Atmospheric Hydrodeoxygenation of bio-oil oxygenated model compounds; a review

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Abstract

Hydrodeoxygenation (HDO) of various bio oil oxygenated model compounds in low H₂ pressure has been discussed in this study. Because of the high yield of aromatic mixtures in bio-oil, they carry great potential for fuel efficiency. Nevertheless, due to its high viscosity, abundance of

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acid, and heteroatom contaminants, the bio-oil ought to be upgraded and hydrotreated in order to be applied as an alternative fuel. A continuous low H_2 pressure HDO of bio-oil is favored as it could be simply integrated with conventional pyrolysis systems, functioning at low pressures, as well as supporting a flexible plan for serial processing in respective bio-refineries. Additionally, such a process is cheaper and safer in comparison with the high pressure set ups. This review meticulously elaborates on the operation conditions, challenges, and opportunities for using this process in an industrial scale. The operating temperature, the H_2 flow ratio, the active site, and the catalyst stability are some important factors to be considered when it is intended to reach a high conversion efficiency for the HDO in low H_2 pressure.

Keywords:

Low pressure/Atmospheric H_2 Hydrodeoxygenation; Fast pyrolysis oil; Bio oil upgrading; Guaiacol; Phenolic compounds

1- Introduction

Fast pyrolysis is the most promising thermochemical process among the other procedures to directly produce liquid from lignocellulosic biomass in high yield of up to wt.%75%, commonly referred to as bio-oil. Likewise, it has become of considerable interest due to its moderate operating temperature of around 773 K and very short reaction time of up to 2 s. (1–6). Bio-oil is generally a mixture of primarily phenolic oligomers derived from lignin in an aqueous phase comprising predominantly carbohydrate derived compounds (7–10). Several deteriorating properties such as high acidity, low higher heating value (HHV), high viscosity, poor storage stability and others have made bio-oil undesirable to instant usage as high grade fuels, mainly

due to high amounts of oxygenated compounds as well as complex mixtures of chemical compounds (11–13).

Accordingly, upgrading the crude bio-oil has been acknowledged as the foremost challenge for production of competitive alternatives of petroleum fuels and also chemical feedstock in the chemical industry (14). Hydrodeoxygenation (HDO) and catalytic cracking with zeolite are the two main processes for bio-oil upgrading (15–17). The former is a hydrogenolysis route which uses high hydrogen pressure to exclude oxygen from oxygenated compounds, resulting a high grade product compared to crude bio-oil (10). In the latter process, different kinds of zeolites (HZSM-5, H-mordenite, H-Y, MgAPO-36, SAPO-11, ZnHZSM-5, etc.) are applied for the deoxygenation process without demanding hydrogen (18–22). Due to numerous drawbacks associated with catalytic cracking with zeolite such as the catalyst's very short lifetime, low grade products and a low H/C ratio, HDO is evaluated as the most efficient route for upgrading crude bio-oil (23,24).

The hydrodeoxygenation process could be classified into two chief routes; high pressure HDO and atmospheric HDO. High pressure HDO utilizes high pressure of hydrogen to remove oxygen atoms from the oxygenated compounds as well as hydrogenation of aromatic rings. It can minimize the oxygen contents of several classes of oxygenated groups including esters, phenols, aldehydes, acids, ketons, etc. Depending on the composition of the organic compound, many reactions can occur during this process, among which hydrogenation, decarboxylation, dehydration, hydrogenolysis, hydrocracking and so forth. Various categories of catalysts have been applied by researchers for high pressure HDO which present several characteristics (25–

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27). Among them, metals catalysts including precious and non-precious metals (Pt, Pd, Rh, Ru, Fe, Ni, and Cu) and also conventional hydrotreating catalysts such as Sulfided CoMo and NiMo have exhibited promising properties in HDO processes.

Atmospheric/low H_2 pressure HDO is seems an ideal process since it can be easily integrated to existing plants of the pyrolysis of biomass, operates at near atmospheric pressure. This means no special equipment is needed to be designed and constructed for pressurizing purposes. In addition, the handling and feeding of bio-oil to the atmospheric reactors are more convenient and practicable in terms of safety. As the consequence, this process is considered cheaper and safer than high pressure HDO. Atmospheric HDO has the same procedure with conventional HDO process (high H_2 pressure HDO). Nonetheless, the catalyst type, process conditions, the reaction mechanism and function of hydrogen on the upgrading mechanism contrast with high pressure HDO. There has been a considerable upsurge in the number of researchers focusing on the current process during the present decade in order to overcome the challenges faced by this method including the unstable operation of the reactor, selectivity of the products, the catalyst deactivation and the like. Based on the reviewed articles in this field, the first study in low pressure hydrodeoxygenation of oxygenated compounds dates back to 2010 being executed by H.Y. Zhao et al (28). However, in the hope of using low pressure HDO in industrial scales, several scientists have concentrated on the low-pressure gas phase HDO of lignin-derived components to overcome its challenges.

This contribution thoroughly reviews the latest advances with reference to low consumption of H_2 in bio-oil upgrading processes including the catalysts, the process conditions, the influence of

H$_2$ partial pressure, deactivation of the active sites, reaction mechanism and kinetics of the reaction. Similarly, the bio oil characteristics and its latest upgrading techniques as well as its applications have been reviewed meticulously.

2- Bio-oil characteristics and its upgrading techniques

Pyrolysis liquid, unprocessed bio oil, pyrolysis oil, and pyrolytic oil are some synonyms for bio-oil which can be produced from fast pyrolysis of lignocellulosic biomass with yield up to wt.% 75% (29–32). Bio-oil is an intricate mixture comprising beyond 300 organic compounds including phenolics (phenol, catechol, anisole, syringol, guaiacol, etc.), oxygenates (alcohols, acids, esters, aldehydes and ketons), hydrocarbons (aromatics, alkene) furans, sugars, high molecular species (lignin derived oligomers, lignin, hemicellulose and cellulose) and water (33). The composition and yield of bio oil strictly depend on the pyrolysis process conditions (the heat transfer rate, the time, the temperature, the condensation, and the char removal efficiency, etc.), the moisture content, the particle size, and the feedstock chemical composition (34–37).

