

Recent advances in the catalytic hydrodeoxygenation of bio-oil

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Abstract—Owing to the increasing interest in alternative energy, there is a focus on bio-oil production from biomass because it is an abundant and renewable energy source. Among the various kinds of biomass conversion technologies, pyrolysis has been investigated widely to produce bio-oil. However, the direct use of bio-oil is difficult because of its poor quality due to the large amounts of oxygen-containing compounds, such as acids, ketones, and esters. Therefore, an additional suitable upgrading process for bio-oil is required. Hydrodeoxygenation (HDO) is considered effective for the deoxygenation of bio-oil. This paper reviews the recent progress in the catalytic HDO of bio-oil. In addition, the effects of the solvent and catalyst applied to the HDO of bio-oil are reviewed intensively together with a discussion of the deactivation behavior of the catalyst during HDO.

Keywords: Pyrolysis of Biomass, Catalytic Upgrading, Bio-oil, Hydrodeoxygenation

INTRODUCTION

The global concerns for energy security are increasing constantly due to the intensive use of fossil fuels. Current environmental issues, such as climate change and air contamination, have also encouraged a focus on the development of renewable energy [1-3]. Biomass is a candidate source for alternative energy production because it is abundant and spread evenly across the world [4-12]. The major thermo-chemical processes for biomass conversion are gasification, pyrolysis, and hydrolysis, which can produce syngas, bio-oil (pyrolysis oil), and aqueous sugar, respectively, as the main product [13-21]. Among them, fast pyrolysis is considered the most effective method to obtain large amounts of bio-oil [22], because it is not only a fast, stable, and low-cost investment [23], but can also be applied to most biomass species [24,25]. Previous studies reported that as much as 70% of bio-oil can be produced by biomass pyrolysis [26,27]. The use of solid bio-char and the other byproducts of biomass fast pyrolysis can also increase the economic value or efficiency of the pyrolysis process [28-42].

A number of biomass materials, such as rice husk [43], miscanthus [44], pinewood [45], cellulose [46], and lignin [47] have been used to produce bio-fuel via pyrolysis and the quality of bio-fuel has been upgraded through additional processes, such as cata-

lytic pyrolysis [48] and co-pyrolysis with other polymers [49] or additives [50]. These studies enhanced the technical competitiveness of bio-oil production by biomass pyrolysis and continuous researches by many investigators are underway, making it a promising technology. On the other hand, the use of bio-oil as a transportation fuel is still difficult because of its low quality. Bio-oil contains a range of organic compounds, such as acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and large molecular oligomers produced from lignin [51]. Bio-oil also has a high water and oxygen content, low heating value, high acidity and viscosity, and chemical instability [52]. Therefore, many studies have been conducted to improve the quality of bio-oil.

The methods to upgrade bio-oil can be divided into physical methods, such as filtration using high temperature gas [53] and emulsification [54], and chemical methods, such as solvent addition [55], steam reforming [56], catalytic pyrolysis [57-60], hydrogen processing [61-64], etc. Among them, hydrogen processing is performed to eliminate heteroatoms, such as S, N, and O, at high temperature using high pressure hydrogen gas [65]. Hydrodeoxygenation (HDO) is an effective upgrading process to convert oxygen-containing compounds, such as acids, aldehydes, alcohols, and phenol, to oxygen-free hydrocarbon fuels [66-69] compared to the low conversion efficiencies of other upgrading processes, such as catalytic fast pyrolysis.

To examine the effects of HDO on bio-oil upgrading, many studies have used model compounds because it is difficult to understand the reaction pathways for the HDO of bio-oil consisting of various oxygen-containing compounds. Among them, phenolic

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Table 1. Physico-chemical properties of bio-oil obtained from various kinds of biomass

Biomass		Sawdust ^a	Pine wood	Rice husk	Cotton stalk	Palm shell	Willow	Maize stalk
Elemental analysis (wt%)	C	30.72	48.13	41.7	42.3	49.74	43.17	44.3
	H	6.67	6.32	7.7	7.9	5.32	7.15	6.3
	O	61.54	44.63	50.3	49.4	44.86	49.49	47.5
	N	1.07	0.35	0.3	0.3	0.08	0.10	0.6
	S	NA	0.18	0.2	0.2	0.16	0.10	0.3
Density (kg/m ³)		1050	NA	1190	1160	1051	NA	1220
Viscosity		9.84 (50 °C, cP)	NA	128 (40 °C, mm ² /s)	125 (40 °C, mm ² /s)	3.2 (50 °C, cP)	53.2 (cP)	138 (40 °C, mm ² /s)
H ₂ O (wt%)		39.00	NA	25.2	24.4	53	17.4	22.5
pH		1.85	NA	2.8	3.3	2.5	2.68	3.2
HHV (MJ/kg)		10.93	18.57	17.42 (LHV)	17.77 (LHV)	6.58	18.4	19.6 (LHV)
Ref.		[85]	[45]	[43]	[86]	[87]	[88]	[89]

^aObtained from different wood mixture

compounds derived from the pyrolysis of lignin, such as guaiacol [70], anisole [71,72], and phenol [73], have been used intensively as the model compounds owing to their high portion in bio-oil. The suggestion of a possible HDO reaction mechanism of these phenolic model compounds is considered an important target of many studies because they contain many different functional groups (e.g. hydroxyl, carboxyl, and methoxy) on an aromatic structure [13].

The metal sites of the catalyst and high pressure are necessary to produce aliphatic hydrocarbons from phenolic compounds and other aromatic hydrocarbons via the HDO of bio-oil under high pressure [74]. The use of a catalyst is also very helpful, not only to minimize the carbon loss, but also to increase the efficiency of hydrogen on HDO. The increase in hydrogen efficiency is very important because a huge amount of hydrogen is required in the HDO process. Therefore, the use of a catalyst is essential to reduce the total cost of bio-oil production. Many catalysts, such as noble metals, zeolites, and sulfided catalysts have been tested to find suitable catalysts for the bio-oil HDO process [75-77].

For the HDO reaction test of real bio-oil, batch type reactors are usually used to minimize the other effects except for temperature, pressure, and catalyst. On the other hand, the sequential type reactor should be considered during the scale-up procedure to maximize the bio-oil production efficiency in the commercialized process. However, the feeding of bio-oil in the sequential type reactor is difficult because of the high viscosity of bio-oil, which acts as a technical barrier. Filtration [78] or solvent addition [79] has been suggested to overcome the bio-oil feeding problems. Solvent addition can also increase the overall reaction efficiency of HDO because the solvent can participate in the reaction and act as a supercritical fluid during HDO [80-82].

Although the value of bio-oil in the fuel market can change depending on the oil price, innovative processes for high quality bio-oil production need to be developed to overcome any future energy crisis and reduce the environmental stress caused by the intensive use of fossil fuels.

Therefore, we review here the recent technical trends on the HDO of bio-oil. The HDO reactions for model compounds and actual bio-oil are reviewed together with a discussion of the effects of the catalyst and solvent addition on the HDO reaction.

BIO-OIL

Bio-oil has different chemical distributions depending on the biomass species and applied pyrolysis conditions. As shown in Table 1, bio-oil has high carbon (30-50 wt%), oxygen (44-61 wt%), and hydrogen (6-8 wt%) contents together with low nitrogen (<2 wt%) and sulfur (<0.5 wt%) contents [83]. Bio-oil is corrosive owing to its high organic acid content and its heating value is also low due to the high oxygen content [84]. The viscosity, water content, and pH were also different depending on the biomass species and its pyrolysis condition. Therefore, the selection of bio-oil is important for the HDO reaction of bio-oil.

