INVITED REVIEW PAPER

Upgrading of biofuel by the catalytic deoxygenation of biomass

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Abstract−Biomass can be used to produce biofuels, such as bio-oil and bio-diesel, by a range of methods. Biofuels, however, have a high oxygen content, which deteriorates the biofuel quality. Therefore, the upgrading of biofuels via catalytic deoxygenation is necessary. This paper reviews the recent advances of the catalytic deoxygenation of biomass. Catalytic cracking of bio-oil is a promising method to enhance the quality of bio-oil. Microporous zeolites, mesoporous zeolites and metal oxide catalysts have been investigated for the catalytic cracking of biomass. On the other hand, it is important to develop methods to reduce catalyst coking and enhance the lifetime of the catalyst. In addition, an examination of the effects of the process parameters is very important for optimizing the composition of the product. The catalytic upgrading of triglycerides to hydrocarbon-based fuels is carried out in two ways. Hydrodeoxygenation (HDO) was introduced to remove oxygen atoms from the triglycerides in the form of H_2O by hydrogenation. HDO produced hydrogenated biodiesel because the catalysts and process were based mainly on well-established technology, hydrodesulfurization. Many refineries and companies have attempted to develop and commercialize the HDO process. On the other hand, the consumption of huge amounts of hydrogen is a major problem hindering the wide-spread use of HDO process. To solve the hydrogen problem, deoxygenation with the minimum use of hydrogen was recently proposed. Precious metal-based catalysts showed reasonable activity for the deoxygenation of reagent-grade fatty acids with a batch-mode reaction. On the other hand, the continuous production of hydrocarbon in a fixed-bed showed that the initial catalytic activity decreases gradually due to coke deposition. The catalytic activity for deoxygenation needs to be maintained to achieve the widespread production of hydrocarbon-based fuels with a biological origin.

Key words: Bio-oil, Biodiesel, Catalytic Cracking, Triglyceride, Hydrodeoxygenation

INTRODUCTION

The development of various energy sources to replace fossil fuels has attracted considerable attention [1-4]. Among these, bio-energy derived from biomass is of particular interest because of its potential for mass production within a relatively short period. Because it is carbon-neutral, biomass is a renewable energy source that can counteract global warming.

Bio-oil is a liquid-phase biofuel produced from the pyrolysis of biomass [5-10]. Rapid pyrolysis was designed to maximize the production of bio-oil from a pyrolysis process. Bio-oil can be used directly as a fuel for boilers or turbines operated in power stations. Significant modification, however, is needed before bio-oil can be used widely as a transportation fuel. The catalytic upgrading of bio-oil is a promising method for improving the fuel quality by removing oxygen from organic compounds and converting them to hydrocarbons. The operating cost of this catalytic upgrading (atmospheric catalytic cracking) is relatively low because it can be operated under

atmospheric pressure without the need for added hydrogen gas. On the other hand, the low organic oil yield and deactivation of the catalysts due to carbon deposition are problems that need to be solved. The upgrading of bio-oils over suitable catalysts has been studied extensively over the last decade. One can refer to several review papers on this topic for more detailed information [11-17]. The present authors have published a review paper on the catalytic pyrolysis of biomass in 2011 [18]. The current review paper focuses on studies reported from 2010.

In addition to bio-oil obtained by the pyrolysis of biomass, triglycerides can be a promising feedstock because of its high energy density and the possibility for a stable feedstock supply. The heating value of triglycerides is similar to that of hydrocarbon-based transportation fuels. The mass-production of triglycerides by microalgae cultivation appears to be a solution for the stable supply of feedstock [19]. Although triglycerides are a potential solution for the replacement of transportation fuels, corrosion induced by the long-term storage of triglycerides needs to be solved by the removal of oxygen atoms in triglycerides. Hydrodeoxygenation (HDO) and deoxygenation (DO) without hydrogenation are two major solutions introduced recently. In the case of HDO, many papers and patents

have been published, and two companies have already started the commercial production of hydrogenated biodiesel. Nevertheless, the considerable hydrogen consumption is an obstacle to the widespread use of the HDO process. DO was proposed in 2005 to enhance the economic feasibility of HDO. However, deactivation of the catalysts by coke deposition has been a major problem to be overcome, and many studies have evaluated the potential.