Oxygen is the most problematic element, as bio oils contains 10-40% oxygen. This influences the heating value (HV), acidity, viscosity, polarity, and homogeneity of the bio oil (38). The high water content leads to a polar nature for bio oils, resulting in immiscibility of bio oil with crude petroleum oil (25). Moreover, the high water content causes lower HV, which is around half of the value of heavy petroleum fuel oil. Acetic acid and formic acid are known as the main reasons for low pH of bio oils (2 - 4) that cause harsh conditions for equipment used for processing, transport, and storage. Olefins, phenols, and aldehydes in bio oil are unsaturated, unstable, while easily forming macro-molecules through polymerization, particularly in the presence of acids, which will also grow the viscosity of bio oil and diminish liquidity. Considering some favorable

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properties of bio oil such as good lubricity, less toxicity, and greater bio degradation in comparison with heavy petroleum fuel oil, the application of bio oil is still limited by some undesired properties which are mainly due to oxygenated compounds.

Upgrading the bio oil is essential to elevate its properties for its practical application as liquid fuel (38). Productions of liquid fuels and raw chemicals as well as generation of heat and power are the main utilization of bio-oil produced from fast pyrolysis. As it can be perceived from Table 1, utilization of bio-oil could be categorized into direct and indirect ones. The direct usages include combustion of bio-oil in gas turbines, stirling engines, diesel engines, furnaces, and boilers to produce heat, electricity, etc. Table 1 tabularizes various direct usages of bio-oil. Some merits associated with the direct usage of bio-oil include CO_2 neutral, very low sulfur content, easy transport, and storage. However, most of the investigation has been performed in laboratory scales and some inherent properties of bio-oil have made it challenging to use in large scale applications. There are two main options to solve such inherent problems, either to upgrade the bio-oil before direct usage or to configure the equipment used in direct usages such as diesel engine, stirling engine, gas turbine, and so forth. Substantial endeavors have been exerted on research and development related to the direct usage of bio-oil since it exhibits a much better prospect for high-efficiency energy production in comparison with the traditional biomass fuels. Indirect usages of bio-oil include upgrading bio-oil to liquid fuel and also extraction of chemicals from whole/fraction of bio-oil (Table 1). Bio-oil is a rich source of commercially valuable chemicals such as acetic acid, formic acid, furfural, levoglucosan, acetol, phenolics, etc. Many efforts have been exerted by researchers to find a proper route to recover these compounds from bio-oils from different sources (Table 1). Yet, there are significant complications to establish

markets for these compounds including inefficient separation technologies, high production costs, and availability of appropriate refining methods (39–44).

Table 1. Bio- oil applications

Direct usage of bio-oil				
Process	**Product**	**Application**	**Country**	**Ref.**
Combustion in Furnace & Boiler	Energy	Heat & Electricity	UK	(45)
Combustion in Diesel engines	Energy	Power generation	USA,UK	(46)
Combustion in Gas turbines	Energy	Power generation	Canada	(47)
Combustion in Diesel engines	Energy	Transportation	USA	(48)
Combustion in Stirling engines	Energy	Heat & Electricity	Germany	(49)
Indirect usage of bio-oil				
Upgrading of bio oil to the conventional fuel	Liquid fuel	Transportation	Global	(50)
Production of chemicals	Catalytic pyrolysis	Furfural	Pharmaceutical, pesticide	Italy	(51)
	Wet oxidation	Formic acid	Antibacterial, Preservative	Chile	(52)
	Aqueous extraction	Glycolaldehyde	Meat browning	Netherlands	(53)
	Separation, aqueous extraction	Glycoaldehyde, glyceraldehydes, diacetyl, aceton	Food additive, food flavore	Netherlands	(53)
	Separation	whole bio-oil	Wood preservative	USA	(54)
	Aqueous extract	Calcium salts	Road de- icers	Canada	(55)
	Aqueous extraction	Acetic Acid	Specialty chemical	Korea	(56)
	Solvent extraction	5-hydroxymethyl furfural (HMF)	Fine chemicals, plastics	-	(57)
	Phase seperation	Levoglucosan	Pharmaceutical, food additive, pesticides, surfactants, and polymers	Canada	(58)
	N/A	Methanol	-	UK	(59)
	1- Solvent fractionation 2- Phase separation	Phenolic compounds	Phenol-formaldehyde resin, smoky flavor providing	Korea	(60,61)
	Catalytic pyrolysis	Olefins	Fibers, plastics, clothing	USA	(62)

Intensive investigations have been executed on bio-oil upgrading topics resulting in development of several technologies including emulsification, steam reforming, supercritical fluids (SCFs), hydrotreating (hydrodeoxygenation), and catalytic cracking/ hydrogenolysis (39,63). Several research papers have been discussed regarding the details, process conditions as well as

advantages and disadvantages of the mentioned technologies (25,39,64,65). Among them, hydrodeoxygenation (HDO) has gained the attention of many researchers since it is able to produce a large amount of light products (31). Furthermore, its ability to reach high conversion of oxygenated compounds to hydrocarbons with no CO_2 emission as well as its technology compatibility with conventional hydrotreating technology has made this process (HDO) as the best choice for bio-oil upgrading (26).

HDO is a thermal process to eliminate oxygen atoms from organic compounds under high pressure of hydrogen with a catalyst. It can diminish oxygen contents of various kinds of oxygenated groups such as phenols, acids, aldehydes, esters, ketons, etc. Depending on the composition of the organic compound, many reactions can occur during this process such as hydrogenation, decarboxylation, dehydration, hydrogenolysis, hydrocracking, etc. The HDO general reaction stoichiometry can be written as (25):

$$CH_{1.4}O_{0.4} + 0.7\, H_2 \rightarrow CH_2 + 0.4\, H_2O \tag{1}$$
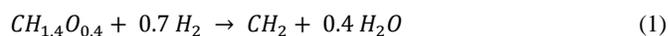
Where $CH_{1.4}O_{0.4}$ symbolizes the carbohydrate in the organic compound. Generally, high operating conditions such as high temperature (573-873 K) and pressure (1000-30000 kPa) have been reported in literature for HDO which is not energy efficient and economical (66). The high pressure has been defined as confirming a higher solubility of hydrogen in the oil and consequently a higher availability of hydrogen in the vicinity of the catalyst. This elevates the reaction rate and further diminishes coking in the reactor (67).

