Production of Renewable Diesel through the Hydroprocessing of Lignocellulosic Biomass-derived Bio-oil: A Review

Madhumita Patel and Amit Kumar[1]*

4-9 Mechanical Engineering Building, Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G8

Abstract

Due to the scarcity of fossil fuels and to population increases, there is an urgent need for renewable energy sources that can replace petroleum-derived fuels. Lignocellulosic biomass, a renewable resource, can be converted to bio-oil by fast pyrolysis and further upgraded to renewable diesel through hydroprocessing. The upgrading of oil by fast pyrolosis is the main focus of this paper. Bio-oil has a higher energy density and heating value than biomass, but it cannot be used in place of petro-diesel as it is highly unstable, polar, and immiscible with hydrocarbons. Thus upgrading is necessary as it removes oxygen-containing compounds from bio-oil. Hydroprocessing was chosen for this review paper as a the method of upgrading bio-oil because there are hydrotreating units in place in refineries. To upgrade bio-oil, hydrodeoxygenation (HDO) in the presence of both a catalyst and hydrogen can replace hydrodesulfurization (the removal of sulfur compunds from crude oil). A sulfided NiMo/CoMo catalyst supported on gamma alumina is used as a benchmark catalyst for a hydrodesulfurization reaction in refineries and is considered the reference catalyst for HDO in the production of renewable diesel. The properties of renewable diesel made through hydroprocessing are similar

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[1] Corresponding Author. Tel.: +1-780-492-7797.

E-mail address: Amit.Kumar@ualberta.ca (A. Kumar).

to those of petro-diesel. Catalyst deactivation and techno-economic assessments of the whole pathway are areas that need more attention before renewable diesel can be commercialized. This review paper concentrates on the reaction mechanism in bio-oil upgrading, process parameters, and the limitations of hydroprocessing technology. This paper will be helpful for further modelling of techno-economic analysis in renewable diesel production from lignocellulosic biomass.

Keywords: Bio-oil; hydroprocessing; hydrodeoxygenation; catalyst; lignocellulosic biomass

Abbreviations

HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HDN	Hydrodenitrogenation
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
C	Carbon
S	Sulfur
Co	Cobalt
Mo	Molybdenum
ZrO_2	Zirconium oxide
CeO_2	Cerium oxide
TiO_2	Titanium oxide
GHG	Greenhouse gas emission

1. Introduction

Increasing environmental concerns and the depletion of fossil fuels are the main factors behind the urgent need for renewable fuels. Canada's Federal Renewable Fuels Regulations requires that at least 5% renewable fuel (based on the volume of petroleum based fuel) [1]. Biomass is a renewable product that, when processed and upgraded to a transportation fuel, can be used in place of petroleum-based liquid fuels.

Ethanol, biodiesel, and renewable diesel are the three renewable fuels that satisfy current regulations and policies of many jurisdictions [2, 3]. Ethanol is produced from grains and thus is considered a first-generation biofuel. Ethanol, produced by the fermentation, is also considered as a clean biofuel and a gasoline alternate. Extensive research has been done on ethanol production from biomass over the last two decades [4-8]. A major challenge in the use of first generation liquid biofuels is that they are also used as food [9].

Biodiesel is produced from the transesterification of vegetable oils produced from grains and has been proven to be a promising renewable fuel with the potential to reduce GHGs significantly of [2]. Biodiesel produces less pollution than petro-diesel and biodegradable; it has no sulfur, which increases the life of the catalytic converter; it is miscibile with hydrocarbons and nontoxics; and it has lubricating properties, which can increase the life of diesel engines [10]. But there are some drawbacks to biodiesel that need specific attention. Biodiesel performs poorly in cold temperatures [10, 11]. In addition, biodiesel alone is not sufficient to fill consumer demand for clean energy.

Biodiesel production technologies and technical aspects of production have been studied extensively [12-16]. Ma et al. [13] have investigated different biodiesel production technologies from vegetable oils, animal fats, and waste vegetable oils. They have also explored the mechanism and kinetics of transesterification. The effects of different reaction parameters (reaction conditions, molar ratio of alcohol to oil, types of alcohol, etc.) have been studied by Meher et al [12]. Biodiesel production from microalgae is discussed in detail by Meta et al. [14], who researched the cultivation, harvesting, and processing of microalgae. Leung et al. [15] reviewed various approaches of reducing fatty acids in the raw oil and refinement of crude biodiesel by controlling different reaction parameters such as reaction time, reaction temperature, and catalyst concentration during the transesterification.

The third option, a renewable diesel derived through hydrodeoxygenation (HDO), also known as "green diesel" and "second generation biodiesel," is produced from the catalytic hydroprocessing of vegetable oil from grains and has been used interchangeably with petro-diesel [17]. Several governments have mandated that diesel from renewable sources should be blended with conventional diesel (e.g., the Canadian government has mandated that all diesel fuel should have an average of 2% renewable diesel [18]). Renewable diesel is composed primarily of long-chain

alkanes and short- and branched-chain alkane and negligible aromatics. The cetane number is high for long-chain alkanes and low for short- and branched-chain alkanes. For cold countries like Canada, shorter alkanes and isomerized compounds are preferred over long-chain alkanes due to their high cloud point, which allows the fuel to flow more easily [17]. Table 1 shows a comparison of biodiesel, renewable diesel, and petro-diesel [17, 19]. Some properties of renewable diesel are similar to and some are superior to petro-diesel. The low aromatic content of renewable diesel leads to cleaner combustion and better cold-flow properties than biodiesel.

Table 1: Comparison between biodiesel, renewable diesel, and petro-diesel [17, 19-23]

Property	Biodiesel	Renewable diesel	Petro-diesel
Density (g/ml)	0.885-0.9	0.77-0.83	0.85
Sulfur (ppmwt)	0 - 0.012	<10	12
Cetane number	45 -72.7	80 – 99	54.57
Flash point (^{0}C)	96-188	68-120	52-136
Net heating value(MJ/kg)	37.1-40.4	42-44	42-45
CFPP (^{0}C)	(-13)-15	>20	-6
Cloud point (^{0}C)	(-3) – 17	(-25) – 30	-5
Pour point (^{0}C)	(-15) -16	(-3) – 29	-21
Kinematic viscosity (mm^2/sec)	1.9 - 6.0 (@ 40^{0}C)	1.9 - 4.1(@ 40 ^{0}C)	1.9 - 4.1(@ 40 ^{0}C)

There have been few studies done on the production of renewable diesel from hydroprocessing technology using lignocellulosic biomass-based intermediates. A number of different catalytic technologies, such as fluid catalytic cracking, gasification with the Fischer-Tropsch process, and high pressure temperature treatment, are used to upgrade bio-oil to renewable diesel [24-27]. Fluid catalytic cracking is a process of upgrading heavy, larger, and complex hydrocarbon molecules to diesel and gasoline in the presence of a catalytic agent. Gasification through the Fischer-Tropsch process involves converting syngas to liquid hydrocarons mostly in presence of transition metal catalysts. High pressure temperature treatment is a non-catalytic means of upgrading bio-oil at high temperatures (> 250 ^{0}C) and pressure (around 250 bar). Coke formation at the time of the reaction is the main disadvantage of the catalytic cracking process, and high pressure temperature treatment and the formation of large amounts of gaseous components are

drawbacks of the gasification process [27-29] . Hence, among these technologies, hydroprocessing was chosen for this review paper for bio-oil upgrading. The detailed understanding of different pathways for the conversion of model compounds/fast pyrolysis oil to renewable diesel and the effect of different process parameters on hydroprocessing need to be addressed. The overall objective of this paper to conduct a review of renewable diesel production from lignocellulosic biomass-based intermediates, i.e. bio-oil. The specific objectives are:

- to review lignocellulosic biomass feedstocks used in renewable diesel production;
- to review bio-oil production as an intermediate for production of renewable diesel;
- to review and summarize the reaction mechanism during the hydrodeoxygenation of bio-oil and model compounds;
- to review and discuss different operating parameters, such as the catalyst, temperature, feedstock, and catalyst deactivation, that have a significant role during HDO;
- to review the status of renewable diesel production around the world; and
- to identify the gaps in knowledge relevant to the development of large-scale commercialization of renewable diesel.

2. Biomass feedstock

Biomass is a generic term for organic hydrocarbon materials, primarily carbon, hydrogen, oxygen, nitrogen, and sulfur, though sulfur and nitrogen are present only in insignificant amounts. Biomass contains some inorganic impurities such as ash, whose concentration varies from species to species. Ash concentration is around 5-10% by weight in agricultural residues and much less in softwood, approximately 1% by wt [30, 31].

Figure 1 shows biomass feedstock classifications. These feedstock are divided into two categories depending on their end use: food and non-food/lignocellulosic biomass feedstock.

Biomass food feedstocks are classified into two categories, starch sugar crops and oil seed vegetable plants. The major starch sugar crops are rice, wheat, maize, root vegetables (potatoes and cassava), sugarcane, and barley. This feedstock contains primarily starchand is made up of a large number of glucose units. Bioethanol and biodiesel are formed from starch sugar crops through fermentation and transesterification, respectively, using different catalysts. Oil seed vegetable plants, the other food category, include coconut, corn, cottonseed, olive, palm,

rapeseed, sunflower, sesame seed, soybean, mustard, canola, camellia, jatropha, and pine. The vegetable oil is extracted through solvent extraction process.. Feedstocks differ from one country to the next depending on climate and soil conditions [32].

