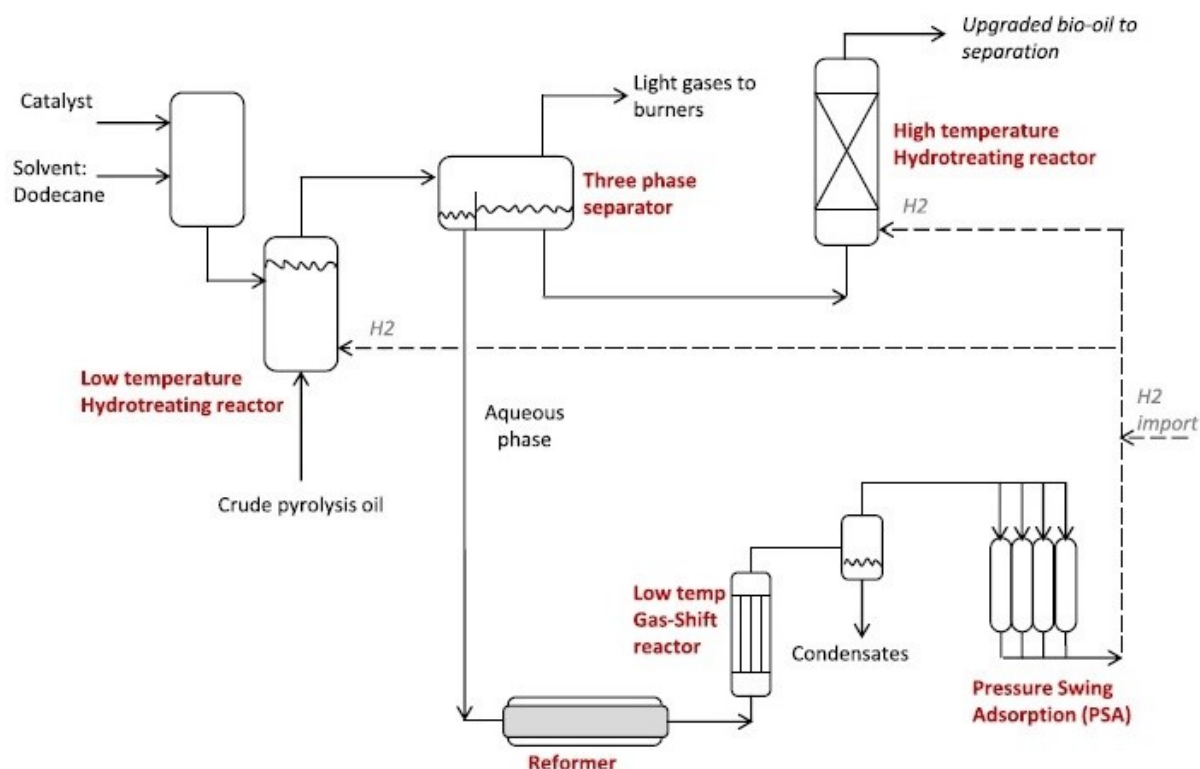


Figure 3.3.5 Hydrotreatment of bio-oil

The elemental analysis of the water, oil and residue phases and the GCMS results of the water and oil phases were used in the simulation. Assumptions were made where necessary to scale up the products to make up the mass deficit in the experiment. The yield of products in the high temperature hydrotreating reactor was adapted from Jones et al. [17]. Simulation results are reported in Table 3.3.19.

Table 3.3.19 Key process indicators of hydrotreatment

Description	Value	Note
Feul/bio-oil (kg/kg)	0.652	Overall efficiency of the process
H_2 required/bio-oil (kg/kg)	0.042	Total H_2 required for the process
H_2 produced/bio-oil (kg/kg)	0.017	H_2 produced from the water phase
Net H_2 requirement/bio-oil (kg/kg)	-0.025	
Energy requirement/bio-oil (kJ/kg)	2396	Energy input to sustain the process
Dodecane/bio-oil (kg/kg)	2.14	

3.3.4.2 The integrated upgrading

Besides the hydrotreating method to upgrade the bio-oil, a study was conducted on non-catalysed hydrothermal treatment of bio-oil in near-supercritical water [9]. The hydrothermal upgrading was conducted in stainless steel batch reactors (8 mL) at 380 °C with a water-to-oil rate of 3 in the absence of catalyst. Results show that approximately 40% of the carbon in the original bio-oil exists in the form of water soluble compounds if the reactor is quenched immediately after reaching 380 °C. The distributions of these groups decrease with residence time. The high solubility of these compounds is because of hydrophilic nature of alcoholic OH, carbonyl C=O and acidic COOH groups.

Contrary to the hydrotreatment, hydrothermal process can produce H₂. This provides the possibility that, if the bio-oil is split between the two processes, an integrated process for bio-oil upgrading can be H₂ self-sustained. Based on this concept, the following scheme is proposed.

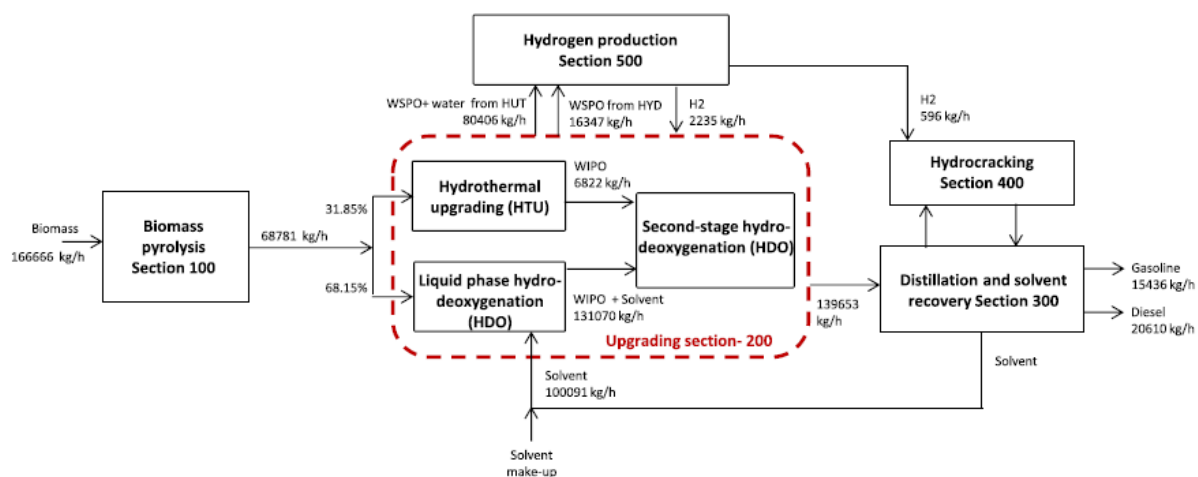


Figure 3.3.6 Process block diagrams of the integrated upgrading section

3.4 CONCLUSIONS

Deoxygenation is required if the bio-oil is going to be used in the current transportation infrastructure as fossil fuel substitutes or blending components. The study investigated a first-stage hydrotreating upgrading (i.e. HDO) of bio-oil with the consideration of different catalysts and operating conditions. Promising laboratory results were used in a modelling study in which an integrated H_2 self-sustainable upgrading process was proposed.

Supported catalysts of Pd/C, Ru/C, Co/ Al_2O_3 and Ni/ Al_2O_3 were tested at 175 °C with 3 hr of batch time under 50 bar of H_2 (cold). Ru/C produced an oil phase with least oxygen content while it consumed much more H_2 than other catalysts, including the hydrogenation of the solvent. Ni/ Al_2O_3 had a better performance on deoxygenation and hydrogenation than Pd/C under the same level of H_2 consumption. Co/ Al_2O_3 was relatively inactive under the operating conditions.

Due to the merits of the unsupported catalysts, NiMo nano sulphided catalyst was selected as an example to be tested in the bio-oil upgrading under various conditions to optimise the process. Results reveal that, under mild conditions, raising the temperature (from 200 to 250 °C) improves the degree of deoxygenation of the bio-oil and reduces the relative extent of hydrogenation of the products. A 2000 ppm of Mo loading is not necessary for the HDO of the bio-oil and the amount of the catalyst being used can be reduced. Though the addition of 100 ppm of sulphur reduces the H_2 consumption, it is not essential. Extending the batch time (from 3 to 13 hr) promotes both deoxygenation and hydrogenation. However, the deoxygenation reaction rate decreases along the time suggesting the batch time can be optimised. As for the solvent, the catalyst has a better performance in dodecane than in tetralin. Besides, a saturated hydrocarbon solvent is preferred for the in-situ catalyst synthesis and it can also simplify the solvent recovery. Indeed, recycled fully hydrotreated bio-oil would be a preferred solvent.

Based on the experimental results, a simulation study was conducted. A model process with high fuel yield is established. However, it suffers H_2 deficit. The hydrothermal process, on the contrary, is able to generate excess H_2 . Accordingly, a combined hydrotreating-hydrothermal process is proposed. This integrated configuration can produce the maximum fuel and would be self-sufficient with respect to the hydrogen requirement.

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4 p-CRESOL HYDRODEOXYGENATION OVER Co/Al₂O₃ AND Ni/Al₂O₃ CATALYSTS

4.1 INTRODUCTION

Phenols form a significant proportion of bio-oils because they are refractory species. They are also important intermediates in the HDO of oxygenated aromatics. Hence, it is necessary to elucidate the catalytic HDO processes of bio-oil by using phenols as model compounds. In order to provide better knowledge to understand the HDO mechanism of the bio-oil and to control the product selectivity, p-cresol, as a representative component of the bio-oil derived from Norwegian spruce, has been studied as a model phenolic compound.

As mentioned in Chapter 2, the alumina supported cobalt and nickel selective hydrogenation catalysts have potential for deoxygenation applications. Tests with selected model compounds have demonstrated favourable results over Ni/Al₂O₃ in the literature [1]. However, Co/Al₂O₃ is mainly used for selective hydrogenation/reduction of unsaturated aldehydes [2, 3]. There is a lack of information in the literature on the HDO performance of Co/Al₂O₃ catalyst, nor on the impact of sulphur on both catalysts in deoxygenation use. Herein, a systematic investigation of the hydroprocessing of p-cresol over alumina supported cobalt and nickel catalysts with and without added sulphur is reported. The catalysts were available in reduced (stabilised) form from a commercial source.

According to the original research works on the HDO of p-cresol reviewed in Chapter 2, the HDO process temperatures normally range from 225 to 400 °C and hydrogen pressures range from 25 to 110 bar. In order to be comparable to the literature and to be consistent with previous bio-oil upgrading (Chapter 3), the experiments of HDO of p-cresol and its intermediate (i.e. 4-methylcyclohexanol) were conducted at temperatures between 250 and 375 °C under 50 bar of hydrogen. Hexadecane was used as solvent under sulphur-free circumstances while dodecane was used when sulphur was added.

Catalysts were characterised in as-received status. X-ray diffraction (XRD), x-ray fluorescence (XRF), transmission electronic micrograph (TEM), temperature programmed reduction (TPR) and Brunauer-Emmett-Teller (BET) analysis was carried out.

Complete deoxygenation of p-cresol could be achieved over both of the catalysts. Methylcyclohexane and toluene were main deoxygenated products. High temperature

would favour toluene production. 4-Methylcyclohexanol, as an intermediate, was observed at low temperatures. The impact of sulphur and catalyst pre-reduction were examined. It is shown that sulphur suppressed the HDO of p-cresol yet it promoted the deoxygenation of alicyclic alcohol.

4.2 EXPERIMENTAL METHODS

This section gives the experimental methods used in the study of p-cresol HDO. Procedures are provided where necessary and details can be found in the Appendix.

4.2.1 Catalyst characterisation

The metal content of each of the catalysts was determined by a Bruker S4 explorer X-ray Fluorescence spectrometer. A pressing force of 20 tons was used to make the pellet for XRF analysis. The X-Ray Diffraction (XRD) results were obtained using a PAnalytical X'Pert Pro X-ray diffractometer with Ni filtered Cu K α radiation (wavelength 1.54 Å) at 40 kV and 30 mA. The analysis was performed using a standard 15° - 80° 2 θ method with a step size of 0.076°/s. In order to determine the catalyst reduction behaviour, Temperature Programme Reduction (TPR) was carried out in 10% Hydrogen/Nitrogen. For the Co/Al₂O₃, the sample was heated from room temperature to 850 °C at a ramp rate of 10 °C/min. However, Ni/Al₂O₃ catalyst was heated up only to 650 °C with the same rate, as there was no peak observed and the signal was back to baseline after 550 °C. The hydrogen consumption was measured by a thermal conductivity detector (TCD) calibrated by ultra-pure copper oxide (Sigma-Aldrich, 99.9999%). Transmission Electron Microscopy (TEM) images were taken with a JEOL 2010 system (80-200 kV) to investigate the crystallinity of the catalyst. The resolution of the instrument was 0.23 nm. BET analysis was performed at 77 K using a Micromeritics Tristar 3000 apparatus on 100 mg catalyst which was held overnight under nitrogen prior to adsorption measurements. Samples were degassed at 120 °C for 12 hrs. Details on the catalyst characterisation can be found in the Appendix.

4.2.2 Hydrodeoxygenation procedure

Parr 4590 100 ml hastelloy pressure vessels (Figure 4.2.1) were used for the study of HDO reactions. Hexadecane (anhydrous, ≥99%, Sigma-Aldrich) was mainly used as solvent. A feed was prepared by mixing 0.6 g reactant p-cresol (99%, Sigma-Aldrich) with 19.4 g solvent. Besides, toluene (CHROMASOLV, 99.9%, Sigma-Aldrich), methylcyclohexane (anhydrous, ≥99%, Sigma-Aldrich), 4-methylcyclohexanol (Purum, cis+trans, ≥98%, Fluka) and 1-Methyl-1-cyclohexene (97%, Sigma-Aldrich) were also investigated as independent model compounds with the same reactant to solvent ratio. In order to investigate the effect of added sulphur on HDO and catalysts, experiments were specially carried out at 350 °C with dodecane (≥99%, Sigma-Aldrich) as solvent by introducing certain amount of dibutyl disulphide (97%, Sigma-Aldrich) into the reaction

mixture. For the comparison of the activities of the catalysts, reaction kinetics was measured with p-cresol and 4-methylcyclohexanol with dodecane as solvent at 250 °C and 300 °C, respectively. The reasons to use dodecane in the later part of the research are that hexadecane is prone to crack at high temperatures and the fragments from the hexadecane increase the complexity of identifying the product peaks from the gas chromatograms.

Catalyst particles (as-received) were crushed and sieved to a fine powder (106-250 µm) before use. To catalyse the HDO process, particles were freely suspended in the liquid phase.



Figure 4.2.1 Parr Hastelloy autoclaves and gas control panel

The autoclave was charged with 20 g of the feed and a certain amount of catalyst, and then it was purged by nitrogen 3 times to displace air and then 5 times with hydrogen. The reactor was initially filled with 30 bar of hydrogen (cold pressure). The temperature was raised while the stirring speed was gradually increased to 1000 rpm to prevent external mass transfer limitation. Fresh hydrogen was supplied when the temperature was near the set point to ensure that the pressure at the beginning of the experiment reached the desired pressure, i.e. 50 bar. The batch time was counted when the process temperature reached the target value. No more hydrogen was added throughout the remaining experiment.

Experiments were also conducted with pre-reduced catalysts to investigate the effect of pre-reduction. The pre-reduction of the Co/Al₂O₃ and Ni/Al₂O₃ catalysts was carried out with 5% hydrogen balanced by nitrogen for 4 hr at 450 and 350 °C, respectively. Figure 4.2.2 shows the schematic diagram of the catalyst reduction rig. The reduced catalyst

was transferred to the reactor with the reduction gas passing by to prevent re-oxidation in a fume cupboard. Other procedures of the runs with pre-reduced catalysts were the same as those with as-received ones.

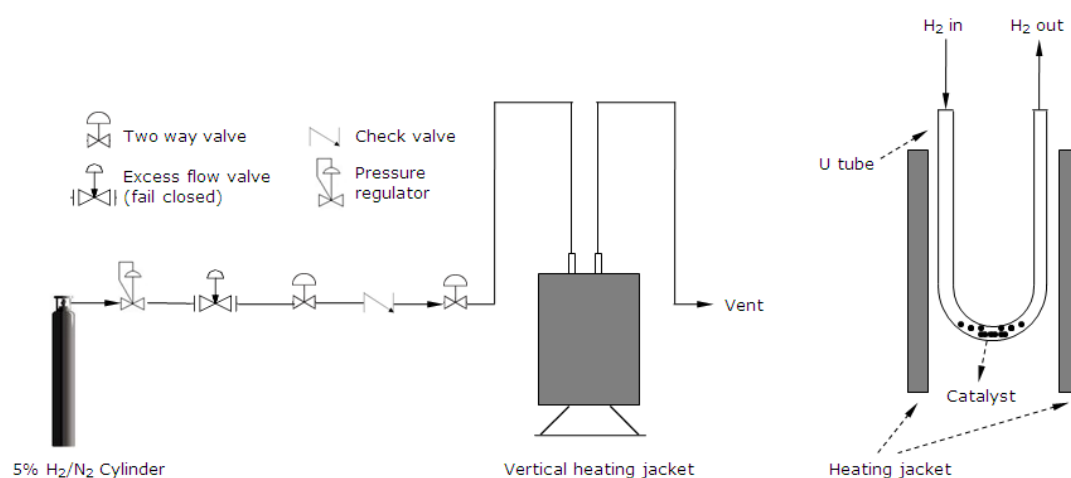


Figure 4.2.2 Catalyst reduction rig

4.2.3 Product analysis

Liquid samples were analysed by gas chromatography (SHIMADZU, GC-2014 with FID) with a BP1 column (film thickness 0.5 μ m, length 25 m and ID 0.32 mm). Peak areas were measured with the software provided by SHIMADZU (GC lab solution). Ethylcyclohexane was used as internal standard for the quantitative analysis. The standard solution was prepared by adding 0.6 g of ethylcyclohexane ($\geq 99\%$, Sigma-Aldrich) into 19.4 g of solution (hexadecane or dodecane).

Response factors and the retention times of reactants and products, including p-cresol, 4-methylcyclohexanol, methylcyclohexane, methylcyclopentane, toluene, 1-methyl-1-cyclohexene, 4-methylcyclohexene, benzene and cyclohexane were determined by the calibration of GC with pure samples. Results can be found in Appendix, including the methods used for sample preparation and GC analysis. Figure 4.2.3 is a typical gas chromatogram of reaction mixture.

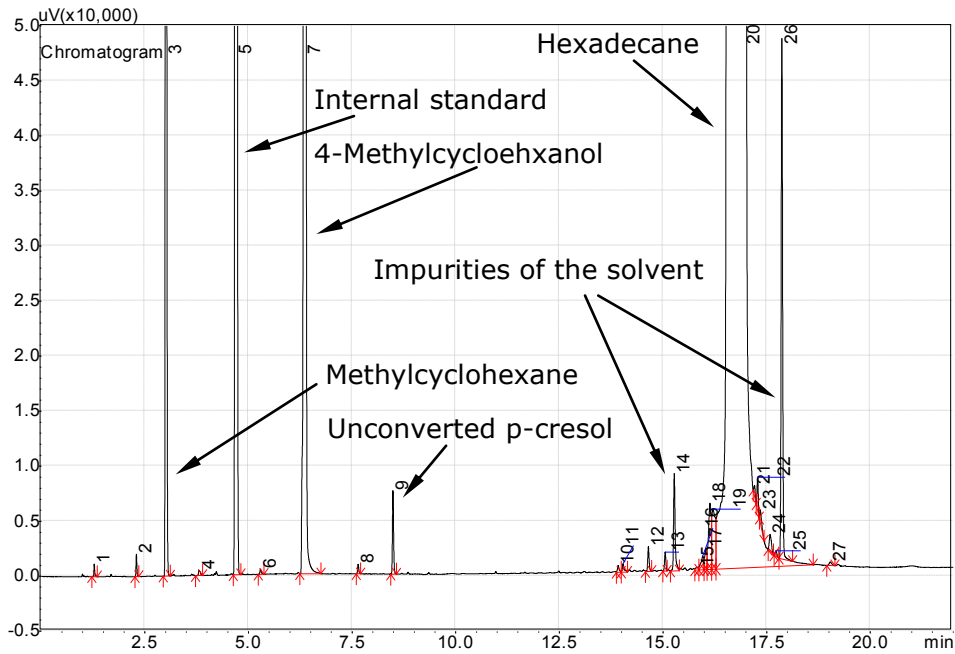


Figure 4.2.3 Typical gas chromatogram of reaction mixture (post-reaction liquid)

The conversion is defined as the ratio of the model compound reacted to the total model compound added.

Conversion

$$= \frac{\text{Weight of the model compound}_{\text{feed}} - \text{Weight of the model compound}_{\text{post reaction liquid}}}{\text{Weight of the model compound}_{\text{feed}}} \quad (4)$$

The product distribution is given by the ratio of the weight of a certain product to the total weight of all detected compounds in the post-reaction liquid.

Product distribution

$$= \frac{\text{Weight of a certain compound in the post reaction liquid}}{\text{Total weight of all detected compounds in the post reaction liquid}} \quad (5)$$

The percentage of HDO is the sum of the product distributions of all the deoxygenated products.

HDO%

$$= \frac{\text{Total weight of all detected deoxygenated compounds in the post reaction liquid}}{\text{Total weight of all detected compounds in the post reaction liquid}} \quad (6)$$

The product selectivity is only being as a general guidance of evaluating the catalyst performance wherever necessary when the feed conversion is low. It is given by the following equation.

$$\text{Product selectivity} = \frac{\text{Mole of feed converted to a certain product}}{\text{Total mole of feed converted}} \quad (7)$$

4.3 RESULTS AND DISCUSSION

Repeat experiments were carried out and also the effect of different solvents was considered. In all cases, the product distribution values at the same conditions varied within $\pm 4\%$, indicating good reproducibility of the work.

In all runs, the total amount of detected compounds in the post-reaction liquid was able to account for ≥ 84 wt% of the starting material. The loss was probably due to the reasons, such as the formation of phenates, chemisorbed by acid support alumina, covering the most of the alumina surface [4], the incomplete recovery of the relatively small amounts of components from the post-reaction liquid [5], and the condensates of light components on the head, the formation of coke by the polymerisation of reactant and/or products and the cracking at high temperatures [6]. Generally, the weight loss and the intensity of the fragment peaks in the gas chromatograms increased with temperature, suggesting that cracking certainly was an issue. Nevertheless, the incomplete recovery could be the main source of loss, since the problem existed even at the lowest temperature tested.

The HDO results are mainly given in the form of figures and associated tables can be found in Appendix (i.e. full data by both weight and mole percent). The data is represented as the percentage of the product distribution by weight together with the degree of HDO and the conversion of feed as a function of a certain controlled condition (e.g. temperature, batch or sulphur level).

4.3.1 Catalyst characterisation

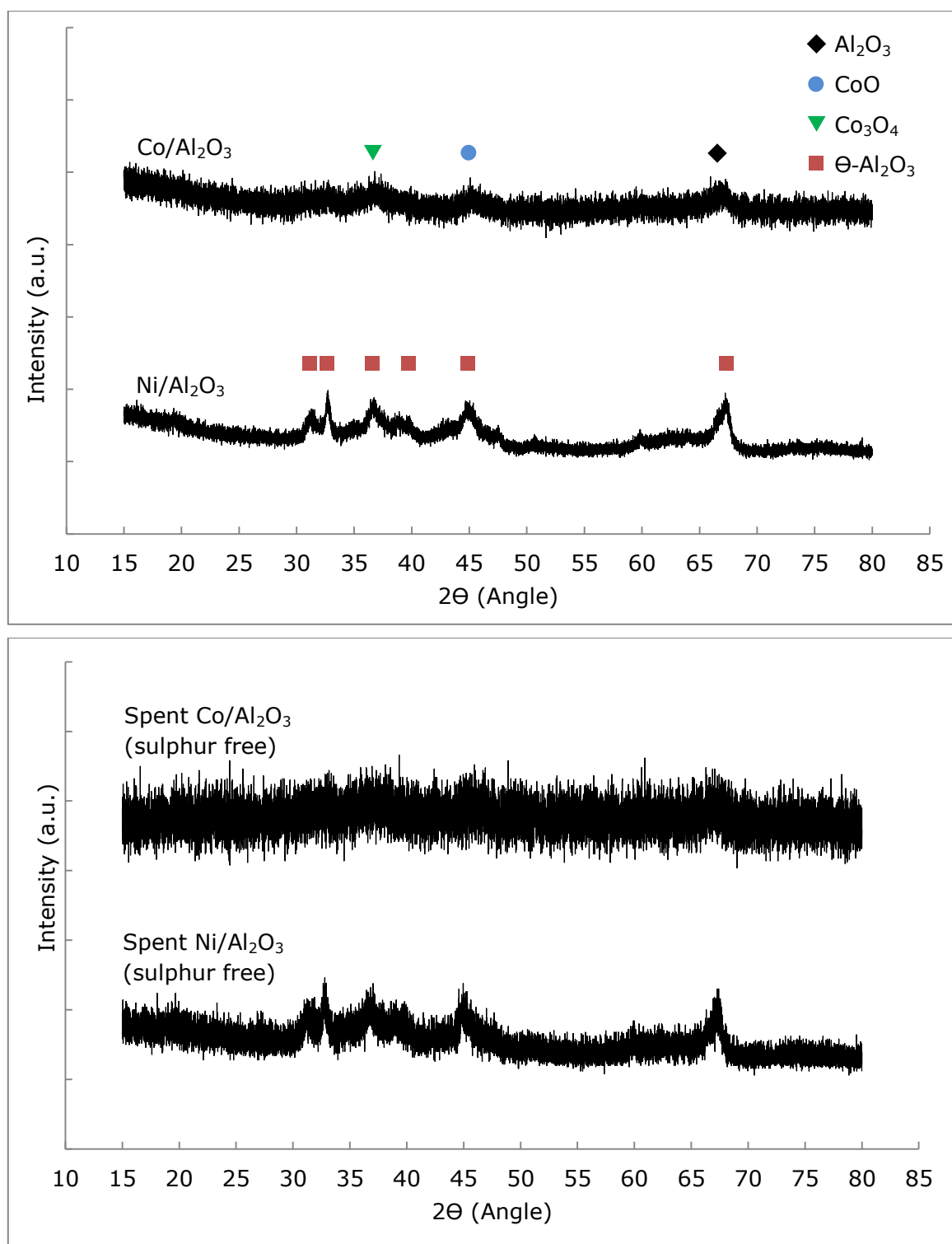
XRF analysis reveals that Co/Al₂O₃ has a metal content of 20 wt% while Ni/Al₂O₃ has 15 wt%. Figure 4.3.1 shows the XRD patterns of the as-received catalysts. The Co/Al₂O₃ catalyst (as-received) examined had very weak peaks indicating that it was XRD-amorphous. Crystallites, if any, were therefore very small or highly dispersed on the support. However, the diffraction profile is analogous to that obtained by Yang et al. [7]. Thus, it is reasonable to assume that the peaks may be due to the existence of Co₃O₄ and CoO species. For the analysis of Ni/Al₂O₃, the peaks observed were assigned to γ -Al₂O₃. Unfortunately, XRD could not prove the existence of nickel oxide species. Samples of spent catalysts (both Co/Al₂O₃ and Ni/Al₂O₃), with and without added sulphur, were recovered and XRD scanned. Same results as those of fresh catalysts were obtained and no significant changes of their XRD patterns were observed on either of the catalysts. In general, the XRD was not able to establish the state of the metals of the catalysts, as no

distinct peaks could be observed.

Figure 4.3.2 shows the TEM images. The areas of lighter contrast could be assigned to alumina support whilst the areas of darker contrast were due to metal oxide and/or metallic species. It can be seen that Co/Al₂O₃ was mostly amorphous with multi-crystal morphology (e.g. platy and needle shaped) and the Ni/Al₂O₃ contained fine crystals.

BET surface areas of as-received Co/Al₂O₃ and Ni/Al₂O₃ were measured to be 120 m²/g and 107 m²/g, respectively. Co/Al₂O₃ had a pore volume of 0.46 cm³/g while that of Ni/Al₂O₃ was 0.37 cm³/g. The average pore diameter of Co/Al₂O₃ was 12.67 nm and that of Ni/Al₂O₃ was 10.66 nm.

The TPR profiles are shown in Figure 4.3.3. Co/Al₂O₃ exhibited three peaks at around 290 °C (peak A), 450 °C (peak B) and 620 °C (peak C). Peak B and C overlaid with each other resulting a broad reduction range between 400 and 700 °C. According to a two-step reduction of cobalt oxide [7-9], peak A was assigned to the reduction of Co₃O₄ to CoO and peak B was assigned to the reduction of CoO to Co⁰. There exist interactions between the cobalt species and alumina support producing xCoO·yAl₂O₃ which constitutes a constraint for the reduction to Co⁰ [9, 10]. The formation of mixed oxides would extent the TPR spectra to higher temperatures. Thus, peak C was associated with the reduction of xCoO·yAl₂O₃. A α-type NiO species are defined to describe those free nickel oxides having a weak interaction with support [11, 12] and they normally have the reduction peaks in the temperature range of 300 to 400 °C [13]. The reduction peak of Ni/Al₂O₃ catalyst (peak D) was therefore assigned to this α-type NiO. The shoulder of peak D was mainly due to the reduction of a small portion of oxide which had stronger interaction with alumina. The hydrogen uptakes for Co/Al₂O₃ and Ni/Al₂O₃ were 3.46 and 1.53 mmol/g_{cat}, respectively. Assuming the metals of the catalysts were entirely in the form of cobalt (III) oxide and nickel (II) oxide, then the minimum percentage of reduction achieved for Co/Al₂O₃ was 68% and that for Ni/Al₂O₃ was 60%. Details on catalyst reduction can be found in the Appendix. The TPR profiles reflect the fact that the catalyst as supplied (as-received) were pre-reduced and stabilised by oxidation.