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3- Low H_2 pressure HDO

A continuous low or even atmospheric HDO of vapor-phase is preferred as it could be easily combined with conventional pyrolysis setups, operates at near atmospheric pressure, as well as enabling a flexible strategy for sequential processing in respective bio-refineries. Furthermore, it is cheaper and safer than high pressure set ups. Unstable operation of the reactor caused by pressure buildup in the upgrading reactor as well as catalyst deactivation caused by destructive components especially phenolic compounds are the main challenges of the researchers at low pressure conditions. What follows is a succinct account of the most outstanding process criteria being applied in recent studies (68,69). As can be observed from Table 2, the criteria being discussed encompass the active phase, the support, H_2 partial pressure, the temperature, the feed composition, efficiency, and major products. The subsequent section (Sub-chapter 3-1) elaborates precisely on the most essential process criterion, the active phase, which brings us better understanding of catalyst selection for atmospheric HDO.

Table 2. The latest development systems for atmospheric H_2 hydrodeoxygenation

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Entry	Active phase	Support	H_2 partial pressure (kpa)	T (K)	Feed Composition	X (%)	WHSV (h^{-1})	Remarks	Major products	Ref
1	MoO₃	-	19.6	673	Acetone 2-hexanone Cyclohexanone Anisole 2- methyl furan 2,5-dimethylfuran	96.8 81.2 100 65 53.1 43.4	14.70	MoO₃ displays great tolerance to water poisoning and coke creation. By calcination process, MoO₃ can easily be regenerated fully.	Propylene Benzene Pentenes Hexenes	(70)
2	Mo₂C	-	104	533-553	m-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol	>90	-	The applied operation conditions and the catalyst in this study can result to high product selectivity to aromatics.	Benzene Toluene	(71)
3	NiMo	Al₂O₃	20.68-103	723.15	Acetic acid	60-65	0.06	By elevating the partial pressure of H_2, acid acetic conversion rate increases. Maximum conversion rate occurs at H_2 partial pressure 103 kpa.	Ethanol Acetaldehyde Acetone Ethyl acetate	(72)
4	MoO₃	-	140	593-623	Phenol, m-cresol, anisole, guaiacol, diphenyl ether	28.7 - 97.5	0.002-0.035	MoO₃ is capable of selectively converting model compounds into aromatic hydrocarbons with high yields under atmospheric H_2 pressures.	Benzene Toluene Phenol Methane	(73)
5	Mo₂C	-	140	420–520	Anisole	-	0.05	low reaction temperature, and low H_2 pressure were required to break the phenolic C–O bond.	Benzene	(74)
6	MoO₃	-	140	723	Acetone, Guaiacol	52	0.9-1.8	The level of HDO of the biomass pyrolysis vapors was not significant at temperatures below 400 °C. At 450 °C catalyst temperature and 93 vol % H_2 concentration, the wood pyrolysis vapor was more active toward cracking forming gas species instead of performing the desired HDO forming hydrocarbons.	Phenol Benzene Propene Propane	(75)
7	MoO₃	γ-Al₂O₃ SiO₂ TiO₂ ZrO₂ CeO₂	140	593	m-cresol	8-78	2.06-8.27	The data from product distribution specify that the deoxygenation process on all catalysts involved a selective C-O bond cleavage rather than a path involving hydrogenation/dehydration as observed for supported noble metals.	Toluene	(76)
8	Pt	γ-Al₂O₃	0-140	573	Guaiacol	-	9.9-20	By elevating the hydrogen partial pressure, selectivity for HDO enhanced gradually.	anisole , phenol.	(77)
9	Pt	HBETA SiO₂	140	673	Anisole	80 – 100	0.25	Rate of HDO and methyl transfer reactions were accelerated by addition of Platinum to the zeolite. This results to lower hydrogen consumption as well as lower carbon losses as methane.	benzene, toluene, xylenes	(78)
10	Pt	Al₂O₃	140	573	Guaiacol	-	-	The results indicate that there is no reaction in the absence of hydrogen	Anisole Benzene toluene	(79)

11	Pt	MgO γ-Al$_2$O$_3$	140	573	Guaiacol	70	11	Pt/MgO catalyzed the formation of the cyclic deoxygenated product cyclopentanone at a relatively high selectivity along with C4 hydrocarbons and carbon monoxide.	phenol, catechol, cyclopent-anone	(80)
12	Pt	Al$_2$O$_3$	40	573	Guaiacol, anisole, 4-methylanisole, cyclohexanone	-	0.01-0.12	Metal function and hydrogen are essential factors for any hydrogenolysis reaction	Phenol, Benzene Anisole	(81)
13	Pt	γ-Al$_2$O$_3$ SiO$_2$ H-BEA	140	573	m-cresol	0-80	0.09-12.5	High acid sites density results to coke formation which is detrimental for catalyst stability.	Toluene	(82)
14	Pt	γ-Al$_2$O$_3$	140	573	m-cresol	74 – 90	0.02-10	By increasing the metal loading from 0.05 wt.% to 1.7 wt.%, high selectivity turned from light hydrocarbons into toluene.	Toluene Benzene Methylcyclohex ane	(83)
15	Fe	SiO$_2$	70	673	Guaiacol	77.7	0.8	-	Benzene Toluene	(84)
16	Fe	SiO$_2$, Activated carbon	70	673	Guaiacol	100	1.66	By increasing the metal loading from 10 wt.% to 15 wt.%, high selectivity turned from phenol and cresols into benzene and toluene.	Benzene, Phenols	(85)
17	Fe	SiO$_2$	20-90	623 – 723	Guaiacol	74	0.66-9	Partial pressure of H$_2$ has negligible effect on product distribution.	benzene, toluene, xylenes	(86)
18	Ga	HBETA SiO$_2$ ZSM-5	140	673-823	m-cresol	80-85 (HBETA)	0.04-0.5	Without hydrogen partial pressure, the hydrogenolysis process is quickly depleted.	toluene, benzene, xylene,	(87)
19	Ru	TiO$_2$	58	673	Biomass pyrolysis vapors	-	0.1-0.15	With methoxy methyl groups transferred to the ring, the phenolic compounds in the bio-oil were transformed to less oxygenated compounds.	-	(88)
20	W	Carbon	140	653	propanol/propanal	-	-	The catalyst is very selective in breaking the C–O/C=O bond of propanol and propanal, resulting to the production propene as the main product.	propene	(89)
21	Ni	Al$_2$O$_3$ SiO$_2$ HZSM-5 ZSM55	100	488-533	1-octanol	87.4	2.5-10	Decreasing of pressure and WHSV, and also increasing of nickel loading and the reaction temperature resulted to increase in the conversion rate.	Octenes	(90)
22	Zn Ce Ni	Al$_2$O$_3$	0-140	838	Sunflower stalk bio-oil	92	-	2.5 wt.% metal (Zn, Ce or Ni) loading on the support exhibited the highest catalyst selectivity and activity.	Benzene Toluene Xylene	(91)
23	Cu Fe Pd	Carbon	140	523 - 723	Guaiacol	65	4-20	Base metal catalysts exhibit lower activity than the precious metal catalysts, but selectively form benzene along with small amounts of toluene,	Toluene Benzene	(92)