Biofuels from first-generation biomass (food feedstock) are limited in their ability to achieve government targets for the replacement of fossil fuels. Increasing concern about these issues has led to an increase in the interest in developing biofuels from non-food biomass.

Non-food biomass, also known as lignocellulosic or second-generation biomass, is emerging as a source for biofuel production that can replace refinery crude oil as a feedstocks for the production of transportation fuels. In this review paper, the focus is on lignocellulosic biomass feedstock due to its advantages over other feedstocks. Non-food biomass feedstock can be divided into three broad categories, shown in Figure 1. They are mainly agricultural, forest, and municipal waste feedstock. Lignocellulosic biomass is the non-edible portion of major food crops that is currently underused and could be used for biofuel production. Agricultural feedstock has four categories ,shown in Figure 1. Straw and vegetation waste include bagasse, vegetable wastes, and residues from the production of cereals. Energy crops such as willow, poplar, and switchgrass are grown specifically for energy production. They have a high yield per unit area compared to conventional crops and trees [33] and are commonly used for the production of biofuels. The moisture content of agricultural residues is between 10 and 20 wt%, which is an advantage for the fast pyrolysis process [34]. Forest biomass includes whole tree, forest residue, and wood waste. Forest residues consist of tree branches and tops, and wood waste includes saw mill wastes and rotten and dead trees. These types of feedstock are always available and accesible for bio-oil production.

As mentioned, municipal wastes can be used to produce biofuels [35]. Waste from the paper industry accounts for up to 40% of all the waste in the United States that has biodegradable components [36]. Municipal waste also includes everyday items such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, etc. Around 80% of these wastes are biodegradable and could be considered an alternate sustainable source of biofuels [36, 37]. The main advantage of using municipal waste as feedstock for biofuel production is because in most jurisdictions, municipal waste is landfilled, its use will save land because the amount of material sent to landfills will decrease.
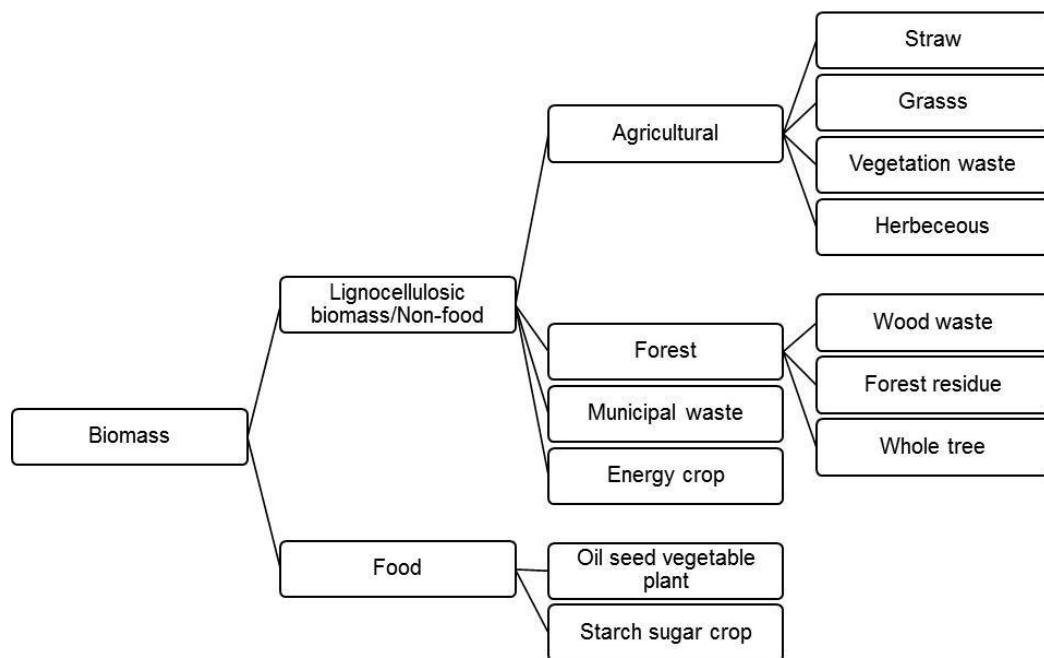
Figure 1: Classification of biomass [30, 33, 38, 39]

Cellulose, hemicelluloses, and lignin are the three important organic compounds in biomass. Their weight percentages are in the ranges of approximately 30-50, 20-40, and 10-20, respectively [33, 40-44].. Feedstock is categorized based on the proportion of cellulose and lignin. For example, hardwood consists of tightly bound cellulose with low concentrations of lignin; softwood is the opposite. Table 2 summarizes the composition of woody biomass [45].

Table 2: Composition of woody biomass [45, 46]

Biomass	Cellulose	Hemicellulose	Lignin	Extractives
Softwood	42% +/- 2%	27% +/- 2%	28% +/- 3%	3% +/- 2%
Hardwood	45% +/- 2%	30% +/- 2%	20% +/- 4%	5% +/- 3%
Sawdust	45.2%	20%	24.3%	9%

3. Bio-oil

Several thermal, mechanical, and biological methods are used to convert lignocellulosic biomass to more valuable products. Renewable diesel production from lignocellulosic biomass requires converting lignocellulosic biomass to an intermediate known as bio-oil. Bio-oil can be produced through fast pyrolysis. Its production depends significantly on the feed type, moisture content, temperature, residence time, and ash content. In this process, biomass is heated in a pyrolyzer in absence of oxygen to 450-550 ^{0}C at an atmospheric pressure for a residence time of < 2s [47-52]. As residence time is very short, liquid yield is high and there is low ash content in the product. A product analysis found that liquid yield is around 75-80 wt% and the rest are gaseous components and char, which is a solid [47]. The bio-oil obtained from this process has a higher heating value than raw biomass and can be directly used as an intermediate to convert lignocellulosic biomass into a transportation fuel [53, 54].

In general, bio-oil is a viscous, polar, dark-brown, free-flowing liquid. It is a complex mixture of different organic compounds derived from the thermal decomposition of cellulose, hemicellulose, and lignin. Bio-oil mainly consists of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, nitrogen compounds, and a large proportion (20-30wt%) of lignin-derived oligomers [37, 55-57]. Table 3 shows the major organic compounds in bio-oil that result from the fast pyrolysis of lignocellulosic biomass, determined by gas chromatography-mass spectroscopy equipment. As biomass contains a significant amount of moisture, the bio-oil derived from this process carries significant amounts of water (around 30 wt%), which leads to phase separation, either aqueous or organic oil, in bio-oil. All organic compounds are present in the organic oil phase, whose density is more than that of water and gives bio-oil high viscosity. The acidity of bio-oil promotes a condensation reaction that accelerates aging and a declination of bio-oil properties and makes the bio-oil immiscible with petro-fuels. Therefore bio-oil should be upgraded so that it can directly be used as a fuel or mixed with crude oil. Moreover, bio-oil is highly unstable because of the presence of unsaturated carbon, which is active during polymerization and condensation [58-62].

Table 3: Major organic compounds in crude bio-oils [63-66]

Bio-oil	Area%[1] (Area of analyte/total area of all peaks)
Acids	13.7-15.6
acetic acid palmitic acid 2-methyl, propanoic acid hexanoic acid, 3-hydroxy-, methyl-	
Esters	2-5
ethyl acetate 2-oxopropyl acetate ethyl orthoformate	
Phenols	10-18
phenol phenol, 4-methyl- phenol, 4-ethyl- 1,2-benzenediol 1,2-benzenediol, 4-methyl- phenol, 2-methoxy-4-(1-propenyl)- phenol, 2,6-dimethoxy- phenol, 2,6-dimethoxy-4-(2-propeny) phenol, 4-ethyl-2-methoxy- 2-methoxy-4-vinylphenol phenol, 2-methoxy-4-methyl-	
Aldehydes	3-9
furfural vanillin 4-methyl benzaldehyde	

4-hydroxy-3-methoxy benzaldehyde	
Ketones	8-10
1-hydroxypropan-2-one	
1-hydroxybutan-2-one	
butan-2-one	
3-methylfuran-2(3H)-one	
4-methylfuran-2(5H)-one	
furan-2(5H)-one	
ethanone, 1-(4-hydroxy-3-methoxyph 1.93	
1,2-cyclopentanedione, 3-methyl-	
2-methylcyclopent-2-enone	
2-hydroxy-3-methylcyclopent-2-enone 3.38	
4-(4-hydroxy-3-methoxyphenyl)	

[1]Area% refers to the weight percentage of the dilute in the solution

The heating value of bio-oil is 16-20 MJ/kg [46, 67, 68], which is significantly higher than that of raw biomass but lower than that of crude oil, whose value is around 35-40 MJ/kg [19, 21]. The low heating value of bio-oil compared to crude oil is due to the presence of high molecular-weight oxygenated compounds. The highly unstable nature of bio-oil can be attributed to its deteriorating heating values. This deterioration occurs over time due to polymerization and condensation between the oxygen compounds themselves.