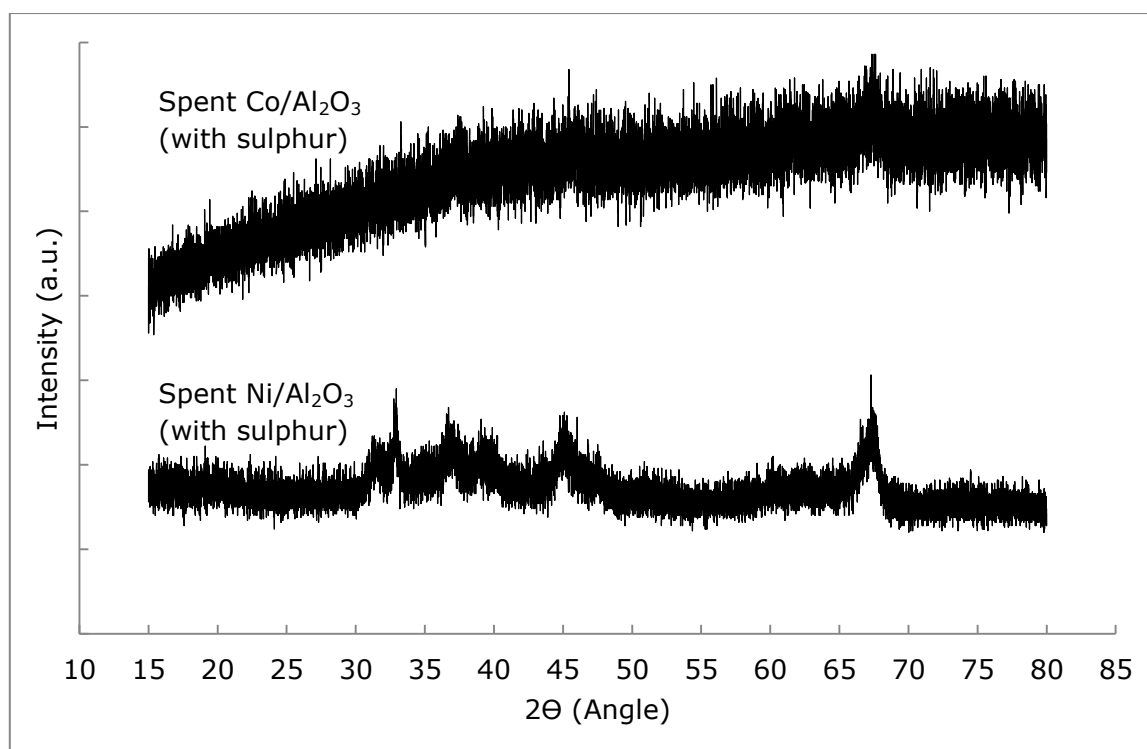


Figure 4.3.1 Catalysts XRD profiles

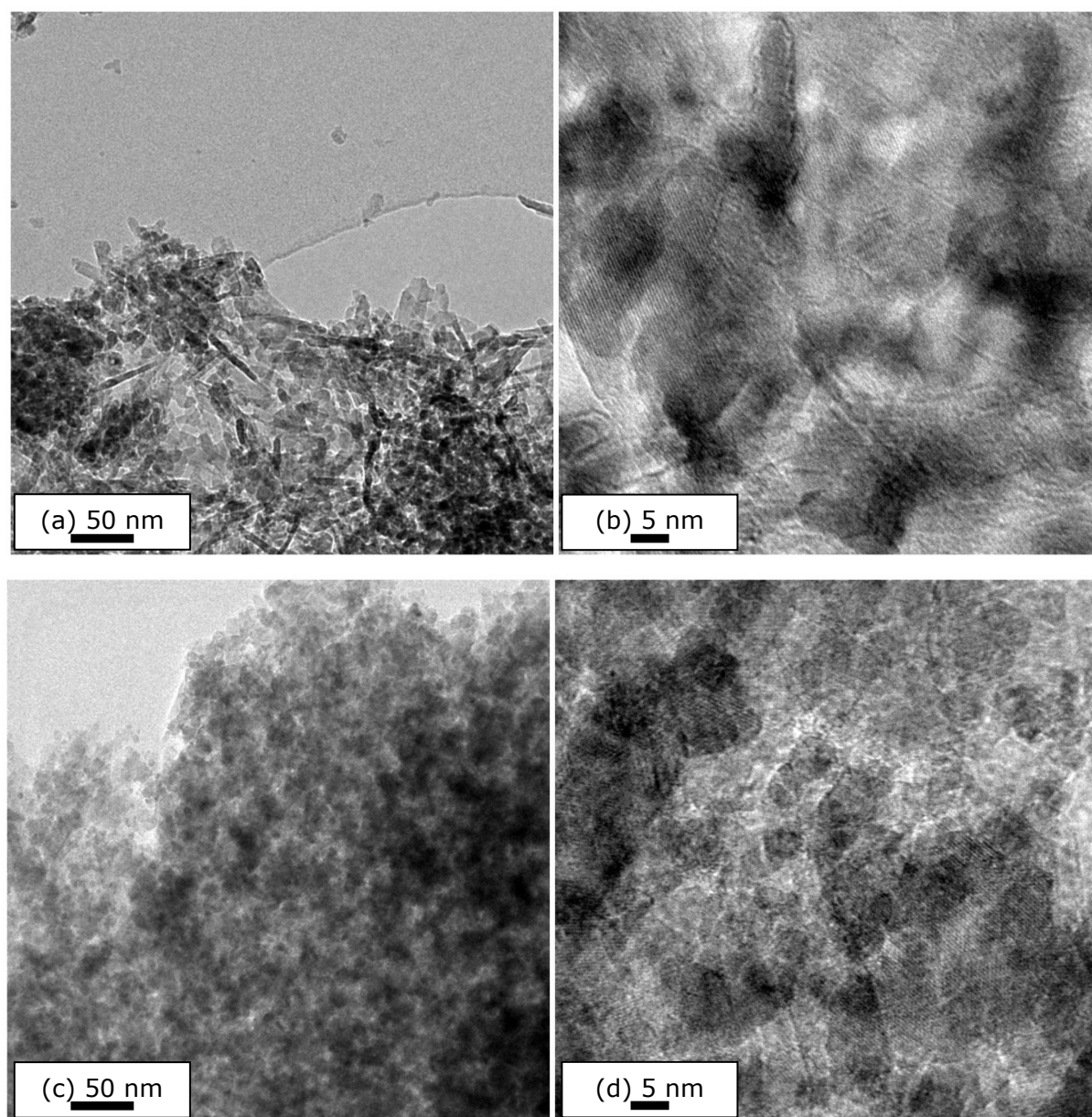
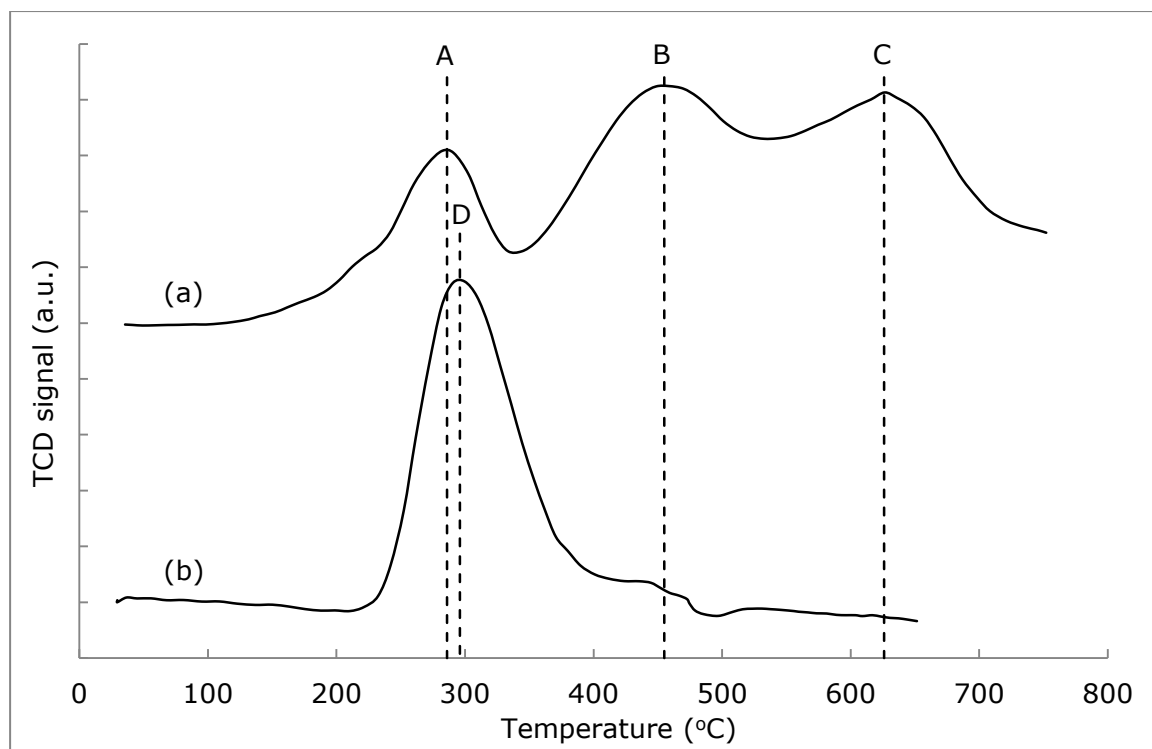


Figure 4.3.2 TEM-micrographs: (a, b) Co/Al₂O₃, (c, d) Ni/Al₂O₃

Figure 4.3.3 TPR profiles: (a) Co/Al₂O₃, (b) Ni/Al₂O₃

4.3.2 HDO of p-cresol

The HDO of p-cresol is known to follow two routes [6, 14-17]. One is the aromatic ring hydrogenation followed by deoxygenation producing naphthenic hydrocarbon and it is believed that methylcyclohexenes are precursors of methylcyclohexane [6, 14, 15] (Figure 4.3.4). The other is a direct hydrogenolysis process, namely deoxygenation of phenol, forming aromatic product. The former route is favoured at high hydrogen pressure [6, 14] and the latter is favoured at high temperature.

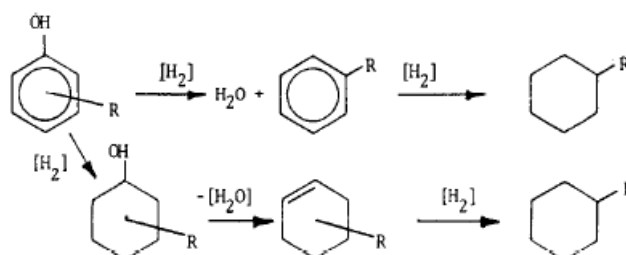


Figure 4.3.4 HDO reaction pathways of cresols [16]

As emphasised in Chapter 2, cresols are important chemical models and widely studied. Though the overall pathway is catalyst dependent, the general HDO mechanism of cresols based on sulphide CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts has been proposed [15]. Effective parameters on reaction selectivity of catalytic HDO of cresols have been studied,

such as catalyst active phase [18], catalyst support [19] solvent [20] and operating conditions [21]. Reaction kinetics of phenols and cresols has also been investigated [22].

Results were obtained from the HDO of p-cresol over Co/Al₂O₃ and Ni/Al₂O₃. In this study, four parameters were investigated, namely temperature, added sulphur, catalyst loading and batch reaction time.

4.3.2.1 Effect of temperature

Experiments were conducted between 250 and 375 °C to determine the effect of reaction temperature on the feed conversion and product distributions. Except the temperature, standard conditions of batch time (i.e. 2 hrs), amount of catalyst (i.e. 0.04 g) and ratio of feed to solvent (i.e. 0.6 g/19.4 g) were used.

The results were generally similar for both catalysts (Figure 4.3.5). The conversions of p-cresol were high ($\geq 98\%$) at all temperatures. The degree of HDO increased considerably with temperature until it reached 300 °C. Above 300 °C, the dominating product changed from 4-methylcyclohexanol to methylcyclohexane. When the temperature was further increased, the production of toluene became significant. Cyclohexane, benzene and methylcyclopentane were observed at temperatures beyond 300 °C as minor products. Minor product distributions at 325, 350 and 375 °C are given in Table 4.3.1.

The equilibrium concentration of benzene in cyclohexane (Figure 4.3.6) shows that the former cannot be obtained by the dehydrogenation of the latter under the studied conditions. Thus, it suggests that benzene was produced by the dealkylation of toluene and the cyclohexane was produced by the dealkylation of methylcyclohexane and by the hydrogenation of benzene. Methylcyclohexene, as intermediate, was not detected in the products, indicating that its conversion was not rate limiting at these conditions.

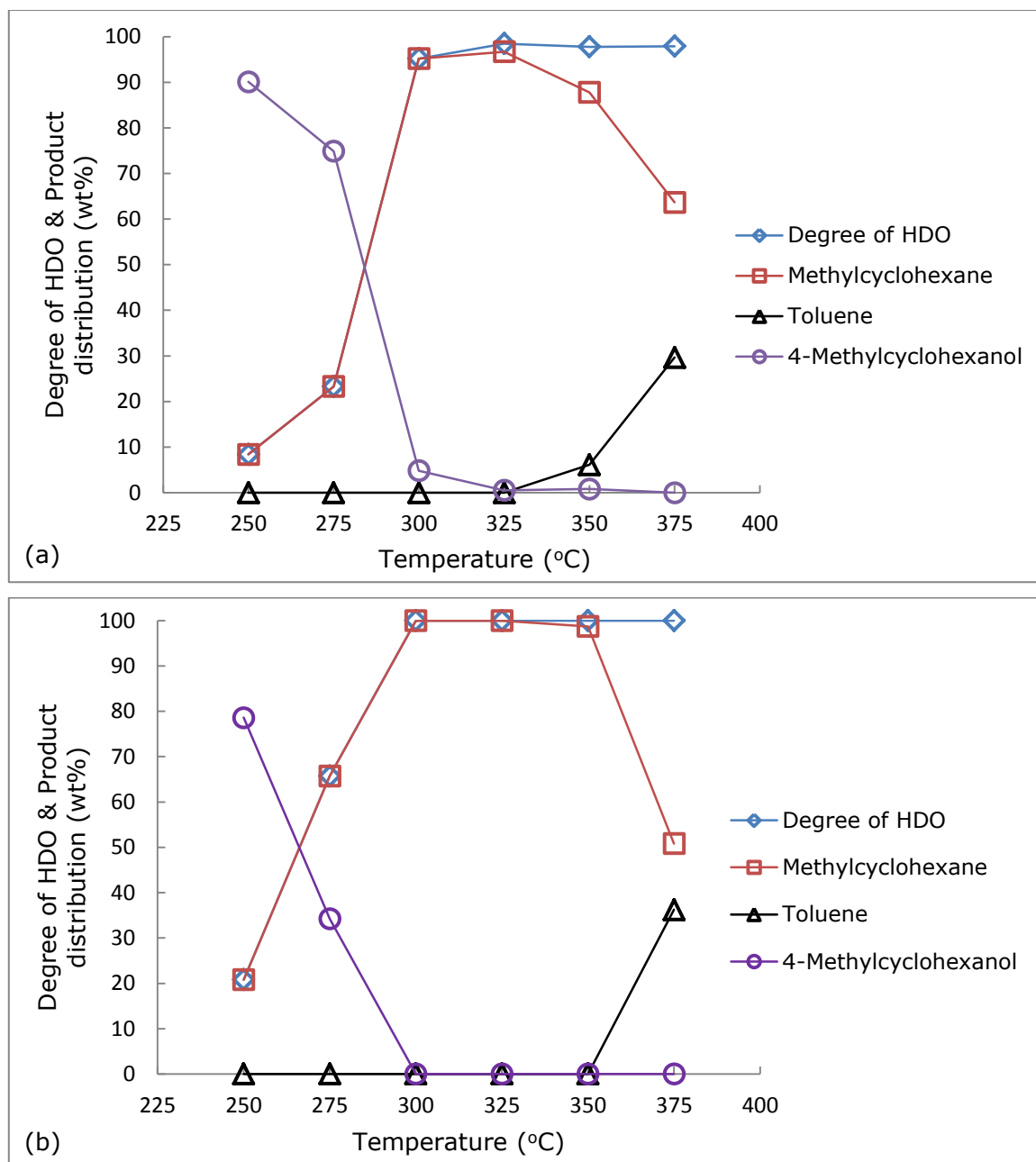


Figure 4.3.5 Effect of temperature on the HDO of p-cresol (0.04 g catalyst and 2 hr batch time): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

Table 4.3.1 p-Cresol HDO minor product distributions over Co/Al₂O₃ and Ni/Al₂O₃ catalysts

Catalyst	Temperature (°C)	Product distribution (%)		
		Cyclohexane	Benzene	Methylcyclopentane
Co/Al ₂ O ₃	325	1%	0%	1%
	350	2%	0%	2%
	375	1%	1%	2%
Ni/Al ₂ O ₃	350	1%	0%	0%
	375	7%	6%	0%

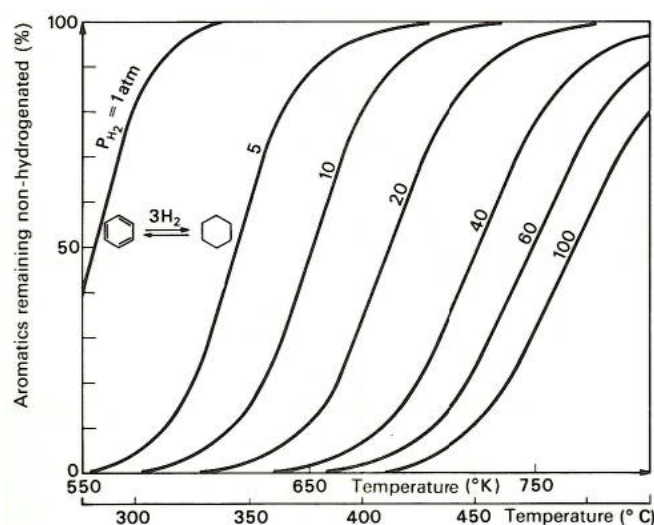


Figure 4.3.6 Effects of hydrogen pressure and temperature on equilibrium concentration of benzene and cyclohexane [23]

The production of methylcyclohexane involves subsequent reactions of p-cresol hydrogenation on hydrogenation sites (i.e. metal sites) and 4-methylcyclohexanol deoxygenation on hydrogenolysis sites (i.e. acid sites) [24]. For both catalysts, the evidence that the complete conversion of p-cresol to 4-methylcyclohexanol as a major product at the lowest temperature tested indicates the hydrogenation sites are highly active.

Base on the study conducted by Faglioni and Goddard [25], which suggests that hydrogen surface coverage over Co and Ni catalysts decreases with temperature, the decrease in the content of hydrogenation products (4-methylcyclohexanol and methylcyclohexane) and the increase in that of the direct deoxygenation product (toluene) at temperatures higher than 325 °C can be due to the availability of hydrogen on catalyst surface. In other words, high hydrogen coverage facilitates aromatic ring hydrogenation while low hydrogen coverage results in direct hydrogenolysis producing toluene [5]. In addition, judging from the fact that the phenolic C-O bond energy (110.8 kcal/mol) is higher than that of the cyclohexanol (95.3 kcal/mol) [26], the direct deoxygenation of p-cresol producing toluene would require a higher temperature to proceed comparing with the deoxygenation of 4-methylcyclohexanol.

4.3.2.2 Effect of added sulphur in the feed

Impurities can modify the activity and selectivity of the catalyst. Among which, sulphur compounds (sulphides, disulphides, thiophenes and etc.) always accompany the

petroleum feedstocks. Though, bio-oil has negligible content of sulphur. It is necessary to understand the impact of sulphur on the HDO performance of Co/Al₂O₃ and Ni/Al₂O₃, as they are normally used with added sulphur or in sulphide form. Here, sulphur was added up to 155 ppm.

Toluene, as an important p-cresol HDO product, was produced to a certain amount only at 350 and 375 °C and it is necessary to understand its product distribution with added sulphur. However, the fragments from solvent cracking at 375 °C may affect the analysis of minor products. Therefore, experiments were conducted at 350 °C to investigate the effect of added sulphur on catalyst performance. Standard conditions of batch time (i.e. 2 hrs), amount of catalyst (i.e. 0.04 g) and ratio of feed to solvent (i.e. 0.6 g/19.4 g) were used. Catalysts were tested with different levels of sulphur and results were compared with sulphur-free ones (Figure 4.3.7). Due to the low conversion of p-cresol in the sulphur environment, product selectivity was used in addition to extract more information from the results (Figure 4.3.8). It is noteworthy that though the product selectivity is subject to weight loss, it can be used to generally evaluate the impact of added sulphur.

For Co/Al₂O₃, the methylcyclohexane concentration was found to be less than 3% and the amount of toluene produced was negligible for all runs with sulphur. Minor amounts of methylcyclohexene isomers (≤ 2 wt%) as deoxygenation intermediates were detected. The selectivity of these isomers rose while that of methylcyclohexane dropped, suggesting that the added agent clearly had an inhibiting effect on the hydrogenation sites. As for Ni/Al₂O₃, the impact on hydrogenation sites was the same, however, the catalyst was less sensitive to sulphur. Toluene was produced with added sulphur and its amount increased first and then dropped. The cause of the fluctuation will be discussed in the later section. Generally, judging from the degree of HDO over both catalysts, results agree with the literature that sulphur containing agents inhibit the deoxygenation of phenolic compounds [14, 15, 27].

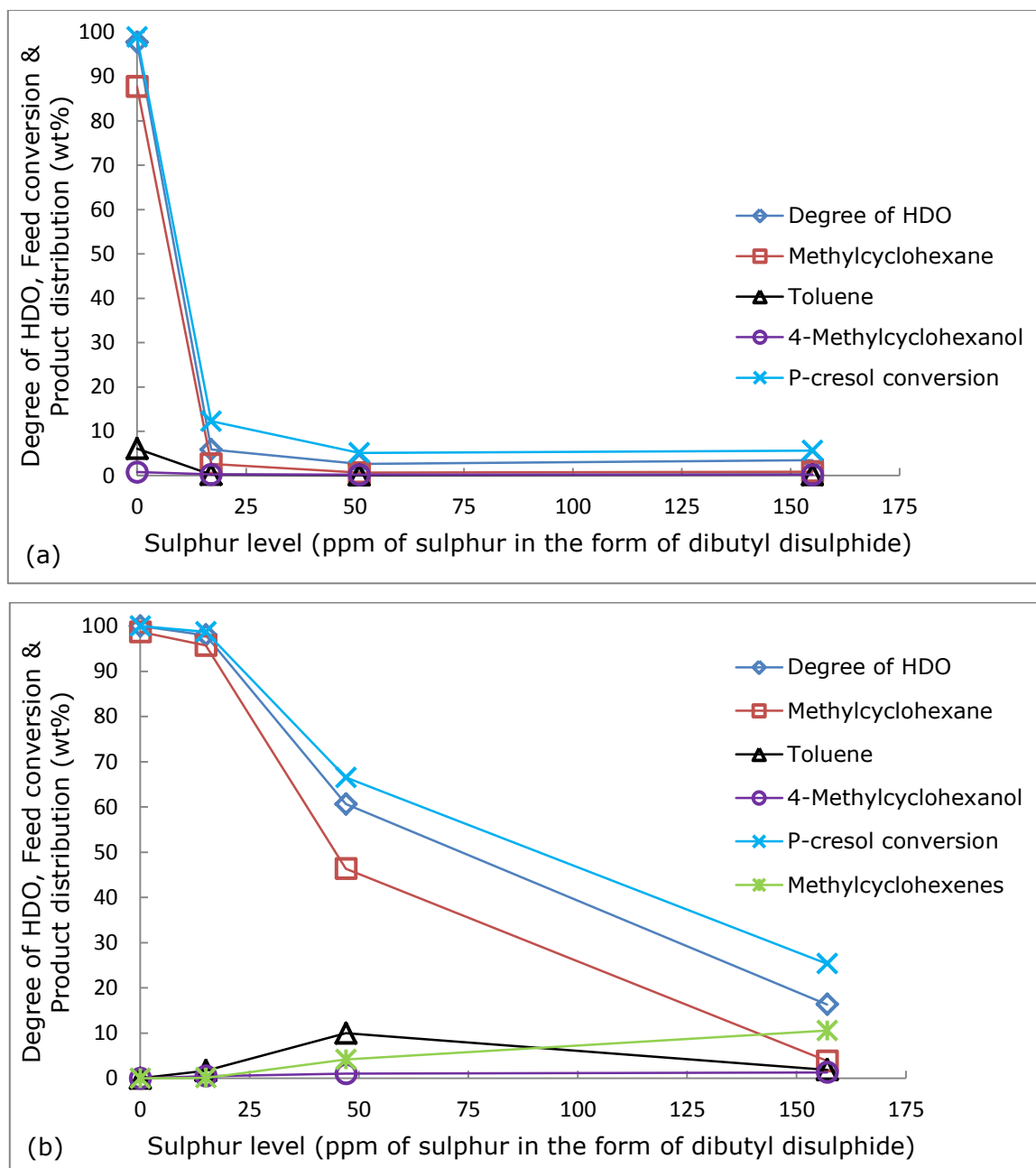


Figure 4.3.7 Effect of added sulphur on the HDO of p-cresol (0.04 g catalyst and 2 hr batch time at 350 °C): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

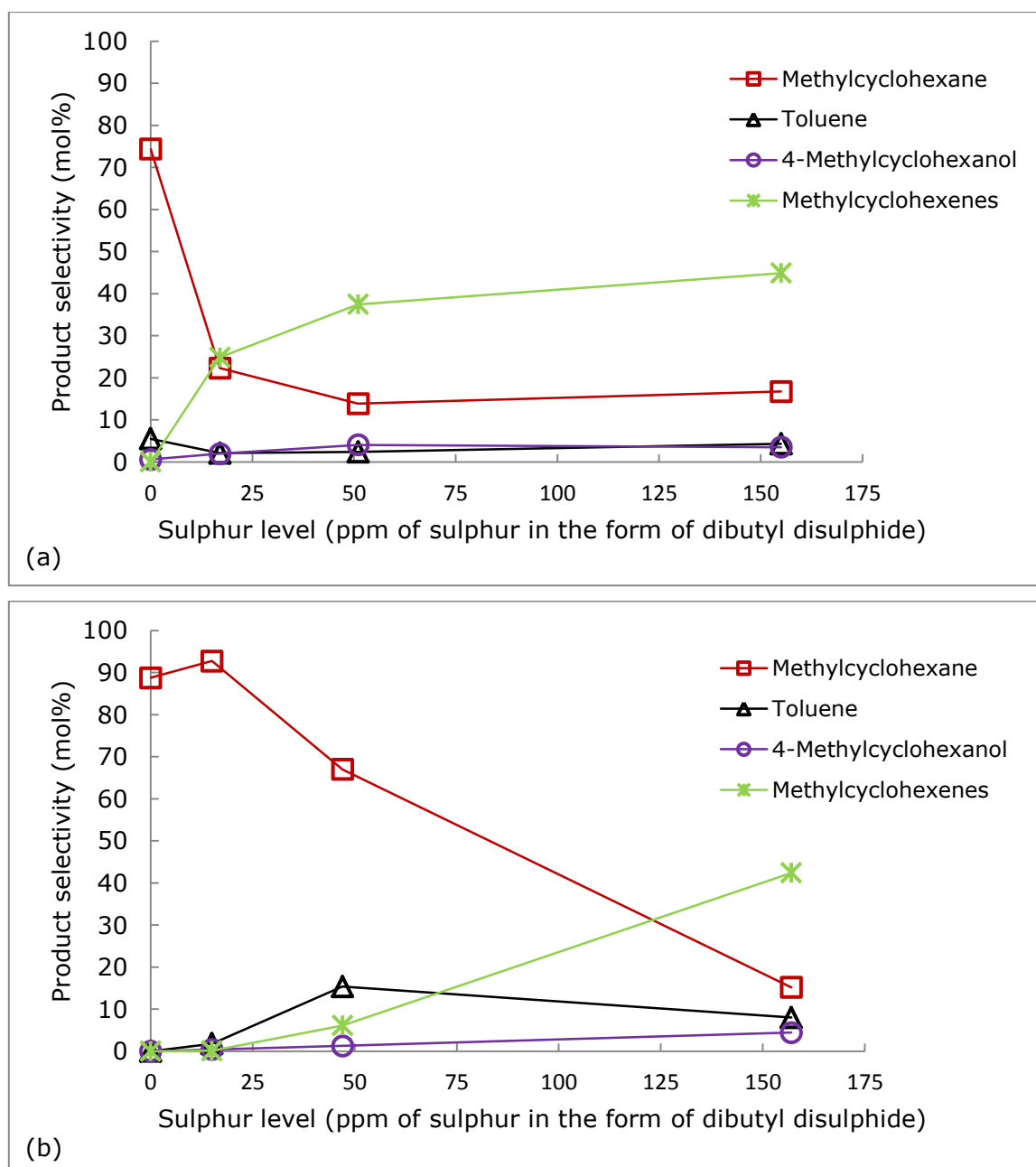


Figure 4.3.8 Effect of added sulphur on the product selectivity of HDO of p-cresol (0.04 g catalyst and 2 hr batch time at 350 °C): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

In general, the inhibition effect of added sulphur is greater on the Co/Al₂O₃ catalyst than that on the Ni/Al₂O₃ one. This could be explained by the status of the active metal sites. According to the TPR profiles (Figure 4.3.3), the majority of the Ni/Al₂O₃ catalyst could be fully reduced around the experimental temperature (i.e. 350 °C), and therefore the added sulphur only adsorbed on the metal sites, leading to limited inhibition effect. As for the Co/Al₂O₃ catalyst, it might be only partially reduced. The cobalt oxides are not stable in-situ and are prone to react with sulphur agents to form cobalt sulphides, which are less active forms for HDO (see section 4.3.5.1 for discussion). Hence, the presence

of cobalt sulphides might be the cause for the catalyst to be more sensitive to sulphur.

