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The Upgrading of Bio-Oil via Hydrodeoxygenation

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2.1 Introduction

The production of liquid transportation fuels from biomass has received increased attention in the last two decades due to environmental concerns [1–4]. Bio-oil, a product of fast pyrolysis or hydrothermal liquefaction (HTL), is a promising renewable energy carrier and a means of producing liquid transportation fuels from biomass [2, 5–9]. Bio-oil is a dark brown liquid, and its physical properties are a function of its composition (various oxygenated organic compounds) [10]. The advantages of using bio-oil as a liquid fuel include the abundance of biomass, its renewability, negligible nitrogen and sulfur content, and nearly zero net-carbon emissions [2, 11, 12]. However, bio-oil produced from fast pyrolysis has several challenges that need to be addressed as the bio-oil can significantly impact the supply chain of liquid transportation fuels. The main challenge is the oxygen content of bio-oil, which can be up to 50% for bio-oil from fast pyrolysis, and leads to chemical and thermal instabilities, polymerization, and storage difficulties; in addition, bio-oil with high oxygen content has a low heating value and is immiscible with crude oil from fossil sources [2, 9, 13, 14]. The polymerization tendency of bio-oil causes it to quickly form a solid coke-like product when distilled, and heavier compounds are formed by polymerization and condensation reactions during prolonged storage [1]. Since upgrading bio-oil through hydrodeoxygenation (HDO) partially or totally eliminates the oxygenated compounds, it is essential to stabilize the bio-oil through this process before it can be widely accepted as a conventional liquid transportation fuel.

Several approaches, broadly categorized as physical and chemical, have been developed and tested for bio-oil upgrading and stabilization [15]. Emulsification and hot vapor filtration are examples of physical methods [16–18]; chemical methods include hydrogen processing, steam reforming, solvent addition, catalytic pyrolysis, and rapid thermal processing [13, 14, 19–22]. Hydrogen processing involves the elimination of heteroatoms such as oxygen (O), nitrogen (N), and sulfur (S) via HDO, hydrodenitrogenation (HDN), and hydrodesulfurization

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(HDS), respectively [13, 23]. The HDO of bio-oil is considered to be the most effective method for bio-oil upgrading and involves the hydrotreating of bio-oils with high-pressure H_2 gas at moderate temperatures (300–600 °C) in the presence of catalysts [13] to convert oxygen-containing compounds to oxygen-free liquid transportation fuels. As bio-oil contains a number of oxygen-containing compounds such as phenols, aldehydes, alcohols acids, esters, and ketones [24–28], it is challenging to fully understand all the reaction pathways for the HDO reaction [29]. According to a review by Patel and Kumar [5], most oxygen compounds found in the bio-oil produced through fast pyrolysis are water (20–30%), lignin-derived components (10–15%), acids (13–15%), phenols (10–18%), aldehydes (8–10%), esters (2–5%), and ketones (8–10%). The quantity and the quality of the bio-oil depend on the chemical composition of biomass, thermochemical conversion approach – fast pyrolysis, intermediate pyrolysis, catalytic pyrolysis, or HTL – reactor type, and operating conditions. As bio-oil is made up of multifunctional compounds, the process conditions and catalysts for HDO vary depending on the bio-oil reactivity. Table 2.1, which lists the attributes of the bio-crudes obtained from HTL and pyrolysis, shows that HTL is superior to fast pyrolysis in most regards, except for sulfur content [30]. Indeed, HTL-derived bio-oil has a lower O (oxygen) and moisture content, giving it a higher heating value than pyrolytic oils. Bio-oils have low pH values of 2–3 as a result of their high amounts of carboxylic acids, such as acetic and formic acids, and this strong acidity makes the oils extremely unstable [31]. The condensation reactions that accelerate bio-oil aging and cause its properties to decline are promoted by the acidity of bio-oil, which also causes bio-oil immiscibility with petro-fuels [5]. Strong acidity also makes bio-oil very corrosive and extremely unstable at elevated temperatures. Therefore, stringent requirements are needed in the construction of the vessels used for both storage and the upgrading processes applied before bio-oil can be used as transportation fuels [31].

This chapter presents recent trends in the HDO of bio-oil with an emphasis on catalyst design issues for HDO such as structure–activity relationships, selectivity, stability, and catalyst deactivation.

Table 2.1 Comparison of bio-crude obtained from the HTL and the pyrolysis of biomass.

Attributes	HTL	Pyrolysis
C (wt%)	73	58
H (wt%)	8	6
O (wt%)	16	36
S (ppm)	<45	29
High heating value (HHV) (MJ/kg)	35.7	22.6
Moisture	5.1	24.8

Source: Gollakota et al. 2018 [30]. Reproduced with permission of Elsevier.

2.2 Hydrodeoxygenation (HDO)

HDO is a process in which carbon–oxygen bonds are cleaved in the presence of hydrogen and a catalyst resulting in the removal of oxygen atoms from oxygen-containing compounds. This process is very similar to HDS, which removes sulfur atoms from petroleum crude oil to form stable petro-fuels. The efficiency with which oxygen is removed and upgraded oil is stabilized depends on the catalyst type, hydrogen pressure, temperature, and bio-oil quality.

HDO is divided into two broad categories: low temperature HDO (mild or partial HDO) and high temperature HDO (deep or complete HDO). In mild HDO, extremely unstable compounds (acidic oxygen compounds) are stabilized, and dissolved water is separated to enhance the energy density. The temperature is maintained between 175 and 250 °C and the pressure is typically >100 bar of hydrogen in the presence of a catalyst [5]. In contrast, high temperature HDO involves the complete conversion of oxygen-containing compounds into both high molecular-weight alkanes and aromatic hydrocarbons. The conversion occurs at a temperature of 350–400 °C and a pressure of >200 bar of hydrogen in the presence of a catalyst [5]. In this chapter, major types of oxygenated

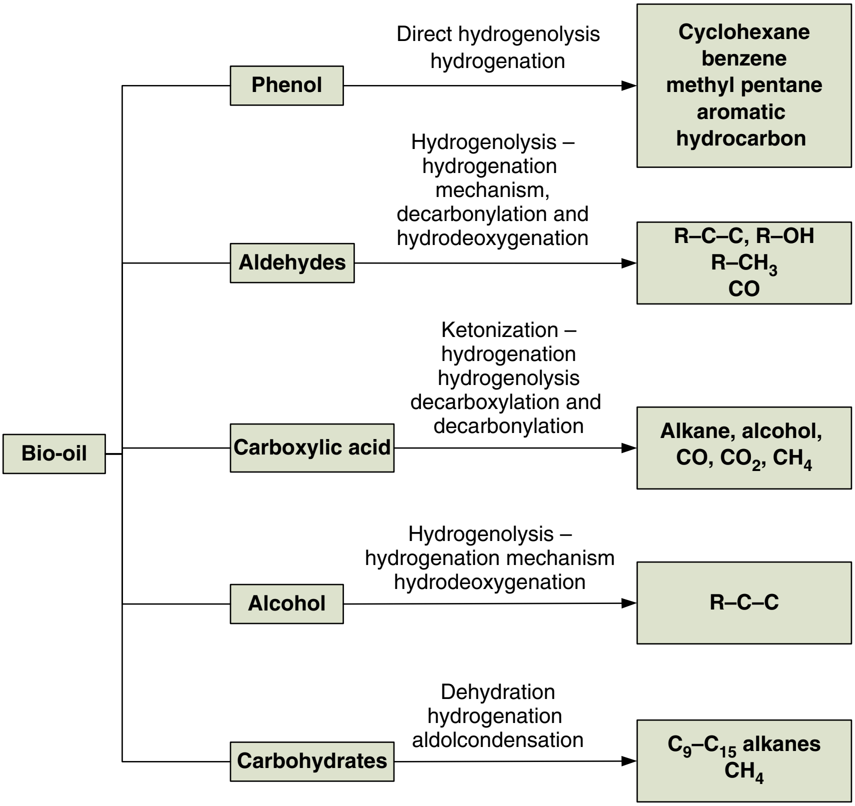

Figure 2.1 Hydrodeoxygenation pathways for major oxygenate compounds in bio-oil.

compounds are considered including phenol, aldehyde, carboxylic acid, alcohol, and carbohydrate model compounds (see Figure 2.1).

2.2.1 Hydrodeoxygenation of Phenol as a Model Compound

In general, different phenol-derived compounds present in bio-oil range between 10 and 18 wt%; however, because of phenol's standard structure, it is considered a key compound in bio-oil and is the model compound most often used during HDO studies. Therefore, it is essential to understand the detailed HDO reaction mechanism of phenol. Theoretically, phenol degradation occurs through three routes:

(1) Direct HDO to sequentially form benzene, cyclohexane, and methyl pentane in the presence of hydrogen.
(2) A combination of hydrogenation and hydrogenolysis of phenol to form an intermediate (cyclohexanol), which further undergoes dehydration to form cyclohexane.
(3) A combination of direct HDO and hydrogenation of phenol to form cyclohexanone followed by dehydration and hydrogenation reactions to form methyl pentane.