The catalyst has a significant effect on the fast pyrolysis process. According to Wang et al. [69], bio-oil from a fast catalytic pyrolysis process in the presence of a mesoporous ZSM-5 zeolite catalyst was more stable than bio-oil from a non-catalytic pyrolysis process. Generally the oxygen content in non-catalytic bio-oil is around 40-50 wt%, but in the catalytic pyrolysis process, the oxygen content could be reduced significantly depending on the catalyst type and feed condition [69]. Wang et al. [69] found that oxygen can be removed partially or fully by the catalytic pyrolysis. However, the catalytic pyrolysis is uneconomical due to the high cost of catalysts.

Table 4 shows the elemental composition and physical properties of bio-oil derived from different lignocellulosic biomass.

Table 4: Elemental composition and physical properties of bio-oil

Feedstock for bio-oil	C	H	O	N	S	HHV (MJ/kg)	pH	Moisture content	Reference
beech wood	51.1	7.3	41.6			20.3	3		[67]
typical wood	55-58	5.5-7	35-40	0-0.2		16-19	3	15-30	[68]
pine wood	40.1	7.6	52.1	0.1					[70]
rice husk	39.92	8.15	51.29	0.61	0.03	16.5	3	28	[71]
beech wood	58.6	6.2	35.2					27.8	[61]
pine sawdust	38.8	7.7	53.4	0.09	0.02			26	[72]
eucalyptus	44.8	7.2	48.1	0.2					[59]
hybrid poplar	46.7	7.6	45.7	0.2	0.03			18.9	[59]
whole tree poplar	49.06	6.3	43.6	1			2	18.7	[73]
white spruce	49.6	6.4	43.1	0.2			2	22.4	[73]
red maple	48.5	6.1					2	18	
poplar	49.5	6.05	44.4	0.07			2	18.6	
sawdust	60.4	6.9	31.8	0.9		21.3			[46]

Bio-oil can be stored at a refinery before transportion. There are two ways to store oil. For short periods, it can be stored in a stainless steel or olefin polymer vessel that does not get corroded by the bio-oil [52]. For long periods, the oil is blended with methanol (10% by weight), which prevents polymerization and condensation [74].

4. Hydroprocessing to convert bio-oil into renewable diesel

4.1 Hydroprocessing

Hydroprocessing is a generic term for a combination of two technologies, hydrocracking and hydrotreating [58]. Figure 2 shows the general flow for the hydroprocessing process. Through hydrocracking and hydrotreating, bio-oil is processed into a product with properties similar to those of petroleum fuel. In hydroprocessing technology, feed is initially processed in a hydrotreating unit and then it is put into a hydrocracker unit [58]. The hydrotreating unit is a primary pretreatment unit that hydrogenates unsaturated hydrocarbons and removes heteroatoms from the feedstocks. The basic reactions in the hydrotreater are hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrodearomatization (HDA). In biomass-derived oil, oxygenates are the main components (sulfur and nitrogen compounds are found in insignificant quantities). Therefore, HDO is critical in ther removal of the oxygen heteroatom from the feedstock. Hydrodealkylation, hydrocracking, isomerization of alkanes, and hydrodecyclization are key reactions that occur simultaneously in the hydrocracking unit. A few more reactions occur in the hydrotreater and hydrocracker without hydrogen: decarboxylation, decarbonylation, the water-gas shift reaction, methanation, and coke formation [75]. The general reactions involved in hydroprocessing are summarized in Table 5.
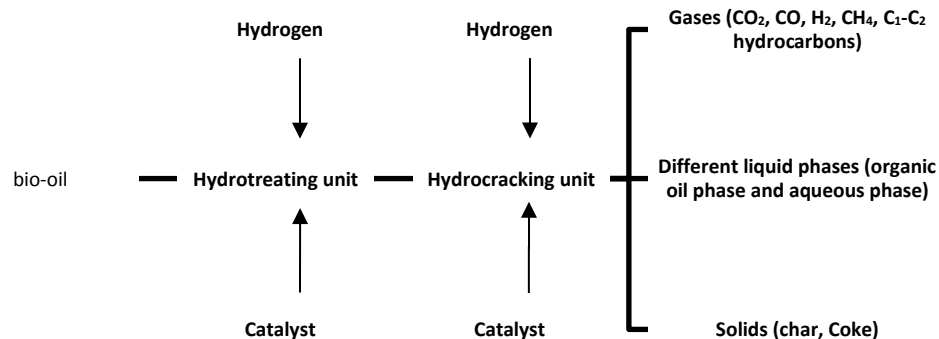
Figure 2: General flow diagram for hydroprocessing

Oxygen, nitrogen, and sulfur are removed in the hydrotreater in the form of water, ammonia, and hydrogen sulfide, respectively. These reactions take place in the presence of hydrogen and a catalyst. The main component of the hydrotreating unit is the reactor, which consists of a high-

pressure reactor vessel, the proprietary catalyst, and internal technology. The pressure range is considerable, between 50-200 bars, and the temperature varies from 300-400 °C [59, 60]. Different researchers have used different kinds of reactors. Tang et al. reported that hydrotreating is an efficient way to convert aldehydes and unsaturated compounds into more stable compounds by removing oxygen atoms from the compounds [76]. Through this process, an unstable form of bio-oil is converted to a stable one through the removal of unsaturated oxygen compounds [61]. Depending on the temperature, the hydrotreating process is considered to be high severity or low severity [77]. High-severity hydrotreating is complete hydrodeoxygenation and low-severity hydrotreating is partial hydrodeoxygenation.

Table 5: Reactions involved in hydroprocessing

Hydrotreating unit (removal of heteroatom)
███████████████████████████████████
Hydrocracking unit
███████████████████████████████████
Other simultaneous reactions
███████████████████████████████████

As the moisture content of bio-oil is high, the liquid product derived from hydrotreating unit has two phases: the aqueous phase and the oil phase [78]. Depending on the severity of

hydrotreatment, the treated oil from the hydrotreating unit is free of heteroatoms, but it has non-polar, high-molecular weight organic compounds in the oil phase. Therefore the oil is further processed in a hydrocracking unit in the presence of a catalyst and hydrogen at high temperature and pressure conditions. As the name suggests, higher molecular compounds break into smaller molecular weight compounds through hydrodealkylation, hydrocracking, and isomerization (see Table 5). During hydroalkylation, the branched alkane is removed from the main alkane chain by the addition of hydrogen, thus forming two individual alkane molecules whose molecular weights are significantly lower than the original alkane molecules. During a hydrocracking reaction, one long-chain alkane is broken down into two small molecular weight alkanes in the presence of hydrogen. During isomerization, the branched alkanes, which are formed during the isomerization reaction, have the same carbon atoms as the reactant.

Among other reactions, decarboxylation, decarbonylation, and the water-gas shift reaction are desired, whereas methanation and coke formation are undesired [75]. Reaction mechanisms for the hydroprocessing of bio-oil and model compounds involve different reactions depending on the catalyst and operating conditions and are discussed in the next section of this paper.

4.2 Typical reaction pathways during hydrodeoxygenation

4.2.1 Bio-oil

Venderbosch et al. [27] developed a reaction network for the hydroprocessing of bio-oil using a Ru/C catalyst; the network is shown in Figure 3. Ardiyanti et al. [70] studied bio-oil on non-sulfide bimetallic Ni-Cu catalysts with an alumina support and deduced that the reaction network of this bio-oil was the same as that described by Venderbosch et al.[27]. The authors consider two modes for bio-oil: catalytic hydrogenation (hydroprocessing) and thermal, non-catalytic repolymerization. Because hydroprocessing takes place at high temperature and pressure conditions, repolymerization leads to the formation of soluble, higher molecular weight fragments in the absence of a catalyst, which, following further condensation reactions, gives char. This is undesired and should be reduced as much as possible. The hydrogenation of bio-oil takes place in the presence of a catalyst and hydrogen, which should be dominating in the mechanism. In the initial phase of hydrotreating, the unstable, polar, and highly viscous bio-oil is converted to stabilized oil by hydrogenation at a temperature greater than 80 ^{0}C. Then