	Pt PdFe Ru							trimethylbenzene (TMB), and cresol without forming ring saturated or ring-opening products.		
24	Pt (Co, Ni)	γ-Al$_2$O$_3$	50/50 (H$_2$ to N$_2$ ratio)	533	m-cresol	38	0-140 W/F (gcat.h/mol)	The additions of Ni and Co into Platinum modified the product distribution as well as improving the overall HDO conversion.	toluene , methylcyclohexane.	(93)
25	Pt, Sn	monolith	101	673	Anisole, Guaiacol	74 (anisole) 90 (guaiacol)	0.42-3.85	In case of CNFs coating, surface area of the monolith increased dramatically (more than 10 times), which results to a higher metal loading in active phase incorporation.	Phenol, benzene	(94)
26	Ni/P	SiO$_2$	101	573	Guaiacol	-	10.68	Maximum deactivation rate (78%) of guaiacol belongs to Ni/P=1 sample whereas the Ni/P=3 sample had the lowest.	-	(95)
27	Ni$_2$P Co$_2$P Fe$_2$P WP MoP	SiO$_2$	112	573	Guaiacol	80 70 64 60 54	0.37	The activity order of the applied catalysts for guaiacol HDO are: Ni$_2$P>Co$_2$P>Fe$_2$P, WP, MoP.	Phenol, benzene	(28)
28	Pd-FeO$_x$	SiO$_2$	100	573-623	Furan	100	-	Using 5%Pd-2.5%FeOx/SiO$_2$ as catalyst resulted to 100% conversion of furan.	Methyl-decane Methyl-nonane	(96)
29	Ni$_2$P	Alumina, Zirconia, Silica	-	573	Guaiacol	-	0.67-5.34	Ni$_2$P/SiO$_2$ enhances DMO and DDO reactions, while Ni$_2$P/ZrO$_2$ and Ni$_2$P/Al$_2$O$_3$ promote DME.	catechol, anisole, cresol, phenol, benzene, cyclohexanone, cyclohexanol	(97)
30	Ni$_2$P	SiO$_2$	112	573	Guaiacol	100	GHSV = 8000 h^{-1}	Selectivity profile by using this catalyst is pentenes as primary products, 2-pentanone as a secondary product, and pentane as a final product.	Phenol benzene	(98)
31	Ni$_2$P	SiO$_2$	140	573	2-MTHF	-	-	The Ni$_2$P catalyst is outstanding in producing desired alkanes in the HDO of the biomass model compound 2-methyltetrahydrofuran.	n-butane n-pentane	(99)

As it can be observed from Table 2, various kinds of supports have been applied in atmospheric HDO of bio-oil oxygenated compounds including SiO_2, γ-Al_2O_3, Zeolites, carbon, TiO_2, ZrO_2, MgO, CeO_2, and monolith. Based on Table 2, H_2 partial pressure fluctuates from 0 to 140 in different studies. In most of the cases, the balance gas is N_2. The majority of researches has acknowledged that the higher partial pressure, the higher selectivity. The temperature fluctuates between 420 K and 838 K, while the prevalent temperature is 573 K. Taking into account the feed composition, it is realized that guaiacol is the most common model compound applied in these papers. However, various kinds of feeds have been used in this process including m-cresol, anisole, 2-hexanone, cyclohexanone, phenol, pyrolysis bio-oil vapors, furan, propanol, 2-MTHF, etc. Based on the mentioned feeds in this process, certain main products are expected such as benzene, toluene, propene, phenols, and others.

Reactors play an essential role in the chemical profile and yield of upgraded-bio-oil from pyrolysis vapors since it associates with the heating rate of system, heat transfer method, residence time of volatiles and conversion efficiency of oxygenated compounds (100). Each reactor has known advantages and disadvantages in operation and scaling. Fixed-bed reactor is the mostly used reactor in atmospheric HDO system (75). For those reactions in need of high temperature, the staged reactor can be used, which can adjust the reaction temperature to achieve the best catalytic effect and the lowest rate of catalyst deactivation (101). Batch reactors are applying in the HDO investigations when intermediate products are needed or fundamental studies are the objective of the studies.

Selection of a stable and active catalyst is crucial since it should overcome specifics operation conditions such as low H_2 pressure and moderate to high temperatures. Until now, various kinds of catalysts have been tested in this process such as metal oxides, transition metal sulfides, phosphides, precious metals, etc. Characterization of the applied catalysts are meaningful since it helps to understand the common nature of each catalyst facing different bio oil model oxygenated compounds. To suit this purpose, almost all the so far applied catalysts for low H_2 pressure HDO have been reviewed and discussed in the following sections.

3-1-1 Molybdenum

Molybdenum has been used by many researchers for HDO of various oxygenated components such as 2,5-dimethylfuran, 1,2-dimethoxybenzene, 2-methylfuran, diphenyl ether, 2-hexanonephenol, acetic acid, m-cresol, cyclohexanone, acetone, guaiacol, and anisole (28,70,71,73–75,102). T. Prasomsri et al. (28) reported that MoO_3 effectively converts bio-mass derived oxygenated compounds (Acetone, 2-hexanone, Cyclohexanone, Anisole, 2- methyl furan, 2,5-dimethylfuran) into unsaturated hydrocarbons (Propylene, Benzene, Pentenes, and Hexenes). According to their results, MoO_3, at low H_2 pressures, converts Phenolics and cyclic ketons to aromatics, and cyclic ethers and linear ketons to olefins with high yield. In another study by T.Prasomsri et al. (73), it was pinpointed that MoO_3 is capable of selectively converting various oxygenated compounds to aromatic hydrocarbons without ring saturated products. The results revealed that MoO_3 specifically cleaves phenolic Ph-OMe (CAromatic and OMethoxy) bond over the weaker aliphatic Ph-o-Me (OPhenolate and CMethoxy) bond which results in higher aromatic products. G. Zhou et al. (75) recently studied the atmospheric HDO of two bio-

oil model compounds as well as a real biomass vapor in a fixed bed catalyst reactor at 773 K. They found that the best process conditions for conversion of the real biomass pyrolysis vapor are 723 K and 89%vol H_2 concentration resulting in 16.2 wt% organic liquid with 11.5 wt% oxygen content. They also overstated that water inhibition, steric hindrance effects, and strong adsorption of pyrolysis vapor molecules to the catalyst active sites are the main reasons for harder upgrading of the pyrolysis vapor in comparison with the model compounds.