4.3.2.3 Effect of catalyst loading

p-Cresol HDO reactions with lower catalyst loading (i.e. 0.01 g) were carried out at temperatures of 250, 300 and 350 °C over the Co/Al₂O₃ catalyst with a 2 hr batch time. The conversions of p-cresol were high ($\geq 98\%$) at all circumstances. It can be clearly seen from the results (Figure 4.3.9) that high catalyst loading (i.e. 0.04 g) increases the production of methylcyclohexane from 4-methylcyclohexanol at 300 °C, which suggests that the reaction is rate limiting at this temperature. On the contrary, increase the amount of the catalyst has a negative effect on toluene production, although the amount of toluene is small in both cases. This may be due to the hydrogenation of the toluene product from direct deoxygenation. In fact, for the higher catalyst loading (i.e. 0.04 g), a minor amount of toluene could have been produced before it is consumed at medium temperatures and therefore it cannot be detected (e.g. at 300 °C). It has been shown in the later section that the equilibrium consists predominantly of methylcyclohexane at all temperatures tested. Accordingly, a higher catalyst loading exerts a greater driving force on the system to reach equilibrium status, and as a result, less toluene was observed. Cyclohexane and methylcyclopentane were detected only at 350 °C as minor products (≤ 2 wt%) and their product distributions slightly increased with catalyst loading. This may due to the availability of the acid sites, as acid-catalysed reactions (i.e. dealkylation and isomerisation) are involved.

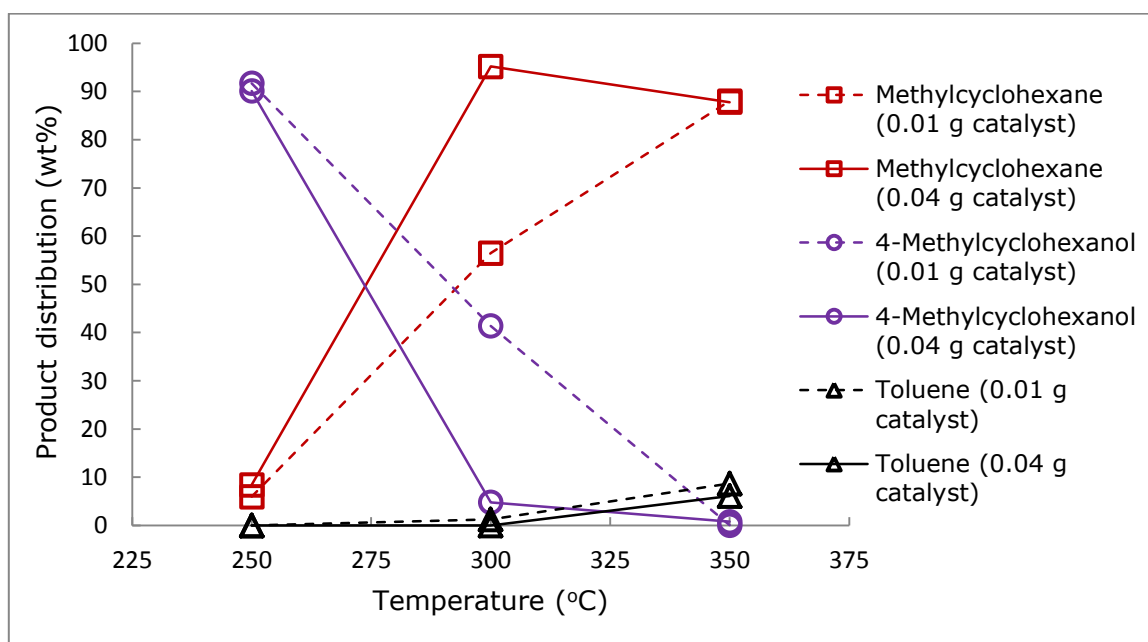


Figure 4.3.9 Effect of catalyst loading on the HDO of p-cresol (2 hr batch time over Co/Al₂O₃)

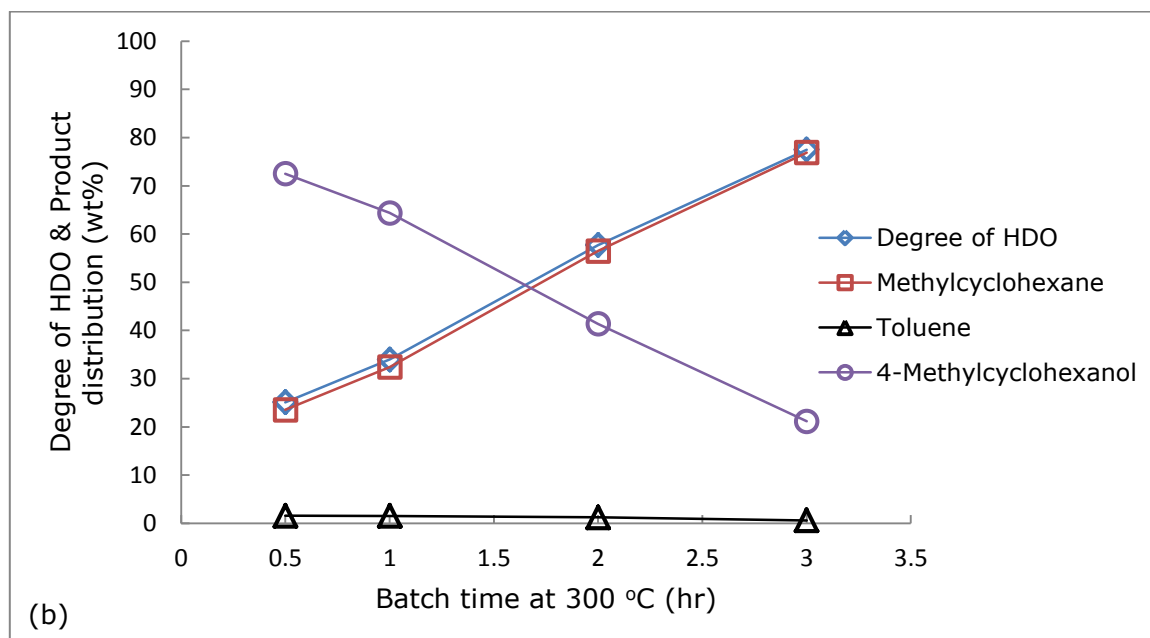
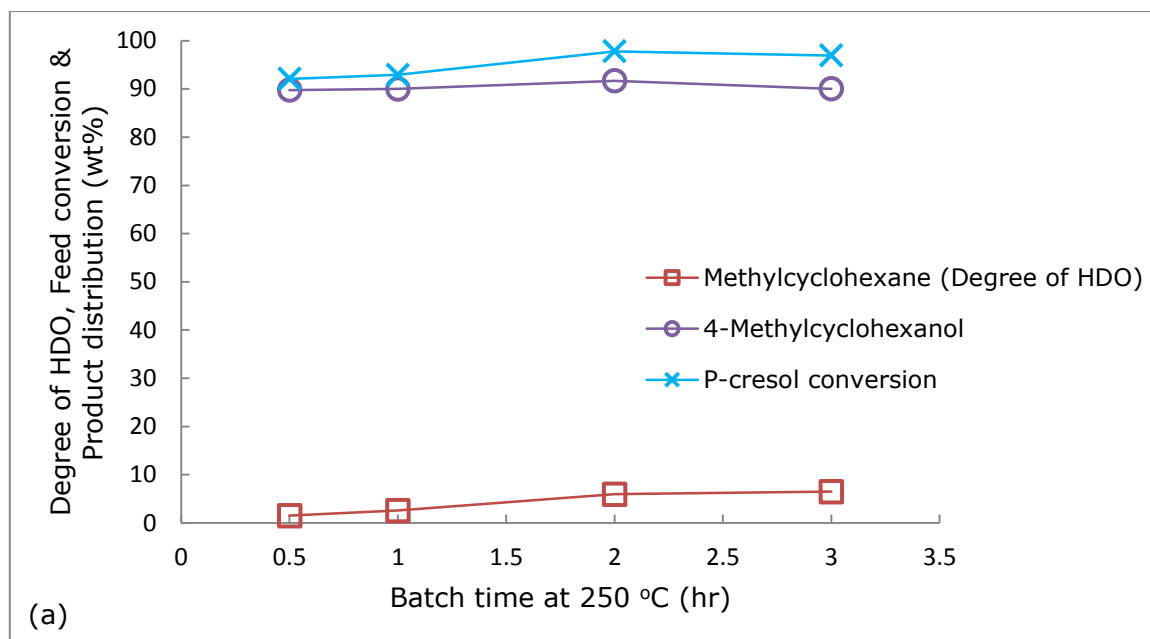
4.3.2.4 Effect of batch time

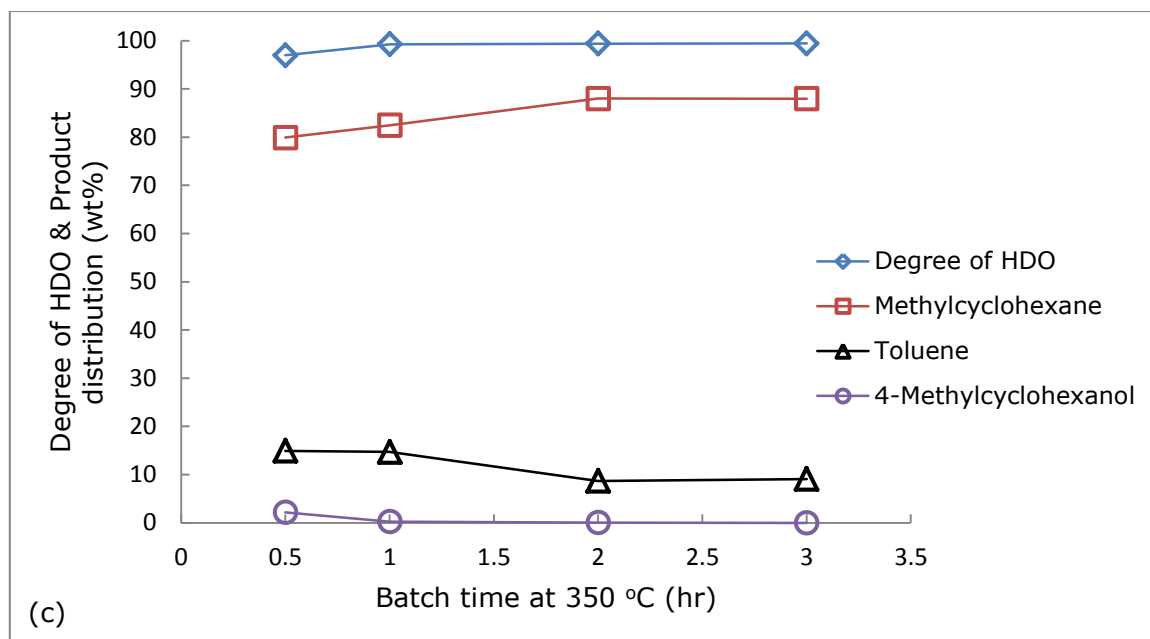
The effect of batch reaction time (ranging from 0.5 to 3 hr) was investigated with different reaction temperatures (i.e. 250, 300 and 350 °C) over Co/Al₂O₃ (0.01 g of catalyst loading). Except for 250 °C, the conversions of p-cresol were nearly complete ($\geq 98\%$).

At the lowest temperature tested (Figure 4.3.10-a), the batch time had little effect on 4-methylcyclohexanol content. Both the p-cresol conversion and the amounts of methylcyclohexane in the product increased slightly with batch time. 4-Methylcyclohexanol might be gradually consumed via hydrogenolysis sites to yield methylcyclohexane under the circumstances, yet it could be produced by the hydrogenation of p-cresol. In such a way, the concentration of 4-methylcyclohexanol remained whereas the conversion of p-cresol increased.

At 300 °C (Figure 4.3.10-b), the content of 4-methylcyclohexanol decreased with the batch time whilst that of methylcyclohexane increased. The increasing amount of methylcyclohexane against the batch time at 250 and 300 °C again indicates that the deoxygenation of 4-methylcyclohexanol is rate limiting over the Co/Al₂O₃ catalyst. Minor amount of toluene was detected and it decreased against time to approach equilibrium.

For 350 °C (Figure 4.3.10-c), the batch time had a less effect on the product distributions. Extending the batch reaction time resulted in a loss of toluene production. Same as the effect of catalyst loading, this may due to the hydrogenation of the toluene product from direct deoxygenation.



Figure 4.3.10 Effect of batch time on the HDO of p-cresol (0.01 g Co/Al₂O₃ catalyst)

4.3.3 Toluene/Methylcyclohexane system equilibrium

The equilibrium between toluene and methylcyclohexane was studied over Co/Al₂O₃ in this section for the better understanding of the above experimental results.

Runs were carried out using toluene as initial feed at the temperatures between 250 and 375 °C to evaluate the degree of toluene hydrogenation in the current system. Standard conditions of batch time (i.e. 2 hrs), amount of catalyst (i.e. 0.04 g) and ratio of feed to solvent (i.e. 0.6 g/19.4 g) were used. Figure 4.3.11 shows the weight ratios of toluene over the sum of toluene and methylcyclohexane of the final products.

A simulation was also conducted based on the work conducted by Schildhauer et al. [28]. They determined the equilibrium constant for the toluene/methylcyclohexane system



where K_{eq} is the equilibrium constant. This constant of the above equation can be expressed by:

$$K_{eq} = \frac{P_{H_2}^3 P_{C_7H_8}}{P_{C_7H_{14}}} \quad (9)$$

where P_{H_2} , $P_{C_7H_8}$ and $P_{C_7H_{14}}$ are the equilibrium partial pressure of hydrogen, toluene and methylcyclohexane at the corresponding temperature, respectively. The correlation is then given by the following equation,

$$K_{eq} = 3.60 \times 10^9 \text{ kPa}^3 \cdot \exp[-217650 \text{ J/mol} \cdot R^{-1} \cdot (1/T - 1/650 \text{ K})] \quad (10)$$

where R is the gas constant and T is the temperature in Kelvin. In order to provide a general reference of the equilibrium concentration of toluene, assumptions were made in order to simplify the calculation when using Equations (9) and (10). At 350 °C for example, take the value of R as $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and the partial pressure of hydrogen P_{H_2} as 50 bar, then the $K_{\text{eq-350C}}$ given by Equation (10) is $6.34 \times 10^8 \text{ kPa}^3$. Therefore, the equilibrium weight ratio of toluene over the sum of toluene and methylcyclohexane, which is 0.5 wt%, can be calculated from Equation (9). The calculated theoretical ratios are plotted in Figure 4.3.11.

The black dots in Figure 4.3.11 represent the ratios of toluene over the sum of toluene and methylcyclohexane obtained from p-cresol HDO at certain conditions while the black triangle represents that obtained from 4-methylcyclohexanol HDO at 375 °C with 2 hr batch time and 0.04 g of Co/Al₂O₃ catalyst (see the following section for 4-methylcyclohexanol HDO). The blue solid line indicates the ratios from the toluene test and the dashed red line shows the theoretical equilibrium values. At 300 and 350 °C, increasing the batch time and catalyst loading would generally shift the ratio towards equilibrium as the black dots descended towards the theoretical positions. In other words, the changes would favour toluene hydrogenation as discussed above.

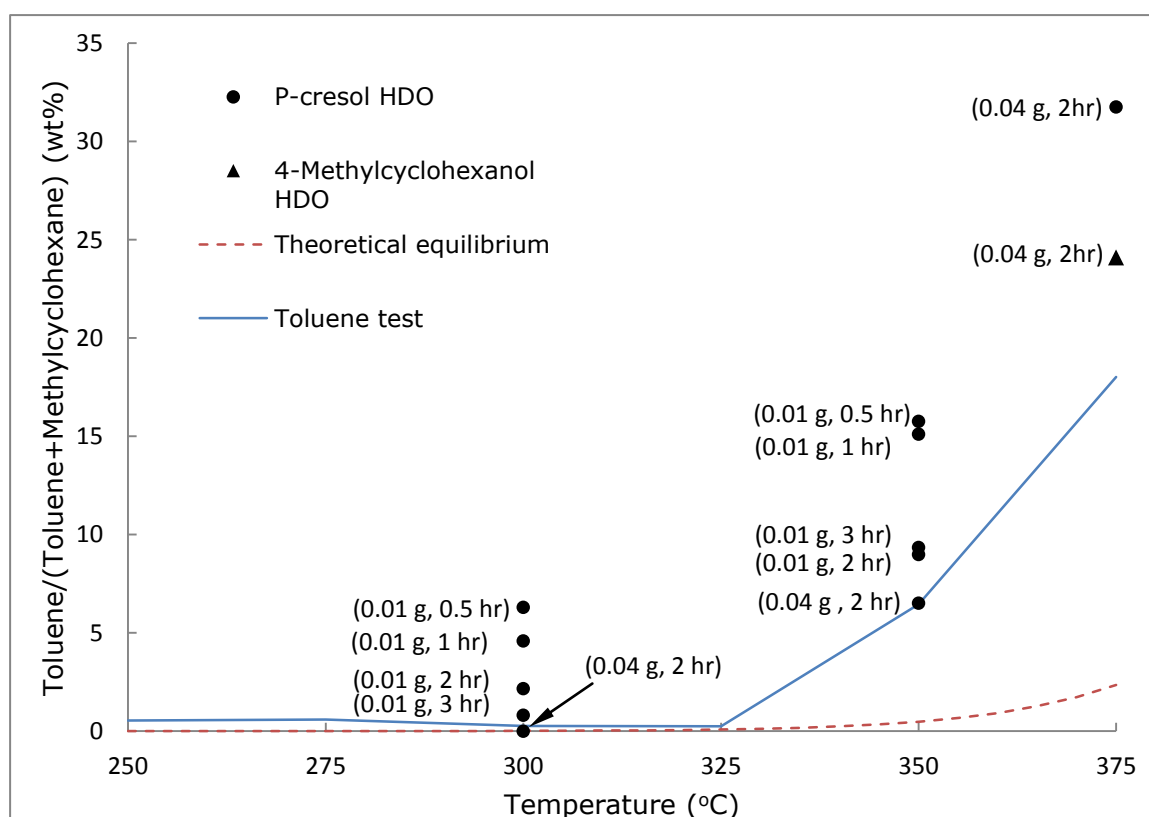


Figure 4.3.11 Toluene equilibrium test (0.04 g catalyst and 2 hr batch time, all results obtained over Co/Al₂O₃)

4.3.4 HDO of 4-Methylcyclohexane

4-Methylcyclohexanol is an important intermediate of p-cresol HDO. The study of the intermediate can help to probe the mechanisms of the p-cresol deoxygenation. Hence, experiments were performed with 4-methylcyclohexanol and the results were discussed in this section.

4.3.4.1 Effect of temperature

Experiments were conducted between 250 and 375 °C to determine the effect of reaction temperature on the feed conversion and product distributions. Except the temperature, standard conditions of batch time (i.e. 2 hrs), amount of catalyst (i.e. 0.04 g) and ratio of feed to solvent (i.e. 0.6 g/19.4 g) were used.

For Co/Al₂O₃, product distributions (Figure 4.3.12-a) were almost the same with those from p-cresol (Figure 4.3.5-a) except at 375 °C, which means HDO of p-cresol would mainly go through 4-methylcyclohexanol as intermediate. At 375 °C, the toluene produced from 4-methylcyclohexanol as initial reactant was less than that from p-cresol. This, therefore, confirms the existence of the direct hydrogenolysis route of p-cresol to toluene during HDO. Interestingly, at 375 °C the product toluene content from 4-methylcyclohexanol HDO exceeded that from the toluene test (Figure 4.3.11). This suggests that the formation of toluene may go through the disproportionation of methylcyclohexenes as intermediates. The reaction of methylcyclohexenes self-dehydrogenation and hydrogenation, producing toluene and methylcyclohexane, is referred to herein as disproportionation reaction. The evidence of methylcyclohexenes disproportionation can be found elsewhere [29, 30]. Hence, the production of toluene in p-cresol HDO most likely involves both the direct hydrogenolysis and hydrogenation-disproportionation routes at high temperatures over Co/Al₂O₃.

Similar to Co/Al₂O₃, the product distributions of 4-methylcyclohexanol HDO and that of p-cresol below 350 °C were alike over Ni/Al₂O₃ catalyst. The direct hydrogenolysis route also exists over Ni/Al₂O₃ catalyst as can be inferred from a higher product distribution of toluene from p-cresol HDO than that of 4-methylcyclohexanol HDO at 375 °C.

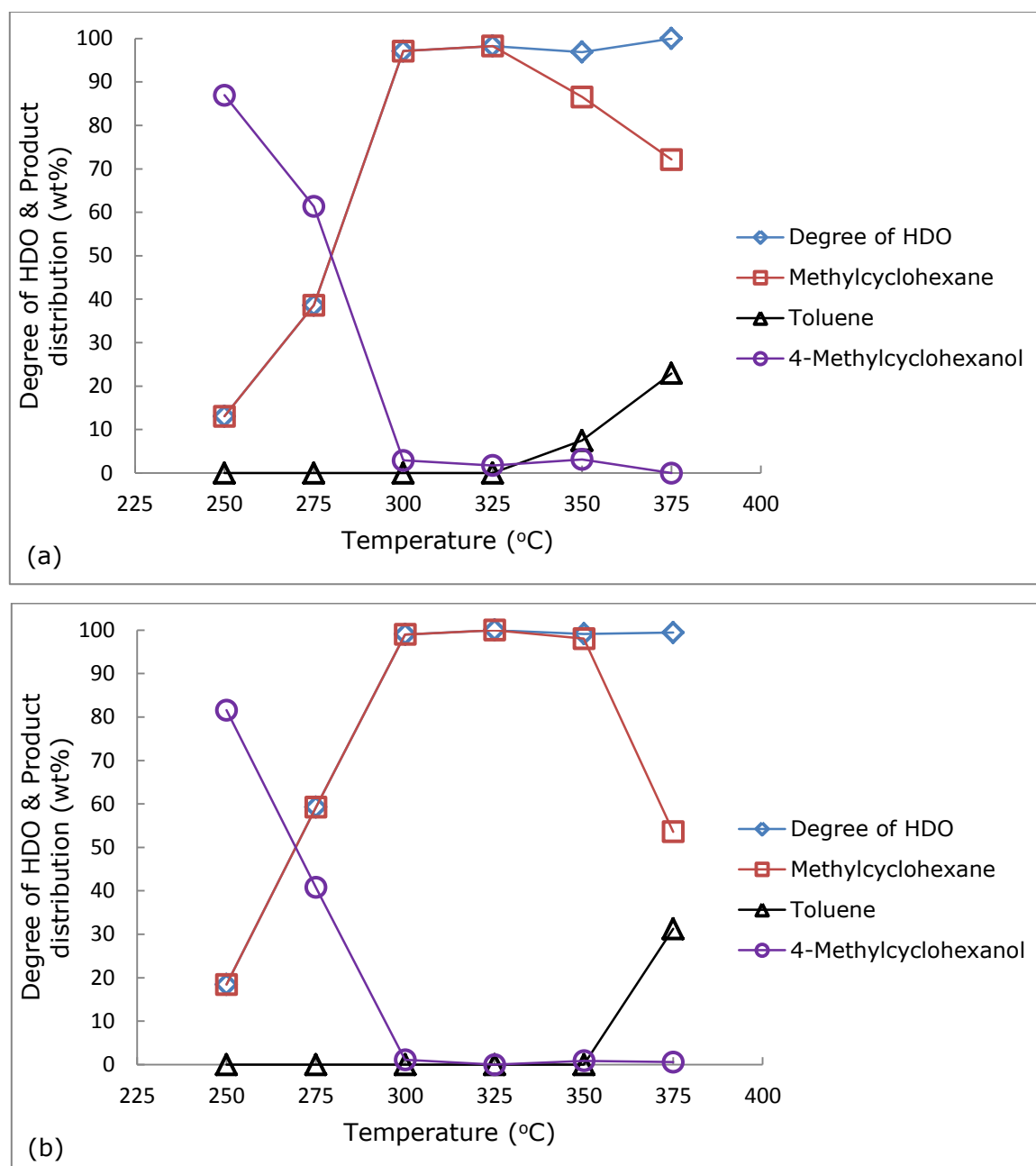


Figure 4.3.12 Effect of temperature on the HDO of 4-methylcyclohexanol (0.04 g catalyst and 2 hr batch time): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

4.3.4.2 Effect of added sulphur in the feed

It has been pointed out that the deoxygenation of alicyclic alcohols is highly active in a sulphur-containing environment [27]. For the same reasons as in the HDO of p-cresol with added sulphur and for the purpose of comparison, experiments were conducted at 350 °C under standard conditions (i.e. 0.04 g of catalyst and 2 hr batch time). As expected, the conversions of 4-methylcyclohexanol were nearly complete ($\geq 98\%$) at all sulphur levels on both catalysts (Figure 4.3.13). Methylcyclohexane, toluene

methylcyclohexenes were main products. Minor products included cyclohexane, methylcyclopentane, etc. Detailed information on the products can be found in Appendix. Sulphur had a large impact on the product distributions. The concentration profiles for methylcyclohexane and methylcyclohexenes reveal that adding sulphur has a strong negative effect on the hydrogenation sites, yet it does not appear to compromise the activity of the hydrogenolysis sites.

For Co/Al₂O₃, ethylcyclopentene isomers were detected (ca. 5 wt%) at the highest sulphur level tested. This may be due to the isomerisation of methylcyclohexenes in the presence of large amount of sulphur. For Ni/Al₂O₃, though the HDO activity of p-cresol was inhibited by added sulphur, toluene product distributions from p-cresol HDO were higher than that of 4-methylcyclohexanol at all sulphur levels, again, indicating the existence of hydrogenolysis route of p-cresol HDO over this catalyst. In illustration of this, Figure 4.3.14 compares the product distributions of toluene and the HDO conversions between p-cresol and 4-methylcyclohexanol. It also shows that, in both cases of p-cresol and 4-methylcyclohexanol HDO, certain amount of sulphur promotes the production of toluene. The HDO behaviours of aromatic oxygenates are related to the availability of the vacancy sites and hydrogen [27]. The competitive adsorption of sulphur on the active sites would effectively reduce the hydrogen availability. Adsorbed hydrogen on a catalyst surface reduces the rate of dehydrogenation [31]. Due to the lack of hydrogen on hydrogenation sites, intermediates (i.e. methylcyclohexenes) may undergo the disproportionation reaction. However, as the added sulphur continued to increase, methylcyclohexane and toluene all reached their minimum values, yet the product distribution of methylcyclohexenes had its maximum. The different effects of added sulphur on the products may be explained as follows. Excess amount of sulphur occupies the hydrogenation sites, diminishing the hydrogen surface coverage, and even limiting the adsorption of intermediates (i.e. methylcyclohexenes) on to the sites. With less activated intermediates available, neither of the subsequent hydrogenation nor disproportionation reactions can proceed normally. Hence, the distributions of methylcyclohexane and toluene dropped. As mentioned, the hydrogenolysis sites for the cleavage of the oxygen from oxygenates are resistant to sulphur. Methylcyclohexenes were being produced by deoxygenation while they were being less consumed by hydrogenation and disproportionation. As a result, methylcyclohexenes accumulated.