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hydrodeoxygenation is the dominating reaction in the hydrotreater, when the temperature is increased to more than 250 ^{0}C and the pressure is maintained at 200 bars. The liquid product from the hydrotreater contains non-polar, high molecular weight fragments in the oil phase associated with an aqueous phase. After that, in the hydrocracker, non-polar, high molecular weight compounds along with the aqueous phase are converted into lower molecular weight fragments at high temperature and pressure conditions. The resulting blend from the hydrocracker has properties similar to petro-diesel. This is the generic reaction mechanism for the hydroprocessing of bio-oil [27].
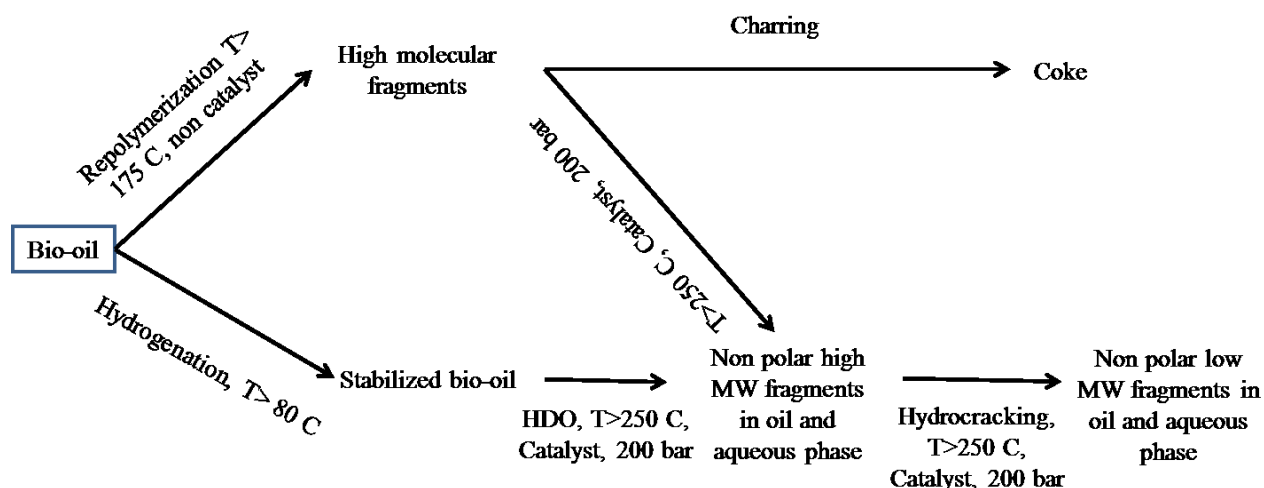
Figure 3: Reaction mechanism for the hydroprocessing of bio-oil [27]

4.2.2 Guaiacol

Guaiacol is considered another important model compound of bio-oil obtained from lignin fractions of lignocellulosic biomass fast pyrolysis. Guaiacol contains two oxygen molecules, hydroxyl (C-OH) and methoxy (C-OCH$_3$) groups. There are three positions of the methoxy group in guaiacol molecules: para, meta, and ortho.

The reaction mechanism for the conversion of guaiacol to hydrocarbons on different catalysts has been studied by several researchers [62, 79-83]. The general reaction scheme of guaiacol conversion to hydrocarbons is summarized in Figure 4. The conversion of guaiacol to phenol takes place in two different paths. The first is the direct conversion of guaiacol to phenol by demethoxylation (elimination of –OCH$_3$) without any intermediary. The second path consists of

two consecutive steps: the conversion of guaiacol to catechol by demethylation and the conversion of catechol to phenol by hydrogenolysis. Phenol then directly forms benzene by hydrodeoxygenation or follows subsequent hydrogenation of the aromatic ring to give cyclohexane and methylpentane as the final products. Guaiacol and catechol have a tendency to form coke due to polymerization depending on the acidity of the catalysts, but the detrimental effect of these molecules can be avoided by proper selection of a catalyst system. The reaction mechanism varies for different catalyst systems mainly depending on the metals and support used.
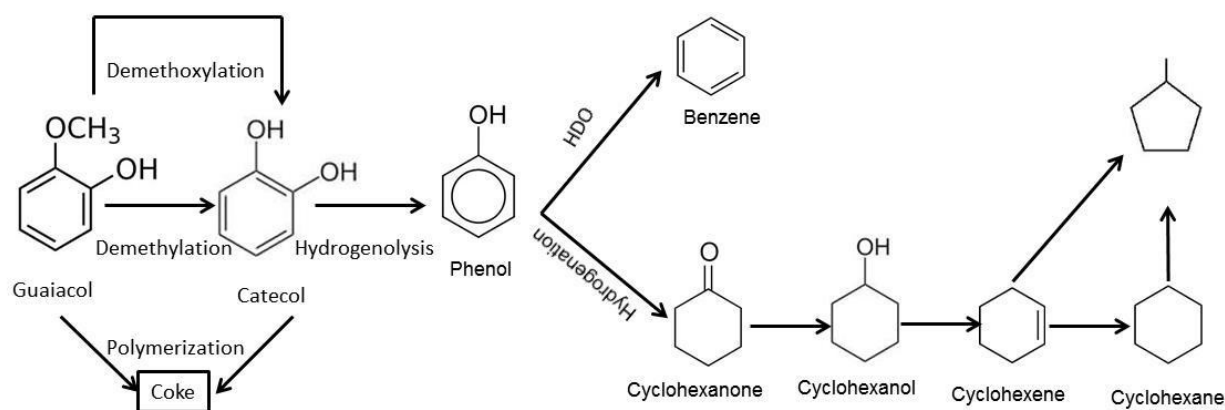

Figure 4: Reaction mechanism for guaiacol [62, 79-83].

4.2.3 Phenol

Bio-oil derived from the fast pyrolysis process contains around 10-20 wt% phenol and phenol-derived compounds. Therefore phenols were considered a model compound with low reactivity in HDO. The conversion pathways of phenol into high-valued hydrocarbons by hydroprocessing have been studied by different researchers [84-89]. The reaction mechanism for phenol is shown in Figure 5.
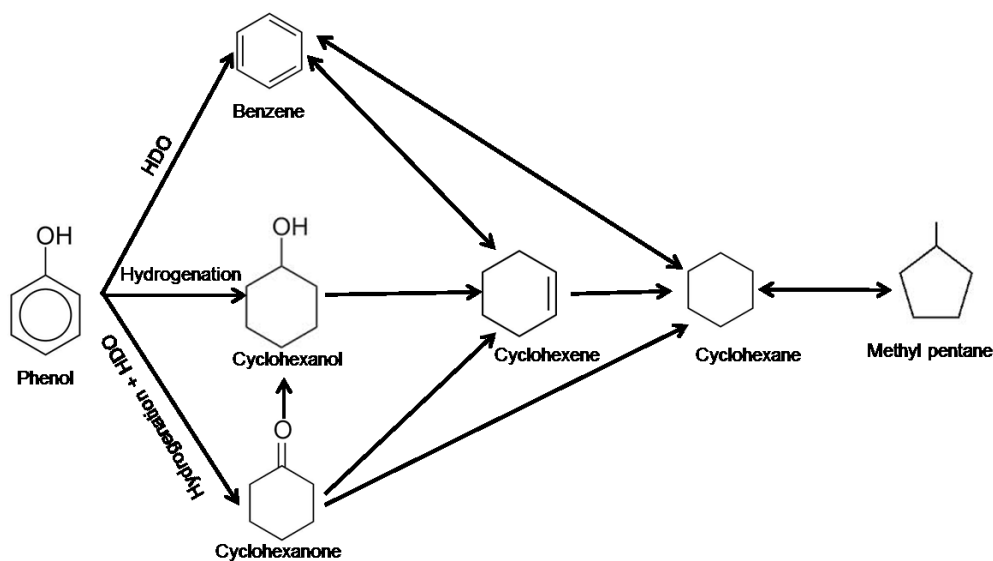
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Figure 5: Reaction mechanism for phenol [84-89].

There are three independent paths for the HDO of phenol: the first is direct elimination of oxygen from the aromatic chain by C-O bond cleavage (direct hydrodeoxygenation) in the presence of hydrogen to form benzene followed by cyclohexene and cyclohexane; the second path is hydrogenation of the aromatic ring (phenol) to form an intermediate, i.e., cyclohexanol, which is immediately followed by oxygen removal to form cyclohexene and cyclohexane; and the third pathway is a combination of hydrogenation and hydrodeoxygenation of phenol to cyclohexanone followed by subsequent hydrogenation to form cyclohexanol, cyclohexene, and cyclohexane. All three pathways ultimately lead to the formation of cyclohexane, which can also isomerize to form methyl cyclopentane. These paths are completely dependent on the operating parameters of the hydroprocessing reactions. Depending on the surface morphology, compositions of metal, support, and temperature, different intermediate and products are formed [84-89].

5. Operating parameters

5.1 Catalyst

A catalyst plays an important role in the final composition of renewable diesel. Researchers have used a variety of catalysts to hydroprocess bio-oil. Mainly the catalysts fall into one of two categories: transition metal catalysts and sulfide catalysts. Either sulfide Ni-Mo or sulfided Co-Mo supported on gamma alumina is used as a catalyst for removing sulfur compounds from

crude oil [58]. Since both hydrodeoxygenation and hydrodesulfurization use hydrogen as a reactant to remove the heteroatom from the respective feedstock, sulfide Ni-Mo/sulfide Co-Mo supported on gamma alumina is considered to be the reference catalyst for hydroprocessing bio-oil. In these catalysts, Mo acts as the active site for these heteroatoms and Co/Ni as the promoter for hydrodeoxygenation. Tables 6 and 7 show the operating conditions used for hydroprocessing bio-oil and model compounds.