The reaction mechanism is largely driven by the catalyst employed. The performance of different types of catalysts, from commercial to noble, has been investigated for the upgrading of phenol-derived compounds [5, 32–38]. On commercial catalysts (Ni–Mo or Co–Mo on alumina), phenol is upgraded through two independent reactions: direct deoxygenation of phenol to aromatics, which is the primary product, and deoxygenation through aromatic hydrogenation to form naphtha compounds [33–35]. On the surface of Ni–W catalysts supported on active carbon, phenol conversion follows two routes: the first is the hydrogenolysis reaction to form benzenes by breaking of the C—O bond and the second route is a combination of hydrogenation and hydrogenolysis to form cyclohexanol, which is converted to cyclohexane and methyl cyclopentane via further hydrogenation [32]. However, noble metal catalysts such as Pd supported on carbon follow a different pathway than typical commercial catalysts [38]. The first step in this route is a metal-catalyzed aromatic ring hydrogenation, which is followed by naphthenic alcohol dehydration and metal-catalyzed cycloalkene hydrogenation [37, 38].

While a number of studies have considered phenol compounds in general as the model compounds used to investigate the HDO mechanism, others have focused on phenol-derived compounds – such as guaiacol, anisole, and cresole – to probe the HDO mechanism and have assessed specific catalysts in the HDO of each model compound.

2.2.1.1 HDO of Phenolic (Guaiacol) Model Compounds

Guaiacol, with its one methoxy functional group ($-OCH_3$) and one phenolic functional group ($-OH$), is considered a representative model compound for bio-oil originating from high lignin content biomass [29, 39, 40]. During the HDO of guaiacol (shown in Figure 2.2), the oxygen atom of the phenolic

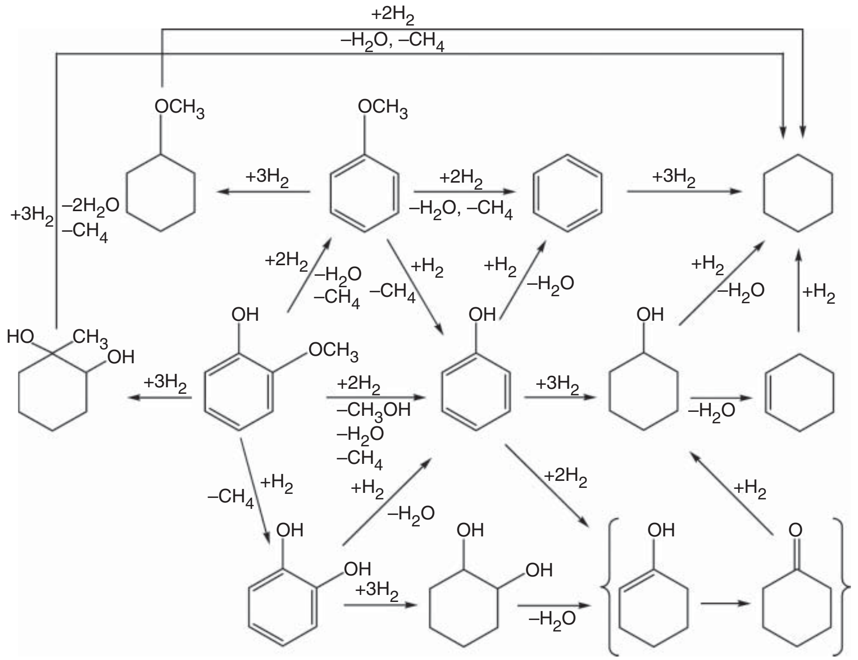

Figure 2.2 Guaiacol HDO conversion pathways. Source: Bykova et al. 2012 [1]. Reproduced with permission of Elsevier.

functional group is removed through two different reaction routes: (i) the hydrogenation of the aromatic ring followed by the elimination of the –OH group and (ii) the cleavage of the bond between the oxygen atom of the phenol group and the carbon atom of the aromatic ring [1, 29, 41]. The methoxy functional group is also eliminated through two reactions: (i) demethoxylation, which results from the rupture of the bond between the oxygen atom and the carbon in the aromatic ring to form phenol and methanol as byproducts, and (ii) demethylation, which comprises the cleavage of C—O bond of the $–OCH_3$ group to form catechol and methane as products [1, 41].

The effect of the catalyst on reaction selectivity in the HDO of guaiacol over noble metal catalysts – including Pt, Rh, Ru, and Pd supported on $SiO_2–Al_2O_3$, Al_2O_3, and nitric acid-treated carbon black – was studied by Lee et al. [42]. The reaction was conducted in a batch reactor at 40 bar of hydrogen pressure and 250 °C, and the acid-site-measurement-dependent catalyst results were used to elucidate the catalytic roles of acidic supports and metal nanoparticles. The results show that acidic supports were indispensable to the deoxygenation of oxygenates and that the metals were responsible for the hydrogenation of aromatic rings. The highest cyclohexane yield was obtained over $Ru/SiO_2–Al_2O_3$ and $Rh/SiO_2–Al_2O_3$ among the various combinations of metals and supports [42].

Lee et al. [39] used platinum-loaded HY zeolite (Pt/HY) catalysts with different Si/Al molar ratios for the HDO upgrading of guaiacol to various hydrocarbons. The yield of the main product, cyclohexane, increased with decreasing Si/Al molar ratio and results suggested that the ratio of the platinum metal particles to Brønsted acid sites must be optimized to realize maximum production of alkylated cyclic compounds and cyclohexane with high octane number.

Bykova et al. [1] carried out the HDO of guaiacol using a series of Ni-based catalysts with different stabilizing components in an autoclave at 17 MPa H_2 and 320 °C. Their results show that Ni-based catalysts prepared by a sol–gel method and stabilized using ZrO_2 and SiO_2 are the most active catalysts in the HDO of guaiacol and the main products formed are cyclohexanone, 1-methylcyclohexane-1,2-diol, and cyclohexane. These authors also investigated the effect of temperature on catalyst activity and product distribution in the HDO process and found that the degree of hydrodeoxygenation increases with temperature, while guaiacol conversion decreases due to catalyst coking at elevated temperatures [1]. The authors used a two-stage bio-oil HDO approach to prevent intense coking of the catalysts. The first stage involved the hydrogenation and partial deoxygenation of unsaturated oxygen-containing organics in the low temperature range of 175–250 °C, while the second stage comprised the hydrotreatment of the bio-oil at elevated temperatures in the range of 350–400 °C.

2.2.1.2 HDO of Phenolic (Anisole) Model Compounds

Anisole consists of an aromatic ring with a single methoxy group ($-OCH_3$) and its hydrodeoxygenation follows two reaction pathways [29, 43], as shown in Figure 2.3:

1. Transalkylation to toluene, cresols, and xylenols and demethylation of anisole to phenol.
2. Ring hydrogenation and hydrogenation of phenol to cyclohexane and benzene.

Of all the phenol-containing model compounds in bio-oil, anisole has been studied the least even though it has a similar structure to the main products of lignin depolymerization during the fast pyrolysis of wood [43]. The direct cleavage of the methoxy group in anisole is weak because the $C_{aromatic}$—O bond is stronger than the C_{methyl}—O bond [43]. The hydrogenolysis and hydrocracking of the $C_{aromatic}$–O–C_{methyl} in the anisole model compound required a bifunctional catalyst consisting of a metal and an acid [44].

Shi et al. [46] investigated the adsorption and reaction of anisole on Pt and Pt/Zn catalysts using both high surface area and model single crystal-supported metal catalysts. The authors demonstrated that the bonding configuration of anisole on Pt facilitates hydrogenation of the aromatic ring, while the bonding configuration of anisole on Pt/Zn limits this hydrogenation. However, the Zn-modified Pt exhibits high selectivity for C—O bond scission in anisole. The authors concluded that the Pt/Zn catalyst is the most effective catalyst for the hydrodeoxygenation of lignin-derived aromatic oxygenates, especially since this formulation displays low activity for ring hydrogenation.

2.2.1.3 HDO of Phenolic (Cresol) Model Compounds

The HDO mechanism of cresol depends on the position of the methyl group, the three isomers of the cresol molecule being *p*-cresol, *m*-cresol, and *o*-cresol. The two main reaction pathways in the HDO of cresol are hydrogenolysis of the bond

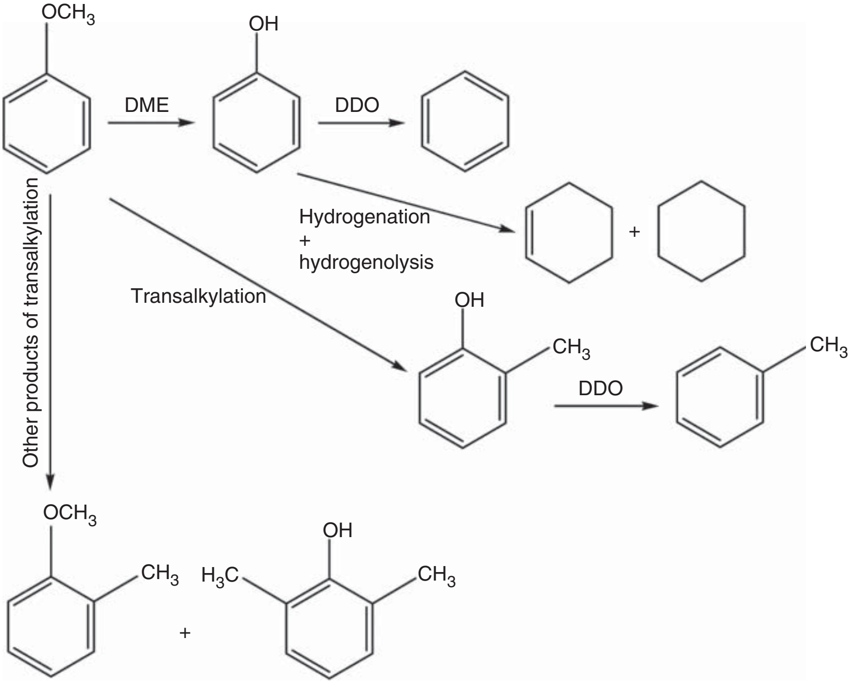

Figure 2.3 Anisole HDO conversion pathways. DME, Demethylation; DDO, Direct deoxygenation. Source: Viljava et al. 2000 [45]. Reproduced with permission of Elsevier.

between the aromatic ring and the –OH group and the rapid dehydration of cresol followed by ring hydrogenation, which produce toluene and methylcyclohexane as the two main products, respectively [35]. These two products have high octane numbers due to the presence of the methyl group, which favors the production of aromatics in the HDO process relative to the phenol molecule [47, 48]. The HDO conversion pathway for *p*-cresol is presented in Figure 2.4.