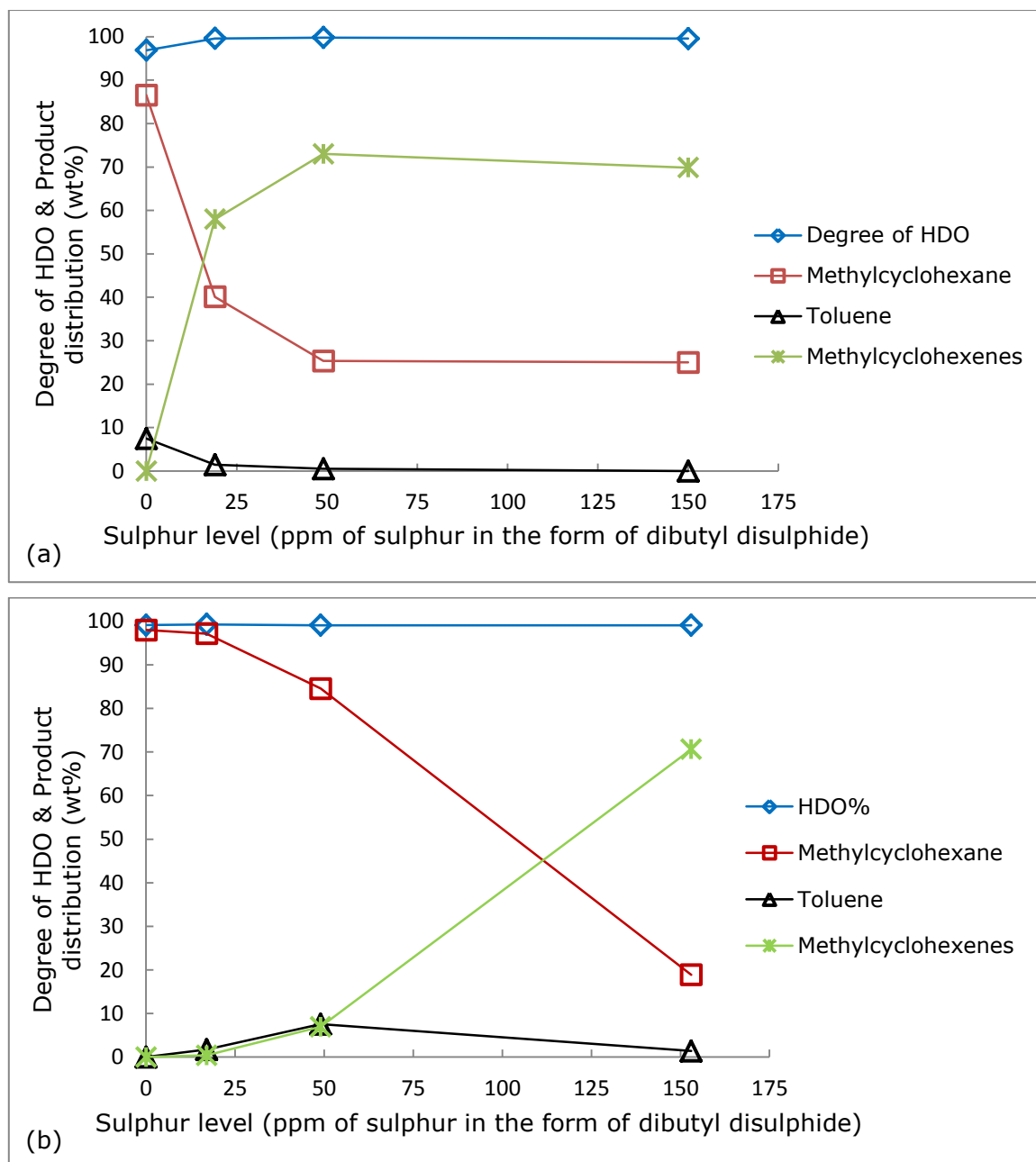


Figure 4.3.13 Effect of added sulphur on the HDO of 4-methylcyclohexanol (0.04 g catalyst and 2 hr batch time at 350 °C): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

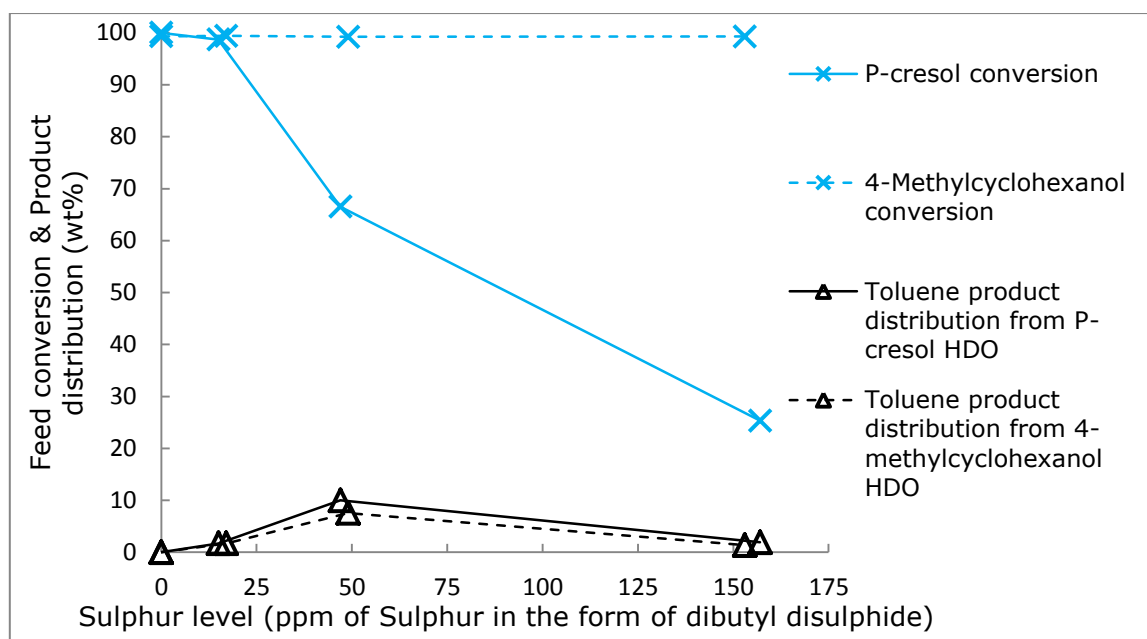


Figure 4.3.14 Effect of added sulphur on toluene production distribution over Ni/Al₂O₃ (0.04 g catalyst and 2hr batch time at 350 °C)

The results of p-cresol and 4-methylcyclohexanol HDO under sulphur environment (≤ 50 ppm) demonstrate that Ni/Al₂O₃ has a better activity and hydrogenation ability than Co/Al₂O₃. A more detailed study of Ni/Al₂O₃ catalyst was conducted with 50 ppm of added sulphur and the results were summarised in Figure 4.3.15. No 4-methylcyclohexanol was detected from the HDO of p-cresol. In addition, toluene was found to be hydrogenated to methylcyclohexane rather than methylcyclohexenes. The facts, together with the presence of methylcyclohexenes in the products of p-cresol HDO, prove that the formation of methylcyclohexenes is mainly through methylcyclohexanol as an intermediate, not by toluene consecutive hydrogenation. The same conclusion can also be drawn based on the complete conversion of 4-methylcyclohexanol HDO producing definite amount of methylcyclohexenes, and on the similarity of the product distributions of the runs starting with 4-methylcyclohexanol and 1-methyl-1-cyclohexene, respectively. The test with methylcyclohexane gave no conversion, and yet toluene was produced by 1-methyl-1-cyclohexene as initial feed. Clearly, a disproportionation reaction exists, and it has an important role in the production of toluene as a parallel route to direct hydrogenolysis in the HDO of p-cresol under the studied conditions. Based on the results and analysis presented here, a modified reaction network of p-cresol HDO catalysed by Co/Al₂O₃ and Ni/Al₂O₃ can be inferred and is shown in Figure 4.3.16.

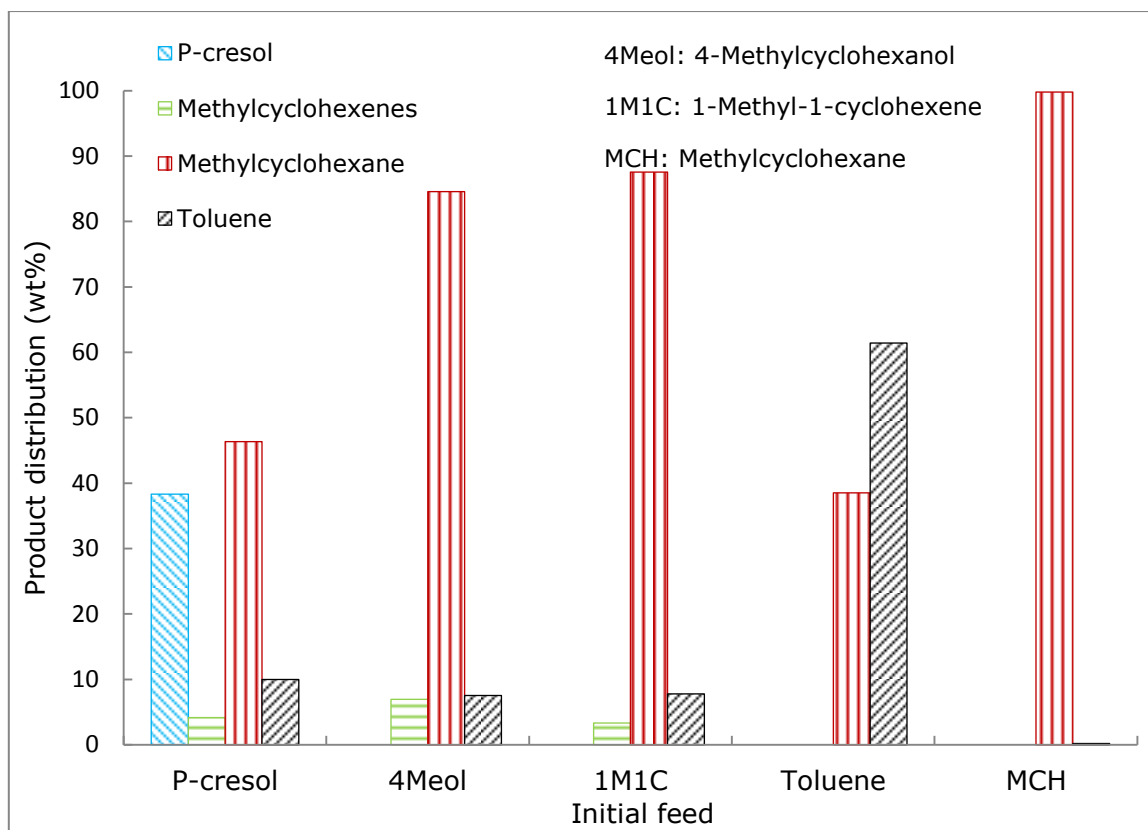


Figure 4.3.15 Product distributions of different initial feeds (0.04 g Ni/Al₂O₃ and 2 hr batch time at 350 °C with 50 ppm of sulphur)

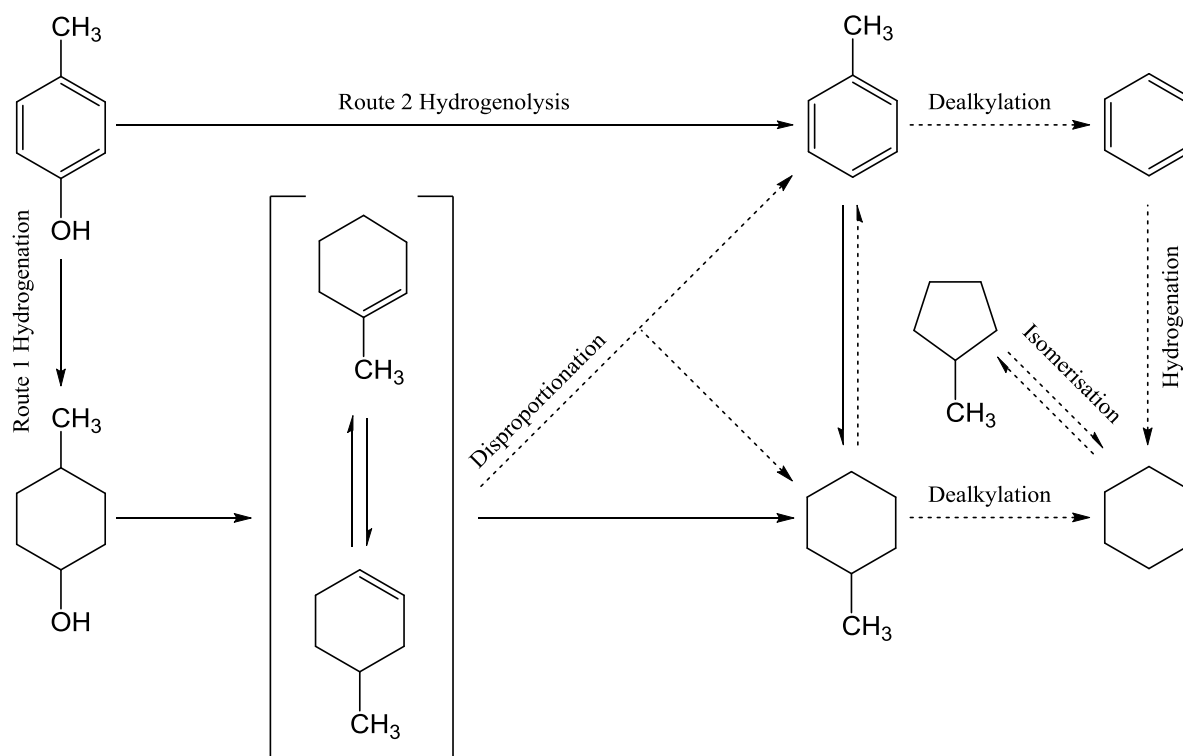


Figure 4.3.16 p-Cresol HDO reaction network (solid line, major reaction; dash line, side reaction)

4.3.5 Reaction kinetics and impact of added sulphur and pre-reduction

The purposes of this section are to compare the relative activities of both catalysts, and to clarify the impact of added sulphur and pre-reduction on the catalyst performance.

For the following hydrogenation reaction:



where A is the reactant, let r_A , c_A , and N_A be the reaction rate, molar concentration and mole number of the reactant A at time t. Assuming pseudo first-order reactions, the following equations apply:

$$r_A = \frac{1}{w} \frac{dN_A}{dt} = -kc_A \quad (12)$$

$$v \frac{dc_A}{dt} = -kwc_A \quad (13)$$

where v is the solution volume at time t; w is the catalyst weight and k is pseudo first-order rate constant for the disappearance of the feed A. Rearrangement of Equation (13) gives:

$$\int \frac{dc_A}{c_A} = -k \left(\frac{w}{v} \right) \int dt \quad (14)$$

The integration of Equation (14) leads to:

$$-\ln(1 - X_A) = k \left(\frac{wt}{v} \right) \quad (15)$$

where X_A is the conversion of reactant A at time t.

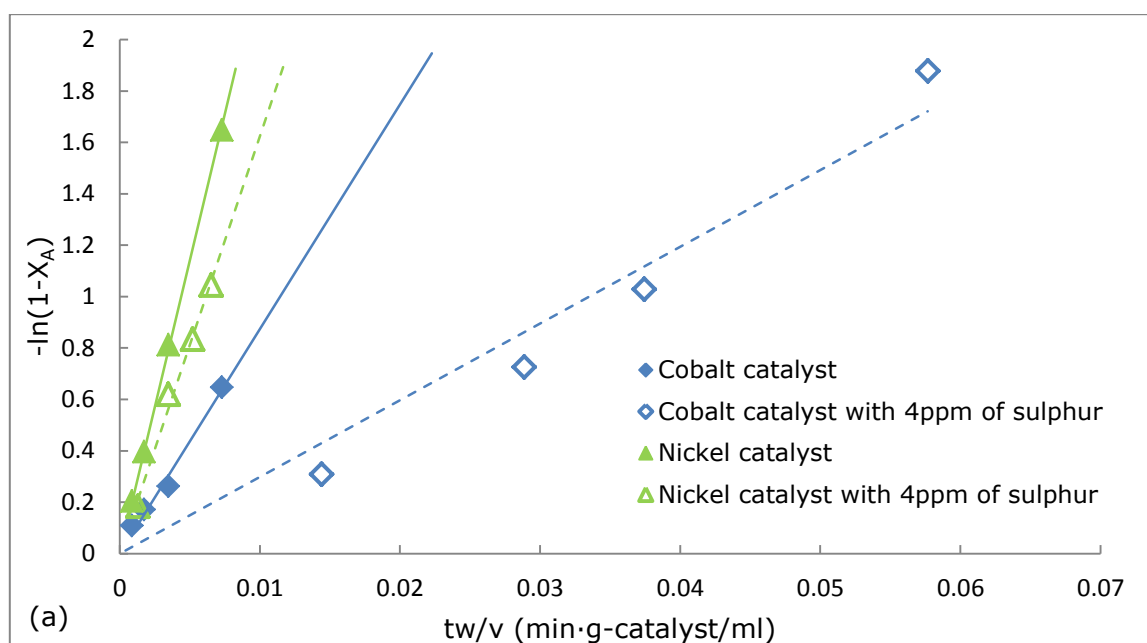
4.3.5.1 Effect of sulphur

Two sets of experiments were carried out with p-cresol and 4-methylcyclohexanol at 250 °C and 300 °C, respectively. According to the results, p-cresol feed is mainly hydrogenated to 4-methylcyclohexanol with negligible amount of methylcyclohexane being produced and 4-methylcyclohexanol feed can only be deoxygenated to methylcyclohexane at selected temperatures.

The p-cresol and 4-methylcyclohexanol conversions with and without sulphur are all adequately represented by pseudo first-order behaviour as shown by the linearity of the plots of $-\ln(1-X_A)$ versus (wt/v) as shown in Figure 4.3.17. Table 4.3.2 presents pseudo first-order rate constants for runs with p-cresol at 250 °C and with 4-methylcyclohexanol at 300 °C. Although Co/Al₂O₃ has a higher metal content and a larger surface area, Ni/Al₂O₃, again, is more active than Co/Al₂O₃ in both cases of p-cresol hydrogenation and 4-methylcyclohexanol deoxygenation, regardless of added sulphur. Nevertheless, they both have better performance comparing with the commercial catalysts used in similar

studies reported by the literature. Gevert et al. [14] tested the activity of sulphided commercial CoMo catalyst with p-cresol (50 bar, 300 °C) and the pseudo first-order rate constant of the catalyst based on the disappearance of p-cresol is 3 ml·min⁻¹·g-catalyst⁻¹, which is approximately two orders of magnitude larger than that given by Odebunmi and Ollis [16] over a similar catalyst (69 bar, 350 °C) according to the review by Girgis and Gates [17].

Certain amount of sulphur inhibits p-cresol hydrogenation whereas it promotes 4-methylcyclohexanol deoxygenation. These two distinct effects prove the fact that two kinds of sites are involved, one for hydrogenation and the other for deoxygenation. The inhibition effect on hydrogenation may be because of the competitive adsorption of sulphur on the active sites and/or the formation of metal sulphides. As for the deoxygenation, it is an acid-catalysed reaction. According to Şenol et al. [27], the dissociative adsorption of the sulphur agent increases the acidity of the catalysts and therefore it has a promoting effect on the cleavage of the C-O bonds.



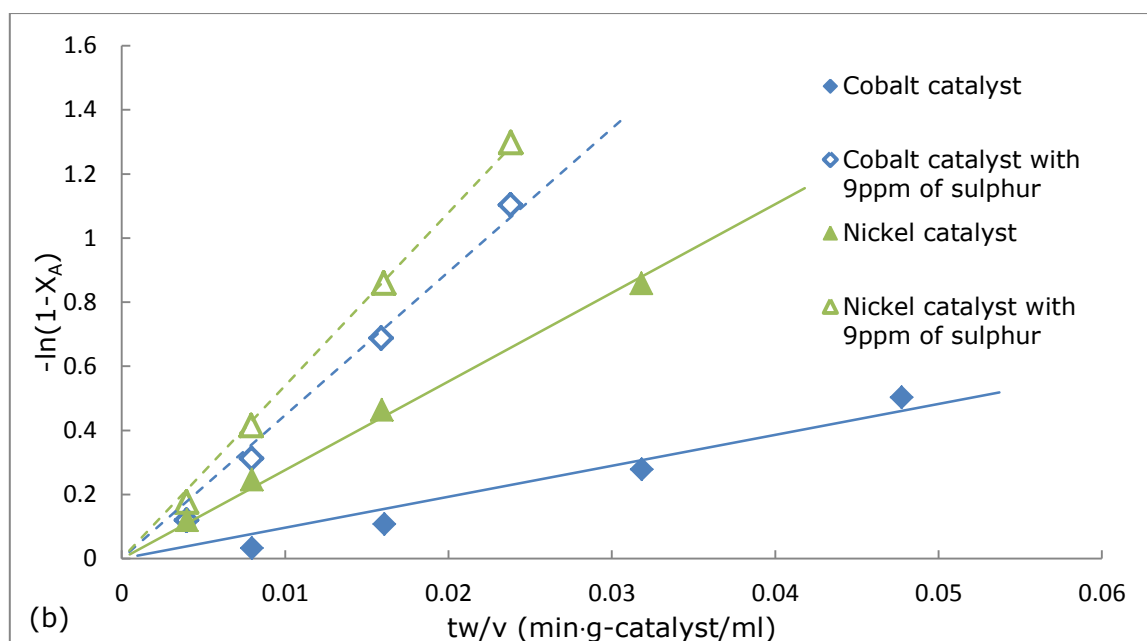


Figure 4.3.17 Pseudo first-order plots: (a) Runs of p-cresol at 250 °C, (b) Runs of 4-Methylcyclohexanol at 300 °C

Table 4.3.2 Pseudo first-order rate constants for p-cresol and 4-methylcyclohexanol

Catalyst	Pseudo first-order constant k (ml·min ⁻¹ ·g-catalyst ⁻¹)			
	p-Cresol feed (250 °C)		4-Methylcyclohexanol feed (300 °C)	
	Sulphur free	With Sulphur	Sulphur free	With Sulphur
Co/Al ₂ O ₃	87	30	10	45
Ni/Al ₂ O ₃	228	162	28	54

4.3.5.2 Effect of pre-reduction

Catalysts were reduced before the p-cresol HDO process to investigate the impact of pre-reduction on catalyst activities. The comparison is made at 250 °C. Results obtained are summarised in Table 4.3.3 and Table 4.3.4 (detailed calculations of the relative rate constant can be found in Appendix). As expected, sulphur reduced the activities of both as-received and pre-reduced catalysts, according to the relative rate constant. Nevertheless, the pre-reduced catalysts were more active than as-received ones, especially for Co/Al₂O₃. The relative weak impact of pre-reduction on Ni/Al₂O₃ may be explained as follows. Ni/Al₂O₃ is more active than Co/Al₂O₃. The active sites of as-received Ni/Al₂O₃ are efficient and adequate to catalyse the reactions, and therefore the extra sites generated by the pre-reduction would have limited effect on increasing the catalyst activity. Also, according to the catalyst TPR profiles (Figure 4.3.3), Ni/Al₂O₃ is easy to be reduced comparing with Co/Al₂O₃. Another possible reason is that the as-

received Ni/Al₂O₃ could be reduced in-situ during the HDO reaction. Therefore, the pre-reduction had limited effect on the catalyst.

Table 4.3.3 The effect of pre-reduction and added sulphur on the activity of Co/Al₂O₃ catalyst at 250°C

Catalyst status	Batch time	Feed/Catalyst ratio	Sulphur	Conversion	Product distribution				HDO	Relative rate constant
					P-cresol	4Meol	MCH	4M1C		
As-received	8 min	20/0.1	0ppm	69%	32%	68%			0%	1.0 (standard)
As-received	8 min	20/0.1	4ppm	54%	49%	51%			0%	0.7
Pre-reduced	8 min	20/0.1	0ppm	100%	0%	99%	1%		1%	1.6 (based on H ₂ consumption)
Pre-reduced	8 min	20/0.1	4ppm	98%	2%	96%	2%		2%	1.4 (based on H ₂ consumption)

4Meol: 4-methylcyclohexanol; MCH: methylcyclohexane; 4M1C: 4-methyl-1-cyclohexene

Table 4.3.4 The effect of pre-reduction and added sulphur on the activity of Ni/Al₂O₃ catalyst at 250 °C

Catalyst	Batch time	Feed/Catalyst ratio	Sulphur	Conversion	Product distribution				HDO	Relative rate constant
					P-cresol	4Meol	MCH	4M1C		
As-received	15 min	20/0.015	0ppm	95%	5%	93%	1%		1%	1.0 (standard)
As-received	15 min	20/0.015	4ppm	77%	23%	75%	1%		1%	0.5
Pre-reduced	15 min	20/0.015	0ppm	97%	3%	95%	2%		2%	1.2
Pre-reduced	15 min	20/0.015	4ppm	77%	23%	73%	3%	1%	4%	0.5

4Meol: 4-methylcyclohexanol; MCH: methylcyclohexane; 4M1C: 4-methyl-1-cyclohexene

Results regarding the impact of pre-reduction with and without sulphur at 350 °C are shown in Table 4.3.5 and Table 4.3.6. In sulphur free conditions, the pre-reduction had little effect on feed conversion and product distributions because both catalysts were active at elevated temperatures. However, it increased the activity of the Ni/Al₂O₃ slightly and that of Co/Al₂O₃ two fold with background sulphur.

Table 4.3.5 The effect of pre-reduction and added sulphur on Co/Al₂O₃ catalyst at 350 °C

Catalyst	Batch time	Feed/Catalyst ratio	Sulphur	Conversion	Product distribution					HDO	Relative rate constant
					P-cresol	methylcyclohexenes	Toluene	MCH	Cyclohexane		
As-received	2hr	20/0.04	0ppm	99%	1%			6%	88%	98%	
As-received	2hr	20/0.04	50ppm	5%	97%	2%		0%	1%	3%	1.0
Pre-reduced	2hr	20/0.04	0ppm	99%	1%			7%	86%	96%	
Pre-reduced	2hr	20/0.04	50ppm	11%	93%	3%		1%	2%	7%	2.3

MCH: methylcyclohexane

Table 4.3.6 The effect of pre-reduction and added sulphur on Ni/Al₂O₃ catalyst at 350 °C

Catalyst	Batch time	Feed/Catalyst ratio	Sulphur	Conversion	Product distribution					HDO	Relative rate constant
					P-cresol	methylcyclohexenes	Toluene	MCH	Cyclohexane		
As-received	2hr	20/0.04	0ppm	100%				99%	1%	100%	
As-received	2hr	20/0.04	47ppm	66%	38%	4%	10%	46%		61%	1.0
Pre-reduced	2hr	20/0.04	0ppm	100%				98%	2%	100%	
Pre-reduced	2hr	20/0.04	50ppm	78%	26%	4%	13%	57%		74%	1.4

MCH: methylcyclohexane

4.4 CONCLUSIONS

The HDO of p-cresol involves two paths, aromatic ring hydrogenation and direct deoxygenation. Two kinds of active sites are involved. The hydrogenation sites are responsible for the reactions between saturated and unsaturated bonds (e.g. p-cresol aromatic ring hydrogenation, methylcyclohexene hydrogenation and disproportionation, and toluene/methylcyclohexane conversion) while the hydrogenolysis sites catalyse C-O bond cleavage (e.g. p-cresol and methylcyclohexanol deoxygenation).

4-Methylcyclohexanol, methylcyclohexane and toluene were formed as major products in sulphur free environment. The studies reveal that temperature, among all the parameters investigated, plays a vital role in the product distributions at the catalyst loading and batch time used. 4-Methylcyclohexanol and methylcyclohexane were mainly produced under low temperatures (≤ 300 °C). At temperatures in between 300 and 350 °C, methylcyclohexane was the predominant product. For Co/Al₂O₃, toluene was observed above 325 °C. Its content increased with temperature whilst that of methylcyclohexane reduced because the former was thermodynamically favourable at high temperatures. Despite the fact that there is no clear evidence showing the mechanism of the formation of toluene between 325 and 350 °C, it has been proven that toluene can be obtained via the direct deoxygenation of p-cresol and the disproportionation of methylcyclohexenes at 375 °C. As for Ni/Al₂O₃, toluene was only observed at 375 °C and was produced by the two routes.

The effect of catalyst loading and that of batch time are analogous. For the rate limiting reaction (i.e. 4-methylcyclohexanol deoxygenation at temperatures ≤ 300 °C), increasing catalyst loading and batch time increase the conversion of the reactant to deoxygenated products. In respect of toluene and methylcyclohexane distributions, the same changes facilitate products to reach the thermodynamic equilibrium with each other.

Adding sulphur suppresses the hydrogenation of aromatic ring and thereby reduces the degree of HDO of p-cresol. Although the poisoned hydrogenation sites are able to break the double bond of cycloolefins making alicyclics, they are less active than those in a non-sulphided environment. The sulphur does not appear to constitute a constraint for the activity of the hydrogenolysis sites. It has no impact on the deoxygenation of 4-methylcyclohexanol at 350 °C and even has a promoting effect at 300 °C. Compared with Co/Al₂O₃, Ni/Al₂O₃ is more active and less sensitive to sulphur. It is worth noting that certain amount of sulphur promotes the toluene production over Ni/Al₂O₃ by disproportion reaction.

Pre-reduction increases the activities of the catalysts and it has a greater impact on Co/Al₂O₃. This may be due to the fact that Co/Al₂O₃ is hard to be fully reduced according to TPR analysis. Adding sulphur deactivates pre-reduced catalysts, as it does on as-received catalysts.

In conclusion, both of the catalysts are active for the HDO of p-cresol. The performance of the HDO process and the product distributions are mainly depend on the temperature. The addition of sulphur containing agent dibutyl disulphide deactivates the hydrogenation sites of both catalysts whereas it promotes acid-catalysed reactions.

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5 GUAIACOL HYDRODEOXYGENATION OVER Ni/Al₂O₃ AND Co/Al₂O₃ CATALYSTS

5.1 INTRODUCTION

Bio-oils, derived from biomass pyrolysis, contain organic oxygenates. Their high oxygen content, which is an order of magnitude higher than that of conventional fossil fuels, appears to constitute a constraint for the commercialisation of the alternative energy sources. Therefore, hydroprocessing, i.e. HDO, the bio-oils is of necessity. However, bio-oils contain numerous compounds and their upgrading is complex. In this regards, the main strategy to understand the mechanisms of upgrading bio-oils and optimise the products is to study model compounds. Guaiacol is normally used to represent large number of mono- and dimethoxy phenols exist in woody based bio-oil [1]. It is indeed a major compound in the Norwegian spruce derived bio-oil, which was investigated in Chapter 3. To serve the same purpose as the work of p-cresol, a similar study was conducted on guaiacol over the same commercially supplied Co/Al₂O₃ and Ni/Al₂O₃ catalysts.

To keep the consistency of the work, the same reaction conditions were used in this chapter as in Chapter 4 of HDO of p-cresol. Experiments of HDO of guaiacol and its intermediate (i.e. methoxycyclohexanol and cyclohexanol) were carried out at temperatures between 250 to 375 °C. The standard batch time was 2 hr. A pressure of 40 bar of H₂ (cold pressure) was used. The impact of temperature, pressure batch time and sulphur were investigated.

Both catalysts demonstrated favourable activities depending on the temperature. Cyclohexane, benzene, cyclopentane and methylcyclopentane were found to be the main deoxygenated products. Oxygen-containing intermediates were methoxycyclohexanols and cyclohexanol. The studies revealed that the degree of deoxygenation was temperature dependent and increased with it as expected. The impact of batch reaction time was generally small regardless of the temperature. The degree of deoxygenation was found to be insensitive to the H₂ pressure in the range studied but an increase in the pressure would hydrogenate toluene producing more cyclohexane at high temperatures. Sulphur was a constraint for the HDO process but it promoted acid catalysed reactions (e.g. dealkylation reactions). Catechol was found to be the main product in the presence of sulphur and its product distribution increased with this added agent. Cyclohexane, ring contraction products, benzene, etc. were also observed. Primary reaction networks of guaiacol HDO with and without sulphur are proposed.

5.2 EXPERIMENTAL METHODS

5.2.1 Catalyst characterisation

The same catalysts were used in the research covered in this chapter as those in Chapter 4 concerning p-cresol HDO. Characterisation details were given in Chapter 4, section 4.2.1.

5.2.2 Hydrodeoxygenation procedure

Parr 4590 100 ml hastelloy pressure vessels were used for the HDO reactions. Dodecane was used as the HDO solvent. A feed was prepared by mixing 0.6 g reactant guaiacol (99%, Sigma-Aldrich) with 19.4 g dodecane (anhydrous, ≥99%, Sigma-Aldrich). 2-Methoxycyclohexanol (99%, Alfa Aesar), cyclohexanol (99%, Sigma-Aldrich), methylcyclopentane (≥99.5%, Sigma-Aldrich) and cyclohexane (≥99.9%, Sigma-Aldrich) were also investigated as independent model compounds with the same reactant to solvent ratio. Runs with sulphur were carried out by introducing certain amount of dibutyl disulphide into the feed. Catalyst particles were crushed and sieved to fine powder (106-250 µm) and were freely suspended in the liquid phase.

The autoclave was charged with 20 g of the feed and 0.04 g of catalyst. Air was purged by N₂ first and then H₂. The reactor was then pressured with H₂ (the H₂ pressure mentioned in this chapter referred to the cold pressure of H₂ at room temperature). Take the HDO of guaiacol over both Co/Al₂O₃ and Ni/Al₂O₃ catalysts for example, the autoclave was charged with 40 bar of H₂ at room temperature. Normally, depending on the temperature, the stable autogenic pressure could reach from 46 to 57 bar. The temperature was raised while the stirring speed was gradually increased to 1000 rpm to prevent external mass transfer limitation. The batch time was counted when the reactor reached the target temperature.