5.1.1 Sulfided NiMo/CoMo metals

Sulfided forms of NiMo/CoMo metals have been studied on different supports for hydroprocessing bio-oil and model compounds [82, 90, 91]. Ni and Co are used as promoters to increase the activity of molybdenum sulfide, and it is believed that promoters donate electrons to Mo, which weakens the metal-sulfide bond. The reactions for different oxygenate compounds have been studied on this sulfide NiMo/CoMo catalyst, and it can be deduced that reaction paths depend on the catalyst surface. The activity of the sulfided catalysts rapidly decreases with time due to the loss of MoS_2 active sites and the presence of H_2O due to HDO; thus, a continuous supply of a sulfiding agent such as H_2S is required to preserve the sulfided catalysts from oxidation by oxygenated compounds or a reduction of the sulfided phase by hydrogen [92].

The effect of H_2S and H_2O on sulfide NiMo/CoMo catalysts has been studied for different model compounds [86, 93]. Senol et al. [93] have studied the effect of water on the HDO of aliphatic esters on sulfide NiMo/CoMo catalysts supported on gamma alumina. They concluded that water decreases the conversion of esters and suppresses the deoxygenation reaction. Between dehydration and the decarboxylation reaction, water mainly affects the decarboxylation reaction and suppresses the formation of C_6 hydrogen.

Laurent et al. [94] studied the effect of H_2S and water on the HDO of carbonyl, carboxylic, and guaiacyl groups with sulfide NiMo/CoMo catalysts supported on gamma alumina and deduced that H_2S increases the Bronsted acidity on the sulfide phase during the reaction. The Bronsted acidity is also responsible for the decarboxylation reaction. Isomerization and hydrocracking are also promoted by the presence of H_2S. Hydrogen sulfide enables the fine control of the activity and selectivity of sulfided hydrotreating catalysts. Among CoMo and NiMo, it was concluded that H_2S depresses the activity of Ni compared to Co for the ketonic and carboxylic model

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compounds. The superior promoting effect of Co has also been agreed upon by Bui et al. [82] for the HDO of guaiacol.

The impregnation order of metals in a bimetallic catalyst is an important parameter for catalyst activity and selectivity of hydrodeoxygenation. Ferrari et al. [95] have investigated the impregnation order for metals (Co and Ni) loading on carbon support at the time of catalyst preparation. According to these authors, Co was dominantly impregnated on the external surface of the support and Mo was deposited inside the micropores of the support. Therefore, it seemed better to add Co after Mo so that Co became responsible for the remobilization of Mo that had migrated to the external part of the grain. Changing the impregnation order caused Mo-Co interactions to form a thick layer of metal oxide crystal. This layer covered the external surface, leading to a reduction in catalyst activity and product selectivity.

The addition of phosphorus as a promoter to a Mo-based traditional refinery catalyst was studied for a hydrotreating activity of bio-oil and model compounds [46, 87, 96]. Phosphorus enhances Mo dispersion on the support, reduces coke formation, increases packing of MoS_2 crystallites, and creates new Lewis and Bronsted acid sites on the support surface [46, 87, 97]. At the time of catalyst preparation, phosphorus forms phosphor molybdate complexes that augment HDN reactions in the hydroprocessing unit. Zhang et al. [46] found that in the presence of P, the oxygen content in raw bio-oil obtained from sawdust was reduced from 41.8% to 3% by weight and the heating value increased from 21.3 to 41.4 MJ/kg.

5.1.2 Noble metals

Studies have also been conducted on noble metals used as catalysts for hydroprocessing bio-oil and model compounds (see Tables 6 and 7). It was seen that noble metals perform better than traditional refinery catalysts in terms of oil yield and degree of hydrodeoxygenation. While Ru is widely used, Rh, Pt, and Pd are commonly used noble metal catalysts for the hydroprocessing of bio-oil and model compounds.

Table 6: Summary of operating conditions for hydroprocessing bio-oil

Feedstock	Reactor Type	Reactor Dimension	Catalyst Used	Temperature ^{0}C	Pressure bar	SV(h^{-1})	Reference	HHV MJ/kg
Beech wood	Autoclave	100ml volume	Ru/C, Ru/TiO$_2$, Ru/Al$_2$O$_3$, Pt/C, and Pd/C	250 &350	100 & 200		[67]	40
Pine wood	Parr	100ml volume	Ni-Cu/Al$_2$O$_3$	350	100		[70]	98
Vacuum pyrolysis oil	Autoclave		Ru/γAl$_2$O$_3$ & NiO-WO$_3$/ γAl$_2$O$_3$	325	172		[98]	
Pine sawdust and bark	Trickle bed	¾" OD, 0.065" thickness & 32" long	Pt/Al$_2$0$_3$/Si0$_2$, sulfided CoMo/γ-Al$_2$0$_3$, Ni-W/γ-Al$_2$0$_3$, Ni-Mo/γ-Al$_2$0$_3$.	350-400	52.72-104.33	WHSV 0.5-3	[99]	
Rice husk	Autoclave	100ml	Pd/SO$_4$$^{2-}$/ZrO$_2$/ SBA-15	280	85-105		[76]	20.1
Fast pyrolysis oil	Stainless steel parr	50ml	Pt/Al$_2$O$_3$. &Pt/MZ-5 (MZ-mesoporous zeolite)	200	40	LHSV 2,4,6	[69]	
Fast pyrolysis oil	Batch autoclave	100 ml	Ru/C	350	200		[100]	
Beech wood	Batch autoclave	100ml	Ru/C	350	200		[61]	
Pine sawdust	Fixed-bed catalytic reactor	1" ID & 32"long	Sulfide Ru/C, NiMoS, CoMoS, NiMoS/C, CoMoS/C, CoMoS/Al$_2$O$_3$	150-450	138	LHSV=0.19	[72]	
Pinewood	Batch autoclave	100ml	Rh/ZrO$_2$Pd/ZrO$_2$Pt/ZrO$_2$RhPt/ZrO$_2$ RhPd/ZrO$_2$PdPt/ZrO$_2$ CoMo/Al$_2$O$_3$	350	35		[78]	
Sawdust from Pinus insignis	Fixed-bed	9mm ID	HZSM-5	400,450 &500	1.01	WHSV = 0.237 & 0.474	[101]	
Eucalyptus & hybrid poplar	Continuous feed fixed bed		NiMo/Al$_2$O$_3$&CoMo/Spinel	355-365		WHSV = 0.54-0.7	[77]	
Rice husk	Autoclave	100ml	Aluminum silicate	260	78		[63]	21
Sawdust	Autoclave	500 ml	Sulfided CoMoP/γAl$_2$O$_3$	340-400	1.6-2.8		[46]	41.4

Table 7: Summary of operating conditions for hydroprocessing model compounds in bio-oil

Model Compound	Reactor Type	Reactor Dimension	Catalyst Used	Temperature ^{0}C	Pressure bar	SV(h^{-1})	Ref e
Benzofuran	Fixed-bed	4 mm i.d.	Sulfided Ni-Mo/ γAl$_2$O$_3$	200-320	35		[90]
Guaiacol	Fixed-bed tabular		MoS$_2$,CoMoS MoS$_2$/ γAl$_2$O$_3$	300	40		[82]

			$CoMoS/ \gamma Al_2O_3$				
Phenol and substituted phenol	Conversion		$CoMo/ \gamma Al_2O_3$	250-400	3.0 - 8.2		[10
Guaiacol Cresol Dibenzofuran	Continuous flow fixed-bed	10mm ID & 420mm long	$Pt/ \gamma Al_2O_3$. &Pt/MZ-5 (MZ- mesoporous zeolite)	200	40	LHSV = 2,4,6	[69
Phenol	Parr autoclave	100ml	Ru/C	250	100		[61
Guaiacol	Batch reactor		Mo_2N/C	300	50		[79
D-Glucose D-Cellobiose D-Sorbitol	Batch autoclave	100ml	Ru/C	250	100		[10
Anisole	Continuous fixed bed	3mm ID	$Ni-Cu/ \gamma Al_2O_3$	300	10	WHSV = 3-6	[70
2-ethylphenol	Fixed-bed	1,25cm ID & 40cm long	$Mo/ \gamma Al_2O_3$, $CoMo/ \gamma Al_2O_3$, $NiMo/\gamma Al_2O_3$	340	70		[10
Phenol	Micro reactor system	14ml	CoMo/MgO, CoMoP/MgO	300-450	50		[87
Phenol	Bench-scale fixed-bed catalytic	9mm ID & 300mm long	Ni-W/C	150-300	15	WHSV – 0.5	[88
Methyl substituted phenol	Batch autoclave	$300cm^3$	$CoMo/ \gamma Al_2O_3$	300	50		[89
Guaiacol	Stainless steel batch	40 ml	Rh/ZrO_2, Pd/ ZrO_2, Pt/ ZrO_2, $RhPt/ ZrO_2$, $RhPd/ ZrO_2$, $PtPd/ ZrO_2$	100 & 300	80		[81

Ardiyanti et al. [70] investigated mono- and bimetallic noble catalysts (Pt, Pd, and Rh) on zirconia support for the catalytic hydrotreatment of bio-oil. The results were compared with the traditional sulfided CoMo catalyst. Among noble metals, Pd showed the highest activity, followed by Rh, with Pt having the lowest due to incomplete reduction at the time of reaction. Ardiyanti et al. reported the activity based on hydrogen uptake as follows:

$Pd/ZrO_2 > Rh/ZrO_2 > RhPd//ZrO_2 \approx \mathbf{PdPt/ZrO_2} > RhPt/ZrO_2 > Pt/ZrO_2 > CoMo/Al_2O_3$

There is not much difference in oil yield for a bimetallic catalyst as compared to a monometallic one. The extent of leaching determined for metal and support were done by inductively coupled plasma-optical emission spectroscopy ICP-OES. Ardiyanti et al. [78] observed that with a sulfided CoMo on an alumina catalyst, Co and Al leached to the aqueous phase after reaction, whereas leaching was negligible for noble metal catalysts.