Foster et al. [49] investigated the HDO of *m*-cresol using Pt catalysts supported on γ-Al_2O_3 and SiO_2 at 0.5 atm H_2 and 260 °C to produce methylcyclohexane and toluene. They found that the HDO reaction involves the combination of acid-catalyzed dehydration and Pt-catalyzed hydrogenation reactions, the dominant reaction pathway to toluene involving the formation of a partially hydrogenated oxygenated intermediate. Increasing the hydrogen pressure increases the selectivity to methylcyclohexane, and modifying the support material had a dramatic impact on the rate of *m*-cresol conversion.

2.2.2 Hydrodeoxygenation of Aldehyde Model Compounds

The HDO of aldehydes involves four major routes [50–53]: (i) direct hydrogenolysis to form alkanes, (ii) hydrogenation followed by hydrogenolysis to yield alkanes, (iii) direct hydrogenation followed by dehydration and additional hydrogenation, and (iv) decarbonylation to afford CO and alkanes.

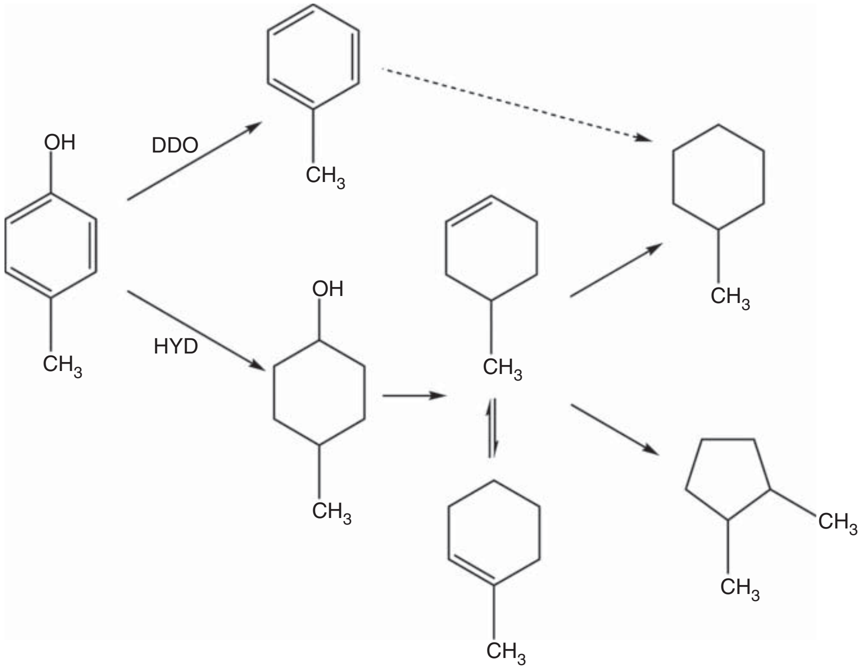

Figure 2.4 *p*-Cresol HDO conversion pathways. HYD, Hydrogenation; DDO, Direct deoxygenation. Source: Laurent and Delmon 1993 [35]. Reproduced with permission of American Chemical Society.

The hydrodeoxygenation of benzaldehyde was studied by Procházková et al. [54] over Pd/ZSM-5 in an autoclave using a temperature range of 30–130 °C and pressure ranging from 1 to 6 MPa. The reaction scheme for the HDO of benzaldehyde is shown in Figure 2.5. Benzaldehyde (A) forms toluene (C) through direct hydrogenolysis – with benzyl alcohol (B) as intermediate – or via the direct cleavage of the carbonyl bond (C—O) in a hexane environment. Toluene can also be produced from HDO of benzaldehyde in a methanol environment through several intermediates including dimethylacetal benzaldehyde (D), benzyl alcohol (B), and benzylmethyl ether (E) [54].

Saadi et al. [52] investigated copper-based catalysts supported on Al_2O_3, SiO_2, TiO_2, CeO_2, and ZrO_2 for the hydrogenation of benzaldehyde at atmospheric pressure and 100–350 °C. These authors found that the production of benzyl alcohol, toluene, and benzene depend on the nature of the support and the reaction temperature. Hydrogenolysis and hydrogenation are the dominating reactions in the upgrading of aldehydes to alkanes.

Zhang et al. [55] studied the HDO mechanism of acetaldehyde in a high pressure stainless steel fixed bed reactor over bimetallic Ni–Mo carbide supported on SiO_2. The authors concluded that the HDO of acetaldehyde can proceed via a number of reaction mechanisms including the following:

(1) Direct hydrogenation to form alcohol.
(2) Decarbonylation to form methane.

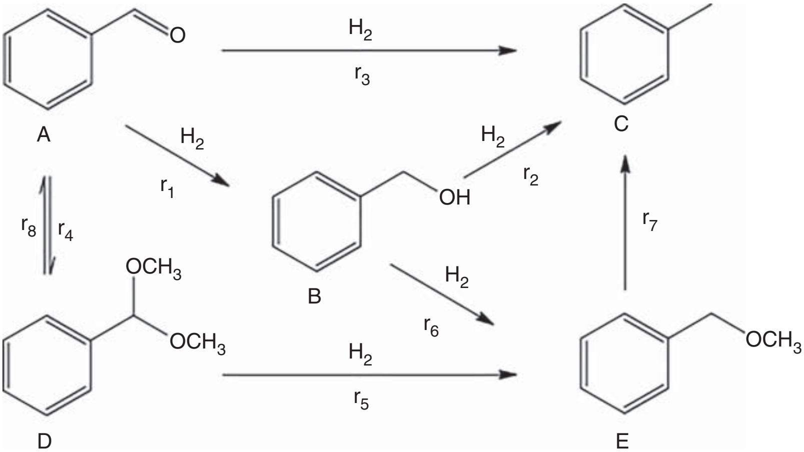

Figure 2.5 Hydrodeoxygenation of benzaldehyde. Source: Procházková et al. 2007 [54]. Reproduced with permission of Elsevier.

(3) Self-aldol condensation of acetaldehyde (side reaction) on the acid sites to form aldol alcohol, which undergoes dehydration and hydrogenation to yield butyl aldehydes.

Saliently, Snell et al. [56] investigated in detail the aldol condensation reaction of acetaldehyde, which takes place during the HDO reaction over a bifunctional aluminophosphate catalyst. The products of this condensation are as follows:

(1) Crotonaldehyde through self-aldol condensation of acetaldehyde with acetaldehyde.
(2) 3-Penten-2-one through cross-aldol condensation of acetaldehyde and acetone.
(3) 3-Methyl-3-penten-one and 4-hexen-3-one through cross-condensation of acetaldehyde and methyl ethyl ketone.

2.2.3 Hydrodeoxygenation of Carboxylic Acid Model Compounds

Carboxylic acids (acetic acid, formic acid, benzoic acid, etc.) present in bio-oil are the most unstable compounds and are responsible for the high total acid number (TAN) number and low pH value of bio-oil. The HDO of carboxylic acid takes place in three major steps, as several authors have described [57–60]:

(1) The dissociation of the carboxylic acid to carboxylate on the catalyst surface, followed by hydrogenation to alcohol.
(2) The decomposition of the C—C bond (through decarbonylation and decarboxylation) to form CO, CO_2, and alkanes with one less carbon atom (with further hydrogenation of CO and CO_2 to CH_4).
(3) The conversion of the alcohol formed in step 1 to an alkane through the dehydration–hydrogenation mechanism.

Serrano-Ruiz and Dumesic [59] studied the HDO of lactic acid over Pt/Nb_2O_5 at 573 K and 57 bar. The authors proposed that two major intermediates are formed: primary intermediates – such as propanoic acid (through the removal of the hydroxyl group following the cleavage of the C—O bond) and acetaldehyde along with CO and CO_2 (through decarbonylation and decarboxylation) – and the secondary product, ethanol (through direct hydrogenolysis). These intermediates are further upgraded to alkanes, ketones, and carbonyls through dehydration–hydrogenation, ketonization, and aldol condensation, respectively. Chen et al. [61] investigated the kinetics of aqueous phase HDO of a mixture of lactic acid and propionic acid in a three-phase stirred batch reactor at 343–423 K and 3.4–10.3 MPa, ultimately developing a two-site Langmuir–Hinshelwood (L–H) kinetic model for the hydrogenation of the feed to produce alcohols.

Olcay et al. [58] studied the aqueous phase hydrogenation of acetic acid over different types of transition metal catalysts (Ru/C, Pt/C, Pd/C, Rh/C, Ir/Al_2O_3, Raney Ni, and Raney Cu) over a temperature range of 110–290 °C and a pressure of 5.17 MPa. They proposed that on Ru and Ni, acetate converts to acetyl and oxygen; on Rh, Pt, Ru, and Ir, acetic acid converts to acetyl and a hydroxyl group; and on Cu, acetic acid converts to ethane-1-ol-1-olate.