3-1-2 Platinum

Platinum is another frequently used metal as an active site for atmospheric HDO of model compounds. T. Nimmanwudipong et al.(77) studied the conversion of a model compound using platinum supported on Alumina. They found that the platinum function catalyzes the hydrogenolysis and hydrogenation reactions while the alumina support catalyzes the transalkylation reaction. From the experiments results, they concluded that the HDO selectivity rises with decreasing temperature elevating H_2 partial pressure. In another study by T.Nimmanwudipong et al. (79), a comparative study was undertaken by using Pt/Al_2O_3 with H_2, HY zeolite, and Pt/Al_2O_3 without H_2 as the catalyst. Their results indicated that H_2 is significant for oxygen removal from guaiacol. Also, the acidic catalysts without metal function (HY zeolite) produces similarly to those identified in the conversion catalyzed by the Pt/Al_2O_3 in the absence of H_2 (only transalkylation products). T. Nimmanwudipong et al.(80) further studied the HDO of guaiacol catalyzed by Pt/MgO in atmospheric H_2 pressure. The study results could be summarized as follows: (I) the selectivity to deoxygenated products in the reactions on Pt/MgO was higher, almost double the value achieved with $Pt/C-Al_2O_3$, (II) sequential reactions (ring opening, ring closing, and decarbonylation) occurred on Pt/MgO, (III) Pt/MgO catalyzed the

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formation of cyclopentanone at a relatively high selectivity, (IV) basic supports had higher conversion efficiency rather than acidic ones for noble metal hydrodeoxygenation catalysts. Ron C.Runnebaun et al. (81) scrutinized HDO of model compounds representative of lignin-derived bio oils such as guaiacol, anisole, 4-methylanisole, and cyclohexane using $Pt/\Upsilon-Al_2O_3$ as the catalyst. Here it was found that when selective deoxygenation is a goal, partial pressure of H_2 plays an important role in increasing the conversion efficiency. They also pointed out that Υ-Al_2O_3 is not active for oxygen removal reactions and only catalyzes the transalkylation reactions.

3-1-3 Other metals

Lately, some transition/post-transition metal based catalysts such as Fe, Ga, W, and Ni have been employed by some researches (84–87,89,90). R.N. Olcese et al. (84–86) investigated HDO of guaiacol over Fe/SiO_2, concluding that Fe/SiO_2 is an active and selective catalyst for the conversion of guaiacol even at high temperatures [673 K]. Although, Fe/SiO_2 is less active in comparison with the co-based catalysts, it is a more versatile catalyst. It also enjoys the benefits of being low-cost and environmental friendly. A. Ausavasukhi et al. (87) studied HDO of m-cresol using gallium (Ga) modified catalysts. They found that the yield of the desired products such as toluene and benzene undergoes a rise with Ga content, H_2 partial pressure, space time (W/F), and reaction temperature. According to their results, SiO_2 is not a proper support for Ga due to its inability to stabilize suitable Ga species which are the active sites for hydrogenolysis under atmospheric H_2 flow. In another study by V.C.S. Palla et al. (90), the supported Ni catalysts (Ni/SiO_2, $Ni/\Upsilon-Al_2O_3$, and Ni/HZSM) were examined in HDO of 1-octanol as a model aliphatic alcohol of bio oil at atmospheric H_2 pressure. Table 3 tabulates the products and their selectivity percentages. According to the results, Ni/ZSM55 has the highest conversion

efficiency among the other catalysts. Furthermore, the main products of HDO of 1-Octanol are n-Heptane, heptane, n-octane, octenes, DOE, and 1-octanal.

Table 3. The role of various supports on hydrodeoxygenation of 1-octanol (90)

Catalyst	Conversion rate	Selectivity,%					
		n-Heptane	Heptenes	n-octane	Octenes	1-octanol	DOE
Ni/ ɤ-Al$_2$O$_3$	45.1	50.9	24.9	0.7	0.4	10.7	10.1
Ni/SiO$_2$	43	52.7	32.8	0.3	0.2	10.8	2.6
Ni/ZSM23	40.2	8.2	0	5.9	73.2	6.2	6.5
Ni/ZSM55	61.5	10.6	0	4.0	69.5	6.2	6.9

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3-1-4 Bi-functional active sites

Bi-functional catalysts such as Pt-Co/ɤ-Al$_2$O$_3$, Ni$_2$P/SiO$_2$, Pd-FeO$_X$/SiO$_2$, Ru/TiO$_2$, etc. represent superior stabilities and activities among the other catalysts which can convert the oxygenated compounds through more than one reaction mechanism resulting in a surge in the yield of the desired products. M.A. Gonzalez-Borja and D.E. Resasco (94) elaborated on HDO of anisole and guaiacol using monolithic Pt-Sn catalysts at atmospheric pressure. The authors concluded that bimetallic Pt-Sn/CNF/Inconel catalyst is able to fully deoxygenate anisole and guaiacol at atmospheric pressure for a long time on stream (TOS). Nonetheless, the monometalic catalysts applied in this study (Pt/Inconel, and Sn/Inconel) deactivate much faster than the bimetallic catalysts and also have shorter TOS. In addition, P.T.M. Do et al. (93) investigated HDO of m-cresol on Pt/ɤ-Al$_2$O$_3$, Pt-Co/ɤ-Al$_2$O$_3$, Pt-Ni/ɤ-Al$_2$O$_3$ at near atmospheric H$_2$ pressure. They reported that HDO proceeds through two successive routes; hydrogenation of aromatic rings on the metal sites and dehydration of intermediates on the support (ɤ-Al$_2$O$_3$). Addition of 3D metals, including Co and Ni, into the catalyst significantly improved the products (toluene, and methylcyclohexane) distribution and the conversion rate. In another study by N. Joshi and A. Lawal (72), pre-sulfided NiO/MoO$_3$/Al$_2$O$_3$ was used as catalyst for HDO of acetic acid.