5.2.3 Product analysis

The conversion is defined as the ratio of the model compound reacted to the total model compound added into the autoclave. The product distribution is given by the ratio of the weight of a certain compound to the total weight of all detected compounds in the post-reaction liquid (including the unconverted reactant). The percentage of HDO is the sum of the product distributions of all the oxygen-free products. The equations and detailed explanations were given in Chapter 4, section 4.2.3.

As all the products from the model compounds HDO without added sulphur were miscible with dodecane, the same GC sample preparation methods and temperature programme were used for guaiacol HDO as those for p-cresol HDO (see below for runs with added sulphur). Details can be found in Appendix. Figure 5.2.1 is a typical gas chromatogram of the post-reaction mixture.

Catechol, as a major product from guaiacol HDO at the presence of sulphur, is immiscible with solvent dodecane at low temperatures. Therefore, different procedures were used for the analysis. The post run mixture was collected from the autoclave as much as possible to a centrifuge tube-A. Then, the residue left in the autoclave was washed with ethyl acetate (Sigma-Aldrich, 99.8%) to a centrifuge tube-B. For the GC analysis, ethyl acetate (ca. 5 g) was added into tube-A to dissolve the catechol and to make a homogeneous phase. Spent catalyst was recovered and the weight of the homogeneous liquid in tube-A was corrected by subtracting the weight of the spent catalyst. Liquid samples of tube-A and tube-B were sent for GC analysis (methods to prepare the GC vials can be found in Appendix) to obtain their chemical information both qualitatively and quantitatively. Consequently, the absolute weight of a certain compound in the post-reaction liquid was the sum weight of this compound in both tube-A and tube-B.

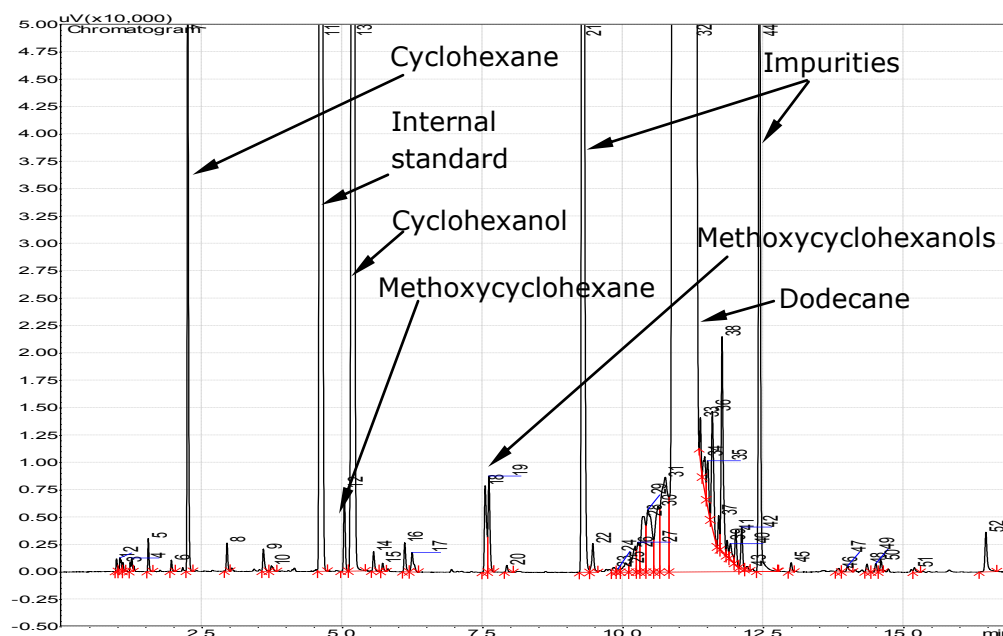


Figure 5.2.1 Typical gas chromatogram of reaction mixture (post-reaction liquid)

5.3 RESULTS AND DISCUSSION

The guaiacol HDO reaction network was studied over both Co/Al₂O₃ and Ni/Al₂O₃ catalysts. Parameters, i.e. temperature, batch reaction time, H₂ pressure and added sulphur, were examined. How the reaction network of guaiacol HDO was modified in the presence of sulphur was explored on both catalysts. The HDO results are mainly given in the form of figures and associated tables can be found in Appendix (i.e. full data by both weight and mole percent).

5.3.1 Effect of temperature

Experiments were conducted between 250 and 375 °C at 25 °C intervals. The results in Figure 5.3.1 indicate that high temperature facilitates the HDO process. Except the run on Co/Al₂O₃ catalyst at 250 °C giving a 95 % of the conversion, guaiacol feeds were fully converted at all other temperatures on both catalysts, indicating high catalytic activities. For Co/Al₂O₃, cyclohexanol, methoxycyclohexanols and cyclohexane were products at and below 300 °C. At 325 °C and above, cyclohexane and benzene were mainly produced with certain amount of oxygen-free ring contraction products (i.e. cyclopentane and methylcyclopentane). Other products such as methylcyclohexane, toluene, methoxycyclohexane, phenol, 1,2-dimethoxybenzene, cyclopentanol and cyclohexanediols were observed in minor amount. For Ni/Al₂O₃, the main products were similar to Co/Al₂O₃ but the total distributions of ring contraction products were higher over Ni/Al₂O₃ compared to those over Co/Al₂O₃ at all temperatures.

In order to construct the guaiacol HDO reaction network, the major oxygen-containing intermediate products from guaiacol (i.e. methoxycyclohexanol and cyclohexanol) were tested as individual model compounds with the same conditions. The results are summarised in Figure 5.3.2 and Figure 5.3.3. The products and trends of the product distributions of 2-methoxycyclohexanol HDO and that of guaiacol were generally the same, suggesting that the methoxycyclohexanols were primary intermediates. Judging from the product distribution profiles of cyclohexanol and cyclohexane in the HDO of 2-methoxycyclohexanol and cyclohexanol (Figure 5.3.2 and Figure 5.3.3), cyclohexane should be a product from the deoxygenation of cyclohexanol. Therefore, in the guaiacol reaction network, there exist consecutive reactions starting from guaiacol hydrogenation producing methoxycyclohexanols then methoxycyclohexanols deoxygenation to cyclohexanol and finally to cyclohexane. In addition, it is worth noting that the HDO of guaiacol (Figure 5.3.1) could produce more cyclohexanol than that of 2-methoxycyclohexanol (Figure 5.3.2) at low temperatures (e.g. 250 and 275 °C).

Consequently, guaiacol appears to be able to produce cyclohexanol directly.

Considerable amounts of benzene were produced at the highest temperature tested from all the three model compounds (i.e. guaiacol, 2-methoxycyclohexanol and cyclohexanol). In order to clarify the reactions involved, experiments were carried out at 375 °C with cyclohexane as initial feed with the same conditions as those of HDO runs. Full analysis results on the cyclohexane tests can be found in Appendix as well, including the conversions and product distributions. The order of product distribution of benzene at 375 °C obtained from 4 different model compounds is indicated from the results to be guaiacol > 2-methylcyclohexanol > cyclohexanol $\approx$ cyclohexane on Co/Al₂O₃, and to be guaiacol > 2-methylcyclohexanol > cyclohexanol > cyclohexane on Ni/Al₂O₃. Therefore, at 375 °C and probably higher temperatures, guaiacol, 2-methylcyclohexanol and cyclohexane each should have a route leading to benzene, and only over Ni/Al₂O₃ can cyclohexanol produce benzene directly.

The production of oxygen-free ring contraction products might involve ring-opening/closing and/or dealkylation. The metal sites may promote the ring-opening reactions [2] and the acid support may facilitate the dealkylation reactions. At all temperatures tested, the sum of their product distributions from different model compounds followed the order of: 2-methoxycyclohexanol $\geq$ guaiacol > cyclohexanol. The products were also observed in experiments with cyclohexane as model compound at 375 °C, but only in minor amount.

Based on the product distributions of the model compounds, a preliminary reaction network given in Figure 5.3.4 can be inferred for guaiacol conversion catalysed by Ni/Al₂O₃ and Co/Al₂O₃ in the presence of H₂. It differs from that proposed by Zhao et al. [3] mentioned in Chapter 2 (Section 2.2.1.2). The transition metal phosphides (e.g. Ni₂P/SiO₂ and Fe₂P/SiO₂) mainly give aromatics (i.e. benzene and phenol) while the hydrogenation catalysts used in the present work, namely Ni/Al₂O₃ and Co/Al₂O₃, give saturated products (e.g. cyclohexane and cyclohexanol).

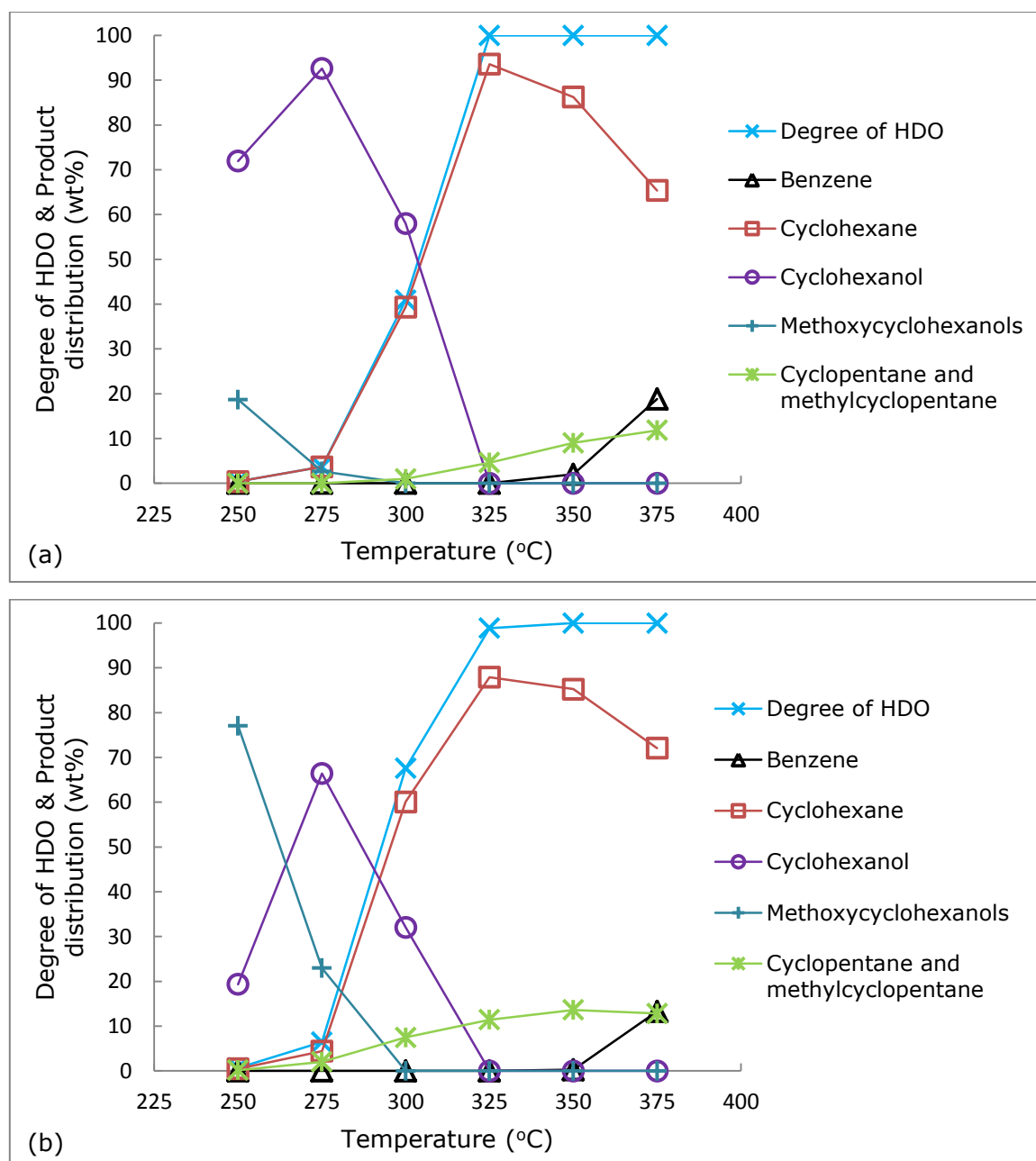


Figure 5.3.1 Effect of temperature on the HDO of guaiacol (0.04 g catalyst, 2 hr batch time and 40 bar of H₂): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

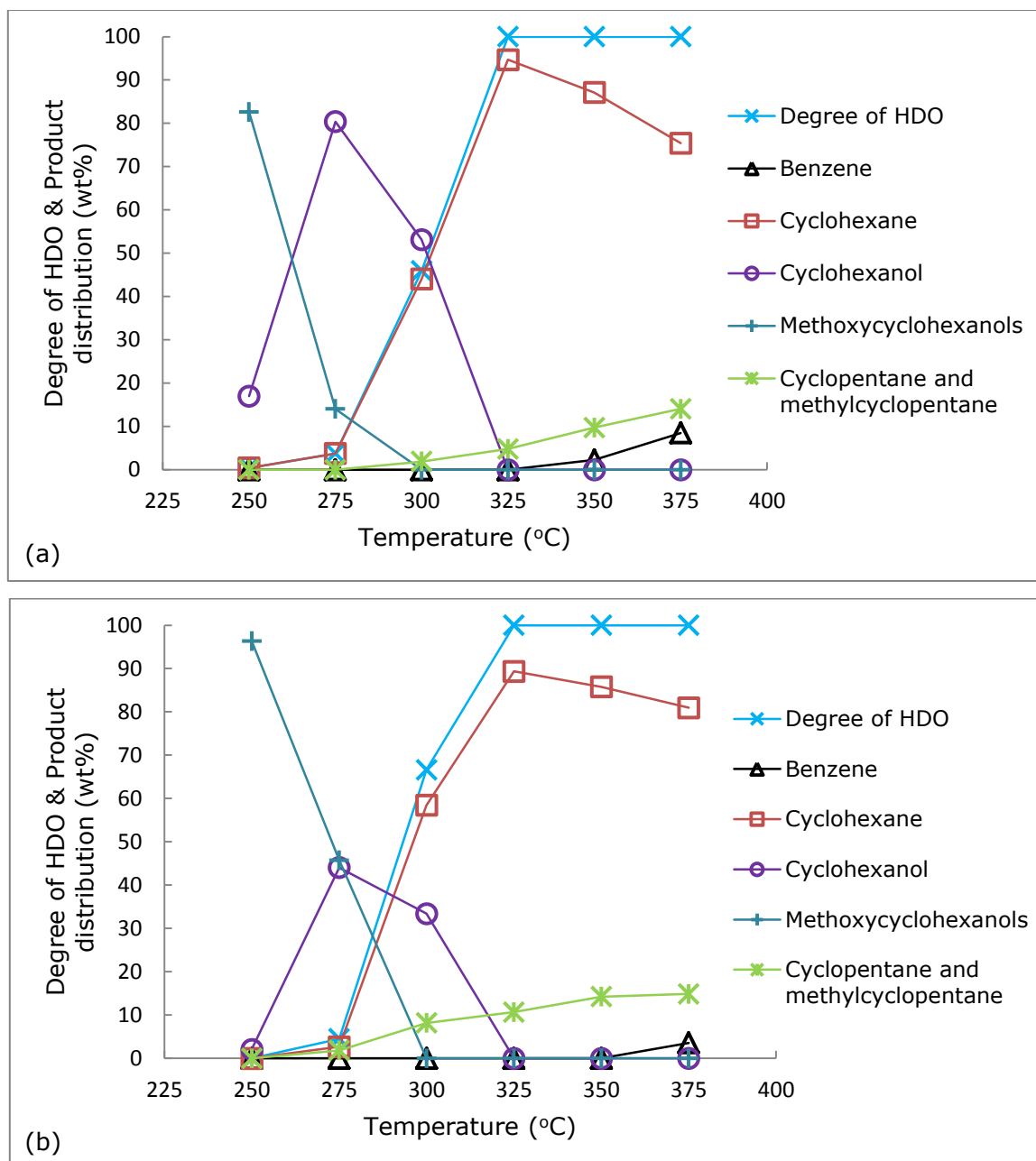


Figure 5.3.2 Effect of temperature on the HDO of 2-methoxycyclohexanol (0.04 g catalyst, 2 hr batch time and 40 bar of H₂): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

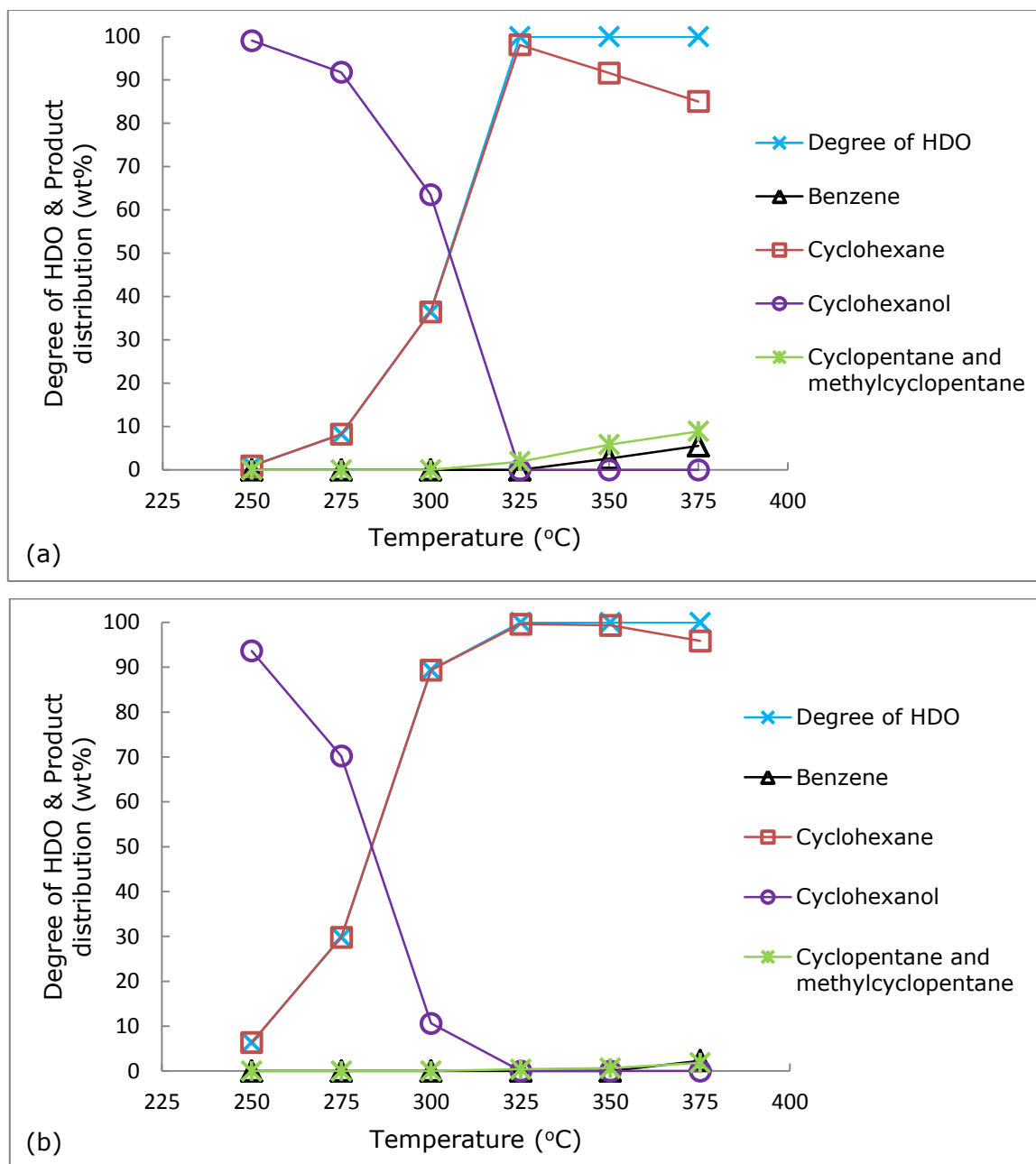
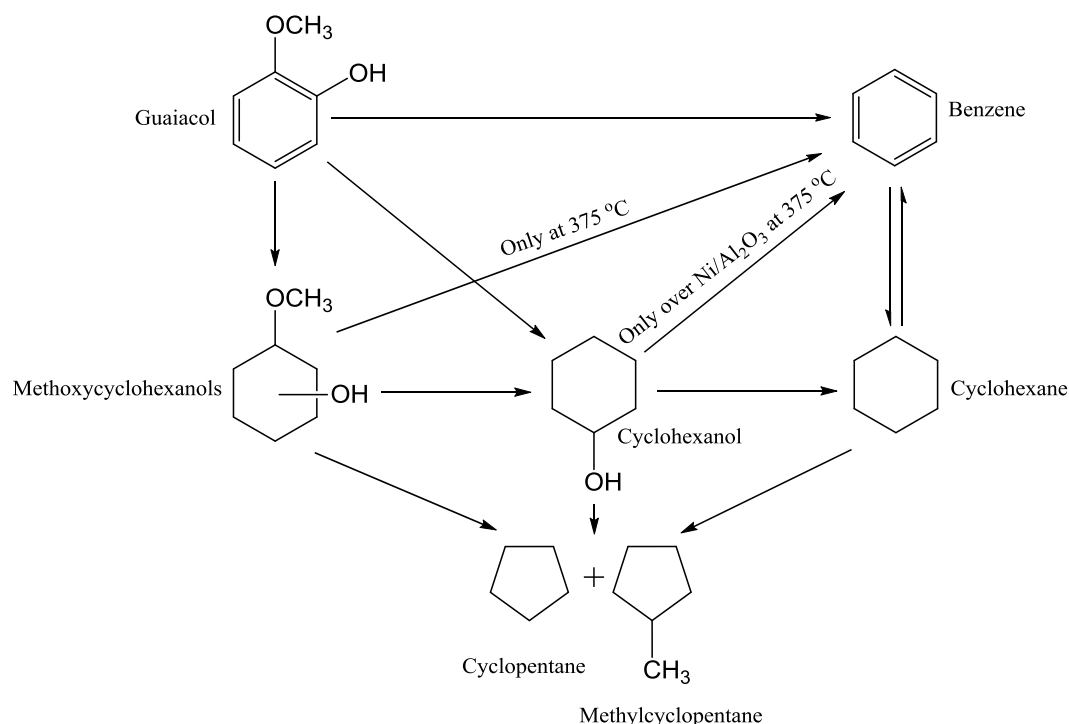


Figure 5.3.3 Effect of temperature on the HDO of cyclohexanol (0.04 g catalyst, 2 hr batch time and 40 bar of H₂): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

Figure 5.3.4 Guaiacol HDO reaction network over Co/Al₂O₃ and Ni/Al₂O₃ catalysts

5.3.2 Effect of batch time

The effects of batch time were investigated only over Co/Al₂O₃ catalyst. Results were obtained at 275 and 350 °C and are given in Figure 5.3.5. Guaiacol feeds were fully converted at all other runs, except the one at 275 °C 0.5 hr giving a 91 % of the conversion. At 275 °C, cyclohexanol was the main product. Considering the fact that methoxycyclohexanols only had minor decrease between 0.5 hr and 1 hr batch time, the initial rise of cyclohexanol was probably due to the increase of guaiacol conversion to produce cyclohexanol directly. The extension of the batch time from 1 hr to 3 hr had limited impact on the product distribution of cyclohexanol, whereas methoxycyclohexanols slowly decreased and cyclohexane increased. Since there was no evidence showing that 2-methoxycyclohexanol could produce cyclohexane directly, it is reasonable to assume the following reason of cyclohexanol concentration being stable. Cyclohexanol might be gradually consumed to yield cyclohexane, yet the deoxygenation of methoxycyclohexanols could compensate for the loss. In such a way, cyclohexanol concentration could remain while methoxycyclohexanols dropped to produce cyclohexane via cyclohexanol as an intermediate.

High temperature favours hydrogenolysis [4]. Therefore, at 350 °C, the benzene being produced at the shortest batch time may be because of the direct hydrogenolysis of guaiacol. Then, the formed benzene was hydrogenated to cyclohexane. Besides, the

deoxygenation of cyclohexanol would also contribute to the initial increase of the product distribution of cyclohexane. There were no significant changes of product distributions after 1 hr batch time. However, a rapid increase of cyclohexane product and the degree of HDO during the first 0.5 hr of the reaction can be inferred from Figure 5.3.5 (b), indicating the fact that the reactions involved in the HDO of guaiacol at high temperatures were not rate limiting.

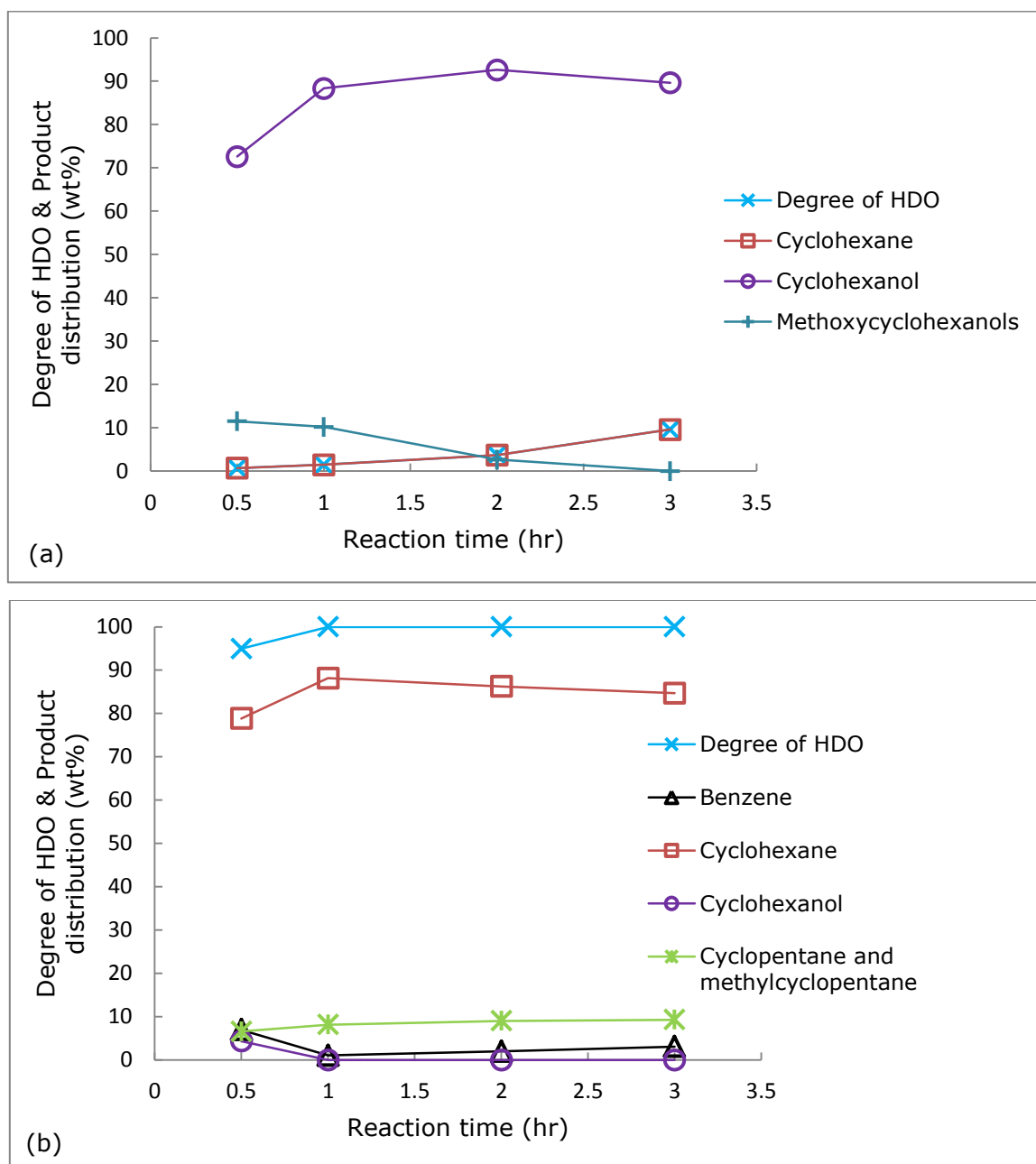


Figure 5.3.5 Effect of batch time on the HDO of guaiacol over Co/Al₂O₃ (0.04 g catalyst, 40 bar of H₂): (a) 275 °C, (b) 350 °C

5.3.3 Effect of H₂ pressure

Experiments with different cold H₂ pressures (i.e. 20, 30 and 40 bar) were conducted at 275 and 350 °C on both the Co/Al₂O₃ and Ni/Al₂O₃ catalysts. Results are presented in Figure 5.3.6 and Figure 5.3.7. In this study, there was no major change in the deoxygenation performance by varying the H₂ pressure. Also, according to the calculation in Appendix, there was always an excess of H₂ for the HDO of guaiacol. Hence, high pressures are not required to remove the oxygen on these two catalysts at these conditions.

For Co/Al₂O₃, H₂ pressure had little effect on product distributions at 275 °C. However, at 350 °C, the product distribution of benzene reduced while that of cyclohexane rose significantly with increasing H₂ pressure. According to the equilibrium concentration of benzene in cyclohexane, only less than 5% of benzene can remain at 350 °C under 20 bar of H₂ [4]. Therefore, the benzene most likely came from the direct hydrogenolysis of guaiacol at low pressures. As the H₂ pressure increased, the production of benzene diminished by hydrogenation, and therefore that of cyclohexane increased. Same observations were reported in a study of guaiacol HDO over Ni/SiO₂ and Co/SiO₂ catalysts [5].