2.2.4 Hydrodeoxygenation of Alcohol Model Compounds

Alcohol HDO has three independent routes, as summarized by Peng et al. [62]:

1. Dehydrogenation of alcohol to ketones followed by dehydration.
2. Direct hydrogenolysis to alkanes.
3. Dehydration followed by hydrogenation.

Wawrzetz et al. [63] discussed the HDO of glycerol in a high pressure tubular reactor over bifunctional Pt/Al_2O_3 at 498 K and a pressure of 29 bar. In carrying out the HDO of glycerol, they found that the presence of a catalyst comprising acid–base and metal functions is required. The initiation steps for the HDO of glycerol are dehydrogenation and dehydration. The dehydrogenation of the hydroxyl group is followed by decarbonylation and subsequent water–gas shift or disproportionation to form a carboxylic acid or alcohol. In the second route, glycerol is dehydrated followed by hydrogenation and decarboxylation reactions to form alkanes. There was no evidence of hydrogenolysis of the C—C or C—O bond on the surface of the Pt catalyst. However, the Pt catalyst favors the hydrogenation reaction. Davda et al. [64] studied the aqueous phase reforming of ethylene glycol over Ni, Pd, Pt, Ru, Rh, and Ir supported on silica catalysts at temperatures of 483 and 498 K and a pressure of 22 bar. The authors also observed that for the upgrading of ethylene glycol, there are two pathways other than the reforming process:

(1) The combination of hydrogenation and dehydration to form alcohols.
(2) The dehydrogenation of ethylene glycol followed by rearrangement to form an aldehyde, which undergoes hydrogenolysis to form alkanes.

2.2.5 Hydrodeoxygenation of Carbohydrate Model Compounds

The carbohydrates present in bio-oil are upgraded to alkanes through acid-catalyzed dehydration followed by aldol condensation to form large organic compounds that are further processed through a combination of hydrogenation and dehydration [65, 66].

Wildschut et al. [67] studied the hydrogenation of three different carbohydrate fractions (D-glucose, D-cellobiose, and D-sorbitol) present in pyrolysis oil using a Ru/C catalyst at a temperature of 250 °C and a pressure of 100 bar. They proposed two pathways for the HDO reaction: (i) hydrogenation of carbohydrates followed by hydrogenolysis to form small polyols (glycols, propanediol) and (ii) an undesired thermal pathway to form 5-hydroxymethyl furfural/levulinic acid/lumen (minor pathway). Verma and Gehlawat [68] studied the kinetics of the hydrogenation of D-glucose to sorbitol in a high pressure, stirred Parr reactor using a Raney Ni catalyst. They found that the reaction between dissolved hydrogen and D-glucose was very slow and the reaction followed homogenous kinetics with a reaction order of 1 with respect to both hydrogen and D-glucose.

Yan et al. [69] investigated the one-step conversion of cellobiose to alcohols using four transition metal catalysts (Ru, Rh, Pt, and Pd nanocluster) and a Parr autoclave at 120 °C and 4 MPa H_2. Of all the catalysts, Ru clusters could selectively cleave the C—O bond to accomplish one-step hydrogenation to form C_1-alcohols.

2.3 Chemical Catalysts for the HDO Reaction

The catalyst employed has an important role in HDO reactions. The reaction mechanisms discussed for different model compounds are completely dependent on the catalyst, reaction conditions (temperature, pressure, space velocity), and feedstock composition. A catalyst basically consists of two components: active phase and support.

Table 2.2 summarizes the catalyst, reactor type and dimensions, and temperature and pressure, as well as the degree of HDO achieved in the reactor during the upgrading of fast pyrolysis oil produced from different biomass feedstocks. HDO technology is similar to crude oil refinery upgrading via HDS, which removes sulfur as H_2S. To do so, sulfided Ni–Mo or Co–Mo supported on γ-alumina are used, these commercial catalysts also being used as the reference catalyst for the HDO reaction to remove oxygen in the form of water. Besides commercial catalysts, researchers have investigated both noble metal and base metal catalysts on various supports. Of the noble metal catalysts, Rh, Ru, and Pd are widely used. In the transition metal category, Ni, Co, W, and Cu are employed. The noble metal catalysts provide a higher oil yield than the transition metal catalysts. The reason might be due to the bonding between the reactant and the active sites during the reaction phase, which enhances reactant conversion to the desired product. Supports also play an important role in the HDO reaction. Most contain oxygen, which reduces catalyst deactivation, provide sites for the active metal to settle on, enhance the reactivity of the reaction, etc. Alumina, silica, carbon, titania, zirconia, and ceria are generally used as catalyst supports in this reaction. Support selection is determined by the desired end product and the nature of the reactant. Ahmadi et al. [70] compared transition metal catalysts on a number of supports (Co–Mo/SBA-15, Co–Mo/MCM–41, Co–Mo/γ-Al_2O_3, Co–Mo/HZSM-5,

Table 2.2 Catalysts, operating conditions, and HDO yields for HDO processing of bio-oil.

Feedstock	Reactor type	Reactor dimensions	Catalyst used	Temperature (°C)	Pressure (bar)	HDO (wt%)	References
Pine sawdust	Autoclave reactor	500 ml, Parr 4575	Co/SiO_2, Fe–Co/SiO_2, Fe/SiO_2, Co/HZSM-5	300	3.45 MPa	15–35	[72]
Loblolly pine	Stainless steel, high-pressure autoclave reactor	1.8 l Parr batch	Nickel/silica–alumina catalyst	340	1000 psig	31.4–35.6	[73]
Pine wood chips	Fixed bed continuous reactor	ID 1″, height 30″	CoMo/γ-Al_2O_3	375–400	10.34 MPa	35	[74]
Raw pine sawdust	Autoclave reactor	500 ml, Parr 4575	Ni–Zn/Al_2O_3	400	5000 psig	20–45	[75]
Raw pine sawdust	Autoclave reactor	500 ml, Parr 4575	Zinc powder with zero valence and 5.00 wt% Pd/C	200, 250, and 300	1–4.45 MPa	20–25	[76]
Raw pine sawdust	Autoclave reactor	500 ml, Parr 4575	Zinc metal with zero valency and zinc oxide	250, 300, 350, and 400	3.45 MPa	10–15	[77]
Raw pine sawdust	Stainless steel high pressure reactor	500 ml, Parr 4575	Zn–Pd/C	150, 200, and 250	1.38, 2.76, and 4.14 MPa	35–45	[78]
Dried cornstalk	High pressure stainless steel airtight pilot-scale autoclave	24 l	Bimetallic ammonium nickel molybdate	280, 310, 340, and 370	4 MPa	26.7–16.3	[79]
Pyrolysis oil	Stirred autoclave reactor (Parr)	Nominal internal volume of 500 ml	CoMo/SBA-15, CoMo/MCM-41, CoMo/γ-Al_2O_3, CoMo/HZSM-5, CoMo/C-Pellet, and CoMo/C-Powder	300 and 350	20.7 and 22.5 MPa,	45–65 (light oil and heavy oil)	[70]

Pyrolysis oil from lignocellulosic biomass	Batch autoclave	100 ml	Ru/C, Ru/TiO_2, Ru/Al_2O_3, Pt/C, and Pd/C Sulfided NiMo/Al_2O_3 and CoMo/Al_2O_3	250 and 350	100 and 200 bar	Up to 60	[80]
Miscanthus sinensis	Autoclave		Ru/C and Pt/C	250, 300, or 350	3 MPa	60–80	[81]
Yellow poplar	Stainless steel (SUS316) autoclave reactor	200 ml	Ni/C, Ni/SBA-15, and Ni/Al-SBA-15	300	3 MPa	55–75	[82]
Switchgrass, *Eucalyptus benthamii*, and equine manure feedstock	Parr bench-top reactor	100 ml	Pt, Ru, or Pd on carbon supports	320	2100 psi		[83]

Co–Mo/C-pellet, and Co–Mo/C-powder) with commercial Ru/C catalysts. Of all the catalysts, the noble metal catalyst Ru/C performed better than any other because of its high activity. However, Ru is very expensive and difficult to regenerate after the HDO reaction. Less coke formed on the surface of SBA-15 and MCM-41 due to their mesoporous nature, and the activity of fresh and regenerated MCM-41 was the same in the HDO reaction. The coke deposition rate depends on the support's acidity, which was highest for HZSM-5 followed by alumina, MCM-41, and SBA-15.

Venderbosch et al. [71] studied the HDO mechanism for the production of biofuel from pyrolysis oil in the presence of a Ru/C catalyst. In the first step, bio-oil is processed in the first stage hydrotreater to produce stabilized bio-oil by removing the unstable, polar, and viscous oxygen compounds through the hydrodeoxygenation reaction. The stabilized oil from the first hydrotreater contains high molecular weight compounds that need to be processed in a high temperature hydrotreater. In this second stage hydrotreater, complete hydrodeoxygenation takes place to convert high molecular weight stabilized compounds to low molecular weight compounds that can be hydrocracked to form gasoline and diesel range compounds. In general, bio-oil consists of different oxygenated compounds; therefore, most researchers study individual model compounds and their reaction mechanisms to understand their conversion in the hydrotreater.

2.3.1 Catalyst Promoters for HDO

In petroleum hydroprocessing technology, metal sulfide catalyst activity is modified through promoting MoS_2-supported Al_2O_3 with cobalt or nickel [84]. Chemical catalyst promoters affect the reaction selectivity through chemical properties such as the type of active site and physical properties such as particle size, pore volume, and catalyst surface area [29]. In short, catalyst promoters influence the performance of chemical catalysts during the HDO process largely through the structure of the catalyst and its active sites [29].