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Acetaldehyde, ethyl acetone, and acetone are the main products of HDO of acetic acid at 723 K and 80% H_2 gas. Supported nickel phosphide catalysts (Ni_2P/ZrO_2, Ni_2P/Al_2O_3, Ni_2P/SiO_2) were used in HDO of guaiacol by S. K. Wu et al. (97). According to the analysis results obtained from this study, Ni_2P/ZrO_2 is the most whilst Ni_2P/SiO_2 is the least reactive catalyst, based on the pseudo first order kinetics results at 573 K. However, TOS results revealed that Ni_2P/SiO_2 promotes direct deoxygenation (DDO) as well as DMO routes for removing oxygen, resulting in benzene and phenol, respectively. They established that Ni_2P/SiO_2 is the most promising catalyst, in comparison with its counterparts, for HDO of Guaiacol in atmospheric pressure. In the other study conducted by S.K. Wu et al. (95), the effect of phosphorous composition of nickel phosphide catalysts was scrutinized. Using various initial Ni/P molar ratios, they prepared three catalysts with different active phases (Ni_2P, $Ni_{12}P_5$, and Ni_3P). The authors reported that although Ni_2P has the highest deactivation rate, its product distribution is more stable compared to the other catalysts, which is mainly due to its bi-functional nature (protonation on PO-H and hydrogenation on Ni). In a study by S. Wan et al. (88), 5%Ru/TiO_2 was applied for HDO of oak and switchgrass pyrolysis vapors at low H_2 pressures. They found that noble metals play a role in generating vacancy sites on the support surface (TiO_2) that promotes ketonization besides its main role which is to function for deoxygenation. Furthermore, according to the Van krevel diagram results, catalytic treatment of the pyrolysis vapors contributed to a rise in O/C and H/C in the combined aqueous phase (0.93 and 1.92 respectively). In a very recent investigation by J. Yang et al. (103), a new bi-functional catalyst (Pd-FeO$_X$/SiO_2) was used for atmospheric HDO of furfural. Based on their results, 5%Pd-2.5%FeO$_X$/SiO_2 represents a full conversion of furfural with high efficiency of jet fuel range alkenes at 573 K- 623 K. The modification of Pd/SiO_2 with FeOX results in (I) restraining of the decarbonylation reactions, (II) lowering the coordination

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number of Pd-Pd species, (III) promoting the hydrogenation of carbonyl group over Pd, and (IV) generating Pd-Fe alloy. All these effects contribute to a high HDO activity of the catalyst at atmospheric pressure.

3-1-5 Supports

Material carrier plays an essential role in catalytic preparation. Two main features should be considered in the selection of a support for at HDO; ability to activate oxygenated compounds and low affinity for carbon formation (25,104).

Due to the presence of water in bio-oil, Al_2O_3 is an unsuitable support for this process since it will convert to boehmite in the presence of a large amount of water (2,67,105). Formation of boehmite further results to the oxidation of metals on the catalysts that are inactive with respect to HDO and also could block other active sites on the catalysts. Furthermore, according to Popov et al (1), two third of the alumina covers with phenolic compounds at 400 ˚C that are potential carbon precursors.

As an alternative to Al_2O_3, SiO_2 has been found to be a more promising support mainly due to its neutral nature features to a lower tendency for carbon formation compared to Al_2O_3 (28). Al_2O_3 dissociates phenol into more strongly adsorbed species on the acid sites, but SiO_2 only interacts with phenol through hydrogen bonds (106). Additionally, Popov et al. (1) revealed that the concentration of adsorbed phenolic compounds on SiO_2 was only 12% comparative to the concentration found on Al_2O_3. TiO_2, ZrO_2, and CeO_2 also have been applied as the catalyst support in atmospheric HDO (76). They thought to have the potential to active oxygenated

3-2 Deactivation

According to the reviewed articles, carbon deposition on the catalyst surface is the main route of catalyst deactivation. Other mentioned causes including metal deposition, sintering of the catalyst, poisoning by water, phosphorous, nitrogen, etc., also happen at HDO at low hydrogen pressure. Lignin derived compounds, such as phenols, due to their great concentrations of unsaturated hydrocarbons elements, are greatly prone to formation of coke. The unsaturated hydrocarbon elements, typically react tightly with catalytic sites on the surface, limiting the access of other oxygenated compounds to the active sites. Some well-known factors for catalyst deactivation are the temperature, the catalyst acidity, the catalyst pore volume, and the space velocity which have been discussed thoroughly elsewhere (107–109). Following some recent discussions regarding low H_2 pressure HDO catalyst deactivation has been reviewed.

In an attempt to find an effective and applicable HDO route as well as understanding the factors influencing the catalyst deactivation, T.Prasomsri et al (70) investigated HDO of acetone with MoO_3 using low H_2 pressure. They found that H_2 partial pressure casts a strong effect on the catalyst performance and the catalyst deactivation profile. The increase in H_2 partial pressure results in regenerating active oxygen vacancy sites while it avoids blocking of active sites by carbonaceous species (71).

R.N. Olcese et al. (84) performed a kinetic and modeling study for low H_2 pressure HDO of guaiacol to aromatic compounds over Fe/SiO_2. They found that the plots for the values of

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kinetics constants of the selected reactions versus TOS fit very well with the following empirical law for the coke-induced catalytic deactivation;

$$K = K^0 \exp(\alpha t)$$

In this equation t stands for the time in minutes, α denotes the coefficient for deactivation in min^{-1}, K^0 is the initial reaction rate, and K symbolizes the reaction rate in kmol/(s.kg).

González-Borja, M. Á., and Resasco, D. E (94) reported that notwithstanding a high reactivity in a typical HDO process, it might have a high rate of catalyst deactivation that is only apparent in the distribution of products. For instance, they observed that the conversion of anisole yields benzene as the main end product, with phenol as the major intermediate, while o-cresol and toluene appear as minor products even after 125 TOS. It is whilst, in the case of guaiacol, after 125 TOS, phenol is the main end product.