Generally, for Ni/Al₂O₃, the product distribution of methoxycyclohexanols was insensitive to an increasing H₂ pressure but that of cyclohexanol slightly increased at 275 °C. It has been reported in the literature [6] that excess H₂ interferes with the adsorption of reactants onto the active sites of catalysts. In this case, the competitive adsorption of H₂ could be a constraint for the deoxygenation of cyclohexanol. The coverage of cyclohexanol decreased as the pressure increased, resulting in lower probability of the sequential deoxygenation reactions. Less cyclohexanol was consumed, and therefore, the amount of the oxygen-free compounds reduced. At 350 °C, considerable amount of benzene was formed by the direct deoxygenation of guaiacol over Ni/Al₂O₃ at low pressure as was over Co/Al₂O₃. Product distributions at medium and high pressures were analogous and cyclohexane was the main product in both cases.

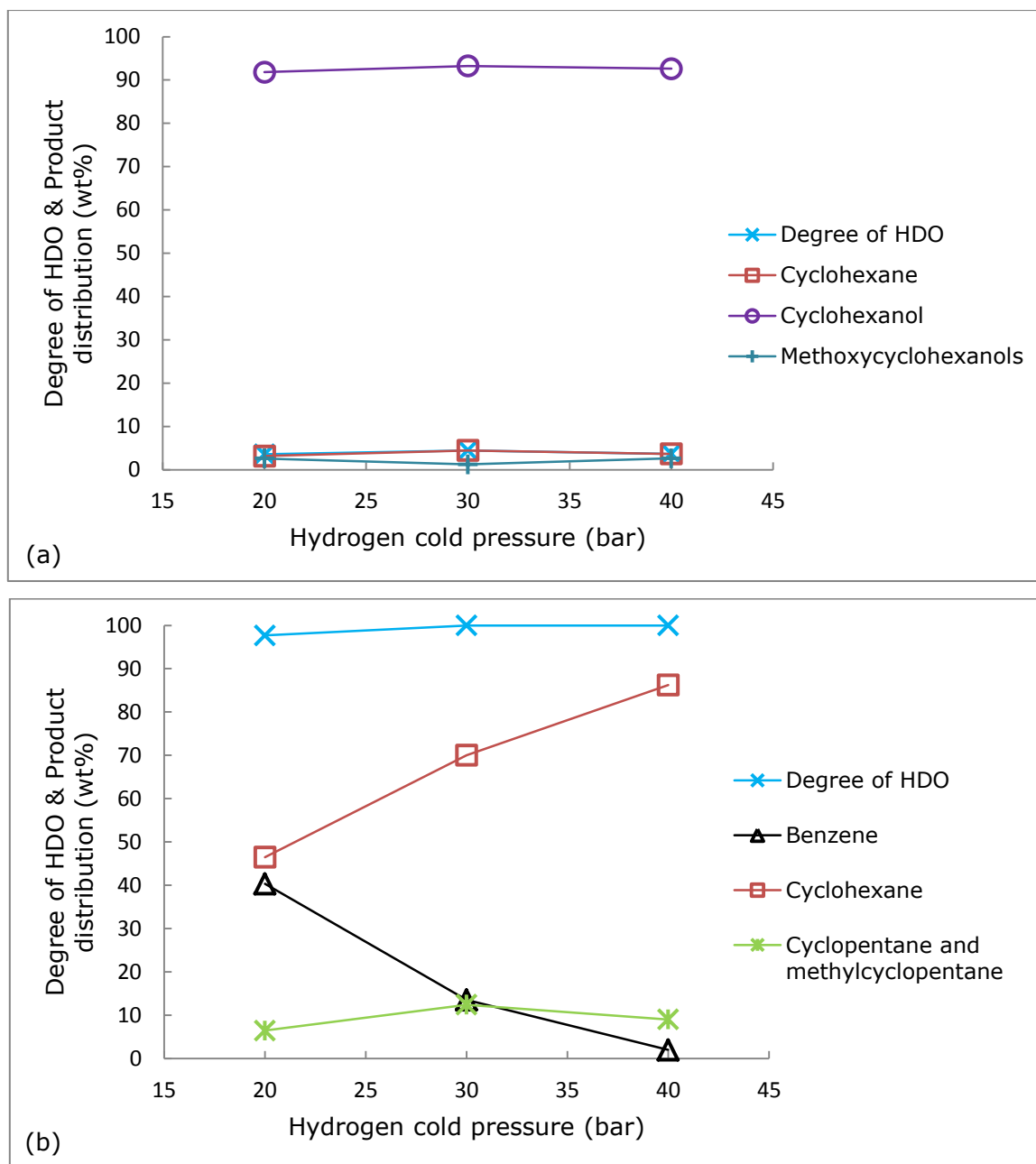


Figure 5.3.6 Effect of H₂ pressure on the HDO of guaiacol over Co/Al₂O₃ (0.04 g catalyst, 2 hr batch time): (a) 275 °C, (b) 350 °C

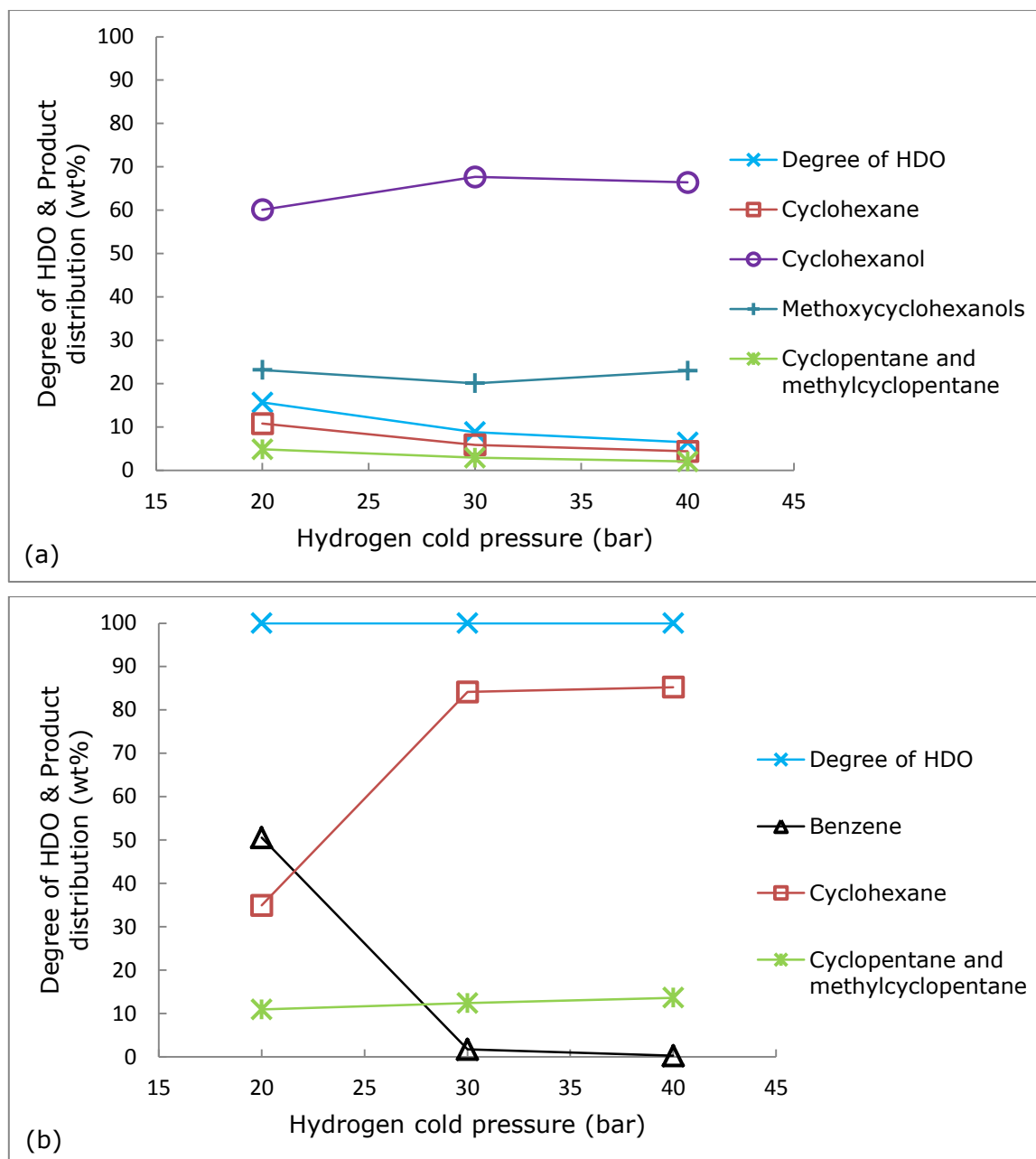


Figure 5.3.7 Effect of H₂ pressure on the HDO of guaiacol over Ni/Al₂O₃ (0.04 g catalyst, 2 hr batch time): (a) 275 °C, (b) 350 °C

5.3.4 Effect of added sulphur

Experiments were conducted at 350 °C with ambient sulphur over both Co/Al₂O₃ and Ni/Al₂O₃ catalysts by adding dibutyl disulphide to the feed. Results are presented in Figure 5.3.8. Different from sulphur free experiments, catechol was the main product over both catalysts. Cyclohexane, ring contraction products, benzene, cyclohexene, cyclohexanone, anisole, phenol and cresols were also observed.

The degree of deoxygenation decreased with increasing the sulphur level. The product distribution of hydrogenated product (i.e. cyclohexane) and that of ring contraction products also decreased. Clearly, sulphur inhibits the deoxygenation, hydrogenation and ring opening reactions by occupying the active sites via adsorption. Therefore, the conversion of guaiacol dropped first. However, as the sulphur level further increased, a divergent effect on the feed conversion was observed. The promoting effect may due to the increase of catalyst acidity [7]. It has been pointed out that higher acidity facilitates dealkylation reactions [8], and also, it has the same effect on the phenol production [9]. Consequently, the increased conversion of guaiacol may arise from the increased production of catechol and that of phenol. Same as in Chapter 4, the Ni/Al₂O₃ catalyst was less sensitive to sulphur comparing to Co/Al₂O₃. As explained, this may due to the formation of cobalt sulphide on Co/Al₂O₃ catalyst.

In order to probe the reaction network of guaiacol HDO in sulphur environment, catechol was tested as a model compound with the same conditions. Results are given in Table 5.3.1. Catechol, cresols and anisole can be expected to be the primary products produced directly from guaiacol. However, by comparing the phenol product distribution of guaiacol and that of catechol, phenol did not appear to be obtained from guaiacol by demethoxylation but mainly from catechol by dehydroxylation [3, 5, 10]. Figure 5.3.9 shows a preliminary reaction network of guaiacol HDO in the presence of sulphur. The network proposed based on Co/Al₂O₃ and Ni/Al₂O₃ has similarity to that in Figure 2.2.4. In both studies, catechol, cresols and anisole are the precursors of phenol. However, the downstream products after phenol are different. Benzene, as an end product, was produced from phenol via cyclohexanol over the silica supported transition metal phosphides [3] while cyclohexanol was not detected over the alumina supported catalysts and benzene was further hydrogenated to cyclohexene and cyclohexane in the present study. Also, as mentioned above, due to the acidity of the alumina support, cyclopentane and methylcyclopentane were produced.

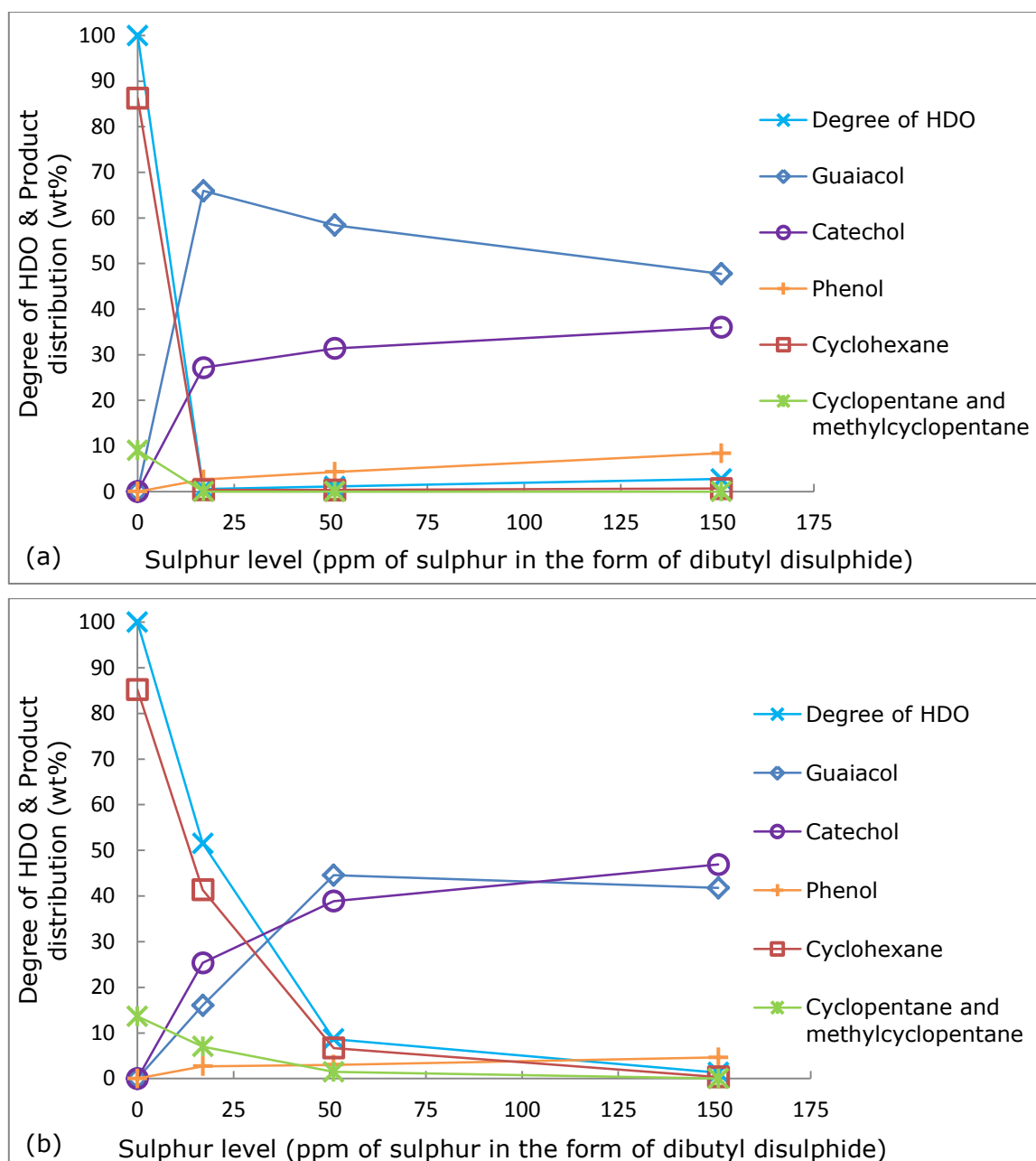


Figure 5.3.8 Effect of sulphur on the HDO of guaiacol (2 hr batch time, 40 bar of H₂ and 350 °C): (a) Co/Al₂O₃, (b) Ni/Al₂O₃

Table 5.3.1 Effect of sulphur on catechol HDO (2 hr batch time, 40 bar of H₂ and 350 °C)

Catalyst	S (ppm)	Product distribution (wt%)							HDO%
		Catechol	Ring contraction products	Benzene	Cyclohexane	Cyclohexene	Cyclohexanone	Phenol	
Ni	16	11.37	16.81	3.72	59.95	0.82	5.37	1.96	81.30
Ni	152	83.36	0.36	0.83	0.88	2.20	6.43	5.94	4.28
Co	152	75.87	0.00	0.42	0.92	4.89	1.98	15.91	6.23

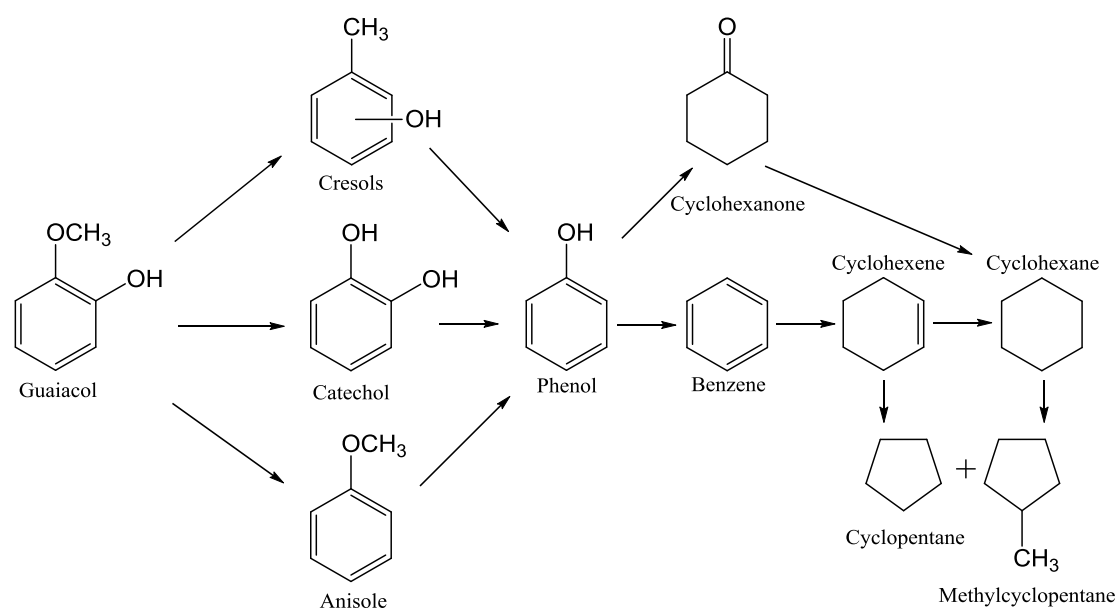


Figure 5.3.9 Guaiacol HDO reaction network over Co/Al₂O₃ and Ni/Al₂O₃ catalysts with sulphur present

5.4 CONCLUSIONS

Saturated hydrocarbons were mainly produced from guaiacol under the studied conditions. Cyclohexanol, methoxycyclohexanols and cyclohexane were dominant products at 300 °C and below as were cyclohexane, benzene and ring contraction at 325 °C and above.

Temperature plays an important role in dictating the HDO of guaiacol. High temperatures facilitate deoxygenation. Generally, as the temperature increases, the methoxyl group is firstly removed and then the hydroxyl group. Direct deoxygenation (i.e. hydrogenolysis) of guaiacol is more favourable at elevated temperatures, so is benzene in the equilibrium with cyclohexane. Therefore, certain amount of benzene exists in the product under these conditions. Judging from the degree of HDO of guaiacol, 2-methoxycyclohexanol and cyclohexanol at different temperatures, both catalysts generally had similar performance at these conditions.

The impact of pressure depends on the temperature. At low temperatures, product distributions are less sensitive to pressure but the importance of pressure increases with temperature. At elevated temperatures, the reactions are more kinetically controlled under low pressures but thermodynamically controlled under high pressures, in the respect of benzene production.

The addition of sulphur changes the guaiacol HDO reaction network. Catechol is the main product under sulphur conditions. Sulphur appears to have a detrimental effect on the HDO of guaiacol. However, it promotes acid catalysed reactions. Due to the complexity of the reaction network, it was not possible to carry out a kinetic study of guaiacol HDO and the impact of sulphur on catalyst activities.

In conclusion, both catalysts are active for the HDO of guaiacol in sulphur-free environment. A high temperature is recommended to remove the oxygen from the model compound. Considering the octane number of the deoxygenated products, pressure should be reduced to preserve the aromatics.

Reference

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6 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The energy crisis and environmental concern have emphasised the importance of generating energy from renewable resources especially from biomass in recent years. Producing fuels from pyrolysis bio-oils is a promising route. Deoxygenation is necessary if the bio-oil is going to be used in the current transportation infrastructure as fossil fuel substitutes or blending components. Bio-oils are composed of numerous compounds and therefore their HDO mechanisms are complicated. Accordingly, model compounds are being used to provide more precise chemical information and enable long time and complicated analysis.

In order to provide knowledge to maximise the production of jet and diesel fuel range hydrocarbons from wood derived pyrolysis oils, the present work examined the HDO performance of various catalysts on a bio-oil (derived from Norwegian spruce) and model compounds (i.e. *p*-cresol and guaiacol), emphasising the impacts of operating conditions (e.g. temperature, pressure, reaction time and added sulphur). The reaction networks of *p*-cresol and guaiacol over the Co/Al₂O₃ and Ni/Al₂O₃ catalyst have also been proposed.

The HDO of the bio-oil produces three phases, i.e. water phase, oil phase and residue. The valuable chemicals (e.g. acetic acid) that can be separated from the water phase and then the remaining water phase can be used for H₂ production. After the separation of the spent catalyst, the residue is co-processed with oil phase in a conventional high temperature hydrotreating reactor to convert remaining oxygenates to hydrocarbons. The upgraded bio-oil consists of gasoline-like and diesel-like components [1].

Generally, for the selected model compounds HDO over Co/Al₂O₃ and Ni/Al₂O₃ catalysts, there are two paths leading to the deoxygenated products, namely, aromatic ring hydrogenation and direct deoxygenation. Two kinds of active sites are involved. The hydrogenation sites are responsible for the reactions between saturated and unsaturated bonds while the hydrogenolysis sites catalyse C-O bond cleavage.

6.1 KEY FINDINGS

Following conditions were investigated on the bio-oil and/or model compounds.

- Effect of temperature

Increase the reaction temperature increases the degree of deoxygenation. Raise the temperature can increase the degree of stacking of the NiMo nanosulphide catalyst. It also facilitates direct deoxygenation over the alumina supported catalysts producing aromatics.

- Effect of added sulphur

The addition of 100 ppm ambient sulphur is not essential to improve the performance of the nanosulphide catalyst in the case of bio-oil HDO. However, it suppresses the hydrogenation of the aromatic rings and reduces the degree of HDO of p-cresol and guaiacol over the alumina supported catalysts. Tests on model compounds HDO intermediates show that sulphur has a detrimental effect on the activity of the hydrogenation sites but it does not appear to be a poison for the hydrogenolysis sites.

- Effect of catalyst loading and batch time

Extending the batch time gives a deeper deoxygenation of the bio-oil over the nanosulphide catalyst. It is not necessary to use 2000 ppm of Mo loading to process the bio-oil and there may be scope for thriftiness of the catalyst. As for model compounds over Co/Al₂O₃ catalyst, the effect of increasing the catalyst loading and that of extending the batch time are analogous. They increase the conversion of those kinetic controlled reactions and drive the products to reach equilibrium with each other by saturating the aromatic rings.

- Effect of solvent

H₂ donor solvent tetralin was used in the bio-oil HDO. However, the nanosulphide catalyst has a better performance in dodecane than tetralin. Also, a saturated hydrocarbon avoids complex downstream solvent recovery.

- Effect of pressure

The effect of pressure was studied on guaiacol HDO over the alumina supported catalysts. At low temperatures, product distributions are less sensitive to pressure but the importance of pressure increases with temperature. At elevated temperatures, the reactions are more kinetically controlled under low pressures but thermodynamically controlled under high pressures, in the respect of benzene production. Therefore, in order to improve the octane number of the upgraded fuels, a relative high temperature and low pressure conditions are suggested.

6.2 CONTRIBUTIONS

This study started with the HDO of bio-oil under mild conditions and extended the investigations to the HDO of key model compounds. The current work provides first-hand experimental data on the utilisation of the dispersed NiMo nano-sulphide catalysts on the HDO of bio-oil and also on that of the selective hydrogenation catalysts on the HDO of model compounds.

The unsupported NiMo nanosulphide catalyst and alumina supported Ni and Co catalysts are active for the HDO of the wood based pyrolysis bio-oil and the model compounds. The chemistry and reaction mechanisms of the model compounds over the supported catalysts have been elucidated. Based on the experimental work, suggestions have been made in order to optimise the fuel production from bio-oils and to improve the efficiency of the HDO process. Though the upgrading of bio-oil by HDO has great potentials, literature suggests that the technique is still in its infancy [2]. This work may be at least a tiny contribution for the utilisation of bio-oils to ease the environmental problems towards a sustainable society.

6.3 RECOMMENDATIONS FOR FUTURE WORK

The bio-oil used in the research was produced from Norwegian spruce by fast pyrolysis. Catalysts can be tested using different bio-oils (derived from different source, e.g. birch and poplar). Also, the effect of additives (e.g. Co) on the HDO performance of Mo nano-sulphide catalysts can be investigated in comparison with Ni. In the current study, naphthenates were used as the precursors to synthesise the catalysts and it is worth examining different metal precursors (e.g. octoates).

The HDO of model compounds was conducted over Co/Al₂O₃ and Ni/Al₂O₃ catalysts. The spent catalysts can be re-cycled and reused. The life expectancy is also an important catalyst characteristic. In addition, it is recommended to study the performance of the Ni or Co promoted Mo nano-sulphide catalysts in consistence with the bio-oil work.

Batch reactors were used for the HDO of bio-oils and model compounds and therefore mass loss was inevitable. This problem, however, could be mitigated by using a continuous system. Indeed, to adapt current knowledge obtained from batch operation to continuous flow systems should be the next step of the current HDO research.

Reference

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7 APPENDICES

7.1 APPENDIX 1: ANALYSIS METHODS AND DETAILED CALCULATIONS

7.1.1 Karl Fischer titration

The water content was determined by METTLER TOLEDO volumetric Karl Fischer compact titrator V20 (Figure S 7.1.1) with HYDRANAL-Coulomat A as reagent. The titrator was calibrated by the manufacturer, and therefore the analysis results were used directly. Procedures are as follows.

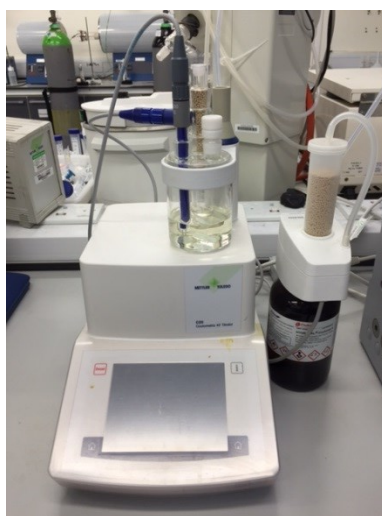


Figure S 7.1.1 Karl Fischer compact titrator V20

For raw bio-oil,

- As the bio-oil was viscous fluid and contained large amount of water, it was dissolved in solvent acetone (Table S 7.1.1).

Table S 7.1.1 Mixture composition

Mixture	Weigh (g)	
	Oil	Acetone
1	0.25303	9.23645
2	0.30620	9.93775
3	0.32961	8.76856

- Pure acetone was injected into the tank filled with HYDRANAL-Coulomat A to determine the water content of the solvent (Table S 7.1.2).

Table S 7.1.2 Water content of acetone

Acetone water content (ppm)				
Test 1	Test 2	Test 3	Test 4	Average
3189.7	3207.3	3169.7	3281.3	3212.0

- Then, the water content of oil-acetone mixture was measured by the titrator (Table S 7.1.3).

Table S 7.1.3 Water content of the mixture

Mixture	Water content (ppm)				
	Test 1	Test 2	Test 3	Test 4	Average
1	12045.8	11792.8	11876.3	11961.6	11919.1
2	13164.2	13123.1			13143.7
3	15273.2	15817.9			15545.6

- The water content of the bio-oil was then calculated by the following equation. The results are showed in Table S 7.1.4.

$$Water_{bio-oil} = \frac{(Weight_{bio-oil} + Weight_{acetone}) \times Water_{mixture} - Weight_{acetone} \times Water_{acetone}}{Weight_{bio-oil}}$$

Table S 7.1.4 Water content of raw bio-oil

Water content of the bio-oil (ppm)			
Mixture 1	Mixture 2	Mixture 3	Average
329759	335476	343653	336296

For the oil phase and water phase of the processed bio-oil

- Samples were injected into the titrator without dilution. Values obtained were used directly.

7.1.2 H₂ consumption analysis

To serve the purposes of comparing the catalyst activities and of evaluating the impacts of bio-oil HDO operation conditions, the H₂ consumption of each experiment in Chapter 3 was estimated from the process pressure drop.

The calculation of the H₂ consumption on the following experiment (Table S 7.1.5) was given as an example.

Table S 7.1.5 Experiment conditions

Catalyst	Temperature (°C)	Reaction mixture (g)		Starting conditions		Finishing conditions	
		Oil	Tetralin	T (°C)	P (bar)	T (°C)	P (bar)
Pd/C	175	7.27303	14.34427	29	49.8	61	42.7

The space volume of the loaded autoclave (7 g oil and 14 g tetralin) at 25 °C was measured to be 76.8 ml. Assuming idea gas law can be used at starting and finishing conditions, then the H₂ consumption per gram of oil is given by the following equation.

$$\begin{aligned}
 n_{\text{H}_2} \text{ consumption per gram of oil} &= (n_{\text{H}_2 \text{ starting}} - n_{\text{H}_2 \text{ finishing}})/\text{Weight}_{\text{oil}} \\
 &= \left(\frac{P_{\text{starting}}V}{RT_{\text{starting}}} - \frac{P_{\text{finishing}}V}{RT_{\text{finishing}}} \right) / \text{Weight}_{\text{oil}} \\
 &= \left(\frac{49.8 \text{ bar} \times 76.8 \text{ ml}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 29^\circ \text{C}} - \frac{42.7 \text{ bar} \times 76.8 \text{ ml}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 61^\circ \text{C}} \right) / 7.27303 \text{ g} \\
 &= 0.0047 \text{ mol/g oil}
 \end{aligned}$$

7.1.3 XRF analysis

The accuracy of the Bruker S4 explorer X-ray Fluorescence spectrometer on Co and Ni elements was calibrated using pure Co_3O_4 (Sigma, 99.5%) and NiO (Sigma, 99.8%), respectively.

Sample (6 g, powder) was mixed with binder (1.5 g, Fluxana-Boreox) using a MU-XRF-Mixing Set (Figure S 7.1.2). The mixed powder was then transferred into a pressing die (Figure S 7.1.3). A pressing force of 20 tons was used to make the pellet for the XRF analysis. Results are shown in Table S 7.1.6.