Jacobs et al. [85] investigated a number of supports – such as Al_2O_3, SiO_2, and ZrO_2 – and several promoters including metal cations and noble metals. The promoters are employed in hydrodeoxygenation, which allows easy access to the active sites available for desired reactions. Some noble metal promoters, including Pt and Ru, undergo reduction at lower temperatures compared with cobalt oxides [86, 87]. Also, textural promoters including certain catalyst supports or support modifiers enhance cluster dispersion, improve resistance due to attrition, and improve S tolerance [85]. Romero et al. [27] studied the influence of nickel and cobalt promoters on Mo/Al_2O_3 activity during the hydrodeoxygenation of 2-ethylphenol in a fixed-bed reactor at 7 MPa and 340 °C in the presence of hydrogen sulfide in order to attain sulfidation. In their study, support acidity generated oxygenated compounds and both Ni and Co improved the rate of deoxygenation; however, Ni was found to promote the hydrodeoxygenation pathway, while Co influenced both direct deoxygenation and hydrodeoxygenation, signifying that route selectivity was affected by the catalyst used. Yoosuk et al. [84] studied the activity of Ni–Mo sulfides and found them to be more active than Ni or Mo sulfides alone, with the maximum activity achieved at an atomic ratio of

0.3. Bui et al. [88] determined the influence of Co as a promoter for MoS_2 catalysts in the HDO of guaiacol and reported enhanced activity through improved direct deoxygenation, the major products being methyl-substituted compounds such as toluene, while methylcyclohexene was produced with unpromoted catalysts. Hence, the addition of promoters to sulfided catalysts has an effect on HDO, although their effect on non-sulfided catalysts is still under investigation [40].

2.3.2 Catalyst Supports for HDO

The material used as catalyst support has a great influence on catalyst performance in general and product selectivity in particular during the HDO process. Extensive studies have been performed using sulfide-supported Co–Mo and Ni–Mo catalysts by changing the catalyst's surface chemistry [89–93]. In this regard, modifiers such as potassium and platinum along with supports including silica as well as activated carbon have been used as a replacement for Al_2O_3 supports [90–92]. The results show that catalyst design has an impact on HDO chemistry. For instance, the incorporation of surface O on activated carbon improves the interaction of the support with the active sites, thereby improving activity and selectivity [94, 95].

Pinheiro et al. [95] and Bui et al. [96] investigated sulfided Co–Mo/Al_2O_3 with the aim of coprocessing straight-run gas oil with model bio-oil compounds at a hydrotreating facility and showed the feasibility of treating oxygenates and other hydrocarbon molecules during HDO and hydrodesulfurization. Zakzeski et al. [97] reviewed and reported various studies showing that sulfided Co–Mo and Ni–Mo with Al_2O_3 supports are active at temperatures ranging from 500 to 700 K at ~3–7 MPa, the main reactions involving six-membered ring structures such as phenol and benzene. A few studies have used expensive noble metal-based catalysts, which have considerable advantages over sulfided catalysts such as higher reactivity and energy efficiency during HDO, low S stripping, and flexibility in catalyst design [98, 99]. Lin et al. [100] studied the catalytic HDO of guaiacol on a supported Rh-based catalyst and found it to have excellent HDO activity, irrespective of its ability to saturate benzene rings during hydrodeoxygenation. Moreover, other supported catalysts such as sulfided Co–Mo and Ni–Mo led to aromatics but also formed coke [100]. When sulfided catalysts are used instead of supported noble metals, the hydrogenation activity is considerably improved [40]. For instance, Şenol et al. [101] reported high hydrogenation activity using a Ni–Mo catalyst, which increased the yield of cyclohexane from phenol.

2.3.3 Catalyst Selectivity for HDO

Catalyst selectivity, which depends on the active phase, support, and promoter type, greatly influences the hydrodeoxygenation mechanism of bio-oil. Hence, an ideal HDO catalyst should display higher selectivity toward C—O cleavage, instead of C—C scission, and must show high stability under HDO conditions [102]. Although most existing HDO catalysts result in C—C cleavage, Mo_2C is found to have relatively higher selectivity toward C—O scission with almost negligible C—C cleavage, thereby producing many stable products including unsaturated compounds with C—C bonds [102]. Sitthisa and Resasco [103] studied furfural hydrodeoxygenation over metal catalysts such as Cu, Ni, and Pd and found higher selectivity using Cu/SiO_2 during furfural alcohol formation. These authors also reported an increase in selectivity to decarbonylation with rising temperature. In general, selective hydrodeoxygenation enhances furfural stability in the formation of gasoline derivatives [103]. Other studies have shown Cu catalysts to be highly selective in C—O hydrogenation during aldehyde formation, these catalysts favoring the reduction of the carbonyl group when supported on acidic SiO_2 [52, 104]. Supported Co–Mo catalysts showed a decrease in the selectivity of oxygenated molecules with an increase in temperature [105]. In bimetallic Ni–Mo catalysts, the selectivity to hydrocarbons was higher than that for Mo/Al_2O_3 and Ni/Al_2O_3 catalysts, which could be attributed to a Ni–Mo synergy in such bimetallic catalysts [106]. In addition, the Ni/Al_2O_3 catalyst formed products through a decarboxylation pathway, while the $Ni–Mo/Al_2O_3$ catalyst resulted in products formed via hydrogenation. Another study involving the HDO of phenol on a Ni–Mo amorphous catalyst also showed a synergistic effect from the active sites of Ni and Mo [107]. However, a zeolite-supported Pt catalyst functions as a bifunctional catalyst, wherein molecules formed via hydrogenation led to enhanced activity and selectivity toward monocyclic and bicyclic compounds, which is relevant for phenolics conversion during the upgrading of bio-oils in the hydrodeoxygenation process [108].

2.3.4 Catalyst Deactivation During HDO

A detailed understanding of the deactivation mechanism for chemical catalysts used in the HDO process is essential to design and develop a more effective system and to guarantee a high yield of desired products. The main reasons for catalyst deactivation are catalyst poisoning due to the presence of sulfur in the bio-oil, coking/fouling through carbon deposition, and thermal degradation of supports and active sites due to the high temperature and pressure of the reaction [5, 109]. Shafaghat et al. [29] recently reviewed the deactivation of HDO catalysts. Simply put, catalyst deactivation refers to the loss of catalytic activity in the hydrodeoxygenation process. Such deactivation occurs as a result of catalyst poisoning from the chemisorption of compounds such as S- and/or N-containing molecules onto active sites, fouling from coke deposition of the catalyst surface, thermal disintegration of the catalyst support, vapor formation, undesirable reactions taking place on supports and/or promoters, and pore loss through attrition [109, 110]. However, the most common form of catalyst deactivation is fouling, which results from coke deposition [5]. Catalysts may facilitate the Boudouard reaction, wherein CO is dissociated into carbon on the surface of catalysts. Coke also forms as a result of the decomposition of tungstic acid on the surface active sites, which blocks pores [32]. Coke deposition is a function of the biomass and the reaction conditions. Centeno et al. [90] used sulfided Co–Mo supported on γ-alumina and reported the formation of coke due to feed interaction with the catalyst support. This phenomenon is acidity related through the interaction of the Lewis sites and the donation of protons by the Brønsted sites. Other supports such as activated C and ZrO_2 are comparatively inert, resulting in less coking [111]. Although Ni acts as a promoter to enhance Mo activity, it has the tendency to produce coke at high temperatures – as illustrated by Ardiyanti et al. [111] – and increases in viscosity due to the release of high molecular weight hydrocarbons. For noble metal catalysts, coking is not a major issue, although it leads to sintering. In the case of oil derived from microalgae, S- and N-containing compounds act as impurities. The chemisorption of S compounds is known to be irreversible; hence, S molecules cause the deactivation of HDO catalysts [5, 112].

The composition of lignocellulosic biomass, reflected in bio-oil, also affects catalyst deactivation. For instance, as bio-oil is known to have ~40–50 wt% O-containing molecules, the compounds produced therefrom are unstable and rapidly polymerize to coke [13]. In general, avoiding coke formation requires careful consideration of the catalyst, support, and reaction conditions.

2.4 Research Gaps

The catalytic HDO of biomass-derived bio-oil offers considerable challenges during the production of transportation fuels. There is considerable research on the implementation of continuous systems at the industrial scale informed by techno-economic analyses. However, there are gaps with respect to the use of appropriate catalyst systems (including supports and promoters) to obtain end products with enhanced quality and quantity that meet fuel requirements and standards compared with petroleum derivatives. To understand the use of promoters and the characterization of the intrinsic activity of catalysts, characterization studies in terms of adsorption and infrared (IR) spectroscopy are needed [27]. Advances in the understanding of HDO mechanisms and surface chemistry at an experimental and theoretical scale would help researchers in both industry and academia design catalysts to target desired products [113]. Moreover, supports and promoters play a crucial role in HDO mechanisms, which are affected by process conditions. When Co–Mo-based catalysts on several supports were used for the HDO reaction, it was observed that increase of the temperature lowered the selectivity with respect to oxygenated products, irrespective of the type of support employed [105]. In addition, ash content during a thermochemical process impacts bio-oil quality and quantity; ash that comes in contact with the upgrading catalyst leads to deactivation. Hence, there is a need to study the influence of HDO pathways with varying ash quantities [114]. Other contaminants such as solids, char, and excess water, as well as reactor materials, can cause deposits and corrosion, thereby negatively impacting the catalyst during the HDO process [115, 116].