CATALYTIC PYROLYSIS OF BIOMASS

Table 1 lists the basic properties of bio- and petroleum-derived oils [20]. Generally, since bio-oils have higher moisture and oxygen content than petroleum-derived oils, it is difficult to mix bio-oils with petroleum-derived oils. The high oxygen content also deteriorates the quality of bio-oil. A range of cracking catalysts has been used to upgrade bio-oils under atmospheric pressure. Microporous zeolite catalysts, such as HZSM-5, HBeta, and HY, are generally used. Mesoporous materials, such as MCM-41, MCM-48 and SBA-15, have also been applied. Recently, hierarchical mesoporous zeo-lite catalysts, such as meso-MFI, have been studied extensively. The pyrolysis products are affected substantially by the shape selectivity and acid properties of the catalyst used. ZSM-5 with strong acidity has high selectivity toward aromatic compounds, whereas mesoporous materials with weak acidity show high selectivity toward phenols and hydrocarbons. The pore size is another important factor. For example, Beta, Y and silica-alumina, whose pose size is larger than that of ZSM-5, can be deactivated easily due to the formation of a large quantity of coke on the catalyst surface. The acid property and pore size need to be optimized to prevent coke formation. In addition, rapid heating and a high catalyst/biomass ratio are beneficial for avoiding excessive thermal decomposition and allowing the pyrolyzed biomass compounds to enter the pores of the ZSM-5 catalyst [20].

Fig. 1 shows the reaction pathways for catalytic deoxygenation [21] consisting of the following: 1) dehydration reactions, 2) cracking of large oxygenated molecules (not shown in Fig. 1), 3) hydrogen-producing reactions, 4) hydrogen-consuming reactions, and 5) C-C bond-forming reactions (aldol condensation or Diels-Alder reactions) [21].

1. Woody Biomass

Woody biomass is used most widely for catalytic pyrolysis. Solid acid catalysts, such as zeolite and mesoporous materials, are commonly used for the catalytic pyrolysis of woody biomass. The acid sites present in these acid catalysts promote a range of various deoxygenation reactions, such as dehydration, decarbonylation, decarboxylation, and cracking, and improve the quality of bio-oils.

Many studies have used these acid catalysts, mostly commercial zeolite materials, for deoxygenation. The effects of the process parameters on the deactivation of catalyst have been investigated. Preservation of the catalyst activity by preventing coke formation is particularly important for the catalytic upgrading of pyrolysis bio-oils. This can be achieved by using a suitable catalyst and reactor configuration as well as by optimizing the processing conditions. Fluid-
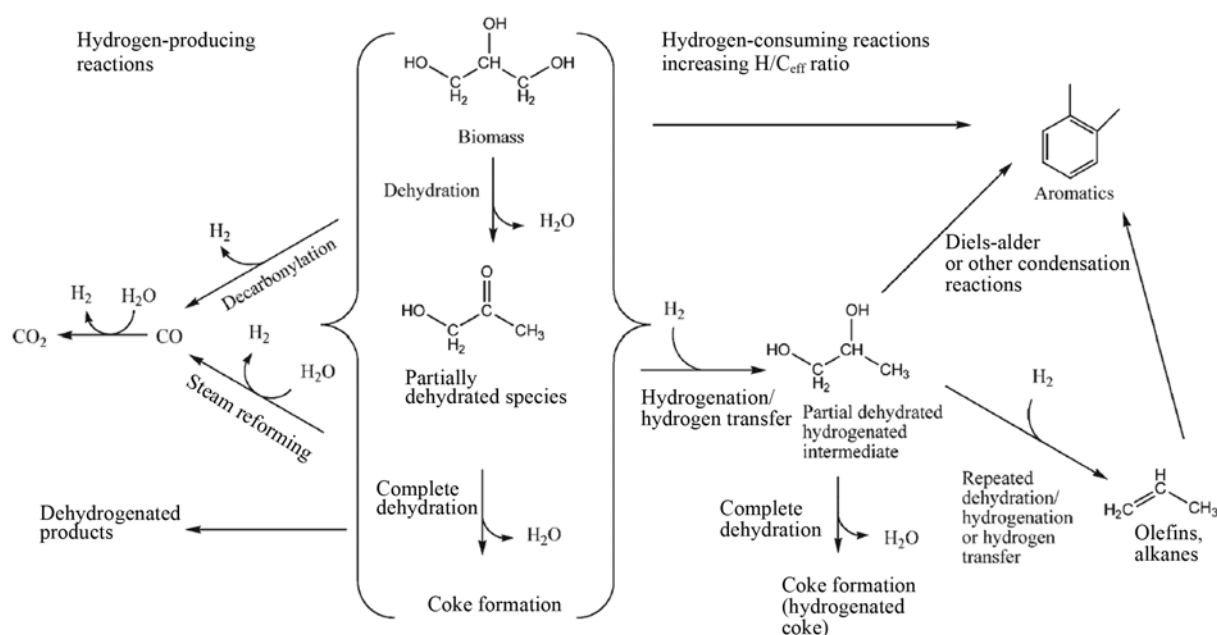
Table 1. Comparison of properties of bio-oil with those of heavy fossil fuel [20]