Figure S 7.1.2 MU-XRF-Mixing Set



Figure S 7.1.3 Pressing die

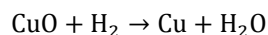
Table S 7.1.6 XRF analysis results

	Sample	Weight (g)	Binder (g)	XRF result (wt%)	Result (wt%)
Calibration	Co ₃ O ₄	6.00561	1.51174	Co element: 76.82	Real value: 73.42
	NiO	5.96401	1.56201	Ni element: 92.24	Real value: 78.58
Catalyst	Co/Al ₂ O ₃	6.05843	1.62217	Co element: 20.97	Calibrated value: 20
	Ni/Al ₂ O ₃	6.01760	1.52526	Ni element: 17.52	Calibrated value 15

7.1.4 Temperature programme reduction analysis

In order to determine the catalyst reduction behaviour, TPR was carried out in 10% Hydrogen/Nitrogen. For the Co/Al₂O₃, the sample was heated from room temperature to 850 °C at a ramp rate of 10 °C/min. However, Ni/Al₂O₃ catalyst was heated up only to 650 °C with the same rate, as there was no peak observed and the signal was back to baseline after 550 °C. The hydrogen consumption was measured by a thermal conductivity detector (TCD) calibrated by ultra-pure copper oxide (Sigma-Aldrich, 99.9999%).

The hydrogen consumption and the minimum percentage of reduction were given below using Co/Al₂O₃ as an example. The original TPR profile of the calibration with CuO is shown in Figure S 7.1.4. The weight of CuO used for the experiment was 0.0245 g. Assuming that all the CuO was reduced and according to the following equation,



the H₂ consumption is ($M_{\text{CuO}}=79.545$ and $M_{\text{H}_2}=2.0158$):

$$m_{\text{H}_2-\text{CuO}} = \frac{m_{\text{CuO}} \times M_{\text{H}_2}}{M_{\text{CuO}}} = \frac{0.0245 \times 2.0158}{79.545} = 6.2087 \times 10^{-4} \text{ g}$$

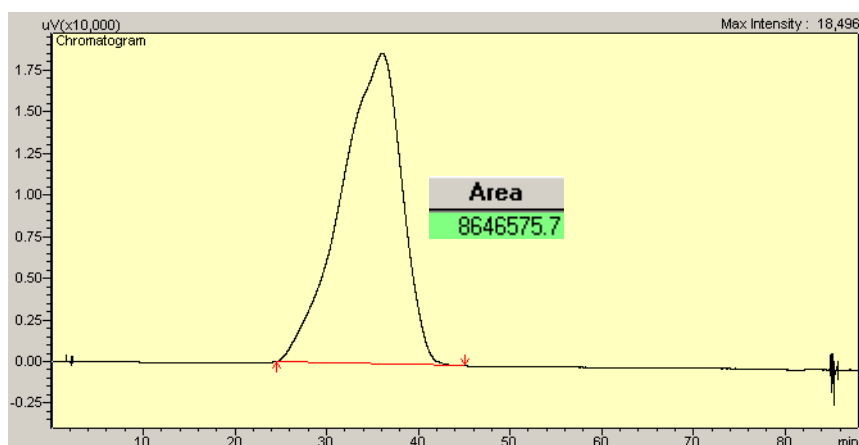


Figure S 7.1.4 TPR profile of CuO

The original TPR profile of Co/Al₂O₃ is presented in Figure S 7.1.5. The weight of the catalyst for the analysis was 0.0561 g. The H₂ consumption due to the reduction of cobalt oxide is:

$$m_{\text{H}_2-\text{Co}_x\text{O}} = \frac{\text{Area}_{\text{H}_2-\text{Co}_x\text{O}} \times m_{\text{H}_2-\text{CuO}}}{\text{Area}_{\text{H}_2-\text{CuO}}} = \frac{5455511.8 \times 6.2087 \times 10^{-4}}{8646575.7} = 3.9173 \times 10^{-4} \text{ g}$$

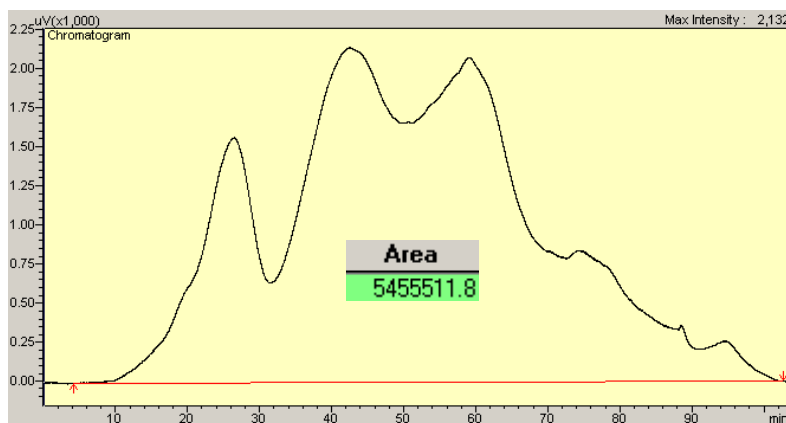
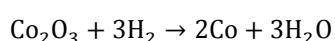


Figure S 7.1.5 TPR profile of Co/Al₂O₃

According to the information regarding the specifications of this Co/Al₂O₃ catalyst provided XRF analysis, the weight percentage of the cobalt element is 20 wt%. There exist mainly three forms of cobalt oxide, namely cobalt (II) oxide, cobalt (II, III) oxide and cobalt (III) oxide. Apparently, if the catalyst contains only cobalt (III) oxide, it will consume more hydrogen than that contains cobalt (II) oxide or cobalt (II, III) oxide. Assuming all this 15 wt% of cobalt exists in cobalt (III) oxide form and according to the following equation:



the hydrogen consumption is:

$$\begin{aligned} m_{\text{H}_2 \text{ consumption}} &= \frac{20 \text{ wt\%} \times \text{weight of catalyst used}}{M_{\text{Co}}} \times \frac{3}{2} \times M_{\text{H}_2} = \frac{20 \text{ wt\%} \times 0.0561}{58.933} \times \frac{3}{2} \times 2.0158 \\ &= 5.7567 \times 10^{-4} \text{ g} \end{aligned}$$

The minimum percentage of the reduction can be estimated from the equation:

$$\begin{aligned} \text{Minimum percentage of the reduction of the Co/Al}_2\text{O}_3 \text{ catalyst} &= \frac{m_{\text{H}_2-\text{Co}_x\text{O}}}{m_{\text{H}_2 \text{ consumption}}} \times 100 \% \\ &= \frac{3.9173 \times 10^{-4}}{5.7567 \times 10^{-4}} \times 100 \% = 68\% \end{aligned}$$

The H₂ uptake of the Co/Al₂O₃ is:

$$\text{The H}_2 \text{ uptake of the Co/Al}_2\text{O}_3 \text{ catalyst} = \frac{m_{\text{H}_2 \text{ consumption}}/M_{\text{H}_2}}{\text{Weight of the catalyst sample}} = 3.46 \text{ mmol/g}_{\text{cat}}$$

The original TPR profile of Ni/Al₂O₃ (0.0435 g sample) had an area of 1873971.4. Assuming the nickel metal was nickel (II) oxide, then the minimum percentage of the reduction of the Ni/Al₂O₃ catalyst was 60%. The H₂ uptake of Ni/Al₂O₃ was 1.53 mmol/g_{cat}.

7.1.5 Gas chromatography calibration

Based on the internal standard method, the concentration of the compound in the GC vial can be calculated from the following equation:

$$\frac{\text{GC Area}_{\text{compound}}}{\text{GC Area}_{\text{ethylcyclohexane}}} = f \times \frac{\text{wt\% in vial}_{\text{compound}}}{\text{wt\% in vial}_{\text{ethylcyclohexane}}} = f \times \frac{\text{Total mass of compound in the vial}}{\text{Total mass of ethylcyclohexane in the vial}}$$

where *f* is the relative response factor.

7.1.5.1 Procedures

The GC calibration response factors were carried out by analysing the gas chromatograms of a set of standard solutions with different concentrations of a certain analyte (e.g. p-cresol). Procedures are described as follows.

- 6 Standard p-cresol/solvent solutions were prepared. The concentrations of p-cresol were 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt%.
- Ethylcyclohexane was used as the internal standard (IS) compound. The IS solution had 3 wt% of ethylcyclohexane.
- Every standard p-cresol solution (0.5 g) was mixed with the IS solution (0.5 g) in a GC vial and was sent for GC analysis. The temperature programme used for the GC is given in Table S 7.1.7.
- The area of a certain peak in the gas chromatogram was measured with the software provided by SHIMADZU (GC lab solution). All areas were measured and referenced to the area of IS (i.e. ethylcyclohexane). A calibration curve was plotted where its X and Y axes represent the area ratio of p-cresol to IS and the weight ratio of p-cresol to IS, respectively (Figure S 7.1.6). Then, the response factor of DBT is the slope of the calibration line.

Table S 7.1.7 GC temperature settings

GC Temperature program procedure	Specification
Hold	Isotherm at 40 °C for 1min
Ramp	Ramp 10 °C/min to 200 °C
Hold	Isotherm at 200 °C for 1 min

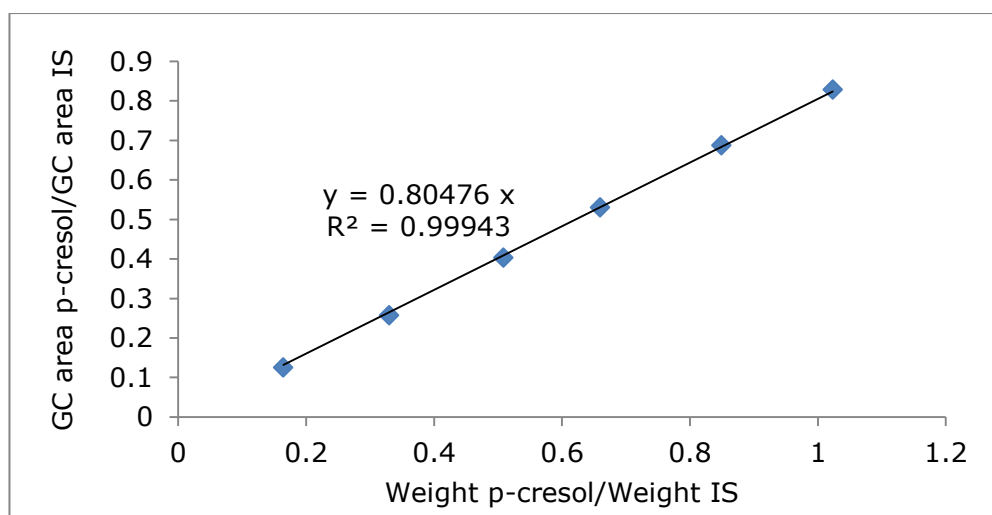


Figure S 7.1.6 Calibration curve of p-cresol

7.1.5.2 Results

The response factors, retention times and etc. of the compounds are given in Table S 7.1.8

Table S 7.1.8 Chemical information

Chemical	MW	B.P.(C)	R. Time	Factor	Purity	Sigma Code
Methylcyclopentane	84.16	72	1.952-1.953	0.97159	≥99.5	66490-10ml
Benzene	78.11	80.1	2.153-2.154	1.04474	≥99.9	12540-5ml-F
Cyclohexane	84.16	80.74	2.243-2.244	0.98011	≥99.9	650455-1L
Methylcyclohexane	98.19	101	2.942-2.949	1.00405	≥99	300306-100ml
4-Methylcyclohexene	96.17	101-102	3.134-3.14	0.99628	99	M39008-5G
Toluene	92.14	110.6	3.402-3.41	1.04726	99.8	244511-1L
1-Methylcyclohexene	96.17	110-111	3.559-3.568	0.92996	97	129801-5G
Ethylcyclohexane (IS)	112.21	130-132			≥99	E19154-25G
4-Methylcyclohexanol	114.19	172	6.26-6.294	0.77750	98	153095-250ml
O-cresol	108.14	191	8.069-8.102	0.83474	≥99	C85700-100ml
P-cresol	108.14	201.8	8.416-8.455	0.80476	≥99	61030-25G-F
Dibutyl disulphide	178.36	229-233			97	B93989
Cyclopentane	70.13	50	1.539-1.54	0.98044	98	459747-500ml
Cyclopentanol	86.13	139-140	3.561-3.59	0.70326	99	C112208-100ml
Methoxycyclohexane	114.19	135	5.023-5.034	0.76995	98	M2374 (TCI)
Cyclohexanone	98.14	155	5.126-5.151	0.73387	99.5	29140-100ml
Cyclohexanol	100.16	160-161	5.162-5.20	0.73971	99	105899-25ml
trans-Methylcyclohexanol	114.19	173-175	6.252-6.292	0.78270	97	104191-10G
Phenol	94.11	182	6.826-6.866	0.81278	≥99.5	P5566-25G
2-methoxycyclohexanone	128.17	185-ish	7.29-7.323	0.58778	97	227331-10G
Guaiacol	124.14	205	8.601-8.64	0.66112	≥99.1	G5502-100G
1,2-Dimethoxybenzene	138.16	206-207	9.457-9.477	0.76647	99	140155-100G
Catechol	110.11	245	10.378-10.426	0.68397	≥99	135011-100G
2-methoxycyclohexanol	130.19	195	7.607-7.645	0.56797	99	L19065 (Alfa Aesar)
1,2-Cyclohexanediol	116.16		8.047-8.063	0.52187	98	141712-10G
Cyclopentanone	84.12	130-131	3.472-3.485	0.61176	≥99	C112402
Anisole	108.14	154	5.708-5.712	0.68196	99	296295
Cyclohexene	82.14	83	2.398-2.399	0.92384	≥99	29240-500ml

7.1.6 Calculation of relative rate constant

A reference run was selected and set as the standard for the calculation. The relative rate constant was given as the ratio of the rate constant of a certain run to that of the reference run. If the pseudo first-order rate constant for the reference run was set to unity, according to Equation (15), the relative rate constant of the run k_a can be obtained from the following equation.

$$k_a = \frac{-\ln(1 - X_a) \times \left(\frac{w_{\text{ref}} t_{\text{ref}}}{v_{\text{ref}}}\right)}{-\ln(1 - X_{\text{ref}}) \times \left(\frac{w_a t_a}{v_a}\right)} = \frac{-\ln(1 - X_a)}{-\ln(1 - X_{\text{ref}})}$$

where X_a and X_{ref} are the feed conversions of the calculated run and that of the reference run at the same batch reaction time; w_{ref} , t_{ref} and v_{ref} are the catalyst weight, reaction time and solution volume at the reaction time t_{ref} of the reference run; w_a , t_a and v_a are the corresponding values of the calculated run.

However, different method was used for the calculations of the relative rate constants of the pre-reduced $\text{Co}/\text{Al}_2\text{O}_3$ catalyst with/without sulphur at 250 °C. As their conversions nearly reached 100%, the above equation was not applicable. Alternatively, the H_2 consumption was used to deduce the relative rate constants. Assume the ideal gas law can be applied and only hydrogenation reaction existed in the experimental conditions, equations below were used.

$$k_a = \frac{-\ln(1 - X_a) \times \left(\frac{w_{ref} t_{ref}}{v_{ref}}\right)}{-\ln(1 - X_{ref}) \times \left(\frac{w_a t_a}{v_a}\right)} = \frac{-\ln(1 - X_a) \times t_{ref}}{-\ln(1 - X_{ref}) \times t_a}$$

In the above equation, the conversion X at batch reaction time t could be obtained by the following two equations.

$$\Delta n_{p\text{-cresol}} = \frac{\Delta n_{\text{H}_2}}{3} = \frac{\Delta P_{\text{H}_2} V}{3RT}$$

where $\Delta n_{p\text{-cresol}}$ is the mole of p-cresol converted within the batch reaction time t ; Δn_{H_2} is the mole of H_2 consumed within the batch reaction time t ; ΔP_{H_2} is the system pressure drop within the batch reaction time t ; V is the reactor headspace volume; R is the ideal gas constant; T is the reaction temperature.

$$X = \frac{\Delta n_{p\text{-cresol}}}{n_{p\text{-cresol initial}}} = \frac{\Delta P_{\text{H}_2} V}{3RT n_{p\text{-cresol initial}}}$$

where X is the feed conversion at reaction time t ; $n_{p\text{-cresol initial}}$ is the mole of p-cresol in the feed. With the data given in Table S 7.1.9, the relative rate constants of the pre-reduced $\text{Co}/\text{Al}_2\text{O}_3$ catalyst with/without sulphur at 250 °C can be obtained.

Table S 7.1.9 Data used for the calculation of relative rate constants of $\text{Co}/\text{Al}_2\text{O}_3$ catalyst at 250 °C

Catalyst	Pressure drop (bar)	Reaction time (s)	Head space volume (ml)	Temperature (°C)	Ideal gas constant (J mol ⁻¹ K ⁻¹)
$\text{Co}/\text{Al}_2\text{O}_3$ as-received, 0 ppm sulphur	2.7	312	76.8	250	8.314
$\text{Co}/\text{Al}_2\text{O}_3$ pre-reduced, 0 ppm sulphur	0.2	12	76.8	250	8.314
$\text{Co}/\text{Al}_2\text{O}_3$ pre-reduced, 4 ppm sulphur	0.5	36	76.8	250	8.314

7.2 APPENDIX 2: RAW EXPERIMENTAL RESULTS

7.2.1 p-Cresol hydrodeoxygenation over Co/Al₂O₃ and Ni/Al₂O₃ catalysts

Table S 7.2.1 Effect of temperature on the HDO of p-cresol (0.04 g catalyst and 2 hr batch time)

Temperature (°C)	Product distribution (wt%)-Co/Al ₂ O ₃							HDO (wt%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Benzene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	8.41	0.00	0.00	0.00	90.10	1.49	8.41
275	0.00	23.28	0.00	0.00	0.00	74.90	1.82	23.28
300	0.00	95.18	0.00	0.00	0.00	4.82	0.00	95.18
325	0.97	96.71	0.00	0.00	0.80	0.54	0.98	98.48
350	2.38	87.77	6.11	0.00	1.53	0.80	1.41	97.78
375	2.47	63.67	29.63	1.01	1.13	0.00	2.10	97.90

Temperature (°C)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Benzene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	9.64	0.00	0.00	0.00	88.81	1.55	9.64
275	0.00	26.06	0.00	0.00	0.00	72.09	1.85	26.06
300	0.00	95.83	0.00	0.00	0.00	4.17	0.00	95.83
325	1.13	96.58	0.00	0.00	0.94	0.46	0.89	98.65
350	2.75	87.06	6.46	0.00	1.77	0.69	1.27	98.04
375	2.81	62.05	30.77	1.23	1.28	0.00	1.86	98.14

Temperature (°C)	Product distribution (wt%)-Ni/Al ₂ O ₃						HDO (wt%)
	Methylcyclohexane	4-Methylcyclohexanol	Toluene	Cyclohexane	Benzene	p-Cresol	
250	20.83	78.60	0.00	0.00	0.00	0.57	20.83
275	65.72	34.28	0.00	0.00	0.00	0.00	65.72
300	100.00	0.00	0.00	0.00	0.00	0.00	100.00
325	100.00	0.00	0.00	0.00	0.00	0.00	100.00
350	98.72	0.00	0.00	1.28	0.00	0.00	100.00
375	50.85	0.00	36.23	6.99	5.93	0.00	100.00

Temperature (°C)	Product distribution (wt%)-Ni/Al ₂ O ₃						HDO (mol%)
	Methylcyclohexane	4-Methylcyclohexanol	Toluene	Cyclohexane	Benzene	p-Cresol	
250	23.42	76.00	0.00	0.00	0.00	0.58	23.42
275	69.03	30.97	0.00	0.00	0.00	0.00	69.03
300	100.00	0.00	0.00	0.00	0.00	0.00	100.00
325	100.00	0.00	0.00	0.00	0.00	0.00	100.00
350	98.51	0.00	0.00	1.49	0.00	0.00	100.00
375	48.39	0.00	36.75	7.76	7.09	0.00	100.00

Table S 7.2.2 Effect of added sulphur on the HDO of p-cresol (0.04 g catalyst and 2 hr batch time at 350 °C)

S (ppm)	Feed conversion (%)	Product distribution (wt%)-Co/Al ₂ O ₃							HDO (wt%)
		4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	p-Cresol	Methylcyclohexenes	
0	98.93	0.80	6.11	87.77	1.53	2.38	1.41	0.00	97.78
17	12.26	0.27	0.23	2.66	0.09	0.00	93.85	2.90	5.88
51	5.12	0.22	0.11	0.66	0.08	0.00	97.18	1.75	2.60
155	5.66	0.22	0.21	0.88	0.07	0.00	96.32	2.31	3.47

S (ppm)	Feed conversion (%)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
		4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	p-Cresol	Methylcyclohexenes	
0	98.93	0.69	6.46	87.06	1.77	2.75	1.27	0.00	98.04
17	12.26	0.26	0.27	2.91	0.11	0.00	93.22	3.24	6.53
51	5.12	0.21	0.13	0.73	0.10	0.00	96.88	1.96	2.91
155	5.66	0.20	0.25	0.96	0.09	0.00	95.91	2.58	3.89

S (ppm)	Feed conversion (%)	Product distribution (wt%)-Ni/Al ₂ O ₃							HDO (wt%)
		p-Cresol	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	Methylcyclohexenes	
0	100.00	0.00	0.00	0.00	98.72	1.28	0.00	0.00	100.00
15	98.70	1.50	0.50	1.72	95.71	0.36	0.08	0.12	97.99
47	66.53	38.33	1.04	9.98	46.35	0.14	0.00	4.16	60.63
157	25.34	82.37	1.31	1.91	3.86	0.00	0.00	10.55	16.32

S (ppm)	Feed conversion (%)	Product distribution (mol%)-Ni/Al ₂ O ₃							HDO (mol%)
		p-Cresol	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	Methylcyclohexenes	
0	100.00	0.00	0.00	0.00	98.51	1.49	0.00	0.00	100.00
15	98.70	1.36	0.43	1.84	95.73	0.42	0.09	0.13	98.20
47	66.53	35.84	0.92	10.95	47.73	0.17	0.00	4.37	63.23
157	25.34	80.78	1.22	2.20	4.17	0.00	0.00	11.63	18.00

S (ppm)	Product selectivity (%) -Co/Al ₂ O ₃					
	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	Methylcyclohexenes
0	0.59	5.52	74.36	1.51	2.35	0.00
17	1.96	2.09	22.32	0.85	0.00	24.84
51	4.06	2.39	13.87	1.95	0.00	37.46
155	3.53	4.31	16.73	1.61	0.00	44.87

S (ppm)	Product selectivity (%) -Ni/Al ₂ O ₃					
	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Methylcyclopentane	Methylcyclohexenes
0	0.00	0.00	88.76	1.34	0.00	0.00
15	0.42	1.78	92.75	0.41	0.09	0.12
47	1.29	15.37	67.00	0.24	0.00	6.14
157	4.44	8.03	15.21	0.00	0.00	42.42

Table S 7.2.3 Effect of catalyst loading on the HDO of P-cresol (2 hr batch time over Co/Al₂O₃)

Temperature (°C)	Product distribution (wt%)-0.04 g catalyst						HDO (wt%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	8.41	0.00	0.00	90.10	1.49	8.41
300	0.00	95.18	0.00	0.00	4.82	0.00	95.18
350	2.38	87.77	6.11	1.53	0.80	1.41	97.78

Temperature (°C)	Product distribution (mol%)-0.04 g catalyst						HDO (mol%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	9.64	0.00	0.00	88.81	1.55	9.64
300	0.00	95.83	0.00	0.00	4.17	0.00	95.83
350	2.75	87.06	6.46	1.77	0.69	1.27	98.04

Temperature (°C)	Product distribution (wt%)-0.01 g catalyst						HDO (wt%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	5.98	0.00	0.00	91.78	2.33	5.98
300	0.00	56.46	1.25	0.00	41.39	0.90	57.71
350	1.64	88.01	8.69	1.04	0.06	0.56	99.38

Temperature (°C)	Product distribution (mol%)-0.01 g catalyst						HDO (mol%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol	
250	0.00	6.88	0.00	0.00	90.70	2.43	6.88
300	0.00	59.94	1.41	0.00	37.78	0.86	61.35
350	1.90	87.17	9.17	1.20	0.05	0.51	99.44

Table S 7.2.4 Effect of batch time on the HDO of p-cresol (0.01 g Co/Al₂O₃ catalyst)

Batch time (hr)	Product distribution (wt%) at 250 °C				HDO (wt%)	Conversion (%)
	Methylcyclohexane	4-Methylcyclohexanol	p-Cresol			
0.5	1.51	89.76	8.73		1.51	92.07
1	2.57	90.00	7.43		2.57	92.92
2	5.98	91.70	2.33		5.98	97.80
3	6.49	90.04	3.47		6.49	96.94

Batch time (hr)	Product distribution (mol%) at 250 °C				HDO (mol%)	Conversion (%)
	Methylcyclohexane	4-Methylcyclohexanol	p-Cresol			
0.5	1.74	89.10	9.16		1.74	92.07
1	2.96	89.26	7.78		2.96	92.92
2	6.88	90.70	2.43		6.88	97.80
3	7.45	88.93	3.62		7.45	96.94

Batch time (hr)	Product distribution (wt%) at 300 °C				HDO (wt%)	Conversion (%)
	Methylcyclohexane	Toluene	4-Methylcyclohexanol	p-Cresol		
0.5	23.54	1.58	72.5	2.39	25.12	97.88
1	32.43	1.56	64.36	1.65	33.99	98.51
2	56.46	1.25	41.39	0.90	57.71	99.24
3	76.87	0.63	21.16	1.34	77.50	98.89

Batch time (hr)	Product distribution (mol%) at 300 °C				HDO (mol%)	Conversion (%)
	Methylcyclohexane	Toluene	4-Methylcyclohexanol	p-Cresol		
0.5	26.23	1.87	69.48	2.42	28.11	97.88
1	35.67	1.83	60.86	1.64	37.49	98.51
2	59.94	1.41	37.78	0.86	61.35	99.24
3	79.29	0.69	18.77	1.25	79.98	98.89

Batch time (hr)	Product distribution (wt%) at 350 °C						HDO (wt%)	Conversion (%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol		
0.5	1.37	79.84	14.94	0.80	2.17	0.87	96.96	99.33
1	1.35	82.45	14.68	0.79	0.26	0.46	99.28	99.65
2	1.64	88.01	8.69	1.04	0.06	0.56	99.38	99.56
3	1.46	87.99	9.07	0.93	0.00	0.56	99.44	99.55

Batch time (hr)	Product distribution (mol%) at 350 °C						HDO (mol%)	Conversion (%)
	Methylcyclopentane	Methylcyclohexane	Toluene	Cyclohexane	4-Methylcyclohexanol	p-Cresol		
0.5	1.58	79.08	15.77	0.93	1.85	0.78	97.37	99.33
1	1.55	81.44	15.46	0.91	0.22	0.41	99.37	99.65
2	1.90	87.17	9.17	1.20	0.05	0.51	99.44	99.56
3	1.68	87.17	9.57	1.07	0.00	0.51	99.49	99.55

Table S 7.2.5 Toluene equilibrium test (0.04 g catalyst and 2 hr batch time, all results obtained over Co/Al₂O₃)

Temperature (°C)	Product distribution (wt%)					Toluene/(Toluene+MCH)
	Toluene	Methylcyclohexane	Cyclohexane	Benzene	Methylcyclopentane	
250	0.54	99.46	0.00	0.00	0.00	0.54
275	0.59	99.41	0.00	0.00	0.00	0.59
300	0.26	99.74	0.00	0.00	0.00	0.26
325	0.25	99.75	0.00	0.00	0.00	0.25
350	6.27	91.04	1.50	0.00	1.18	6.44
375	17.35	78.94	1.62	0.77	1.31	18.02

Temperature (°C)	Product distribution (mol%)					Toluene/(Toluene+MCH)
	Toluene	Methylcyclohexane	Cyclohexane	Benzene	Methylcyclopentane	
250	0.58	99.42	0.00	0.00	0.00	0.58
275	0.63	99.37	0.00	0.00	0.00	0.63
300	0.27	99.73	0.00	0.00	0.00	0.27
325	0.26	99.74	0.00	0.00	0.00	0.26
350	6.63	90.26	1.74	0.00	1.37	6.84
375	18.16	77.53	1.85	0.95	1.51	18.98

Table S 7.2.6 Effect of temperature on the HDO of 4-methylcyclohexanol (0.04 g catalyst and 2 hr batch time)

Temperature (°C)	Product distribution (wt%)-Co/Al ₂ O ₃						HDO (wt%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Benzene	Cyclohexane	Methylcyclopentane	
250	86.94	13.06	0.00	0.00	0.00	0.00	13.06
275	61.37	38.63	0.00	0.00	0.00	0.00	38.63
300	2.90	97.10	0.00	0.00	0.00	0.00	97.10
325	1.74	98.26	0.00	0.00	0.00	0.00	98.26
350	3.14	86.55	7.49	0.00	1.26	1.56	96.86
375	0.00	72.15	22.91	0.83	1.45	2.66	100.00

Temperature (°C)	Product distribution (mol%)-Co/Al ₂ O ₃						HDO (mol%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Benzene	Cyclohexane	Methylcyclopentane	
250	85.13	14.87	0.00	0.00	0.00	0.00	14.87
275	57.73	42.27	0.00	0.00	0.00	0.00	42.27
300	2.51	97.49	0.00	0.00	0.00	0.00	97.49
325	1.50	98.50	0.00	0.00	0.00	0.00	98.50
350	2.68	86.10	7.94	0.00	1.46	1.82	97.32
375	0.00	70.46	23.84	1.02	1.65	3.03	100.00

Temperature (°C)	Product distribution (wt%)-Ni/Al ₂ O ₃					HDO (wt%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Benzene	Cyclohexane	
250	81.55	18.45	0.00	0.00	0.00	18.45
275	40.77	59.23	0.00	0.00	0.00	59.23
300	1.11	98.89	0.00	0.00	0.00	98.89
325	0.00	100.00	0.00	0.00	0.00	100.00
350	0.89	98.01	0.00	0.00	1.09	99.11
375	0.59	53.60	31.25	5.88	8.68	99.41