In a study by Moon et al (110), they surveyed the catalyst deactivation in various pressures and temperatures. At 1 atm, the reduction in reaction temperature dropped the HDO conversion from 80% to 60%, but it was not completely recovered upon the temperature ramping, representing that the catalyst underwent deactivation possibly due to the partial oxidation of the catalyst surface or coke deposition. At 8 atm, the deactivation was not detected and the hydrodeoxygenation activity was retrieved upon the increase in temperature. These results propose that the hydrogenation route (the reaction mechanism at high pressures) is less susceptible to coke deposition or poisoning than the direct deoxygenation route (the reaction mechanism in atmospheric pressure).

3.3 Reaction network and Kinetics of guaiacol HDO at atmospheric pressure

The kinetics of HDO has been investigated by many researchers to better understand the HDO mechanism of pyrolysis oil (111,112). However, the sparse reliable kinetic information of HDO of pyrolysis oil is reported due to the diversity of complex compositions of bio-oils (113); instead, a variety of studies explored the HDO kinetics of different model compounds which were found to be the significant compositions of bio-oils with a lower reactivity, such as guaiacol, phenols, furans, aldehydes and the like (112). The kinetics of HDO of guaiacol had received increasing attentions since it is the most representative model compound for the lignin-derived bio-oil (28,86,114,115). This is mainly due to the fact that guaiacol incorporates two types of C–O bond that represent both lignin and many of its derivatives. Furthermore, the existence of guaiacol in bio oils remarkably affects the results of upgrading of bio oil mainly due to their low reactivity (116,117). Compared to phenol, there is one more methoxy group attached to the aromatic ring. This small change makes the reaction network of guaiacol much more complex than the phenol (118). S.K. Wu et al (119) investigated the atmospheric HDO of guaiacol over Ni_2P catalysts. According to their results obtained from the activity evaluation, they proposed a conceivable network for the reaction. Figure 1 represents a reaction network for the atmospheric guaiacol HDO over Ni_2P catalysts.
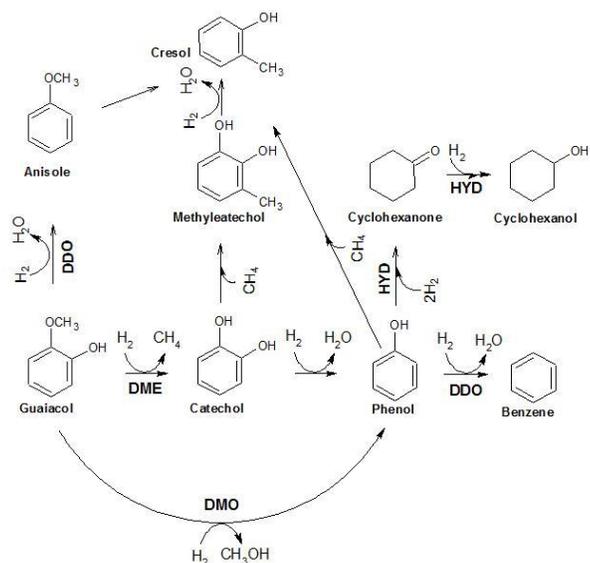
Figure 1. Proposed guaiacol HDO network at atmospheric H_2 pressure (119)

Based on the proposed network, they found four possible reaction routes including Hydrodeoxygenation (HDO), Direct Deoxygenation (DDO), Demethoxylation (DMO), and Demethylation (DME). Among these four routes, DDO and DMO are the only oxygen-atom removal pathways. By comparing the other studies of guaiacol HDO at a low pressure environment, the authors found that the route of guaiacol DDO to anisole is a common point in these studies. According to the findings, they declared that H_2 pressure is an essential factor to mediate the HDO network. T. Nimmanwudipung et al (77) carried out a study on catalytic HDO of guaiacol in a continuous tubular reactor over platinum supported on alumina. The results derived from the logarithmic plot of the experimental data (fraction of the guaiacol unconverted versus the inverse space velocity) showed apparent first order kinetics. 16.2 L (g of catalyst)$^{-1}$ h^{-1} is the pseudo first order rate constant for the guaiacol conversion using platinum as the catalyst.

S.K. Wu et al (119) deployed the same approach to gain the rate constant for the conversion of guaiacol in a low H_2 pressure. The authors applied supported Nickel phosphides as the catalysts. Compared to the above-mentioned study, an order of the magnitude smaller rate constant (1.5 (g catalyst)$^{-1}$ h^{-1}) was achieved, indicating that platinum was much active for this type of reactions. The first order reaction kinetic was also reported in this study for guaiacol HDO.

However, other orders for the reaction kinetic of guaiacol HDO at the atmospheric H_2 pressure have been reported. For instance, R. N. Olcese et al (84) surveyed guaiacol catalytic HDO over Fe/SiO$_2$ catalyst. They carried out the experiments in a fixed bed reactor at the atmospheric pressure. A gas mixture including guaiacol, H_2O, CO, CO_2 and H_2 was applied in this study as the feed to simulate the real gas composition from the pyrolysis of the lignin. According to their offered reaction pathway derived by the experimental results, they proposed the following equation for guaiacol HDO at the atmospheric pressure:

$$\frac{1}{1-n}\left(F_i^{1-n} - F_{0i}^{1-n}\right) = -\frac{k(RT)^n}{Q^{n-1}}t \qquad (2)$$

F_i, F_{0i}, k, R, T, Q and t stand for the molar flow rate of the converted compound, the molar flow rate at the entrance of the catalyst bed, the kinetic constant, the molar gas constant, the temperature of the catalyst bed, the total volume flow rate of the gas phase and the space time, respectively. The authors reported that based on equation 2, the apparent reaction rate can be assumed zeroth order since the molar flow rate of guaiacol, benzene, and toluene exhibit a linear evolution with the space time. The apparent zero order kinetics observed for all the reactions would indicate that the oxygenated species are strongly adsorbed through hydroxyl moieties with a high surface coverage. The second order for this reaction has been proposed by D. Gao et al