Oil from	Pyrolysis of wood	Heavy fossil fuel
Elemental composition (%)		
C	58	86.1
H	7	11.8
O	40	-
N	0.2	0.1
Viscosity (cP)	100	180
Water content (wt%)	15-30	<0.1
Distillation residue (wt%)	Up to 50	1
Heating value (MJ/kg)	19	40

Fig. 1. Reaction pathways for the catalytic cracking of biomass derived oxygenates [21].
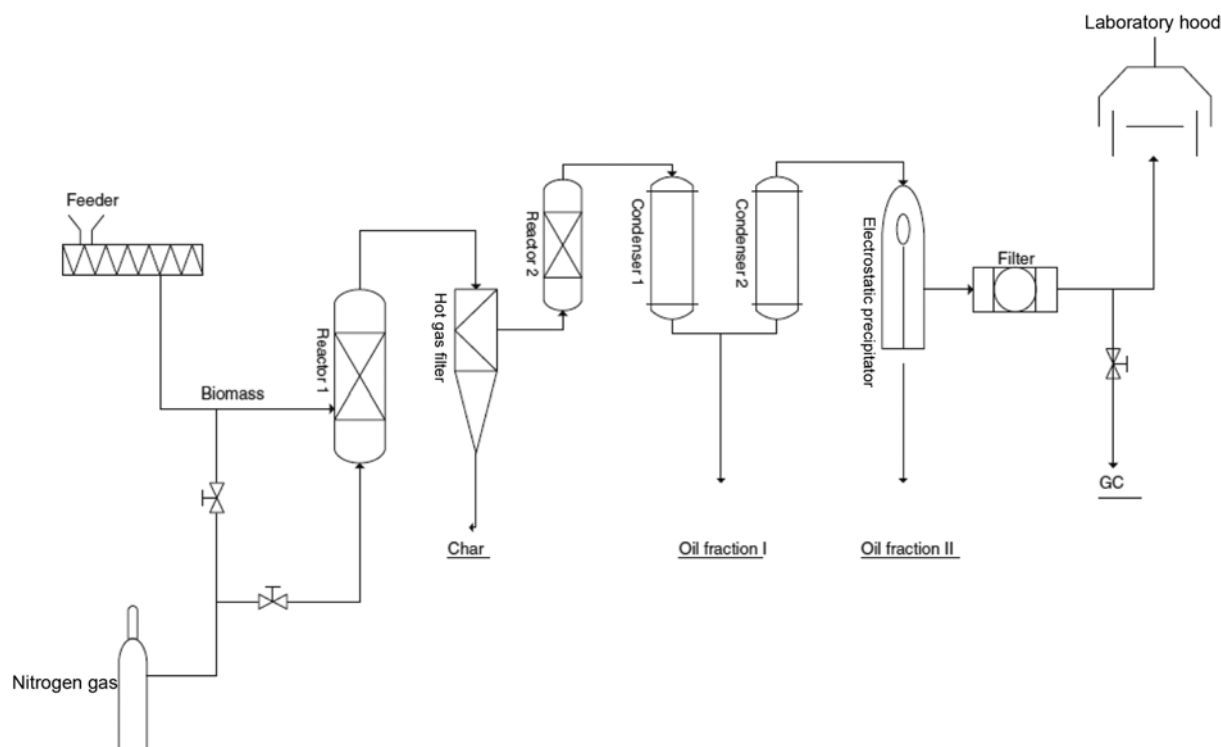
Fig. 2. Schematic diagram of dual fluidized-bed reactor [22].

ized- or fixed-bed reactors are generally used for catalytic pyrolysis. A combination of two different reactor configurations in series can also be used. In this case, non-catalytic pyrolysis occurs in the first reactor, and catalytic upgrading occurs in the second. Mante and Agblevor [22] examined the catalytic pyrolysis of hybrid poplar using HZSM-5. The importance of the reactor configuration was demonstrated. Compared to the fluidized-fixed- or dual fixed-bed reactor, the dual fluidized-bed (fluidized-fluidized-bed) reactor (Fig. 2) could suppress coke formation and extend the life of the catalyst.