Venderbosch et al. [27] studied Ru supported on C to stabilize the bio-oil for mild hydrotreating, which is the first step in hydroprocessing. The coke-formation tendency of this stabilized oil is comparatively low compared to the non-stabilized oil. The same Ru on a C catalyst has also been tested by Wildschut et al. [50] for the hydrotreatment of fast bio-oil from beech wood in a batch reactor. The effect of reaction time on oil yield and elemental composition of product phases was studied. It was inferred that an increase in reduction time leads to a significant decrease in oil yield due to transformation during the liquid phase to the gaseous phase [61].

Figure 6 presents the results from another study of noble metal catalysts. These outcomes were compared with the benchmark catalyst study by Wildschut et al. [67]. Ru/C, Ru/TiO$_2$, Ru/Al$_2$O$_3$, Pd/C, and Pt/C were tested during beech wood oil hydroprocessing in an autoclave following a reaction time of 4h for noble metal catalysts. Three different phases of liquid were reported: a slightly yellow aqueous phase, an oil phase with a density higher than that of water (top oil), and an oil phase with density lower than water (bottom oil). The top oil had a better H/C and O/C ratio than the bottom oil phase. Pd/C appeared better in terms of oil yield and oxygen content, followed by Ru/C. Both Pd/C &Ru/C performed comparatively far better than the benchmark catalysts [67].

The outcome of Pd metal supported on C was investigated by Elliott et al. [72] for a range of bio-oils. The bio-oil was obtained from various mixed wood feedstocks in a bench-scale continuous-

flow fixed-bed reactor for reaction times varying from 8-102 h. The oxygen content in the upgraded oils from different feedstock was reduced to 0-1 wt% from 40-60 wt%.
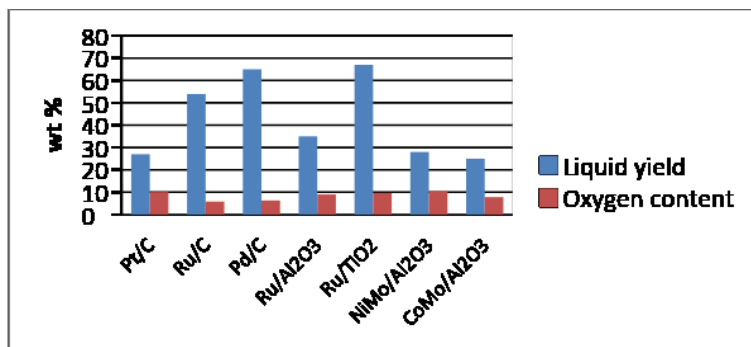

Figure 6: Performance of noble metal catalysts and benchmark catalysts for liquid (oil) yield and oxygen content in oil yield [67].

In summary, noble metals (Rh, Ru, Pd, and Pt) are most promising catalysts for the hydroprocessing of bio-oil obtained from lignocellulosic biomass than the traditional sulfide NiMo/CoMo catalyst supported on gamma alumina. For the benchmark catalyst, metal loading is considerably higher (more than 10 times) than the metal loading for a noble metal catalyst. But the activity on a per gram catalyst basis is higher for noble metals than for benchmark ones by a factor of two [78]. Noble metals have a high selectivity for hydrogenation reactions and require more hydrogen, which in turn raises the operating cost. Noble metals can be easily poisoned by small amounts of sulfur compounds present in bio-oil, and these are expensive. These reasons make them unattractive for the hydroprocessing technique.

5.1.3 Inexpensive transition metals

Although it is difficult to replace a noble metal catalyst in terms of performance, different researchers have tried various alternatives. A series of inexpensive transition metals was tested in hydroprocessing experiments in different reactor systems. Echeandia et al. [88] studied a Ni-W catalyst supported on active C for the HDO of phenol in a bench-scale fixed-bed catalytic reactor with a hydrogen flow of 2.5 lh^{-1} and a reaction time of 4 h. They [88]also studied the effect of W precursors (silicotungstic [SI], phosphotungstic [P], and tungstic acid [W]). Total elimination of oxygen compounds was reported at 573 K over Ni-W(P)/C and Ni-W(SI)/C catalysts. The synergistic effect between Ni and W supported on C reduced the catalyst deactivation during the

reaction. Another study of a Ni-based catalyst, for bio-oil obtained from pine wood, was carried out by Ardiyanti et al. [24] in a batch reactor. The study's results in terms of catalyst activity are as follows:

NiCu/TiO$_2$>NiCu/delta-Al$_2$O$_3$>NiCu/CeO$_2$-ZrO$_2$>NiCu/ZrO$_2$

NiCu/TiO$_2$ catalysts showed the best performance in terms of hydrogen uptake, stability, and catalyst activity, but leaching and coke formation were significant for these catalysts compared to noble metal catalysts.

Ardiyanti et al. [70] studied the variation in ratio of Ni to Cu metal loading on delta alumina support in a batch autoclave for the hydroprocessing of bio-oil obtained from pine wood for a reaction time of 4 h. They reported the activity of catalysts as follows:

Ru/C> 16Ni2Cu> 13.8Ni6.83Cu > 13.3Ni11.8Cu > 9.92Ni18.2Cu

The activity of these catalysts decreased with an increase in Cu content as Ni is excellent for HDO. But leaching and coking tendencies were improved considerably during reaction. It should be noted here that the viscosity of the upgraded oil was higher than the original bio-oil [103, 105-107].

In summary, for the upgrading of bio-oil from lignocellulosic biomass, both benchmark sulfided NiMo/CoMo supported on alumina and transition metal catalysts are available. The ideal selection of proper catalysts for different feedstocks is still in debate. Research is required to learn the properties and morphology of catalysts to determine the most suitable catalyst.

5.1.4 Catalyst support

Support is an important part of a catalyst system in the hydroprocessing of bio-oil. Alumina, carbon, TiO$_2$, ZrO$_2$, and CeO$_2$ are generally used as carriers [24, 62, 78, 80, 81, 108]. Alumina has been widely used in the oil upgrading industry to remove S from crude oil. Therefore, many authors have tried to use gamma alumina for hydrodeoxygenation in bio-oil upgrading. They found that alumina is susceptible to attack by acidic water at elevated conditions and later its reaction with water leads to a reduction of surface area [109]. At the time of reaction, promoters such as Ni/Co can react with Al$_2$O$_3$ as it is not inert and can occupy the octahedral or tetrahedral sites in the external layers depending on the catalyst preparation conditions [86]. This strong interaction between promoter and support reduces the dispersion of the Mo sulfide phase, which

lowers the activity of the HDO. Further, the crystalline phase of gamma alumina converts to the boehmite phase, which is useless for this reaction [67]. Another problem for gamma alumina is the viscosity of the upgraded oil, which is higher than the original bio-oil. The higher viscosity affects the product quality and quantity because of the oil's tendency to stick to the walls, plates, impeller, and piping of the reactor, thereby reducing the reactor's efficiency. Weak Lewis-type acidic sites on the support surface lead to large coke formation during HDO [80]. Centeno et al. [83] reported that alumina-supported CoMo catalysts had the highest rate of decarboxylation and deesterification selectivities for guaiacol hydrodeoxygenation. But at the same time, surface area and pore volume of alumina support decreased with the HDO reaction.

As an alternative, activated carbon has been identified as a promising support for HDO [27, 61, 62, 67, 79, 88, 95, 110]. Compared to gamma alumina, carbon is superior in terms of textural properties (surface area, meso- and microporosity, pore volume), thermal stability, and hydrophobic nature. Ferrari et al. [95] investigated four different kinds of carbon support with different origins for CoMo catalysts: Merck carbon from coconut shells, Norit carbon from chemical activation of wood, and Chemviron and BKK from the thermal treatment of bituminous coal. Even though variation in properties was negligible, the surface area of carbon support varied significantly. Merck and Norit had high surface areas and microporous volumes, followed by Chemviron. The last was BKK, with the most developed non-microporous volume. On the basis of activity of HDO for guaiacol, the order was as follows:

Norit> BKK>Chemviron>Merck

Sepulveda et al. [79] investigated three different types of commercial carbon support (Norit, Pica, and udu) varying in pore size distribution and micropore/mesopore volume ratios for a Mo_2N catalyst for the hydrodeoxygenation of 2-methoxyphenol. They also observed that Mo_2N/Norit had the highest mesopore diameter resulting in the most open porous structure. High mesoporosity in carbon support facilitated reactant diffusion to the internal surface where the active sites were located. Echeandia et al. [88] reported that adsorption of water on active sites produced from an HDO reaction can be prevented by the hydrophobic nature of carbon support that ultimately reduces the rate of deactivation of catalysts. Carbon remains inert at the time of an HDO reaction, which is a great advantage for transition metals because all transition metals present in precursors will be converted into active sulfide forms. According to Wildschut et al.