The thermal and chemical stability of bio-oil were reported to be lower than those of typical petroleum fuels because bio-oil contains large amounts of oxygen-containing compounds and its volatility is high [90]. The stability of bio-oil is important because it needs to be stored and transported safely. A stability test can be performed by checking the change in viscosity, water content, and average molecular weight of bio-oil. The change in carbonyl products, such as aldehydes and ketones, can also be used for the bio-oil stability test because they can accelerate the instability of bio-oil. A range of bio-oils obtained from the pyrolysis of wood (pine, spruce and forest residues), birch wood [91], and softwood [92] were used for the bio-oil stability test. Boucher et al. [92] measured the change in the viscosity and water content of bio-oil from the accelerated aging test (at 80 °C for 24 hours). They suggested that the polymerization and condensation reaction, such as esterification, etherification, and olefinic condensation among hydroxyl, carbonyl, and carboxyl group components are the main reactions for the change in bio-oil stability.

Many studies have attempted to upgrade the quality of bio-oil. Park et al. [93] and Cao et al. [94] attempted to upgrade bio-oil by applying the co-pyrolysis of biomass with waste plastics and tires, respectively. They reported that high quality bio-oil can be obtained via co-pyrolysis with plastics and tires, which have high carbon and low water contents. The catalytic upgrading of bio-oil using HZSM-5 and HY was also reported [95]. Although the yields of benzene, toluene, and xylenes were increased by applying catalytic pyrolysis, its quality was still not high enough to use the product

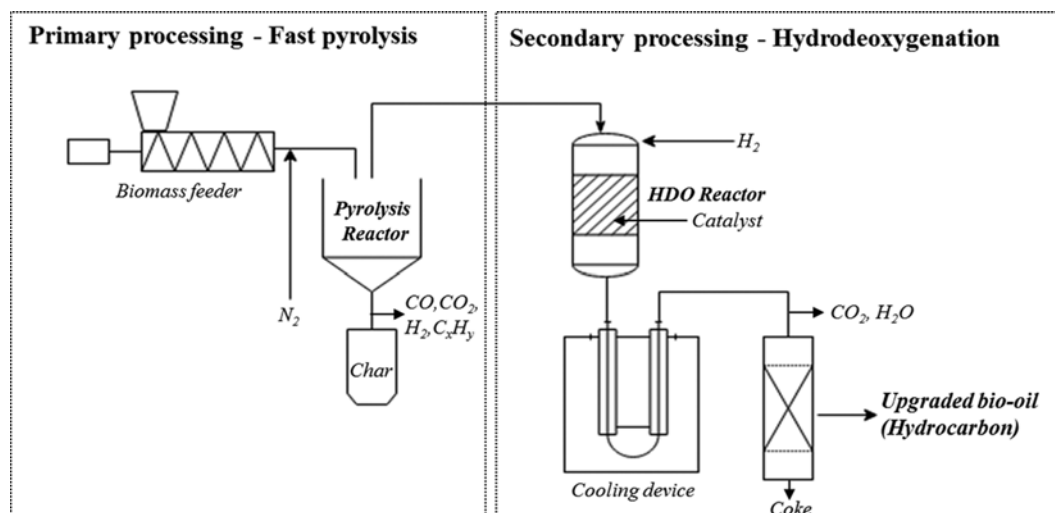


Fig. 1. System diagram of the sequential reactor system for the biomass pyrolysis-HDO reaction [96].

oil as a transportation fuel. In this situation, the HDO of bio-oil has been suggested as an essential process to produce high quality bio-oil.

Fig. 1 presents a specific diagram of the sequential process system for the pyrolysis of biomass followed by the HDO upgrading reaction [96]. In this system, the product vapor biomass pyrolysis emitted from the first reactor is fed into the second reactor for an additional HDO reaction. Most HDO processes, however, are operated using batch-type reactors in many research institutes and most use the bio-oil produced by the simple fast pyrolysis of biomass without the additional use of a catalyst or co-feeding materials. If the catalytic pyrolysis or co-pyrolysis is applied prior to the HDO reaction process, the HDO reaction pathway would be shortened because the amount of oxygenated compounds is decreased with increasing small molecular compounds by catalytic pyrolysis or co-pyrolysis [97]. On the other hand, research on the sequential reaction systems comprised of catalytic pyrolysis or co-pyrolysis with the additional HDO reaction is still in demand.

CATALYTIC HDO OF MODEL COMPOUNDS

Many researchers have used model compounds instead of actual bio-oil to examine the optimal condition, appropriate catalyst, and possible reaction pathway for the HDO reaction of bio-oil, because of the complex chemical composition of bio-oil [97]. Wood-derived biomass contains hemicellulose (25-30%), cellulose (40-50%), and lignin (15-30%) [98]. Although the chemical or biological conversion of lignin is more difficult than that of hemicellulose and cellulose because of its complex structure, many researchers are focusing on lignin conversion to maximize the use of biomass because lignin has great potential for the production of fuels and bulky chemical feedstock [99].

For the efficient conversion of lignin, many researchers used guaiacol [100-102], a monomer unit of lignin containing oxygenated functional groups ($\text{CH}_3\text{O}-$ and $\text{HO}-$), as the model compound for the HDO reaction of lignin derived bio-oil. The other specific pyrolyzates of lignin, such as cresol [103], anisole [104], phenol [105],

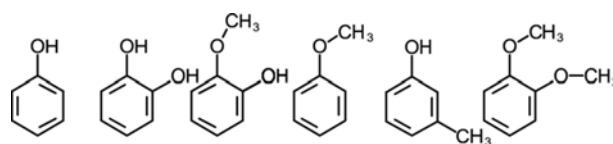


Fig. 2. Model compounds of lignin pyrolysis oil (phenol, catechol, guaiacol, anisole, m-cresol and veratrole).

veratrole [106], and dibenzofuran [107] (Fig. 2) have also been used to study the HDO reaction of lignin derived bio-oil.

Sanna et al. [108] suggested four types of oxygen elimination reaction pathways from the HDO study of model compounds as follows: (1) hydrogenation of C-O and C-C bonds, (2) dehydration of C-OH groups (3) C-C bond cleavage by retro-aldol condensation and decarbonylation, and (4) hydrogenolysis of C-O-C bonds. Cycloalkanes ($\text{C}_6\text{-C}_9$) were produced as the main products via the HDO reaction of lignin-derived model compounds, and the yields of the target products were determined by the catalyst and reaction conditions, such as the reaction time, temperature, and pressure. Table 2 summarizes the reaction conditions, conversion rate, and major products of the HDO reaction of lignin-derived model compounds reported in the literature. As shown in Table 2, many types of catalyst have been used for the HDO of lignin model compounds. Generally, reaction temperatures between 250 and 300 °C and high pressures up to 3 MPa (sequential reactor) or 7 MPa (batch reactor) were chosen, mainly as the condition of the HDO reaction. The effects of the contact time were tested using sequential reactors. In addition, the effects of temperature and pressure on HDO reaction were examined mainly using batch-type reactors.

Ghampson et al. [70] examined the effects of the contact time of the reactant with the catalyst on the HDO of guaiacol by measuring the change in the concentration of major products (phenol, catechol, methylcatechol and heavy products) in the product oil. Yang et al. [74], Saidi et al. [109], and Chang et al. [110] suggested the HDO reaction mechanisms by measuring the product chemicals under different reactant-catalyst contact times. Peters et