Catalyst fouling has been observed during HDO and has an impact on the overall economics of the process [117]. The influence of high pressure thermal treatment on the lifetime of catalysts is still unclear, and the development of this area is the key to understanding catalyst stability and selectivity at optimal reaction conditions [114]. Most studies have been done with model compounds that rely on the structure and chemistry of a particular representative molecule; however, real feedstock poses challenges in terms of bulk effects due to complex molecular interactions. The latter are linked with the adsorption of particular molecules on the active sites of catalysts, leading to the inhibition of other molecules that show considerably weaker active site–support interactions [118–120]. Research with respect to catalyst structure includes the development of an isomerization catalyst function as well as process optimization [106]. Desirable catalysts are expected to have sufficient acidity to allow isomerization and minimize cracking, thereby obtaining high product yields. From an economic and environmental perspective, reducing unnecessary H_2 consumption during HDO is vital, as the H_2 consumption is sensitive to catalyst structure [106].

Most of the studies on chemical catalysts for hydrodeoxygenation have focused on catalyst screening tests without considering catalyst deactivation. Catalyst deactivation for the HDO process should receive more attention in order to fast-track the commercialization of bio-oil upgrading via catalytic hydrodeoxygenation. Technological gaps in the HDO of bio-oils pose additional challenges attributed to low bio-oil quality (i.e. high oxygen content, impurities, and coking), these challenges requiring catalyst systems with effective promoters and supports. The continued development of catalysts with significant economic and environmental perspectives would help improve HDO technology for renewable fuel production.

2.5 Conclusions

The hydrodeoxygenation reaction for bio-oil upgrading involves different reaction mechanisms and pathways to form desired products. The reaction mechanism for different model compounds is dependent on the chemical catalysts used during the upgrading process.

In this chapter, we discussed the upgrading of different model compounds for bio-oil and the impact of various catalysts on the HDO mechanism of these model compounds. The selectivity toward various chemicals was discussed, as well as the effect of promoters for different catalysts. The loss of catalyst activity in the HDO process, or catalyst deactivation, was also reviewed, and we conclude that this is an important research gap that needs to be filled for most catalysts.

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References

1 Bykova, M., Ermakov, D.Y., Kaichev, V. et al. (2012). Ni-based sol–gel catalysts as promising systems for crude bio-oil upgrading: guaiacol hydrodeoxygenation study. *Appl. Catal., B* 113: 296–307.

2 Wang, W., Yang, Y., Luo, H. et al. (2011). Amorphous Co–Mo–B catalyst with high activity for the hydrodeoxygenation of bio-oil. *Catal. Commun.* 12 (6): 436–440.

3 Kumar, M., Oyedun, A.O., and Kumar, A. (2018). A review on the current status of various hydrothermal technologies on biomass feedstock. *Renewable Sustainable Energy Rev.* 81 (Part 2): 1742–1770.

4 Oyedun, A.O., Kumar, A., Oestreich, D. et al. (2018). The development of the production cost of oxymethylene ethers as diesel additives from biomass. *Biofuels, Bioprod. Biorefin.* 12 (4): 694–710.

5 Patel, M. and Kumar, A. (2016). Production of renewable diesel through the hydroprocessing of lignocellulosic biomass-derived bio-oil: a review. *Renewable Sustainable Energy Rev.* 58: 1293–1307.

6 Patel, M., Zhang, X., and Kumar, A. (2016). Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: a review. *Renewable Sustainable Energy Rev.* 53: 1486–1499.

7 Zhao, C., Kou, Y., Lemonidou, A.A. et al. (2009). Highly selective catalytic conversion of phenolic bio–oil to alkanes. *Angew. Chem. Int. Ed.* 121 (22): 4047–4050.

8 Kumar, M., Oyedun, A.O., and Kumar, A. (2017). Hydrothermal liquefaction of biomass for the production of diluents for bitumen transport. *Biofuels, Bioprod. Biorefin.* 11: 811–829.

9 Patel, M., Oyedun, A.O., Kumar, A., and Gupta, R. (2018). A techno-economic assessment of renewable diesel and gasoline production from aspen hardwood. *Waste Biomass Valorization*: 1–16.

10 Xiu, S. and Shahbazi, A. (2012). Bio-oil production and upgrading research: a review. *Renewable Sustainable Energy Rev.* 16 (7): 4406–4414.

11 Chheda, J.N., Huber, G.W., and Dumesic, J.A. (2007). Liquid–phase catalytic processing of biomass–derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem. Int. Ed.* 46 (38): 7164–7183.

12 Huber, G.W., Iborra, S., and Corma, A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.* 106 (9): 4044–4098.

13 Furimsky, E. (2000). Catalytic hydrodeoxygenation. *Appl. Catal., A* 199 (2): 147–190.

14 Maggi, R. and Delmon, B. (1994). Characterization and upgrading of bio-oils produced by rapid thermal processing. *Biomass Bioenergy* 7 (1): 245–249.

15 Lee, H., Kim, Y.-M., Lee, I.-G. et al. (2016). Recent advances in the catalytic hydrodeoxygenation of bio-oil. *Korean J. Chem. Eng.* 33 (12): 3299–3315.

16 Chen, T., Wu, C., Liu, R. et al. (2011). Effect of hot vapor filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor. *Bioresour. Technol.* 102 (10): 6178–6185.

17 Jiang, X. and Ellis, N. (2009). Upgrading bio-oil through emulsification with biodiesel: mixture production. *Energy Fuels* 24 (2): 1358–1364.

18 Jiang, X. and Ellis, N. (2010). Upgrading bio-oil through emulsification with biodiesel: thermal stability. *Energy Fuels* 24 (4): 2699–2706.

19 Chen, T., Wu, C., and Liu, R. (2011). Steam reforming of bio-oil from rice husks fast pyrolysis for hydrogen production. *Bioresour. Technol.* 102 (19): 9236–9240.

20 Garcia, L.A., French, R., Czernik, S., and Chornet, E. (2000). Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Appl. Catal., A* 201 (2): 225–239.

21 Hew, K., Tamidi, A., Yusup, S. et al. (2010). Catalytic cracking of bio-oil to organic liquid product (OLP). *Bioresour. Technol.* 101 (22): 8855–8858.

22 Wildschut, J., Melian-Cabrera, I., and Heeres, H. (2010). Catalyst studies on the hydrotreatment of fast pyrolysis oil. *Appl. Catal., B* 99 (1–2): 298–306.

23 Peters, J.E., Carpenter, J.R., and Dayton, D.C. (2015). Anisole and guaiacol hydrodeoxygenation reaction pathways over selected catalysts. *Energy Fuels* 29 (2): 909–916.

24 Akhtar, J. and Amin, N.A.S. (2011). A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable Sustainable Energy Rev.* 15 (3): 1615–1624.

25 Fisk, C.A., Morgan, T., Ji, Y. et al. (2009). Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. *Appl. Catal., A* 358 (2): 150–156.

26 Joshi, N. and Lawal, A. (2012). Hydrodeoxygenation of pyrolysis oil in a microreactor. *Chem. Eng. Sci.* 74: 1–8.

27 Romero, Y., Richard, F., and Brunet, S. (2010). Hydrodeoxygenation of 2-ethylphenol as a model compound of bio-crude over sulfided Mo-based catalysts: promoting effect and reaction mechanism. *Appl. Catal., B* 98 (3–4): 213–223.

28 Romero, Y., Richard, F., Renème, Y., and Brunet, S. (2009). Hydrodeoxygenation of benzofuran and its oxygenated derivatives (2,3-dihydrobenzofuran and 2-ethylphenol) over NiMoP/Al_2O_3 catalyst. *Appl. Catal., A* 353 (1): 46–53.

29 Shafaghat, H., Rezaei, P.S., and Daud, W.M.A.W. (2015). Effective parameters on selective catalytic hydrodeoxygenation of phenolic compounds of pyrolysis bio-oil to high-value hydrocarbons. *RSC Adv.* 5 (126): 103999–104042.

30 Gollakota, A., Kishore, N., and Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable Sustainable Energy Rev.* 81 (Part 1): 1378–1392.

31 Zhang, Q., Chang, J., Wang, T., and Xu, Y. (2007). Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers. Manage.* 48 (1): 87–92.

32 Echeandia, S., Arias, P.L., Barrio, V.L. et al. (2010). Synergy effect in the HDO of phenol over Ni–W catalysts supported on active carbon: effect of tungsten precursors. *Appl. Catal., B* 101 (1–2): 1–12.

33 Gevert, B., Otterstedt, J., and Massoth, F. (1987). Kinetics of the HDO of methyl-substituted phenols. *Appl. Catal.* 31 (1): 119–131.

34 Yang, Y., Gilbert, A., and Xu, C. (2009). Hydrodeoxygenation of bio-crude in supercritical hexane with sulfided CoMo and CoMoP catalysts supported on MgO: a model compound study using phenol. *Appl. Catal., A* 360 (2): 242–249.

35 Laurent, E. and Delmon, B. (1993). Influence of oxygen-, nitrogen-, and sulfur-containing compounds on the hydrodeoxygenation of phenols over sulfided cobalt-molybdenum/.Gamma.-alumina and nickel-molybdenum/.Gamma.-alumina catalysts. *Ind. Eng. Chem. Res.* 32 (11): 2516–2524.

36 Feng, J., Hse, C.Y., Wang, K. et al. (2017). Directional liquefaction of biomass for phenolic compounds and in situ hydrodeoxygenation upgrading of phenolics using bifunctional catalysts. *Energy* 135: 1–13.