[67] , oil yield and degree of hydrodeoxygenation were highest for carbon support. Carbon support also had a low catalyst deactivation due to the neutral nature of carbon. The presence of some impurities like titanium and strontium in carbon support can change the electronic structure of active sites that might be undesirable for an HDO reaction. The high microporosity is another disadvantage for carbon material because for high molecular weight compounds which remains unused [79].

Silica has been often used for HDO reactions due to its inert character (like carbon) and smaller interaction with the sulfided phase. Popov et al. [111] studied silica support for the HDO of phenolic molecule and reported that the phenolic compound interacted through H bonding. Phenate formation on a silica surface was very low compared to alumina support, as two-thirds of the surface was covered by phenate compounds.

MgO and ZrO_2 support are also recognized as good basic supports for hydroprocessing reactions [78, 87]. Yang et al. [81] investigated CoMo catalysts supported on MgO for the hydroprocessing of phenol [87]. They noticed excellent coke resistance for coking reactions for two reasons: first, MoO_3/MoS_2 was acidic in nature and highly dispersed on the MgO surface due to the basic nature of the support and second, MoO_3/MoS_2 increased the edge plane area for promoters due to the formation of short edge-bonded MoS_2 slabs. ZrO_2 is identified as an inert material for hydroprocessing reactions. ZrO_2 has high stability towards the coke formation because it is less acidic and has less affinity towards water, which increases the activity of the HDO.

In summary, the selection of the appropriate support for the HDO reaction is required to get the desired product. Coke formation is another point of concern to reduce catalyst deactivation for the reaction. Overall, carbon can be thought of as a promising carrier for this process, with appropriate mesoporosity.

5.2 Catalyst deactivation

Catalyst deactivation is loss of catalyst activity and product selectivity with reaction time, which is considered a great loss for an HDO reaction. The cost to replace and regenerate a catalyst is too expensive for industry. Catalyst deactivation takes place due to six reasons: (1) poisoning due to strong chemisorption of impurities like sulfur and nitrogen to active sites, (2) fouling/coking due to physical deposition of coke onto the surface of the catalyst, (3) thermal

degradation/sintering due to collapse of the catalyst and support surface area because of crystallite growth, (4) vapor compound formation accompanied by transport, (5) vapor-solid (catalyst) and/or solid-solid reactions that are reactions of fluid, support, or promoters in the catalytic phase that lead to an inactive phase, and (6) loss of internal pores at the time of attrition/crushing [106, 107]. Although these are the reasons for catalyst deactivation, in the literature the most frequent reason cited is coking/fouling [94, 103, 105, 112, 113].

Carbon and coke are the two main sources of coking. Carbon forms from a Boudouard reaction ($2CO \Leftrightarrow 2CO_2 + C$), where CO dissociates to form carbon on the catalyst surface, and coke is produced from decomposition or condensation of high molecular weight hydrocarbon compounds on the active sites of the metal and support surface. Coke deposits may deactivate the catalyst either by covering the active sites or by pore blocking [88]. The composition of coke (high molecular weight to graphite form) varies depending on the feed composition and reaction conditions. Reactants with two oxygen-containing functional groups in the benzene ring form coke with greater ease than those with one oxygen-containing substituent. Centeno et al. [83] investigated a sulfided CoMo catalyst-supported gamma alumina for a HDO guaiacol model compound present in bio-oil and observed that coke was produced from the interaction of guaiacol with the gamma-Al_2O_3 support rather than with the active metals. This is due to acidity, which plays an important role in coking, as Lewis sites are responsible for binding species to the catalyst surface and Bronsted sites donate protons to the deposited species to form carbonaceous materials. But other supports, like activated carbon and ZrO_2, remain inert at the time of HDO; therefore, coking is comparatively low relative to gamma support [24, 78, 88, 108].

In a traditional catalyst, Ni is used as a promoter to accelerate the activity of Mo. But Ni tends to form coke at high temperatures, and coking tendency increases with reaction time. Ardiyanti et al. [24] reported that the viscosity of the upgraded oil was more than that of the original bio-oil due to the formation of high molecular weight compounds that further converted to coke on the catalyst surface.

Coking is not a big problem in noble metal catalysts as they are mostly affected by sintering. As bio-oil produced from biomass is not completely free from sulfur and nitrogen, sulfur and nitrogen compounds act as impurities for these metals. As chemisorption of sulfur compounds on the catalyst surface is rapid and irreversible, sulfur compounds make the catalyst inactive for

HDO. Ardiyanti et al. [78] studied catalyst deactivation for Rh-based catalysts for a reaction time of 4 h. Deposition of carbonaceous materials after 1 h (2.6 wt%) was similar to after 4 h (2.7 wt%). The reason was high polymerization and char formation at the initial stage of reaction time, but with increased reaction time, the gasification rate of feed was enough to balance the formation of carbonaceous deposits while maintaining a constant temperature [78].

The composition of lignocellulosic biomass plays an important role in the deactivation of a catalyst. As bio-oil contains around 40-50 wt% O-containing compounds, some compounds are highly unstable and may readily polymerize to form coke on the catalyst surface [114]. Coke formation can be reduced by proper selection of the catalyst, support, temperature, and hydrogen pressure during a HDO reaction. The addition of extra hydrogen during the reaction can reduce coke formation by converting unsaturated compounds to a stable saturated molecule.

5.3 Temperature

Temperature is an important controlling factor for the hydroprocessing of bio-oil from lignocellulosic biomass. In terms of temperature, the hydrotreating process is divided into two categories: high-severity hydrotreating or deep HDO, and low-severity hydrotreating or mild HDO. High-severity hydrotreating involves complete hydrodeoxygenation with minimal hydrogenation at temperatures ranging from 350-400 ^{0}C and pressures greater than 200 bar [67]. For low-severity hydrotreating, the temperature is maintained between 175 and 250 ^{0}C, and the pressure is greater than 100 bar, with partial hydrodeoxygenation and reasonable hydrogenation to stabilize the unstable bio-oil. A combination of these steps significantly reduces the oxygen content of bio-oil.

In mild HDO, crude bio-oil becomes more stable through the removal or transfer of unstable compounds to stable ones [59]. Acetic acid makes bio-oil unstable. But there is no significant change in oxygen content and viscosity in the upgraded oil. The dominating reaction in mild HDO is the hydrogenation of carbon-carbon double bond with the partial HDO of aldehydes and ketones. Due to complete hydrodeoxygenation at a deep HDO condition, upgraded bio-oil contains low concentrations of oxygen. But hydrogen consumption increases significantly with the complete removal of oxygen molecules [67].

Wildschut et al. [67] studied the hydroprocessing of bio-oil from beech wood using noble metal carbon-supported catalysts at both low-severity (250 ^{0}C) and high-severity hydrotreating (350

[0]C) temperature conditions. They reported that the yield of both oil and gaseous components increased significantly with a decrease in char yield when the temperature increased from 250 to 350 [0]C. The reason for the increase in liquid yield at high temperatures is due to a complete HDO reaction, which requires excess hydrogen. The excess hydrogen and the carbon dioxide that forms during decarboxylation increases the gas phase concentration at high temperatures [67] . Figure 7 shows the oxygen content of upgraded bio-oil for beech wood after low- and high-severity hydrotreating. It was found that after high-severity hydrotreating, the oxygen content decreased significantly from the initial value of 42 wt% in the original bio-oil.
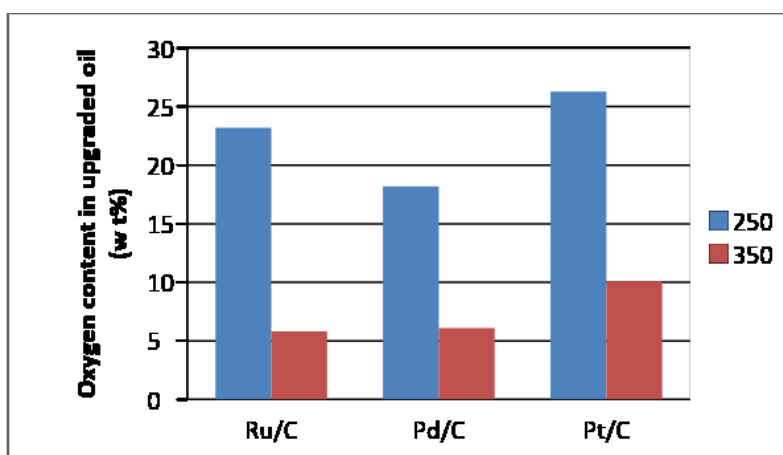

Figure 7: The effect of temperature on the performance of noble metal carbon-supported catalysts [67].