Table 2. Summary of studies on catalytic HDO of model compounds

Model compound	Reaction temperature	Reaction pressure	Reaction time or space velocities	Reactor type	Catalysts	Conversion	Major products	Ref.
Guaiacol	300 °C	5 MPa	4 h	Batch	CoMoN/SBA-15 MoN/SBA-15 CoMoN/Al ₂ O ₃ MoN/Al ₂ O ₃	66%	Catechol	[70]
Guaiacol	300 °C	7 MPa	NA	Batch	Pd/WO _x /Al ₂ O ₃	100%	Cyclohexane	[118]
Guaiacol	250-340 °C	5 MPa	1-8 h	Batch	Ni /ZrO ₂ -SiO ₂ NiCu/ ZrO ₂ -SiO ₂	100%	Cyclohexane Cyclohexene Benzene Toluene	[71]
Guaiacol	300 °C	NA	0.67-5.34 h ⁻¹	Continuous	Ni ₂ P/Al ₂ O ₃ Ni ₂ P/ZrO ₂ Ni ₂ P/SiO ₂	99.6%	Benzene	[97]
Guaiacol	300 °C	1 atm	0.1-0.3 g _{cat} ·h/g _{GUA}	Continuous	Pt/C Pd/C Rh/C Ru/C	87%	Phenol Catechol Cyclopentanone	[120]
Guaiacol	360 °C	10 bar	3 h	Batch	Rh/ZrO ₂ PdRh/ZrO ₂ PtRh/ZrO ₂ Sulfided CoMo/Al ₂ O ₃ Sulfided NiMo/Al ₂ O ₃	100%	Cyclohexane	[121]
Guaiacol/ Anisole	350-450 °C	1.7-15 bar	0.3-4.3 h ⁻¹	Continuous	Ni-based Fe-based FCC (commercial)	99.6%/ 35%	Benzene Toluene	[65]
Anisole	180-220 °C	0.5-3.0 MPa	4 h	Batch	Ni/AC Ni/Al ₂ O ₃ Ni/SBA-15 Ni/SiO ₂	99%	Cyclohexyl methyl ether Cyclohexane Cyclohexanol Benzene	[71]
Anisole	300 °C	1.5 MPa	10-100 h ⁻¹	Continuous	Ni ₂ P/SiO ₂ MoP/SiO ₂ NiMoP/SiO ₂ NiMo/Al ₂ O ₃	95%	Phenol Benzene Cyclohexane	[114]
Phenol	150-300 °C	1.5 MPa	0.5 g _{PHF} /g _{cat} ·h	Continuous	Ni-W/AC	100%	Cyclohexane Cyclohexene Cyclohexanol Methylcyclopentane	[122]
Phenol	230 °C	2.8 MPa Initial pressure	1 h	Batch	Amorphous unsupported Ni-Mo sulfide	96.2%	Cyclohexane Cyclohexene Cyclohexanone Benzene	[123]
Phenol	300 °C	650 psi	1 h	Batch	Ru/SBA-15 Ru/silica gel Ru/MCM-41 Ru/CNF Ru/C Ru/Al ₂ O ₃ Ru/TiO ₂	12%	Cyclohexane Cyclohexene Cyclohexanone Cyclohexanol Benzene	[124]
Phenol	275 °C	100 bar	4 h	Batch	Pt/C Ni/CeO ₂ Ni/CeO ₂ -ZrO ₂	99.8%	Cyclohexanol Cyclohexane Dicyclohexyl	[73]

Table 2. Continued

Model compound	Reaction temperature	Reaction pressure	Reaction time or space velocities	Reactor type	Catalysts	Conversion	Major products	Ref.
Phenol	350 °C	15 bar	0.8 g _{cat} ·min/ml _{PHF}	Continuous	CoMo/Al ₂ O ₃ CoMo/TiO ₂ NiMo/Al ₂ O ₃ NiMo/TiO ₂ NiW/Al ₂ O ₃ NiW/TiO ₂	About 96%	Methylcyclopentane Cyclohexane Cyclohexene Benzene	[125]
Phenol	250 °C	1.5 MPa	0.5 h ⁻¹	Continuous	Pd/Al ₂ O ₃ Pd/HY-Al ₂ O ₃ Pd/HY	63%	Cyclohexene Cyclohexane	[126]
4-Propylphenol	260-300 °C	2 MPa Initial pressure	0-1 h	Batch	Pt/ZrO ₂ Pt-Re/ZrO ₂ Pt-Sn/ZrO ₂ Pt-Ir/ZrO ₂ Pt-Ga/ZrO ₂ Pt-Fe/ZrO ₂ Pt-Au/ZrO ₂ Pt-Pd/ZrO ₂ Pt-W/ZrO ₂ Pt-In/ZrO ₂ Pt-Mo/ZrO ₂ Pt-Bi/ZrO ₂ Pt-Re/TiO ₂ Pt-Re/Al ₂ O ₃ Pt-Re/CeO ₂ Pt-Re/SiO ₂ Pt-Re/AC	100%	n-Propylbenzene	[127]
Dibenzofuran	200-300 °C	3.0 MPa	32 h ⁻¹	Continuous	Ni/P	99%	Bicyclohexane	[128]
Guaiacol Dibenzofuran	250 °C	40 bar	3 h	Batch	Pt/mesoporous Y Pt/mesoporous MFI	61.4	Cyclohexane	[107]
m-Cresol	260 °C	0.5 atm	63 g _{cat} ·h/mol	Continuous	Pt/Al ₂ O ₃ Pt/SiO ₂	44%	Toluene	[103]

al. [65] suggested a mechanism for the benzene and toluene production reaction via the HDO reaction of guaiacol. They explained that catechol and methylcatechol can be produced by the transalkylation of methoxy groups or the demethylation of guaiacol, and benzene and toluene were produced from the additional hydrodeoxygenation of catechol and methylcatechol. Bykova et al. [111] explained the conversion of guaiacol to cyclohexane. Phenol and anisole are generated by the hydrodeoxygenation of guaiacol. Phenol forms benzene via hydrodeoxygenation or cyclohexane via dehydration-hydrogenation reaction. They also detected methylcyclopentane, which can be produced by the isomerization of cyclohexene. Anisole was converted to benzene (hydrodeoxygenation reaction) and cyclohexane (hydrogenation reaction). Mortensen et al. [112] reported the mechanism for the conversion of phenol to cyclohexane by a HDO reaction. They argued that cyclohexanone is formed by the hydrogenation of phenol and converted to cyclohexanol by rapid hydrogenation. Cyclohexane is produced by the additional dehydration and hydrogenation.

Massoth et al. [113] suggested two types of reaction pathways. The first pathway is benzene formation via the direct cleavage of

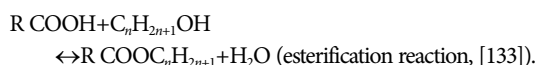
C-O σ bond due to the hydrogenolysis of phenol. In the second pathway, cyclohexanol is produced as a reaction intermediate via the hydrogenation of the aromatic ring of phenol and converted to cyclohexene and cyclohexane. Li et al. [114] reported the HDO of anisole. They explained that phenol and benzene are generated by the demethylation of anisole because the C_{methyl}-O bond is broken more easily than the C_{aromatic}-O bond. The cyclohexyl ether is then converted to alicyclic hydrocarbons by the additional hydrogenation. Zhang et al. [115] suggested cyclohexane formation via the hydrogenation saturation of cyclohexyl methyl ether as the main reaction pathway and the formation of phenol and benzene as side reactions. They indicated that the main reaction pathway includes the formation of cyclohexanol by the demethylation of cyclohexyl methyl ether via the hydrogenolysis of the C_{methyl}-O bond and the additional conversion of cyclohexanol to cyclohexanone by the hydrodeoxygenation of C_{aromatic}-O bond as intermediate reactions. Peters et al. [65] reported that cresol, phenol, and methane are generated by the transalkylation or demethylation of anisole and they were converted to benzene and toluene by subsequent hydrodeoxygenation. Mild reaction conditions were also used for the

HDO mechanism study because of the many reaction pathways and the difficulty in detecting the reaction intermediates under normal reaction conditions [116,117]. Lee et al. [106] suggested the HDO reaction pathways using the HDO reaction test of phenol, anisole and veratrole at 150 and 250 °C because they are known reaction intermediates of guaiacol conversion.

Many reaction pathways for the HDO of model compounds have been studied intensively. More investigation of the HDO reaction of actual bio-oil is also needed because the actual bio-oil has a more complex chemical composition than model compounds.

USE OF SOLVENT ON HDO REACTION

Recently, the addition of solvents, such as water, methanol, ethanol, and butanol, to the HDO of bio-oil has been attempted [129-132]. The solvents act as a hydrogen donor, which can react directly with the acids, such as acetic acid and carboxylic acid, in bio-oil and produce esters and water via the esterification reaction:



The solvents can be classified into polar, dipolar, and non-polar, according to their polarity [134]. Polar aprotic solvents, such as water and alcohols containing the -OH and -NH group in their structure have hydrogen bonding and acidic hydrogen. Dipolar aprotic solvents include 1,4-dioxane and acetone. Non-polar solvents include benzene, toluene, and cyclohexane. Among them, a supercritical reaction with polar aprotic solvents is being used for the HDO of biomass pyrolysis because the supercritical reaction can not only increase heat transfer, but also produce a high density, low viscosity, and a high diffusion coefficient of the reactant and solvents in the system [135].