37 Wang, L., Zhang, J., Yi, X. et al. (2015). Mesoporous ZSM-5 zeolite-supported Ru nanoparticles as highly efficient catalysts for upgrading phenolic biomolecules. *ACS Catal.* 5 (5): 2727–2734.

38 Zhao, C., He, J., Lemonidou, A.A. et al. (2011). Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *J. Catal.* 280 (1): 8–16.

39 Lee, H., Kim, H., Yu, M.J. et al. (2016). Catalytic hydrodeoxygenation of bio-oil model compounds over Pt/HY catalyst. *Sci. Rep.* 6: 28765.

40 Saidi, M., Samimi, F., Karimipourfard, D. et al. (2014). Upgrading of lignin-derived bio-oils by catalytic hydrodeoxygenation. *Energy Environ. Sci.* 7 (1): 103–129.

41 Bykova, M., Bulavchenko, O., Ermakov, D.Y. et al. (2011). Guaiacol hydrodeoxygenation in the presence of Ni-containing catalysts. *Catal. Ind.* 3 (1): 15–22.

42 Lee, C.R., Yoon, J.S., Suh, Y.-W. et al. (2012). Catalytic roles of metals and supports on hydrodeoxygenation of lignin monomer guaiacol. *Catal. Commun.* 17: 54–58.

43 Loricera, C., Pawelec, B., Infantes-Molina, A. et al. (2011). Hydrogenolysis of anisole over mesoporous sulfided CoMoW/SBA-15 (16) catalysts. *Catal. Today* 172 (1): 103–110.

44 Huuska, M.K. (1986). Effect of catalyst composition on the hydrogenolysis of anisole. *Polyhedron* 5 (1): 233–236.

45 Viljava, T.-R., Komulainen, R., and Krause, A. (2000). Effect of H_2S on the stability of $CoMo/Al_2O_3$ catalysts during hydrodeoxygenation. *Catal. Today* 60 (1–2): 83–92.

46 Shi, D., Arroyo-Ramírez, L., and Vohs, J.M. (2016). The use of bimetallics to control the selectivity for the upgrading of lignin-derived oxygenates: reaction of anisole on Pt and PtZn catalysts. *J. Catal.* 340: 219–226.

47 Massoth, F., Politzer, P., Concha, M. et al. (2006). Catalytic hydrodeoxygenation of methyl-substituted phenols: correlations of kinetic parameters with molecular properties. *J. Phys. Chem. B* 110 (29): 14283–14291.

48 Wan, H., Chaudhari, R.V., and Subramaniam, B. (2012). Catalytic hydroprocessing of *p*-cresol: metal, solvent and mass-transfer effects. *Top. Catal.* 55 (3–4): 129–139.

49 Foster, A.J., Do, P.T., and Lobo, R.F. (2012). The synergy of the support acid function and the metal function in the catalytic hydrodeoxygenation of *m*-cresol. *Top. Catal.* 55 (3–4): 118–128.

50 Keane, M.A. (1997). Gas phase hydrogenation/hydrogenolysis of benzaldehyde and *o*-tolualdehyde over Ni/SiO_2. *J. Mol. Catal. A: Chem.* 118 (2): 261–269.

51 Vannice, M.A. and Poondi, D. (1997). The effect of metal-support interactions on the hydrogenation of benzaldehyde and benzyl alcohol. *J. Catal.* 169 (1): 166–175.

52 Saadi, A., Rassoul, Z., and Bettahar, M. (2000). Gas phase hydrogenation of benzaldehyde over supported copper catalysts. *J. Mol. Catal. A: Chem.* 164 (1–2): 205–216.

53 Haffad, D., Kameswari, U., Bettahar, M.M. et al. (1997). Reduction of benzaldehyde on metal oxides. *J. Catal.* 172 (1): 85–92.

54 Procházková, D., Zámostný, P., Bejblová, M. et al. (2007). Hydrodeoxygenation of aldehydes catalyzed by supported palladium catalysts. *Appl. Catal., A* 332 (1): 56–64.

55 Zhang, W., Zhang, Y., Zhao, L., and Wei, W. (2010). Catalytic activities of NiMo carbide supported on SiO_2 for the hydrodeoxygenation of ethyl benzoate, acetone, and acetaldehyde. *Energy Fuels* 24 (3): 2052–2059.

56 Snell, R.W., Combs, E., and Shanks, B.H. (2010). Aldol condensations using bio-oil model compounds: the role of acid–base bi-functionality. *Top. Catal.* 53 (15): 1248–1253.

57 Chen, L., Zhu, Y., Zheng, H. et al. (2011). Aqueous-phase hydrodeoxygenation of carboxylic acids to alcohols or alkanes over supported Ru catalysts. *J. Mol. Catal. A: Chem.* 351: 217–227.

58 Olcay, H., Xu, L., Xu, Y., and Huber, G.W. (2010). Aqueous-phase hydrogenation of acetic acid over transition metal catalysts. *ChemCatChem* 2 (11): 1420–1424.

59 Serrano-Ruiz, J.C. and Dumesic, J.A. (2009). Catalytic processing of lactic acid over Pt/Nb_2O_5. *ChemSusChem* 2 (6): 581–586.

60 Zhang, Z., Jackson, J.E., and Miller, D.J. (2008). Effect of biogenic fermentation impurities on lactic acid hydrogenation to propylene glycol. *Bioresour. Technol.* 99 (13): 5873–5880.

61 Chen, Y., Miller, D.J., and Jackson, J.E. (2007). Kinetics of aqueous-phase hydrogenation of organic acids and their mixtures over carbon supported ruthenium catalyst. *Ind. Eng. Chem. Res.* 46 (10): 3334–3340.

62 Peng, B., Zhao, C., Mejía-Centeno, I. et al. (2012). Comparison of kinetics and reaction pathways for hydrodeoxygenation of C_3 alcohols on Pt/Al_2O_3. *Catal. Today* 183 (1): 3–9.

63 Wawrzetz, A., Peng, B., Hrabar, A. et al. (2010). Towards understanding the bifunctional hydrodeoxygenation and aqueous phase reforming of glycerol. *J. Catal.* 269 (2): 411–420.

64 Davda, R.R., Shabaker, J.W., Huber, G.W. et al. (2003). Aqueous-phase reforming of ethylene glycol on silica-supported metal catalysts. *Appl. Catal., B* 43 (1): 13–26.

65 Huber, G.W., Chheda, J.N., Barrett, C.J., and Dumesic, J.A. (2005). Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* 308 (5727): 1446–1450.

66 West, R.M., Tucker, M.H., Braden, D.J., and Dumesic, J.A. (2009). Production of alkanes from biomass derived carbohydrates on bi-functional catalysts employing niobium-based supports. *Catal. Commun.* 10 (13): 1743–1746.

67 Wildschut, J., Arentz, J., Rasrendra, C.B. et al. (2009). Catalytic hydrotreatment of fast pyrolysis oil: model studies on reaction pathways for the carbohydrate fraction. *Environ. Prog. Sustainable Energy* 28 (3): 450–460.

68 Verma, R. and Gehlawat, J.K. (1989). Kinetics of hydrogenation of D–glucose to sorbitol. *J. Chem. Technol. Biotechnol.* 46 (4): 295–301.

69 Yan, N., Zhao, C., Luo, C. et al. (2006). One-step conversion of cellobiose to C_6-alcohols using a ruthenium nanocluster catalyst. *J. Am. Chem. Soc.* 128 (27): 8714–8715.

70 Ahmadi, S., Yuan, Z., Rohani, S., and Xu, C. (2016). Effects of nano-structured CoMo catalysts on hydrodeoxygenation of fast pyrolysis oil in supercritical ethanol. *Catal. Today* 269: 182–194.

71 Venderbosch, R., Ardiyanti, A., Wildschut, J. et al. (2010). Stabilization of biomass–derived pyrolysis oils. *J. Chem. Technol. Biotechnol.* 85 (5): 674–686.

72 Cheng, S., Wei, L., Julson, J., and Rabnawaz, M. (2017). Upgrading pyrolysis bio-oil through hydrodeoxygenation (HDO) using non-sulfided Fe–Co/SiO_2 catalyst. *Energy Convers. Manage.* 150: 331–342.

73 Luo, Y., Guda, V.K., Hassan, E.B. et al. (2016). Hydrodeoxygenation of oxidized distilled bio-oil for the production of gasoline fuel type. *Energy Convers. Manage.* 112: 319–327.

74 Luo, Y., Guda, V.K., Steele, P.H., and Wan, H. (2016). Hydrodeoxygenation of oxidized and hydrotreated bio-oils to hydrocarbons in fixed-bed continuous reactor. *BioResources* 11 (2): 4415–4431.

75 Cheng, S., Wei, L., Julson, J. et al. (2017). Hydrocarbon bio-oil production from pyrolysis bio-oil using non-sulfide Ni–Zn/Al_2O_3 catalyst. *Fuel Process. Technol.* 162: 78–86.

76 Cheng, S., Wei, L., Alsowij, M.R. et al. (2018). In situ hydrodeoxygenation upgrading of pine sawdust bio-oil to hydrocarbon biofuel using Pd/C catalyst. *J. Energy Inst.* 91 (2): 163–171.

77 Cheng, S., Wei, L., Julson, J. et al. (2017). Hydrodeoxygenation upgrading of pine sawdust bio-oil using zinc metal with zero valency. *J. Taiwan Inst. Chem. Eng.* 74: 146–153.