In another study, Wildschut and co-workers reported that at high-severity hydrotreating conditions, CO_2 was the dominating gaseous component in the gaseous phase due to unfavourable decarboxylation reactions at high temperatures [100]. A methanation reaction also started at high temperatures, a reaction not observed at low temperatures.

Zhang et al. [46] investigated the effect of temperature on the HDO of bio-oil from sawdust in a 500 ml autoclave using a sulfided Co–Mo–P catalyst. Figure 7 shows the effect of temperature on liquid, char, and gas yield. Oil yield was low at low temperatures and increased with temperature, but after a certain temperature there was no change in yield. The yield of char and gaseous components was dependent on the temperature. Char yield decreased with a rise in temperature because at low temperatures unstable components were deposited as char due to low volatility, and gaseous components increased with temperature.

In summary, the HDO of bio-oil is affected to a large extent by temperature. As temperature increases with time, the degree of deoxygenation changes and significantly reduces the oxygen concentration in bio-oil. At high temperatures, coke formation on the catalyst surface could be a main concern and needs more attention.
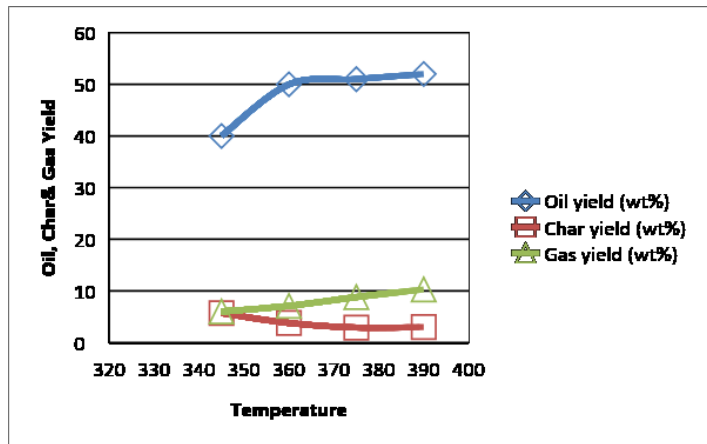

Figure 8: The effect of temperature on oil, char, and gas yield for the HDO of bio-oil from sawdust [46].

6. Status of HDRD production

Today some companies are paying attention to renewable diesel production – for example, ConocoPhillips [115, 116], Neste Oil [117-119], Petrobras in Brazil [120] – and others plan to produce renewable diesel, e.g., Nippon Oil in Japan [121], BP in Australia [122], and Syntroleum [123], Tyson [124], and UOP-Eni in the United States [125]. All the existing companies are using vegetable oil and animal fat as the feedstock for renewable diesel production. ConocoPhilip uses vegetable oil and crude oil, Neste's plant processes vegetable and animal fats, and Brazilian Petrobras uses co-processed vegetable oils. Table 8 summarizes the commercial producers of renewable diesel. However, substantial research is still needed in order for renewable diesel to replace diesel and gasoline on a large scale.

Table 8: Commercial renewable diesel plants

Company	Plant Location	Capacity	On-Stream	Reference
CoconoPhilips	Cork, Ireland	1000 bbl/day	2006	[115]
Neste Oil	Rotterdam, Netherlands	800,000 tonne/year	2010	[117]
Neste Oil	Singapore	800,000 tons/year	2010	[118]
Neste Oil	Porvoo, Finland	190000 tons/year	2007	[119]
Neste Oil	Porvoo, Finland	190000 tons/day	2009	[119]

7. Issues with hydroprocessing

7.1 Economic analysis

Economic viability is an important factor for any process when it is compared with a developed process. According to Elliott and Neuenschwander, there are four major cost considerations in bio-oil hydroprocessing: raw bio-oil cost, capital cost, hydrogen cost, and relative product value [59]. A number of techno-economic studies are available on the production of bio-oil from biomass [126-129], but very limited study has been done on the techno-economic assessment of the upgrading of bio-oil using hydroprocessing technologies [130]. The National Renewable Energy Laboratory (NREL) has completed a techno-economic assessment of bio-oil from corn stover to transportation fuel that includes both naphtha-range and diesel-range distillation fractions [130]. The NREL did the analysis for two scenarios for bio-oil upgrading through hydroprocessing: on-site hydrogen production and a hydrogen purchase scenario. According to their results, costs were lower in the second scenario due to the difference in capital costs of a hydrogen reforming plant. Production costs of transportation fuels from pyrolysis-derived biofuels are competitive with production costs of other renewable fuels (biodiesel); however, the technology is relatively immature, and so there is a high level of uncertainty. Another techno-economic assessment was done by a team from the Pacific Northwest National Laboratory for the production of diesel and gasoline from hybrid poplar via fast pyrolysis, hydrotreating, and hydrocracking [131]. The team observed that this method could be financially attractive if the

pyrolysis plant was located within an existing refinery in order to reduce the capital costs of the hydrotreating unit and the steam reforming unit.

A stand-alone renewable diesel unit requires a large capital investment as the material required for handling bio-oil is expensive. But the overall cost can be optimized by building the new unit near the existing refineries in order to make use of an existing hydrogen facility, as well as electricity, steam, and a recycle gases management unit [132]

Capital costs for a pyrolysis unit, a hydrotreating unit, and a hydrogen reforming unit contribute approximately 85% of the total costs, and each unit has an equal weight.. There could be a large reduction in capital costs if the hydrotreating unit of an existing refinery is used. As the hydrotreating unit is operated at high pressure and temperature conditions, more care should be taken to determine the space velocity (volumetric flow rate of the feed/volume of the reactor) to reduce the capital cost [130].

The cost of the bio-oil is the largest component in the hydrotreating product costs; therefore, the product yield is a primary consideration for process optimization. The composition of renewable diesel varies depending on the composition of the bio-oil. For improved cold-flow properties, we need more short and isomerized alkenes than long-chain alkenes, and these properties depend completely on the elemental composition of the bio-oil.

Hydrogen also makes up a significant portion of the total cost. The optimization of hydrogen could be done following careful study of reaction mechanisms of different oxygenate compounds, where hydrogen is consumed in excess amounts. Unstable compounds such as acetic acid, olefins, etc., could be removed before hydrotreating [130].

7.2 Gaps in knowledge

More experimental work is required to determine optimal operating conditions, e.g., catalyst, catalyst deactivation, temperature and pressure in the hydroprocessing unit, to control product yield. The reactor configuration plays an important role in reaction rates and mass transfer of feed. Channeling, clogging, and entrainment are major problems in reactors due to uneven distribution of materials. Selection of proper metal and support is important to reduce catalyst deactivation, which is reported as the main concern in this upgrading process.

Carbon deposition on a noble metal catalyst is comparatively lower than on the benchmark catalyst (gamma alumina-supported sulfide NiMo/CoMo catalyst), but a noble metal catalyst is affected by small concentrations of sulfur present in feedstock and highly expensive compared to transition metal catalysts. Due to the acidic nature of gamma alumina, gamma alumina is not so effective for this process compared to activated carbon and MgO, which remain inert throughout the reaction. Therefore, the optimization of metal and the support system is required to get catalysts that are technically and economically feasible.

Temperature is another key operating parameter for the hydroprocessing process in the elimination of oxygen compounds in order to increase the heating value of renewable diesel. At high temperatures and pressures, the concentration of oxygen is reduced significantly, from 40-50 wt% to 3-8 wt%, but high temperature hydroprocessing is associated with high hydrogen consumption and low oil yield. Therefore more research is required to optimize the relationship between hydrogen consumption, oil yield, and temperature, given that oil yield and hydrogen consumption significantly affect the costs of crude bio-oil and hydrogen production. In other words, optimization of operating conditions is necessary for better product yield.
More research is required in production of renewable diesel from lignocellulosic biomass to make this economically feasible.

8. Conclusions
Biomass-derived biofuels have the potential to replace fossil fuels and are the only renewable carbon resource that has a short production cycle and is carbon neutral. Among all biofuels, renewable diesel is the only fuel that can directly replace petro-diesel with one of a more superior quality than the minimum diesel standard requirement decided by fuel regulators. Commercialization of renewable diesel is yet to be attained due to the following technological gaps and economical disparities.
- Technological gaps include the consideration of bio-oil composition from different feedstocks, catalyst selection, and the temperature of the hydroprocessing process. The oxygen content of bio-oil makes hydroprocessing more challenging, so effort should be put toward reducing the oxygen content in bio-oil before it is put into the hydrotreater.
- Catalytic pyrolysis should be implemented in place of non-catalytic pyrolysis to reduce the oxygen content and stabilize the bio-oil before further processing.

- More research should be done in the area of catalyst regeneration and recycling to increase the lifetime of catalysts.
- A process can be practically feasible if it is economically sound; however, studies on costs are lacking. Work on different feedstocks ought to be carried out to support the development of large-scale processes.

Although several challenges are associated with hydroprocessing, several factors, such as environmental concerns, population rise, and depletion of fossil fuels, need attention so that energy can be directed toward renewable diesel serving as a transportation fuel to fulfill our future needs. Hence this topic will to continue to be one of the most energetic topics of research until bio-oil is commercialized.

9. Acknowledgements

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