Temperature (°C)	Product distribution (mol%)-Ni/Al ₂ O ₃					HDO (mol%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Benzene	Cyclohexane	
250	79.16	20.84	0.00	0.00	0.00	20.84
275	37.18	62.82	0.00	0.00	0.00	62.82
300	0.95	99.05	0.00	0.00	0.00	99.05
325	0.00	100.00	0.00	0.00	0.00	100.00
350	0.77	97.96	0.00	0.00	1.27	99.23
375	0.48	51.09	31.74	7.04	9.65	99.52

Table S 7.2.7 Effect of added sulphur on the HDO of 4-methylcyclohexanol (0.04 g catalyst and 2 hr batch time at 350 °C)

S (ppm)	Product distribution (wt%)-Co/Al ₂ O ₃							HDO (wt%)	Conversion (%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Cyclohexane	Methylcyclopentane	Ethylcyclopentenenes	Methylcyclohexenes		
0	3.14	86.55	7.49	1.26	1.56	0.00	0.00	96.86	97.83
19	0.40	40.10	1.44	0.10	0.00	0.00	57.97	99.60	99.68
49	0.20	25.34	0.52	0.10	0.00	0.84	73.01	99.80	99.84
150	0.44	25.01	0.00	0.12	0.00	4.59	69.85	99.56	99.65

S (ppm)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)	Conversion (%)
	4-Methylcyclohexanol	Methylcyclohexane	Toluene	Cyclohexane	Methylcyclopentane	Ethylcyclopentenenes	Methylcyclohexenes		
0	2.68	86.10	7.94	1.46	1.82	0.00	0.00	97.32	97.83
19	0.34	39.59	1.51	0.11	0.00	0.00	58.44	99.66	99.68
49	0.17	24.94	0.54	0.11	0.00	0.84	73.39	99.38	99.84
150	0.37	24.63	0.00	0.13	0.00	4.62	70.24	99.63	99.65

S (ppm)	Product distribution (wt%)-Ni/Al ₂ O ₃						HDO (wt%)	Conversion (%)
	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Ethylcyclopentenenes	Methylcyclohexenes		
0	0.89	0.00	98.01	1.09	0.00	0.00	99.11	99.33
17	0.73	1.71	97.17	0.00	0.00	0.40	99.27	99.40
49	0.93	7.55	84.57	0.00	0.00	6.95	99.07	99.23
153	0.91	1.38	18.89	0.00	8.21	70.62	99.09	99.29

S (ppm)	Product distribution (mol%)-Ni/Al ₂ O ₃						HDO (mol%)	Conversion (%)
	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Ethylcyclopentenenes	Methylcyclohexenes		
0	0.77	0.00	97.96	1.27	0.00	0.00	99.23	99.33
17	0.62	1.83	97.15	0.00	0.00	0.40	99.38	99.40
49	0.79	8.01	84.14	0.00	0.00	7.06	99.21	99.23
153	0.77	1.44	18.59	0.00	8.25	70.95	99.23	99.29

Table S 7.2.8 Product distributions of different initial feeds (0.04 g Ni/Al₂O₃ and 2 hr batch time at 350 °C with 50 ppm of sulphur)

Feed	S (ppm)	Product distribution (wt%)							HDO (wt%)	Conversion (%)
		P-cresol	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Ethylcyclopentane	Methylcyclohexenes		
P-cresol	47	38.33	1.04	9.98	46.35	0.14	0.00	4.16	60.63	66.53
4-Methylcyclohexanol	49	0.00	0.93	7.55	84.57	0.00	0.00	6.95	99.07	99.23
1-Methylcyclohexene	51	0.00	0.00	7.76	87.54	0.75	0.64	3.31	0.00	97.81
Toluene	50	0.00	0.00	61.41	38.54	0.00	0.00	0.05	0.00	40.02
Methylcyclohexane	49	0.00	0.00	0.22	99.78	0.00	0.00	0.00	0.00	5.56

Feed	S (ppm)	Product distribution (mol%)							HDO (mol%)	Conversion (%)
		P-cresol	4-Methylcyclohexanol	Toluene	Methylcyclohexane	Cyclohexane	Ethylcyclopentane	Methylcyclohexenes		
P-cresol	47	35.84	0.92	10.95	47.73	0.17	0.00	4.37	63.23	66.53
4-Methylcyclohexanol	49	0.00	0.79	8.01	84.14	0.00	0.00	7.06	99.21	99.23
1-Methylcyclohexene	51	0.00	0.00	8.21	86.93	0.87	0.63	3.36	0.00	97.81
Toluene	50	0.00	0.00	62.91	37.05	0.00	0.00	0.05	0.00	40.02
Methylcyclohexane	49	0.00	0.00	0.24	99.76	0.00	0.00	0.00	0.00	5.56

Table S 7.2.9 Pseudo first-order plots

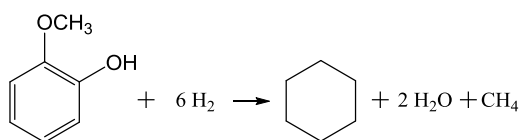
Pseudo 1st order data for p-cresol HDO at 250 °C				
Catalyst	Batch time (min)	Catalyst weight (g)	Feed mixture weight (g)	Conversion (%)
Co/Al ₂ O ₃	15	0.0020	20.0143	10.32
	30	0.0020	20.0037	15.73
	60	0.0020	20.0307	23.01
	120	0.0021	20.0158	47.62
Ni/Al ₂ O ₃	15	0.0020	20.0138	18.50
	30	0.0020	20.0074	32.69
	60	0.0020	20.0125	55.60
	120	0.0021	20.0166	80.75
Co/Al ₂ O ₃ (4 ppm S)	5	0.0999	20.0419	26.52
	10	0.1001	20.0343	51.57
	13	0.0999	20.0474	64.21
	20	0.1000	20.0378	84.70
Ni/Al ₂ O ₃ (4 ppm S)	3	0.0150	20.0303	16.77
	8	0.0150	20.0292	46.19
	12	0.0150	20.0242	56.57
	15	0.0151	20.0295	64.79
Pseudo 1st order data for 4-methylcyclohexanol HDO at 300 °C				
Catalyst	Batch time (min)	Catalyst weight (g)	Feed mixture weight (g)	Conversion (%)
Co/Al ₂ O ₃	30	0.0100	20.0036	3.24
	60	0.0101	20.0058	10.21
	120	0.0100	20.0060	24.26
	180	0.0100	20.0040	39.55
Ni/Al ₂ O ₃	15	0.0100	20.0008	11.25
	30	0.0100	20.0054	21.84
	60	0.0100	20.0099	37.13
	120	0.0100	20.0098	57.63
Co/Al ₂ O ₃ (9 ppm S)	15	0.0100	20.0529	11.26
	30	0.0100	20.0561	26.81
	60	0.0100	20.0558	49.74
	90	0.0100	20.0683	66.82
Ni/Al ₂ O ₃ (9 ppm S)	15	0.0100	20.0594	16.15
	30	0.0100	20.0670	33.95
	60	0.0101	20.0579	57.65
	90	0.0100	20.0552	72.70

7.2.2 Guaiacol hydrodeoxygenation over Ni/Al₂O₃ and Co/Al₂O₃ catalysts

7.2.2.1 Maximum H₂ consumption

Calculations with reasonable assumptions were conducted to prove the fact that there was an excess of H₂ in all runs.

Assuming the guaiacol compound was fully hydrogenated and its oxygen was completely removed in the form of water by the following reaction,



then, 0.6 g (4.833×10^{-3} mol) guaiacol required 0.029 mol H_2 . Experiments conducted at 20 bar (cold pressure) had the minimum amount of H_2 supplied. The space volume of the loaded autoclave at 25 °C was measured to be 76.8 ml. Assuming ideal gas law can be used, then charging the autoclave with 20 bar of cold H_2 at 25 °C would provide 0.062 mol of H_2 . Therefore, H_2 was excessive.

7.2.2.2 Guaiacol HDO results

Table S 7.2.10 Effect of temperature on the HDO of guaiacol (0.04 g catalyst, 2 hr batch time and 40 bar of H_2)

Temperature (°C)	Product distribution (wt%)-Co/Al ₂ O ₃							HDO (wt%)
	Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	1,2-Dimethoxybenzene	Cyclohexane	
250	6.23	0.00	0.00	0.00	0.00	0.43	0.40	
275	0.00	0.00	0.00	0.00	0.69	0.37	3.69	
300	0.00	0.66	0.33	0.00	1.10	0.00	39.35	
325	0.00	2.81	1.81	0.00	0.00	0.00	93.59	
350	0.00	5.44	3.59	2.00	0.00	0.00	86.25	
375	0.00	6.22	5.60	18.82	0.00	0.00	65.38	
Temperature (°C)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
	Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	1,2-Dimethoxybenzene	Cyclohexane	
250	5.33	0.00	0.00	0.00	0.00	0.33	0.50	
275	0.00	0.00	0.00	0.00	0.61	0.27	4.39	
300	0.00	0.87	0.36	0.00	0.90	0.00	43.48	
325	0.00	3.37	1.80	0.00	0.00	0.00	93.30	
350	0.00	6.47	3.55	2.13	0.00	0.00	85.51	
375	0.00	7.30	5.48	19.84	0.00	0.00	63.95	
Temperature (°C)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
	Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	1,2-Dimethoxybenzene	Cyclohexane	
250	0.00	71.95	0.00	0.90	18.69	1.40		0.40
275	0.00	92.61	0.00	0.00	2.65	0.00		3.69
300	0.00	58.03	0.54	0.00	0.00	0.00		40.87
325	0.00	0.00	1.79	0.00	0.00	0.00		100.00
350	0.28	0.00	2.45	0.00	0.00	0.00		100.00
375	1.90	0.00	2.08	0.00	0.00	0.00		100.00
Temperature (°C)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
	Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	1,2-Dimethoxybenzene	Cyclohexane	
250	0.00	76.30	0.00	1.01	15.24	1.28		0.50
275	0.00	92.69	0.00	0.00	2.04	0.00		4.39
300	0.00	53.88	0.51	0.00	0.00	0.00		45.23
325	0.00	0.00	1.53	0.00	0.00	0.00		100.00
350	0.25	0.00	2.08	0.00	0.00	0.00		100.00
375	1.70	0.00	1.74	0.00	0.00	0.00		100.00

Temperature (°C)	Product distribution (wt%)-Ni/Al ₂ O ₃						HDO (wt%)
	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Methoxycyclohexanols	Cyclohexane	
250	0.17	0.00	0.00	0.41	77.06	0.49	
275	2.04	0.00	0.00	0.77	22.95	4.40	
300	7.11	0.35	0.00	0.00	0.00	60.07	
325	10.31	1.12	0.00	0.00	0.00	87.91	
350	11.61	2.02	0.25	0.00	0.00	85.24	
375	10.42	2.39	13.26	0.00	0.00	72.08	
	Cyclopentanol	Methylcyclohexane	Toluene	Cyclohexanol	Cyclohexanediols		
250	0.00	0.00	0.00	19.36	2.51		0.65
275	2.12	0.00	0.00	66.42	1.29		6.45
300	0.00	0.41	0.00	32.06	0.00		67.59
325	0.00	0.66	0.00	0.00	0.00		98.88
350	0.00	0.88	0.00	0.00	0.00		100.00
375	0.00	1.25	0.60	0.00	0.00		100.00

Temperature (°C)	Product distribution (mol%)-Ni/Al ₂ O ₃						HDO (mol%)
	Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Methoxycyclohexanols	Cyclohexane	
250	0.29	0.00	0.00	0.44	72.31	0.71	
275	3.03	0.00	0.00	0.70	18.30	5.43	
300	8.87	0.36	0.00	0.00	0.00	62.42	
325	12.14	1.10	0.00	0.00	0.00	86.21	
350	13.63	1.97	0.26	0.00	0.00	83.39	
375	12.16	2.32	13.88	0.00	0.00	70.06	
	Cyclopentanol	Methylcyclohexane	Toluene	Cyclohexanol	Cyclohexanediols		
250	0.00	0.00	0.00	23.62	2.64		1.00
275	2.56	0.00	0.00	68.83	1.15		8.46
300	0.00	0.36	0.00	27.99	0.00		71.65
325	0.00	0.55	0.00	0.00	0.00		98.90
350	0.00	0.74	0.00	0.00	0.00		100.00
375	0.00	1.04	0.53	0.00	0.00		100.00

Table S 7.2.11 Effect of temperature on the HDO of 2-methoxycyclohexanol (0.04 g catalyst, 2 hr batch time and 40 bar of H₂)

Temperature (°C)	Conversion (%)	Product distribution (wt%)-Co/Al ₂ O ₃					HDO (wt%)
		Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Cyclohexanol	
250	60.23	0.00	0.00	0.00	0.00	16.98	
275	94.53	0.00	0.00	0.00	0.70	80.39	
300	100.00	1.49	0.39	0.00	0.96	53.14	
325	100.00	3.13	1.67	0.00	0.00	0.00	
350	100.00	6.32	3.41	2.26	0.00	0.00	
375	100.00	8.03	6.04	8.48	0.00	0.00	
		Cyclohexane	Methylcyclohexane	Toluene	Methoxycyclohexanols	Cyclopentanol	
250		0.41	0.00	0.00	82.60	0.00	0.41
275		3.77	0.00	0.00	14.04	1.10	3.77
300		44.02	0.00	0.00	0.00	0.00	45.90
325		94.68	0.53	0.00	0.00	0.00	100.00
350		87.13	0.88	0.00	0.00	0.00	100.00
375		75.41	1.26	0.78	0.00	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (mol%)-Co/Al ₂ O ₃					HDO (mol%)
		Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Cyclohexanol	
250	60.23	0.00	0.00	0.00	0.00	20.96	
275	94.53	0.00	0.00	0.00	0.63	82.39	
300	100.00	1.95	0.42	0.00	0.77	48.77	
325	100.00	3.73	1.66	0.00	0.00	0.00	
350	100.00	7.48	3.37	2.40	0.00	0.00	
375	100.00	9.45	5.92	8.95	0.00	0.00	
		Cyclohexane	Methylcyclohexane	Toluene	Methoxycyclohexanols	Cyclopentanol	
250		0.61	0.00	0.00	78.43	0.00	0.61
275		4.60	0.00	0.00	11.07	1.32	4.60
300		48.08	0.00	0.00	0.00	0.00	50.46
325		94.16	0.45	0.00	0.00	0.00	100.00
350		86.00	0.75	0.00	0.00	0.00	100.00
375		73.92	1.06	0.70	0.00	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (wt%)-Ni/Al ₂ O ₃					HDO (wt%)
		Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Cyclohexanol	
250	49.20	0.00	0.00	0.00	0.00	2.06	
275	81.04	1.81	0.00	0.00	0.60	44.02	
300	100.00	7.89	0.27	0.00	0.00	33.40	
325	100.00	9.82	0.82	0.00	0.00	0.00	
350	100.00	12.52	1.69	0.00	0.00	0.00	
375	100.00	13.05	1.80	3.56	0.00	0.00	
		Cyclohexane	Methylcyclohexane	Cyclohexanediols	Methoxycyclohexanols	Cyclopentanol	
250		0.00	0.00	1.58	96.36	0.00	0.00
275		2.67	0.00	3.82	45.74	1.34	4.49
300		58.44	0.00	0.00	0.00	0.00	66.60
325		89.35	0.00	0.00	0.00	0.00	100.00
350		85.78	0.00	0.00	0.00	0.00	100.00
375		80.95	0.65	0.00	0.00	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (mol%)-Ni/Al ₂ O ₃					HDO (mol%)
		Cyclopentane	Methylcyclopentane	Benzene	Methoxycyclohexane	Cyclohexanol	
250	49.20	0.00	0.00	0.00	0.00	2.65	
275	81.04	2.87	0.00	0.00	0.58	48.72	
300	100.00	9.84	0.28	0.00	0.00	29.16	
325	100.00	11.56	0.81	0.00	0.00	0.00	
350	100.00	14.66	1.65	0.00	0.00	0.00	
375	100.00	15.24	1.75	3.73	0.00	0.00	
		Cyclohexane	Methylcyclohexane	Cyclohexanediols	Methoxycyclohexanols	Cyclopentanol	
250		0.00	0.00	1.76	95.59	0.00	0.00
275		3.52	0.00	3.64	38.95	1.72	6.39
300		60.72	0.00	0.00	0.00	0.00	70.84
325		87.63	0.00	0.00	0.00	0.00	100.00
350		83.69	0.00	0.00	0.00	0.00	100.00
375		78.75	0.54	0.00	0.00	0.00	100.00

Table S 7.2.12 Effect of temperature on the HDO of cyclohexanol (0.04 g catalyst, 2 hr batch time and 40 bar of H₂)

Temperature (°C)	Conversion (%)	Product distribution (wt%)-Co/Al ₂ O ₃						HDO (wt%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Methylcyclohexane	Cyclohexanol	
250	6.13	0.00	0.00	0.00	0.93	0.00	99.07	0.93
275	13.85	0.00	0.00	0.00	8.22	0.00	91.78	8.22
300	46.26	0.00	0.00	0.00	36.45	0.00	63.55	36.45
325	100.00	1.00	0.88	0.00	98.12	0.00	0.00	100.00
350	100.00	3.73	2.08	2.59	91.60	0.00	0.00	100.00
375	100.00	5.52	3.37	5.53	85.04	0.53	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (mol%)-Co/Al ₂ O ₃						HDO (mol%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Methylcyclohexane	Cyclohexanol	
250	6.13	0.00	0.00	0.00	1.10	0.00	98.90	1.10
275	13.85	0.00	0.00	0.00	9.63	0.00	90.37	9.63
300	46.26	0.00	0.00	0.00	40.56	0.00	59.44	40.56
325	100.00	1.20	0.88	0.00	97.92	0.00	0.00	100.00
350	100.00	4.43	2.06	2.77	90.74	0.00	0.00	100.00
375	100.00	6.53	3.32	5.88	83.82	0.45	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (wt%)-Ni/Al ₂ O ₃					HDO (wt%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexanol	
250	12.56	0.00	0.00	0.00	6.36	93.64	6.36
275	37.23	0.00	0.00	0.00	29.80	70.20	29.80
300	91.52	0.00	0.00	0.00	89.37	10.63	89.37
325	100.00	0.00	0.39	0.00	99.61	0.00	100.00
350	100.00	0.00	0.64	0.00	99.36	0.00	100.00
375	100.00	0.67	1.18	2.28	95.87	0.00	100.00

Temperature (°C)	Conversion (%)	Product distribution (mol%)-Ni/Al ₂ O ₃					HDO (mol%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexanol	
250	12.56	0.00	0.00	0.00	7.47	92.53	7.47
275	37.23	0.00	0.00	0.00	33.56	66.44	33.56
300	91.52	0.00	0.00	0.00	90.91	9.09	90.91
325	100.00	0.00	0.39	0.00	99.61	0.00	100.00
350	100.00	0.00	0.64	0.00	99.36	0.00	100.00
375	100.00	0.80	1.18	2.44	95.58	0.00	100.00

Table S 7.2.13 Test with cyclohexane (0.04 g catalyst, 375 °C, 2 hr batch time and 40 bar of H₂)

Catalyst	Conversion (%)	Product distribution (wt%)			
		Cyclohexane	Cyclopentane	Methylcyclopentane	Benzene
Co/Al ₂ O ₃	33.87	92.40	1.04	0.73	5.83
Ni/Al ₂ O ₃	24.64	98.52	0.00	0.63	0.85

Catalyst	Conversion (%)	Product distribution (mol%)			
		Cyclohexane	Cyclopentane	Methylcyclopentane	Benzene
Co/Al ₂ O ₃	33.87	91.80	1.23	0.73	6.24
Ni/Al ₂ O ₃	24.64	98.46	0.00	0.63	0.91

Table S 7.2.14 Effect of batch time on the HDO of guaiacol over Co/Al₂O₃ (0.04 g catalyst, 40 bar of H₂)

Batch time (hr)	Conversion (%)	Product distribution (wt%) at 275 °C							HDO (wt%)
		Guaiacol	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Phenol	1,2-Dimethoxybenzene	Methoxycyclohexanols	
0.5	90.77	11.54	0.67	0.00	72.62	3.67	0.00	11.49	0.67
1.0	100.00	0.00	1.45	0.00	88.36	0.00	0.00	10.20	1.45
2.0	100.00	0.00	3.69	0.69	92.61	0.00	0.37	2.65	3.69
3.0	100.00	0.00	9.60	0.75	89.65	0.00	0.00	0.00	9.60

Batch time (hr)	Conversion (%)	Product distribution (mol%) at 275 °C							HDO (mol%)
		Guaiacol	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Phenol	1,2-Dimethoxybenzene	Methoxycyclohexanols	
0.5	90.77	9.76	0.84	0.00	76.06	4.09	0.00	9.26	0.84
1.0	100.00	0.00	1.76	0.00	90.23	0.00	0.00	8.01	1.76
2.0	100.00	0.00	4.39	0.61	92.69	0.00	0.27	2.04	4.39
3.0	100.00	0.00	11.23	0.65	88.12	0.00	0.00	0.00	11.23

Batch time (hr)	Conversion (%)	Product distribution (wt%) at 350 °C							HDO (wt%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Methoxycyclohexane	Methylcyclohexane	Cyclohexanol	
0.5	100.00	3.89	2.69	6.96	78.84	0.67	1.97	4.37	94.96
1.0	100.00	4.82	3.32	1.06	88.14	0.00	2.33	0.00	100.00
2.0	100.00	5.44	3.59	2.00	86.25	0.00	2.45	0.00	100.00
3.0	100.00	5.68	3.61	3.09	84.68	0.00	2.52	0.00	100.00

Batch time (hr)	Conversion (%)	Product distribution (mol%) at 350 °C							HDO (mol%)
		Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Methoxycyclohexane	Methylcyclohexane	Cyclohexanol	
0.5	100.00	4.67	2.69	7.49	78.75	0.49	1.68	3.67	95.84
1.0	100.00	5.75	3.30	1.14	87.54	0.00	1.99	0.00	100.00
2.0	100.00	6.47	3.55	2.13	85.51	0.00	2.08	0.00	100.00
3.0	100.00	6.75	3.58	3.30	83.86	0.00	2.14	0.00	100.00

Table S 7.2.15 Effect of H₂ pressure on the HDO of guaiacol over Co/Al₂O₃ (0.04 g catalyst, 2 hr batch time)

H ₂ pressure (bar)	Conversion (%)	Product distribution (wt%) at 275 °C							HDO (wt%)
		Benzene	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Anisole	1,2-Dimethoxybenzene	Methoxycyclohexanols	
20	100.00	0.40	3.19	0.42	91.81	0.87	0.70	2.62	3.59
30	100.00	0.00	4.50	0.58	93.26	0.00	0.43	1.24	4.50
40	100.00	0.00	3.69	0.69	92.61	0.00	0.37	2.65	3.69

H ₂ pressure (bar)	Conversion (%)	Product distribution (mol%) at 275 °C							HDO (mol%)
		Benzene	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Anisole	1,2-Dimethoxybenzene	Methoxycyclohexanols	
20	100.00	0.51	3.80	0.37	91.99	0.81	0.50	2.02	4.31
30	100.00	0.00	5.33	0.51	92.90	0.00	0.31	0.95	5.33
40	100.00	0.00	4.39	0.61	92.69	0.00	0.27	2.04	4.39

H ₂ pressure (bar)	Conversion (%)	Product distribution (wt%) at 350 °C							HDO (wt%)
		Benzene	Cyclopentane	Methylcyclopentane	Cyclohexane	Anisole	Methylcyclohexane	Toluene	
20	100.00	40.33	3.31	3.15	46.50	2.30	2.18	2.23	97.70
30	100.00	13.52	6.28	6.13	70.03	0.00	2.46	1.58	100.00
40	100.00	2.00	5.44	3.59	86.25	0.00	2.45	0.28	100.00

H ₂ pressure (bar)	Conversion (%)	Product distribution (mol%) at 350 °C							HDO (mol%)
		Benzene	Cyclopentane	Methylcyclopentane	Cyclohexane	Anisole	Methylcyclohexane	Toluene	
20	100.00	42.28	3.86	3.07	45.25	1.74	1.82	1.98	98.26
30	100.00	14.31	7.40	6.03	68.78	0.00	2.07	1.42	100.00
40	100.00	2.13	6.47	3.55	85.51	0.00	2.08	0.25	100.00

Table S 7.2.16 Effect of H₂ pressure on the HDO of guaiacol over Ni/Al₂O₃ (0.04 g catalyst, 2 hr batch time)

H ₂ pressure (bar)	Conversion (%)	Product distribution (wt%) at 275 °C							HDO (wt%)
		Cyclopentane	Cyclopentanol	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Cyclohexanediols	Methoxycyclohexanols	
20	100.00	4.86	0.00	10.80	1.06	60.12	0.00	23.16	15.66
30	100.00	2.92	1.69	5.90	0.77	67.69	0.94	20.10	8.82
40	100.00	2.04	2.12	4.40	0.77	66.42	1.29	22.95	6.45

H ₂ pressure (bar)	Conversion (%)	Product distribution (mol%) at 275 °C							HDO (mol%)
		Cyclopentane	Cyclopentanol	Cyclohexane	Methoxycyclohexane	Cyclohexanol	Cyclohexanediols	Methoxycyclohexanols	
20	100.00	7.04	0.00	13.03	0.94	60.93	0.00	18.06	20.07
30	100.00	4.26	2.01	7.18	0.69	69.22	0.82	15.81	11.44
40	100.00	3.03	2.56	5.43	0.70	68.83	1.15	18.30	8.46

H ₂ pressure (bar)	Conversion (%)	Product distribution (wt%) at 350 °C							HDO (wt%)
		Cyclopentane	Methylcyclopentane	Cyclohexane	Benzene	Toluene	Methylcyclohexane		
20	100.00	9.23	1.68	34.92	50.55	2.65	0.97		100.00
30	100.00	10.52	1.88	84.13	1.73	0.00	1.74		100.00
40	100.00	11.61	2.02	85.24	0.25	0.00	0.88		100.00

H ₂ pressure (bar)	Conversion (%)	Product distribution (mol%) at 350 °C							HDO (mol%)
		Cyclopentane	Methylcyclopentane	Cyclohexane	Benzene	Toluene	Methylcyclohexane		
20	100.00	10.51	1.59	33.14	51.68	2.29	0.79		100.00
30	100.00	12.37	1.84	82.49	1.83	0.00	1.46		100.00
40	100.00	13.63	1.97	83.39	0.26	0.00	0.74		100.00

Table S 7.2.17 Effect of sulphur on the HDO of guaiacol (2 hr batch time, 40 bar of H₂ and 350 °C)

S (ppm)	Conversion (%)	Product distribution (wt%)-Co/Al ₂ O ₃							HDO (wt%)
		Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexene	Methylcyclohexane	
0	100.00	0.00	5.44	3.59	2.00	86.25	0.00	2.45	
17	50.70	65.93	0.00	0.00	0.22	0.36	0.00	0.00	
51	56.65	58.42	0.00	0.00	0.24	0.34	0.54	0.00	
151	66.56	47.77	0.00	0.00	0.32	0.66	1.78	0.00	
		Toluene	Anisole	Phenol	o-Cresol	p-Cresol	1,2-Dimethoxybenzene	Catechol	
0		0.28	0.00	0.00	0.00	0.00	0.00	0.00	100.00
17		0.00	0.92	2.63	1.59	0.00	1.16	27.18	0.57
51		0.00	1.07	4.30	1.81	0.90	0.99	31.39	1.11
151		0.00	1.24	8.41	1.96	1.84	0.00	36.02	2.76

S (ppm)	Conversion (%)	Product distribution (mol%)-Co/Al ₂ O ₃							HDO (mol%)
		Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexene	Methylcyclohexane	
0	100.00	0.00	6.47	3.55	2.13	85.51	0.00	2.08	
17	50.70	62.88	0.00	0.00	0.33	0.50	0.00	0.00	
51	56.65	54.90	0.00	0.00	0.35	0.47	0.76	0.00	
151	66.56	43.65	0.00	0.00	0.47	0.89	2.45	0.00	
		Toluene	Anisole	Phenol	o-Cresol	p-Cresol	1,2-Dimethoxybenzene	Catechol	
0		0.25	0.00	0.00	0.00	0.00	0.00	0.00	100.00
17		0.00	1.01	3.31	1.74	0.00	1.00	29.23	0.83
51		0.00	1.16	5.33	1.95	0.97	0.84	33.26	1.59
151		0.00	1.30	10.14	2.05	1.93	0.00	37.11	3.81

S (ppm)	Conversion (%)	Product distribution (wt%)-Ni/Al ₂ O ₃							HDO (wt%)
		Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexanone	Methylcyclohexane	
0	100.00	0.00	11.61	2.02	0.25	85.24	0.00	0.88	
17	91.94	16.05	4.98	2.04	2.77	41.34	3.71	0.00	
51	72.80	44.56	0.99	0.49	0.49	6.69	3.47	0.00	
151	71.77	41.78	0.00	0.00	0.34	0.35	2.25	0.00	
		Anisole	Phenol	o-Cresol	p-Cresol	Cyclohexene	Catechol		
0		0.00	0.00	0.00	0.00	0.00	0.00		100.00
17		0.00	2.72	1.05	0.00	0.00	25.35		51.13
51		0.00	3.01	1.42	0.00	0.00	38.88		8.66
151		1.15	4.65	1.25	0.70	0.63	46.90		1.32

S (ppm)	Conversion (%)	Product distribution (mol%)-Ni/Al ₂ O ₃							HDO (mol%)
		Guaiacol	Cyclopentane	Methylcyclopentane	Benzene	Cyclohexane	Cyclohexanone	Methylcyclohexane	
0	100.00	0.00	13.63	1.97	0.26	83.39	0.00	0.74	
17	91.94	12.22	6.71	2.29	3.36	46.44	3.57	0.00	
51	72.80	39.96	1.58	0.65	0.69	8.86	3.93	0.00	
151	71.77	38.26	0.00	0.00	0.50	0.47	2.61	0.00	
		Anisole	Phenol	o-Cresol	p-Cresol	Cyclohexene	Catechol		
0		0.00	0.00	0.00	0.00	0.00	0.00		100.00
17		0.00	2.73	0.91	0.00	0.00	21.76		58.79
51		0.00	3.56	1.47	0.00	0.00	39.31		11.77
151		1.21	5.62	1.32	0.74	0.86	48.42		1.83