The supercritical condition of the solvent is different: T=647.096

K and P=22.064 MPa for water [129]; T=512.6 K and P=8.09 MPa for methanol [130]; T=513.9 K and P=6.14 MPa for ethanol [131]; and T=560.2 K and P=4.9 MPa for 1-butanol [132]. Among these polar solvents, ethanol is used most commonly because it can approach the supercritical point at lower temperatures and pressures than other solvents. Recently, the price of ethanol has been decreasing due to the increased production via biomass fermentation [136]. Ethanol is less harmful than methanol and can be handled more easily than butanol. Although methanol is also used in the transesterification process of bio-oil [137] owing to its short chain [138], its stronger toxicity than ethanol is a disadvantage.

Supercritical water is also used frequently because it is safer than alcohols and can be treated more easily than other organic solvents. On the other hand, low yield of water-insoluble oil and high oxygen content in the final oil produced by the HDO using supercritical water has been suggested as potential problems for the use of water as a solvent for the HDO reaction [139]. The use of butanol as a solvent for the HDO reaction is increasing. Butanol has weaker polarity than methanol and ethanol and high solubility in water. Xu et al. [140] applied 1-butanol to the HDO of pine sawdust derived bio-oil and obtained high quality oil with high heating value, low water content, and low viscosity. They also observed a low level of coke formation (0.2%) via the catalytic HDO over the Ru/C catalyst. The synergistic effect of using a co-solvent was also reported. Chen et al. [141] used ethanol-water as a co-solvent and Zhang et al. [142] obtained increased olefin yield and mass transfer using 1-octene/1-butanol as the co-solvent.

Although a high pressure is normally applied to the supercritical HDO reaction to maximize the efficiency, mild conditions (low temperature and pressure) can also be chosen to obtain the desired products. For example, Wahyudiono et al. [143] reported the reaction pathway for the HDO reaction of guaiacol using sub/supercritical water. They explained that catechol is produced as the

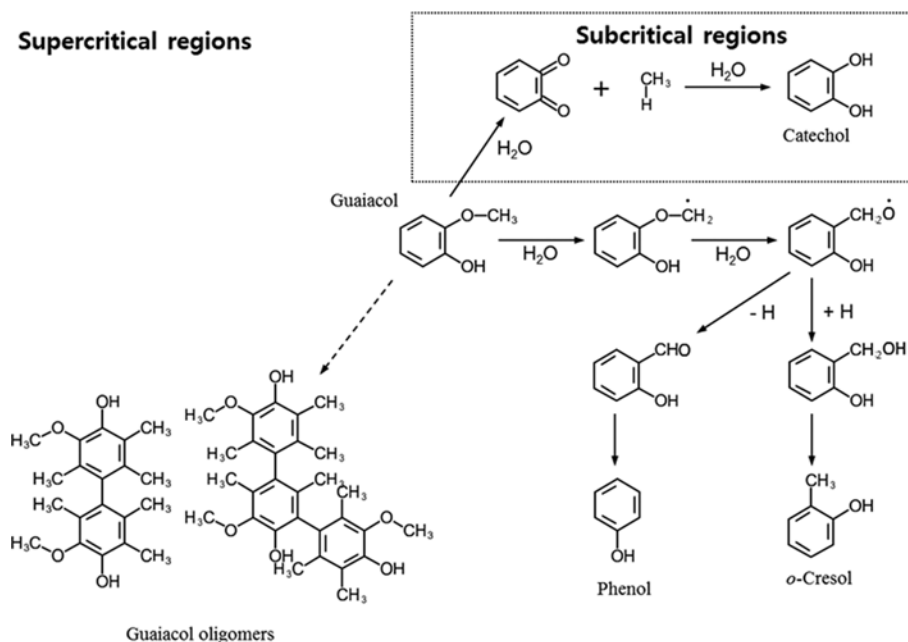


Fig. 3. Possible reaction pathways for the catalytic HDO of guaiacol under sub/supercritical regions [143].

main product via hemolysis of the methoxy bond and a hydrogen abstraction reaction from water. Phenol and cresol were obtained mainly at the high temperature supercritical regions. Fig. 3 presents the possible reaction pathways for guaiacol conversion under the sub/supercritical region.

Although the use of a solvent can have synergistic effects on the

catalytic HDO reaction, the large amount of solvent use is considered a problem in the commercialization process. Dang et al. [81] changed the solvent to bio-oil ratio from 1 : 1 to 5 : 1 during the catalytic HDO of rice husk derived bio-oil over Pt/SO₄²⁻/ZrO₂/SBA-15 and reported that a higher solvent to biomass oil ratio is required to produce high quality oil with a high heating value and

Table 3. Summary of studies on catalytic HDO of bio-oils from pyrolysis with solvent

Biomass pyrolysis	Solvent	Biooil : solvent	Reaction temperature	Reaction pressure	Reaction time	Catalyst	Heating value	Ref.
Rice husk	Ethanol	1 : 1-1 : 5	260-300 °C	7.0-11.8 MPa	3 h	Pt/SO ₄ ²⁻ /ZrO ₂ /SBA-15	29.56 MJ/kg	[81]
Rice husk	Ethanol	1 : 2	280 °C	8.5-10.5 MPa	3 h	SO ₄ ²⁻ /ZrO ₂ /SBA-15	20.1 MJ/kg	[148]
Rice husk	Ethanol	NA	260 °C	7.80 MPa	3 h	Al ₂ O ₅ Si	20.08 MJ/kg	[156]
Rice husk	Ethanol	1 : 2	300 °C	2.0 MPa Initial pressure	5 h	Pt/C Pd/C Ru/C Ru/HZSM-5	31.03 MJ/kg	[147]
Pinus sylvestris L	Methanol or Ethanol	10 : 1	260 °C	7.5-11.5 MPa	3 h	Pt/SO ₄ ²⁻ /ZrO ₂ /SBA-15 Pd/SO ₄ ²⁻ /ZrO ₂ /SBA-15 Pt/HZSM-5 Pd/HZSM-5	NA	[150]
Pinus sylvestris	Ethanol	1 : 10	260 °C	2.0 MPa Initial pressure	3 h	SO ₄ ²⁻ /ZrO ₂ /SBA-15 Pt/SO ₄ ²⁻ /ZrO ₂ /SBA-15	NA	[82]
Hardwood sawdust	Ethanol	1 : 2	300-350 °C	20.7-22.5 MPa	3 h	CoMo/SBA-15 CoMo/MCM-41 CoMo/ Al ₂ O ₃ CoMo/HZSM-5 CoMo/C-Pellet CoMo/C-Powder Ru/C CoMo/MCM-41 CoMo/Al ₂ O ₃ CoMo/C-Powder Ru/C	36.30 MJ/kg	[131]
Pine sawdust	1-Butanol	1 : 1	250-300 °C	8.8-11.5 MPa	3 h	Ru/C	32.0 MJ/kg	[140]
Miscanthus sinensis	Ethanol	4 : 1	250-350 °C	3 MPa Initial pressure	30 min-1 h	Ru/C Pt/C	27.8 MJ/kg	[80]
Corn	Toluene n-Butyl alcohol	3 : 2	250-330 °C	2.0 MPa Initial pressure	1 h	Ni/HZSM-5	37.28 MJ/kg	[157]
Cornstalk	Ethanol	1 : 2	280-370 °C	4 MPa Initial pressure	1 h	((NH ₄)HNi ₂ (MoO ₄) ₂ (OH) ₂)	38.3 MJ/kg	[149]
Yellow poplar wood (Liriodendron tulipifera)	Ethanol	4 : 1	250-370 °C	30 bar Initial pressure	40 min-2 h	Pd/C	34.5 MJ/kg	[158]
Wood	Water	1 : 5	300 °C	60 bar	4 h	Ni/HZSM-5 NiCo/HZSM-5	33.6 MJ/kg	[151]
Switchgrass Eucalyptus benthamii equine manure	Water	40 : 9	320 °C	2100 psi	4 h	Pt/C Ru/C Pd/C	NA	[152]
Microalgae (Nannochloropsis sp.)	Water	1 : 1	400 °C	3.4 MPa Initial pressure	4 h	Pt/C	42 MJ/kg	[79]

low oxygen content. On the other hand, the increased cost of the process and the change in the process conditions due to the increased amount of solvent also needs to be considered to make an efficient HDO process together with the elimination of solvent remaining in the bio-oil after the reaction.