78 Huang, Y., Wei, L., Zhao, X. et al. (2016). Upgrading pine sawdust pyrolysis oil to green biofuels by HDO over zinc-assisted Pd/C catalyst. *Energy Convers. Manage.* 115: 8–16.

79 Yang, T., Jie, Y., Li, B. et al. (2016). Catalytic hydrodeoxygenation of crude bio-oil over an unsupported bimetallic dispersed catalyst in supercritical ethanol. *Fuel Process. Technol.* 148: 19–27.

80 Wildschut, J., Mahfud, F.H., Venderbosch, R.H., and Heeres, H.J. (2009). Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Ind. Eng. Chem. Res.* 48 (23): 10324–10334.

81 Oh, S., Hwang, H., Choi, H.S., and Choi, J.W. (2015). The effects of noble metal catalysts on the bio-oil quality during the hydrodeoxygenative upgrading process. *Fuel* 153: 535–543.

82 Oh, S., Choi, H.S., Choi, I.-G., and Choi, J.W. (2017). Evaluation of hydrodeoxygenation reactivity of pyrolysis bio-oil with various Ni-based catalysts for improvement of fuel properties. *RSC Adv.* 7 (25): 15116–15126.

83 Elkasabi, Y., Mullen, C.A., Pighinelli, A.L.M.T., and Boateng, A.A. (2014). Hydrodeoxygenation of fast-pyrolysis bio-oils from various feedstocks using carbon-supported catalysts. *Fuel Process. Technol.* 123: 11–18.

84 Yoosuk, B., Tumnantong, D., and Prasassarakich, P. (2012). Amorphous unsupported Ni–Mo sulfide prepared by one step hydrothermal method for phenol hydrodeoxygenation. *Fuel* 91 (1): 246–252.

85 Jacobs, G., Das, T.K., Zhang, Y. et al. (2002). Fischer–Tropsch synthesis: support, loading, and promoter effects on the reducibility of cobalt catalysts. *Appl. Catal., A* 233 (1): 263–281.

86 Iglesia, E., Soled, S.L., Fiato, R.A., and Via, G.H. (1993). Bimetallic synergy in cobalt ruthenium Fischer-Tropsch synthesis catalysts. *J. Catal.* 143 (2): 345–368.

87 Bruce, L.A., Hoang, M., Hughes, A.E., and Turney, T.W. (1993). Ruthenium promotion of Fischer–Tropsch synthesis over coprecipitated cobalt/ceria catalysts. *Appl. Catal., A* 100 (1): 51–67.

88 Bui, V.N., Laurenti, D., Afanasiev, P., and Geantet, C. (2011). Hydrodeoxygenation of guaiacol with CoMo catalysts. Part I: promoting effect of cobalt on HDO selectivity and activity. *Appl. Catal., B* 101 (3–4): 239–245.

89 Laurent, E. and Delmon, B. (1994). Study of the hydrodeoxygenation of carbonyl, carylic and guaiacyl groups over sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts: I. Catalytic reaction schemes. *Appl. Catal., A* 109 (1): 77–96.

90 Centeno, A., Laurent, E., and Delmon, B. (1995). Influence of the support of CoMo sulfide catalysts and of the addition of potassium and platinum on the catalytic performances for the hydrodeoxygenation of carbonyl, carboxyl, and guaiacol-type molecules. *J. Catal.* 154 (2): 288–298.

91 Ferrari, M., Maggi, R., Delmon, B., and Grange, P. (2001). Influences of the hydrogen sulfide partial pressure and of a nitrogen compound on the hydrodeoxygenation activity of a CoMo/carbon catalyst. *J. Catal.* 198 (1): 47–55.

92 Ferrari, M., Delmon, B., and Grange, P. (2002). Influence of the impregnation order of molybdenum and cobalt in carbon-supported catalysts for hydrodeoxygenation reactions. *Carbon* 40 (4): 497–511.

93 Ferrari, M., Lahousse, C., Centeno, A. et al. (1998). Influence of the impregnation order of molybdenum and cobalt in carbon supported catalysts for hydrodeoxygenation reactions. *Stud. Surf. Sci. Catal.* 118: 505–515.

94 De la Puente, G., Gil, A., Pis, J., and Grange, P. (1999). Effects of support surface chemistry in hydrodeoxygenation reactions over CoMo/activated carbon sulfided catalysts. *Langmuir* 15 (18): 5800–5806.

95 Pinheiro, A., Hudebine, D., Dupassieux, N., and Geantet, C. (2009). Impact of oxygenated compounds from lignocellulosic biomass pyrolysis oils on gas oil hydrotreatment. *Energy Fuels* 23 (2): 1007–1014.

96 Bui, V.N., Toussaint, G., Laurenti, D. et al. (2009). Co-processing of pyrolysis bio oils and gas oil for new generation of bio-fuels: hydrodeoxygenation of guaïacol and SRGO mixed feed. *Catal. Today* 143 (1–2): 172–178.

97 Zakzeski, J., Bruijnincx, P.C., Jongerius, A.L., and Weckhuysen, B.M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* 110 (6): 3552–3599.

98 Elliott, D.C. and Hart, T.R. (2008). Catalytic hydroprocessing of chemical models for bio-oil. *Energy Fuels* 23 (2): 631–637.

99 Gutierrez, A., Kaila, R., Honkela, M. et al. (2009). Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catal. Today* 147 (3–4): 239–246.

100 Lin, Y.-C., Li, C.-L., Wan, H.-P. et al. (2011). Catalytic hydrodeoxygenation of guaiacol on Rh-based and sulfided CoMo and NiMo catalysts. *Energy Fuels* 25 (3): 890–896.

101 Şenol, O., Ryymin, E.-M., Viljava, T.-R., and Krause, A. (2007). Effect of hydrogen sulphide on the hydrodeoxygenation of aromatic and aliphatic oxygenates on sulphided catalysts. *J. Mol. Catal. A: Chem.* 277 (1–2): 107–112.

102 Ren, H., Yu, W., Salciccioli, M. et al. (2013). Selective hydrodeoxygenation of biomass–derived oxygenates to unsaturated hydrocarbons using molybdenum carbide catalysts. *ChemSusChem* 6 (5): 798–801.

103 Sitthisa, S. and Resasco, D.E. (2011). Hydrodeoxygenation of furfural over supported metal catalysts: a comparative study of Cu, Pd and Ni. *Catal. Lett.* 141 (6): 784–791.

104 Chambers, A., Jackson, S.D., Stirling, D., and Webb, G. (1997). Selective hydrogenation of cinnamaldehyde over supported copper catalysts. *J. Catal.* 168 (2): 301–314.

105 Kubička, D., Šimáček, P., and Žilková, N. (2009). Transformation of vegetable oils into hydrocarbons over mesoporous-alumina-supported CoMo catalysts. *Top. Catal.* 52 (1–2): 161–168.

106 Choudhary, T.V. and Phillips, C.B. (2011). Renewable fuels via catalytic hydrodeoxygenation. *Appl. Catal., A* 397 (1): 1–12.

107 Wang, W.-Y., Yang, Y.-Q., Bao, J.-G., and Luo, H.-A. (2009). Characterization and catalytic properties of Ni–Mo–B amorphous catalysts for phenol hydrodeoxygenation. *Catal. Commun.* 11 (2): 100–105.

108 Hong, D.-Y., Miller, S.J., Agrawal, P.K., and Jones, C.W. (2010). Hydrodeoxygenation and coupling of aqueous phenolics over bifunctional zeolite-supported metal catalysts. *Chem. Commun.* 46 (7): 1038–1040.

109 Bartholomew, C.H. (2001). Mechanisms of catalyst deactivation. *Appl. Catal., A* 212 (1): 17–60.

110 Forzatti, P. and Lietti, L. (1999). Catalyst deactivation. *Catal. Today* 52 (2–3): 165–181.

111 Ardiyanti, A., Khromova, S., Venderbosch, R. et al. (2012). Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni–Cu catalysts on various supports. *Appl. Catal., A* 449: 121–130.

112 Ardiyanti, A., Gutierrez, A., Honkela, M. et al. (2011). Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono-and bimetallic (Pt, Pd, Rh) catalysts. *Appl. Catal., A* 407 (1–2): 56–66.

113 Vlachos, D.G. and Caratzoulas, S. (2010). The roles of catalysis and reaction engineering in overcoming the energy and the environment crisis. *Chem. Eng. Sci.* 65 (1): 18–29.

114 Zacher, A.H., Olarte, M.V., Santosa, D.M. et al. (2014). A review and perspective of recent bio-oil hydrotreating research. *Green Chem.* 16 (2): 491–515.

115 Diebold, J.P. (1999). *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils*. Golden, CO: National Renewable Energy Lab.

116 Elliott, D.C. (1994). Water, alkali and char in flash pyrolysis oils. *Biomass Bioenergy* 7 (1–6): 179–185.

117 Elliott, D.C., Lee, S.-J., and Hart, T.R. (2012). Stabilization of Fast Pyrolysis Oil: Post Processing. Final Report, Pacific Northwest National Laboratory (PNNL), Richland, WA, PNNL-21549.

118 Girgis, M.J. and Gates, B.C. (1991). Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Ind. Eng. Chem. Res.* 30 (9): 2021–2058.

119 Choudhary, T.V. (2007). Structure – reactivity – mechanistic considerations in heavy oil desulfurization. *Ind. Eng. Chem. Res.* 46 (25): 8363–8370.

120 Choudhary, T.V., Parrott, S., and Johnson, B. (2008). Understanding the hydrodenitrogenation chemistry of heavy oils. *Catal. Commun.* 9 (9): 1853–1857.