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(120). They performed a kinetic study based on five 5 sub-reactions for the guaiacol-hydrogen reaction over platinum as the catalyst;

$$guaiacol + H_2 \xrightarrow{k_1} catechol + CH_4$$
$$catechol + H_2 \xrightarrow{k_2} phenol + H_2O$$
$$guaiacol + 2H_2 \xrightarrow{k_3} phenol + MeOH$$
$$guaiacol + 3H_2 \xrightarrow{k_4} cyclopentanone + CH_4 + CO$$
$$catechol + 2H_2 \xrightarrow{k_5} cyclopentanone + CO$$
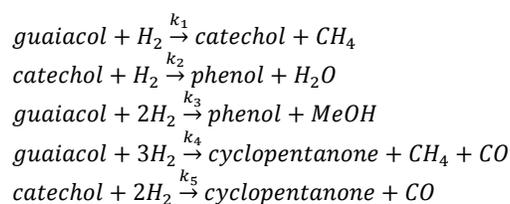
They also integrated the designed equation based on a plug-flow packed-bed reactor assumption and finally concluded that the good fitting was achieved when the reaction order was 2. They explained that under the applied operation conditions, adsorption of guaiacol is the rate controlling and this is the most possible explanation for the second order reaction rate. Based on the various orders for HDO of guaiacol, it could be understood that the experimental conditions used, such as the catalyst, types of the reactors, the method of analysis and the like, will have an influence on the kinetic parameters obtained by different studies. Furthermore, selecting a proper kinetic model to predict the reaction order is critical. Three reaction models are commonly applied for this purpose including Langmuir-Hinshelwood, Rideal-Eley, and power-law models (120). Among them, however, the power-law kinetic model generally represents good fitting results and realistic kinetic parameters for this type of reactions.

3-4 Overall aspects and prospect of low H_2 pressure HDO

Although recently a significant number of relevant studies have focused on the low H_2 pressure HDO process of bio oil oxygenated compounds in the laboratory scale, further investigation is demanded to explore the integration of the current infrastructures of oil refinery for this process

in an industrial prospective. Low H_2 pressure HDO is a promising and attractive process since H_2 consumption is one of the most paramount constituents which affects the total cost of end products in HDO of bio oils. Though, in this process, the most problematic challenge is finding a robust catalyst which is able to tolerate high processing temperature and stand against deactivation by coking and water poisoning. Consistent with the recent surveys, MoO_3 is an outstanding catalyst representing high tolerance to coke formation and water poisoning (70). Further favorable catalysts for this process include Ni_2P/SiO_2, $Pd-FeO_x/SiO_2$, Fe/SiO_2, and Pt/SiO_2. Among all the supports being used so far, SiO_2 represents the best characteristics for the active sites in low H_2 pressure HDO. C.R. Lee et al. (121) reported that the deoxygenation activity of an active site increases when more acidic sites are introduced. The authors reported that 2-methoxycyclohexanol is formed exclusively by hydrogenation of the benzene ring once the conversion is catalyzed by noble metals supported on nitric-acid-treated carbon black, but when the support is $SiO_2–Al_2O_3$, which incorporates acidic sites, the main product is cyclohexane which is a desired product. Nevertheless, as it was mentioned in the catalyst deactivation section at an earlier point, the conversion rate does not reflect the efficiency of the applied catalyst since the main product alters from the deoxygenated ones to the oxygenated compounds although the conversion stays high. Therefore, the judgement should be based on the analytical results from the experiments as the conversion rate does not suffice. According to the literature, the main valuable products from HDO of bio oil oxygenate compounds are benzene, phenol, toluene, and anisole.

The selectivity and conversion rate of the fuels produced from upgrading bio-oil are vital features to consider, but depending on the process conditions, especially H_2 pressure. By

changing the H_2 pressure, different product compositions with various conversion rates will be achieved. As yet, there are a few comparison studies on HDO of a model compound using a catalyst in atmospheric and high pressures of H_2 to explore the exact impact of H_2 pressure on this process.

In a study by Moon et al (110), they investigated the HDO of guaiacol using Ni_2P/SiO_2 as the catalyst in 1 and 8 atmospheric pressure of H_2 as well as various temperatures of the reaction to monitor the selectivity and efficiency of the process. CO chemisorption uptake measurement revealed after hydrodeoxygenation process, the loss of active sites is more pronounced for the catalyst tested at 1 atmosphere in comparison to the catalyst tested at 8 atmospheres. The decrease in the CO uptake was found to be 32% and 9% for the Ni_2P samples tested at 1 and 8 atmospheres respectively. The authors found that at 1 atm guaiacol converts to benzene as the major products with a selectivity of 62%, then anisole (30%), cyclohexane (7%), and phenol (<1%) as minor products, with a guaiacol conversion of 83%. Instead, at 8 atm the conversion of guaiacol resulted to cyclohexane (91%) as the major component and benzene (8%), anisole (1%), and phenol (1%) as minor products, with a guaiacol overall conversion of 100%. Further investigation at elevated pressures (up to 15 atm) proved the same trend, increasing the pressure leads to decrease in benzene production and simultaneously increase in cyclohexane production. The following overall conclusions have been made based on the Moon et al (2014) experimental results followed by DFT studies together with XAFS and in situ FTIR measurements.

- pre-hydrodeoxygenation and direct hydrodeoxygenation occur concurrently over the catalyst, in which the HDO of guaiacol frequently yields phenol or anisole in the early stage of reaction.

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- At 1 atm, the direct hydrodeoxygenation pathway appears dominant to give benzene

- At 8 atm, the pre-hydrogenation pathway becomes prominent to form cyclohexane

- The active spots of the catalysts for the HDO of guaiacol can be proposed in terms of relative populations of OH or H groups on P or Ni sites of Ni_2P surface, influencing whole reaction pathways.

- Direct deoxygenation pathway is preferred by the surface OH groups, whereas the pre-hydrogenation pathway is favored on the more reduced surface of the catalyst. Furthermore, high dispersion of the active sites will be of great importance in facilitating the hydrodeoxygenation process.

Conclusion

Atmospheric hydrodeoxygenation (HDO) of bio-oil/bio-derived oxygenated compounds in pyrolysis oils has been reviewed. The catalysts having a high activity for HDO at atmospheric H_2 pressure as well as great potential to avoid carbon formation are of great challenge in this discipline. MoO_3, Ni_2P/SiO_2, $Pd-FeOx/SiO_2$, Fe/SiO_2, and Pt/SiO_2 are the most promising catalysts efficiently upgrade oxygenated compounds (guaiacol, m-cresol, acetone, furan, 2-methyl furan, 2,5-dimethylfuran, anisole, etc.) to higher octane index compounds. Based on this review, 573 K is the most proper temperature for atmospheric HDO since it maximizes the conversion rate while the coking is still low. However, in order to make this process affordable in an industrial scale in the future, many challenges have to be addressed meticulously through further studies include; lack of advanced kinetic studies to reveal an accurate mechanism of atmospheric HDO, optimizing the reaction conditions, and exploring developed catalysts.

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