A supercritical solvent is also applied to the pyrolysis of biomass to produce low oxygen-content bio-oil [144–146]. But, its actual commercialization is expected to be difficult due to the low possibility of a sequential reaction system. Therefore, many researchers have used bio-oils as the feeding materials for the HDO reaction and focused on the effects of the reaction time, pressure, temperature, and the amount of solvent on the change in the bio-oil quality, as shown in Table 3. Although other solvents have also been used, ethanol was the main supercritical solvent used for the HDO of bio-oil.

Chen et al. [147] compared the effects of the catalyst (Pt/C, Pd/C, and Ru/C) on the HDO of rice husk derived bio-oil and reported different chemical selectivity of each bio-oil produced over the different catalysts. HDO over the Pd/C catalyst showed high selectivity for phenols, alcohols and ethers. Pt/C produced mainly acids and esters, and Ru/C formed alcohols, ethers, esters, and ketones. They also reported catalyst deactivation due to coke deposition and metal particle sintering via BET analysis and transmission electron microscopy (TEM). Ahmadi et al. [130] used CoMo catalysts supported on various kinds of nano-structured materials (activated carbon, alumina, HZSM-5, MCM-41, and SBA-15) and Ru/C as the catalyst for the HDO of fast pyrolysis bio-oil from hardwood sawdust. Among the catalysts tested, Ru/C showed the highest oil yield and the lowest coke formation together with no heavy oil production. Mesoporous supports (SBA-15 and MCM-41) showed similar yields of oil to that over Ru/C and low coke

formation. Zhang et al. [82] applied $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$ catalyst to the HDO of *Pinus sylvestris* derived bio-oil and reported the elimination of acids and aldehydes together with a decrease in phenols, ketones, poly aromatic hydrocarbons (PAHs), and sugars. The esters produced via the esterification of acids and other components were the main components in the final bio-oil and the content of esters produced from the aldolization of aldehydes and ethanol was also high.

Oh et al. [80] reported improved bio-oil quality in terms of the water content, viscosity, acidity, oxygen level, and heating value, through the catalytic HDO of *miscanthus sinensis* derived bio-oil using supercritical ethanol over Pt/C and Ru/C. Compared to Ru/C, Pt/C showed higher durability and thermal resistance. Tang et al. [148] carried out the hydrotreatment, esterification, and cracking of rice husk derived bio-oil over $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$ catalyst under supercritical ethanol conditions and reported an increased heating value together with decreased viscosity and density of bio-oil. They also obtained low yields of aldehydes and ketones from the hydrotreatment and an increased yield of esters from esterification. Yang et al. [149] checked the heating values of bio-oil produced from the HDO performed at different temperatures from 280 to 370 °C.

The bio-oil produced under the supercritical conditions (370 °C) showed a higher heating value (HHV=38.3 MJ/kg) than those (HHV=33.3, 36.3, 37.0 MJ/kg) produced under subcritical conditions (280–340 °C). Zhang et al. [150] compared the effects of ethanol and methanol on the HDO of *Pinus sylvestris* L. derived bio-oil over $\text{Pt}/\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-15}$ and reported that ethanol is a more efficient solvent for eliminating acids and aldehydes and decreasing the level of ketones, phenols and sugars than methanol. They also tested the effect of metals (Pt, Pd) on the HDO reaction. Xu

Table 4. Detected compounds and weight percentage in bio-oil and HDO oil [153]

Class	Detected compounds	Bio-oil	HDO oil
Phenolics	Phenol	0.49	0.00
	3-Methylphenol	0.69	0.00
	2-Methylphenol	2.03	0.00
	3-Ethylphenol	2.93	0.00
	3-Propylphenol	0.82	0.00
Guaiacols	Guaiacol	1.66	0.00
	2-Methoxy-5-methylphenol	2.62	0.00
Syringols	2,6-Dimethoxyphenol	3.28	0.00
Methoxybenzenes	1,2,4-Trimethoxybenzene	4.43	0.00
	Benzene, 1,2,3-trimethoxy-5-methyl-	1.25	0.00
Catechols	Catechol	0.46	0.00
	3-Methoxycatechol	2.24	0.00
Alkanes	Hexadecane	0.04	1.93
	Pentadecane	0.03	0.50
	Methylcyclohexane	0.00	0.26
Cyclohexanols	Cyclohexanol	0.00	2.79
	Methylcyclohexanol	0.00	4.08
	Ethylcyclohexanol	0.00	1.74

et al. [140] applied supercritical 1-butanol as the solvent for the HDO of pine sawdust derived bio-oil over Ru/C and reported an increased HHV and decreased coke formation using butanol as well as a higher efficiency of a supercritical solvent than that of subcritical fluid. On the other hand, they could not remove 1-butanol completely from the upgraded bio-oil. Huynh et al. [151] obtained a high HDO efficiency using water as the solvent for the HDO reaction of wood (PYTEC GmbH) derived bio-oil over a bimetallic catalyst (Ni-Co/HZSM-5), which is a high-performance catalyst for the HDO of phenol. Elkasabi et al. [152] applied the metal-supported charcoal to the HDO of bio-oil obtained from the pyrolysis of biomass, such as switchgrass, eucalyptus, benth-amii, and equine manure and reported the highest HDO efficiency from the HDO of switch grass over Pt/C.

De Wild et al. [153] used dodecane as the solvent for the HDO reaction test (632 K, 100 bar) of lignin derived bio-oil, and the results are shown in Table 4. The bio-oil consisting of alkylphenolics and guaiacols was converted to cycloalkanes, alkyl-substituted cyclohexanols, cyclohexanol, linear alkanes and aromatic compounds by the HDO reaction of bio-oil. They also commented that the formation of a large amount of cyclohexanols is an interesting point because they can be used as the oxygenates in engine fuel.

As shown above, various types of catalysts, solvents, and reaction condition were applied to the HDO reaction of bio-oil and the oxygen content in the final product oil was decreased to approximately 20 wt% by an efficient HDO reaction. Although 20 wt% is much lower than the original oxygen content (40 wt%) of bio-oil, it is still a higher level than that (approximately 0.1 wt% of oxygen) of heavy petroleum fuel oil [154,155]. Therefore, more study will be needed to decrease the oxygen content to the appropriate level for its actual use as a high-heating-value fuel.

BIO-OIL FRACTIONATION TECHNIQUE

Owing to the complexity of bio-oil, research to determine the appropriate conditions and catalyst for the HDO of bio-oil is severely limited. The HDO reaction without the addition of solvent is also difficult due to its high viscosity. Therefore, several studies have suggested the fractionation of bio-oil to increase the homogeneity of bio-oil before the HDO reaction. Fig. 4 shows the

extraction pathways of bio-oil using water and various kinds of solvents. Water addition is generally applied as the first step for bio-oil fractionation. Through water extraction, the bio-oil can be divided into a water-soluble aqueous phase (top layer) and water insoluble organic phase (bottom layer) [159]. Water addition is effective for the extraction of alcohols and acids, which can reduce the viscosity and improve the applicability of bio-oil [160]. In addition, the additional extraction using other solvents, such as methanol, pentane, hexane, ethyl acetate, ether, benzene, and dichloromethane, can make the use of chemicals extracted from bio-oil in various industries [161].

The solvents are applied to chemical extraction from bio-oil differ according to the extraction efficiency and extraction target compounds. Therefore, many studies have applied a range of solvents to the chemical extraction from bio-oil. For example, Mazaheri et al. [164] divided the oil produced from palm fruit press fiber liquefaction into acetone insoluble, benzene soluble, diethyl-ether soluble, and water soluble components. Karagöz et al. [165] also extracted 2-methyl phenol as the main component using diethyl-ether from the bio-oil produced by sawdust liquefaction. Karimi et al. [166] reported the extraction of chemicals from hemp-seed derived bio-oil using the polarity solvents, such as water, methanol, acetone, acetonitrile, ethyl acetate, diethyl ether, and n-hexane.

Oasmaa et al. [162] performed a stability test for the oil separated by water addition to the bio-oil produced from the pyrolysis of pine sawdust and forest residues containing mainly softwood to make a uniform phase. Wang et al. [167] reported the different use of monophenols and pyrolytic lignin separated by water addition to the bio-oil. They explained that monophenols can be converted to hydrocarbons via an additional HDO reaction and that pyrolytic lignin can be used as the feedstock for the synthesis of phenolic resins and adhesives.

The additional upgrading of the extracted bio-oil has also been reported. Han et al. [159] attempted the HDO reaction of water soluble and insoluble phase oil separated by water addition to Ponderosa pine derived bio-oil. They applied the hydrocracking and HDO reaction over Ni-decorated nanosprings catalyst to the water insoluble oil and reported the formation of cycloalkanes, which can be used as green gasoline or jet fuel, in the final prod-

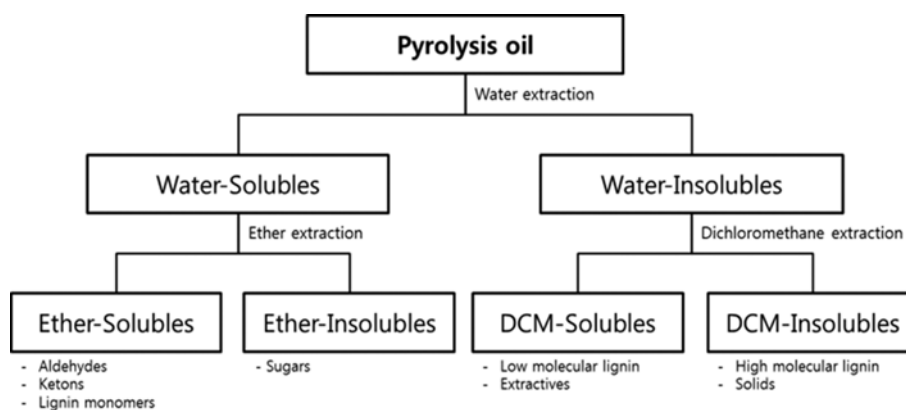


Fig. 4. Solvents fraction technique [160,162,163].

uct [159]. Pucher et al. [163] performed the HDO reaction using an oil with a low water content (7 wt%) through solvent fractionation and found a better HDO reaction performance of Pt/C than those of other catalysts, such as Pd/C and Ru/C. Wildschut et al. [168] obtained a large quantity of hydrocarbons from solvent extraction using n-hexane after the HDO reaction of beech wood derived bio-oil over the Pd/C catalyst. They also extracted lignin monomers containing aldehydes and ketones via ether extraction from a water soluble phase. On the other hand, low-molecular-weight lignin-derived materials and hydrocarbons could be extracted from the water insoluble phase by the addition of dichloromethane. As discussed thus far, solvent extraction can be applied to the HDO reaction process. On the other hand, more intensive studies to increase oil recovery by solvent extraction needs to be performed for its commercialization.

CATALYTIC HDO OF REAL BIO-OIL WITHOUT A SOLVENT

The catalytic HDO of bio-oil without the use of a solvent has also been investigated widely, as shown in Table 5. Guo et al. [172] performed the HDO reaction of the bio-oil obtained from the catalytic pyrolysis of algae biomass using bimetallic Ni-Cu/ZrO₂ as the catalyst for the HDO reaction. After the HDO reaction, the oxygen content and heating value of bio-oil were changed from 7.19 to 1.30% and from 31.5 to 36.0 MJ/kg, respectively. Huang et al. [169] also produced a larger quantity of hydrocarbons with decreased oxygen compounds in bio-oil through the catalytic HDO without solvent use. Cheng et al. [170] accomplished oil quality improvement in terms of the water and oxygen content, pH, and

HHV as well as the hydrocarbon content (C₆-C₁₂; 32.63%) using the HDO of prairie cordgrass derived bio-oil over a Ni/activated carbon catalyst. Wildschut et al. [171] tested various catalysts, such as Ru/C, Ru/TiO₂, and Ru/Al₂O₃ for the HDO reaction of beech wood derived bio-oil. They obtained a high oil yield (60 wt%) and HHV (40 MJ/kg) from the reaction over Ru/C and monitored the decrease in organic acids, aldehydes, ketones, and ethers and the increase in phenolics, aromatics, and alkanes due to the HDO reaction via two-dimensional GC analysis. Although the number of HDO studies without solvent use is much smaller than those using a solvent, the advantage of this process without solvent use is also important. Therefore, more study will be needed to allow the efficient HDO reaction of bio-oil.

EFFECTS OF THE CATALYST ON HDO

The use catalysts that can eliminate oxygen from the bio-oil through efficient HDO reaction is very effective. At the initial research stage, conventional sulfide CoMo and NiMo catalysts were used for the HDO reaction of bio-oil. Sulfided catalysts have a tolerance against the sulfur-containing compounds in biomass and are considered to be an effective catalyst for the HDO reaction [174-176]. Generally, materials, such as γ -Al₂O₃, SiO₂, activated carbon, TiO₂, ZrO₂, and zeolite are used as the supporting materials for sulfided catalyst [174]. Laurent et al. [175] and Bui [176] also used sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ for the HDO of guaiacol. Yang et al. [174] used sulfided CoMo and CoMoP supported on MgO to obtain high yields of hydrocarbons, such as benzene and cyclohexyl aromatics from the HDO reaction of phenol and reported low catalytic behavior. Centeno et al. [177] mod-

Table 5. Summary of studies on catalytic HDO of bio-oils from pyrolysis without solvent

Oil type	Reactor type	Catalyst	Reaction temperature	Reaction pressure	Reaction time or space velocity	Heating value	Ref.
Chlorella <i>Nannochloropsis</i> sp.	Continuous	Ni-Cu/ZrO ₂ Ni/ZrO ₂ Cu/ZrO ₂	350 °C	2 MPa	3.5 h ⁻¹	40.0 MJ/kg (LHV)	[172]
Pine sawdust	Batch	Zinc-assisted Pd/C	150-250 °C	1.38-4.14 MPa	4 h	28.41 MJ/kg	[169]
Prairie cordgrass	Batch	Ni/AC Ni-Fe/AC Ni-Mo/AC Ni-Cu/AC	350 °C	500 psi	5 h	31.61 MJ/kg	[170]
Beech wood	Batch	Ru/C Ru/TiO ₂ Ru/Al ₂ O ₃ Pt/C Pd/C sulfided NiMo/Al ₂ O ₃ sulfided CoMo/Al ₂ O ₃	250-350 °C	100-200 bar	4 h	40 MJ/kg	[171]
Forestry residues	Continuous	Ru/C	400 °C	200 bar	5-10 kg/h ⁻¹ kg _{cat}	Na	[160]
Pine sawdust	Batch	MoNi/Al ₂ O ₃	100 °C	30 MPa	2 h	14.17 MJ/kg (CV)	[173]
Beech wood	Batch	Ru/C	350 °C	200 bar	1-6 h	Na	[168]
Hemp-seed	Batch	Red mud	350-365 °C	800 psi	5 h	Na	[166]

ified the sulfided CoMo and CoMoP by adding K and Pt and applied them to the HDO of guaiacol. Although sulfided catalysts are being studied intensively on the HDO reaction study, their use can cause problems, such as sulfur penetration into bio-oil and the accelerated deactivation of a catalyst. The contamination of water used for the elimination of sulfur is also a potential problem of sulfided catalysts. Therefore, the development of alternative sulfided catalysts is also being investigated [178,179].

The recent interest in the use of a noble metal catalyst on the HDO reaction is becoming amplified among researchers. Metal catalysts, such as Pd, Pt, Rh, and Ru are normally reduced at between 400 and 500 °C under a hydrogen atmosphere to provide a high enough activity for high quality oil production via the HDO reaction [120]. These noble metal catalysts can also be applied flexibly to reactor design because they enable the reactions at a lower temperature under lower pressure in a shorter time than other catalysts. The main disadvantage of the use of noble metal catalysts is their high price. Noble metal alloys, such as RhPd, RhPt, and PtPd, were also used for the HDO reaction [100]. Sulfided catalyst, alumina, and carbon are generally used as the supporting materials for noble metal catalysts. Higher reaction activity can be expected using carbon with a large surface area as the supporting material for noble metal catalysts, even though a small amount of metal is applied. Zhao et al. [180] used Pd/C for the HDO of phenol and Newman et al. [124] studied the HDO reaction of phenol using Ru supported on carbon, silica, alumina, and titania. Recently, zeolites, such as HY, SBA-15, ZSM-5, mesoporous Y, mesoporous MFI, and mesoporous beta, have been used as the supporting materials for noble metal catalysts [182]. Zeolites are used in refining and petrochemical processes because of their strong acidity and proper pore size [157]. Therefore, they can also be considered as strong catalysts for the HDO reaction of bio-oil. On the other hand, the diffusion of large molecules, such as dibenzofuran and phenolic oligomers in bio-oil into the catalyst pore can be limited by the small pore size of zeolite. Mesoporous zeolites are considered to be the solution to overcome the limited diffusion efficiency [70]. Mesoporous materials have very high surface areas, narrow pore size distributions, and large pore volumes. Therefore, mesoporous materials can maximize the dispersion of active metal and catalytic activity per unit mass. The high price of zeolite catalysts is a disadvantage for their actual use as the supporting materials. On the other hand, the price of zeolites has decreased recently due to commercialization of the mesoporous catalyst manufacturing process.

Hong et al. [183] obtained a high oil yield from the HDO reaction over Pt/HY zeolite. Bi-functional catalysts consisting of active metals (reducible site) and acidic center (support or metal-support interface) can allow not only hydrogenation and hydrogenolysis reactions, but also dehydration, alkylation, isomerization, and condensation reactions [184]. Lee et al. [185] and Yao et al. [186] also obtained high oil yields from the HDO reaction over these bi-functional catalysts. Peng et al. [187] focused on the acidity of zeolite influencing the yield of oil during the HDO reaction of rice husk derived bio-oil over HZSM-5. They reported that the strong acidity of the catalyst is quite effective for the cracking of heavy components in bio-oil through bio-oil upgrading tests using cata-

lysts having different acidity (Si/Al ratio; 22, 100 and 300). Zhao et al. [188] tried to increase the effects of the acid catalyst further by adding catalysts, such as H_3PO_4 and H_2SO_4 , to the bio-oil upgrading system.

A nickel catalyst, which is an efficient catalyst for the steam reforming reactions and water gasification, was also used to examine the HDO reaction [71,74,189]. Nickel is a cheaper catalyst than noble metals and has an advantage as non-sulfided catalyst. On the other hand, the activity of nickel, which is checked via the concentration of active metal per unit gram, is not higher than those of noble metal catalysts [190]. Therefore, various nickel catalysts in many different forms, Pt-Ni/ Al_2O_3 [191], La-Ni-Mo-B amorphous [192], and Ni-Cu bimetallic [193], were also applied to the HDO reaction of model compounds. The supporting amount of nickel was also optimized by Zhang et al. [194]. Among the 6, 10 and 14 wt% Ni/HZSM-5 catalysts, 10 wt% Ni/HZSM-5 showed the highest conversion efficiency in the HDO reaction of phenol.

The performance of many catalysts on the HDO reaction has been investigated by many researchers. Mertensen et al. [73] compared 23 types of catalysts containing Ni-based catalyst (Ni/ Al_2O_3 , Ni/ CeO_2 -Zr O_2), noble metal supported on carbon, NiO-Mo O_3 / Al_2O_3 , Cu/ZnO/ Al_2O_3 etc., by checking the HDO reaction efficiency of phenol using batch-type reactor (at 275 °C and under 100 bar). The catalytic activity for the HDO reaction was reported in the following order: Ni/Zr O_2 >Ni-V O_5 /Zr O_2 >Ni-V O_5 /Si O_2 >Ru/C>Ni/ Al_2O_3 >Ni/Si O_2 >>Pd/C>Pt/C. Gao et al. [120] reported that Pt/C had the best catalytic performance in the HDO reaction of guaiacol over noble metal (Pt, Pd, Rh, and Ru) supported on activated carbon catalysts. Wildschut et al. [171] applied Ru/C, Ru/Ti O_2 , Ru/ Al_2O_3 , Pt/C, Pd/C, sulfided NiMo/ Al_2O_3 , and sulfided CoMo/ Al_2O_3 catalysts to the HDO reaction of beech wood derived bio-oil and 90 wt% deoxygenation performance was obtained over the Ru/C catalyst.

As shown above, the reaction performance over different catalysts varies according to the reactant, reactor type, and reaction conditions. Therefore, fundamental research using model components with similar properties to actual bio-oil needs to be performed. Even in the HDO reaction of bio-oil, the feeding oil properties of each biomass also needs to be considered for the optimization of the HDO process.

The HDO reaction pathway also differs according to the applied catalyst. Lin et al. [121] reported different HDO reaction pathways of guaiacol over a Rh-based catalyst, sulfided CoMo and NiMo catalysts. Hellinger et al. [195] also suggested different HDO reaction pathways of guaiacol using noble and non-noble metal catalysts, as shown in Fig. 5. In addition, Nimmanwudipong et al. [196], Bui et al. [197], and Bykova et al. [198] also investigated the HDO reaction pathways of model compounds over different catalysts. According to their results, the HDO reaction mechanism of guaiacol over noble metal catalysts was suggested to be 1) 2-methoxycyclohexanol and 2-methoxycyclohexanone formation via the benzene ring hydrogenation of guaiacol, and 2) cyclohexane formation via additional demethoxylation, and dehydroxylation. In addition, the HDO reaction over non-noble metal catalyst was explained by benzene formation through a parallel demethylation, demethoxylation, and deoxygenation reaction of guaiacol as the

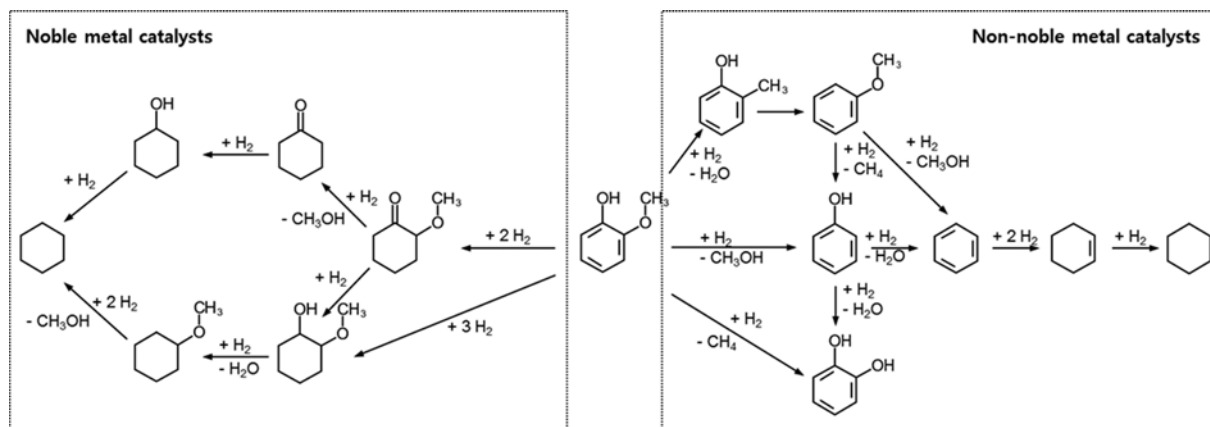


Fig. 5. Different HDO reaction pathways by the use of different catalysts [195].

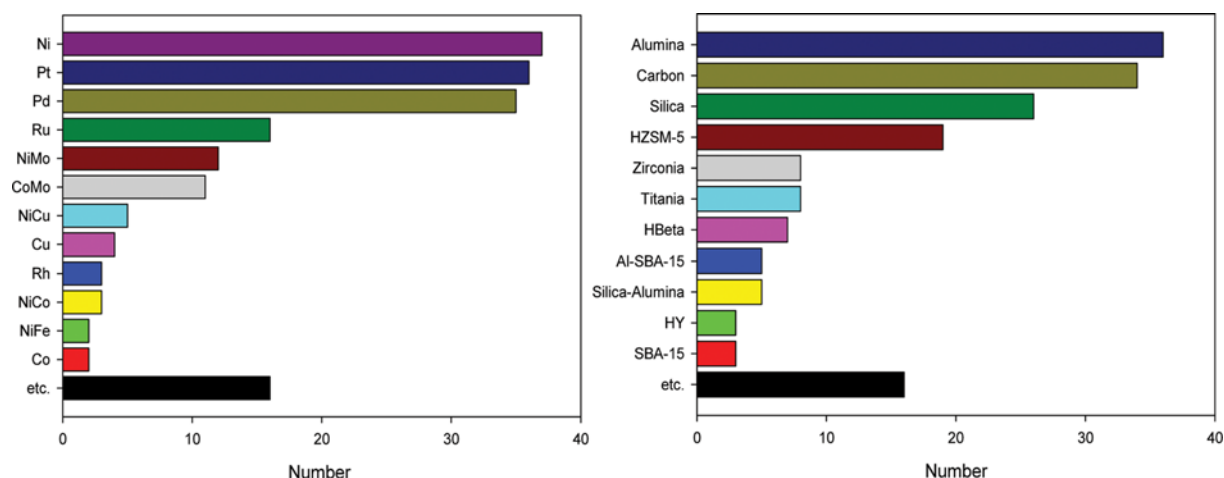


Fig. 6. Active metals and supporting materials mostly used in catalytic HDO reaction (This statistical data were based on the 146 kinds of scientific journal paper with the search term “Hydrodeoxygenation and bio-oil”).

first step and additional hydrogenation of benzene as the second step. Tan et al. [199] confirmed from the HDO test of *m*-cresol over Pt/SiO₂ and Ru/SiO₂ catalysts that the HDO reaction pathway can also differ according to the types of noble metal. Although different reaction pathways were suggested depending on the different catalyst, the use of a proper catalyst can enhance the reaction rate toward to the target chemical.

Fig. 6 presents a summary of the recently reported catalysts for the HDO reaction. As expected, noble metals, such as Ni, Pt, and Pd, were used mostly as catalysts, and alumina, carbon, and silica were generally used as the supporting materials. Sulfided NiMo and CoMo catalysts and ZSM-5, Beta, and HY zeolites have also been used as the catalysts and supporting materials in many HDO reaction studies. In addition, Pd/WO₃/γ-Al₂O₃ [118] and multi-metallic catalysts, such as Ce-Ni-W-B amorphous catalysts [200], were also used to increase the overall efficiency of deoxygenation reaction together with a consideration of mesoporous beta [66], mesoporous Y, mesoporous MFI [107] as the potential supporting materials.

As shown above, a range of catalysts have been applied to HDO reaction of bio-oil together with the development of new catalysts. On the other hand, more active catalysts should be applied to the

actual bio-oil to produce oils with higher quality.

DEACTIVATION OF HDO CATALYST

Although a high activity catalyst is important, the slow catalyst deactivation also needs to be considered to apply the catalyst to a commercial scale HDO reaction plant. The stability of the catalyst is one of the most important factors in choosing an appropriate catalyst because the amount of catalyst required for bio-oil upgrading via the HDO reaction is not small. For example, Huynh et al. [151] used 20% catalyst (1 g of NiCo/HZSM-5) to upgrade 5 g of wood derived bio-oil via the HDO reaction. To obtain a high HDO reaction efficiency, an excess of catalyst is used in many studies, which makes the cost for the catalyst high, even in the commercialized process. In this case, the increase in catalyst stability can provide a solution to decrease the total cost of the process. Deactivation of the catalyst is caused by a complex reaction, which is a difficult problem to solve using simple treatment. Li et al. [157] indicated that the pore and acidity of catalyst, catalytic reaction condition, and properties of the reactant can be related to catalyst deactivation. They also reported that soft and hard coke are

produced via the alkylation, aromatization, hydrogen transfer, and dehydrogenation reaction of organic reactants over catalysts.

Research on catalyst deactivation is normally performed by comparing the physico-chemical properties of the new and used catalysts for the reaction. For this, the crystallinity, surface area, pore size, acidity, and particle size distribution of the used catalyst are measured by X-ray diffraction (XRD), Brunauer, Emmet, and Teller (BET) surface area measurements, temperature programmed desorption, scanning electron microscopy (SEM), TEM, and Fourier transform infrared spectroscopy (FTIR). The amount of carbon coke can also be determined by thermogravimetric analysis (TGA). The degree of catalyst deactivation differs according to the reaction conditions and time. Zhang et al. [119] checked the amount of coke deposited due to the repeated use of the catalyst, and found that 14% of coke was produced after the four sequential uses of NiCu/ZrO₂-SiO₂ for the HDO reaction of guaiacol. Gao et al. [120] monitored a considerable amount of coke deposition (17%) by the one-time HDO reaction over Ru/C and Pt/C catalysts. The particle size of the catalyst increased from 2.40±0.54 (fresh catalyst) to 2.67±0.62 nm (spent catalyst) due to catalyst sintering. Xu et al. [140] checked the deactivation of the Ru/C catalyst during the catalytic upgrading of pine sawdust derived bio-oil by XRD and TEM. XRD showed that the crystallinity of the catalyst obtained from the reaction using a solvent has a smaller size (8.4 nm) than that (Ru=11.0 nm) obtained from the reaction performed with no solvent. Chen et al. [147] obtained a lower amount of desired products (acids, alcohol/ethers, esters, and ketones) in bio-oil due to the sequential use of a catalyst and they attributed it to coke deposition and the sintering of metal particles based on the BET and TEM analysis results.

Although catalyst deactivation is very important, most HDO reaction studies have only focused on the catalyst screening test without deactivation results. Therefore, long-term HDO reaction studies need to be performed for the commercialization of the bio-oil HDO process.

CONCLUSION

Owing to the complex composition of actual bio-oil, model compounds have been used for studies on the HDO reaction. Among the various kinds of model compounds, specific pyrolyzates of lignin, such as guaiacol and phenol, have been used intensively in HDO reaction studies. Many researchers have examined the HDO reaction pathways and efficiency using range of experimental parameters, such as the reaction temperature, pressure, and time, over sulfided NiMo, sulfided CoMo, and noble catalysts (Pt, Pd, Ru, and Ni). Recently, their application to actual bio-oil has also increased. The HDO reaction needs to be performed under a high pressure hydrogen atmosphere, and its overall performance can be increased using a solvent. The use of a solvent as hydrogen donor in the HDO reaction of bio-oil can enhance the formation of esters by the interaction between acids in bio-oil and solvent. The HDO reaction using a solvent can also decrease the deactivation of the catalyst. On the other hand, additional research needs to be performed to find better solvents to achieve more efficient HDO reaction performance. The minimization of residual sol-

vent in the final bio-oil product also needs to be considered.

Although catalytic HDO processes have beneficial effects on the production of high-quality oil from oxygen-containing compounds, their direct application to bio-oil is still difficult because of the high water and oxygen contents in the oil and high viscosity. Therefore, a range of additional solvent extraction technologies are being considered by many researchers and continuous efforts are being made to find more active catalysts. Further research will be needed to achieve the production of stable and high-quality bio-oil that can be used as a petrochemical feedstock and alternative oil of fossil fuel.

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