Aho et al. [23] examined the processing conditions for the catalytic pyrolysis of pine wood over H-Beta using a dual fluidized-bed. The temperatures of the pyrolysis reactor and catalytic upgrading reactor were set to 400 °C and 440 °C, respectively. The effects of the space velocity were examined. The yields of gas, moisture and coke increased with decreasing space velocity, whereas the organic-phase fraction in the bio-oil decreased. The spent catalysts could be regenerated by burning out the coke produced during the reaction, which could recover the surface area and most acid sites. Mullen et al. [24] conducted the catalytic pyrolysis of white oak wood over zeolite catalysts (Ca/Y and proprietary beta-zeolite) using a fluidized-bed reactor. The catalysts used exhibited satisfactory deoxygenation efficiencies and enhanced the hydrocarbon content in the bio-oil produced. On the other hand, the liquid-phase yield decreased and the catalysts became deactivated due to coking. The coking phenomenon was less severe in the case of the Ca-Y zeolite catalyst, for which deoxygenation occurred via the decarbonylation and decarboxylation reaction pathways, than in the case of the proprietary beta-zeolite catalyst, for which deoxygenation took place via the dehydration and dehydrogenation pathways. The coking problem of the proprietary beta-zeolite catalyst was mitigated by in-situ regeneration of the catalyst, enabling the production of partially deoxy-
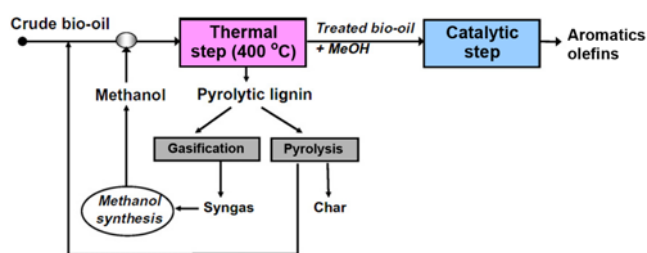

Fig. 3. Two-step process for the transformation of crude bio-oil into hydrocarbons [25].

genated oil over extended periods of time. Catalytic upgrading increased the C/O ratio of the pyrolysis oil considerably from 1.8/1 to 5.9/1. Mullen et al. suggested that in-situ catalytic rapid pyrolysis can be used to produce partially deoxygenated and stable fuel intermediates. The development of a suitable catalytic pyrolysis process is possible if process optimization is conducted by examining the effects of other bench-scale operating conditions, such as temperature and space velocity.

Valle et al. [25] also proposed a two-stage bio-oil upgrading process to solve the deactivation problems (Fig. 3). The reaction system consisted of two consecutive steps: a thermal step and a catalytic step. In the thermal step, polymerization of the components contained in the bio-oil occurred at 400 °C. In the catalytic step, the remaining volatile oxygenates were transformed to hydrocarbons in a fluidized-bed catalytic reactor at 450 °C. They also reported that coke deposition was inhibited significantly by co-feeding methanol, and that the nature of the coke components varied according to the bio-oil/methanol ratio.

On the other hand, Stefanidis et al. [26] used a bench-scale fixed-

bed reactor for the catalytic pyrolysis screening of commercial woody biomass (lignoli HBS 150-500). They used a number of commercial catalysts: E-cat FCC catalyst, various ZSM-5 formulations, MgO, alumina, zirconia/titania, tetragonal zirconia, titania and silica/alumina. Among these, ZSM-5 formulations, which have the highest surface area, and zirconia/titania showed the best performance: moderate selectivity towards hydrocarbons, reduced generation of undesirable compounds and acceptable yield of the organic liquid product. On the other hand, the FCC catalyst appeared to be the worst catalyst because of its low deoxygenation efficiency. This was attributed to the formation of excessive coke on the catalyst surface and the resulting high carbon loss. The above-mentioned studies examined the causes of catalyst deactivation and methods to regenerate the catalysts, which are crucial for commercialization of the process.

The effects of another process parameter, recirculation of non-condensable gases (NCG), on the quality of the product bio-oil were also investigated [27]. The catalytic pyrolysis of hybrid poplar over FCC and FCC/FeCrCu/CoMo/Al_2O_3 catalysts was carried out. The recirculation of NCG increased the bio-oil yield, whereas the char and coke yields were reduced. The recirculation of NCG also improved the quality of bio-oil by increasing the aromatic yield and heating value, and reducing the methoxy, carboxyl and sugar yields as well as the pH. Mante et al. [27] suggested that the presence of reductive gases (CO, H_2, and hydrocarbon) and mild oxidative gas (CO_2) in the recycled gas stream facilitates decarboxylation, decarbonylation and demethoxylation reactions. The effects of NCG need to be examined further using a range of catalysts and biomass materials in the future.

Stephanidis et al. [28] examined the effects of a hydrothermal pre-treatment of beech wood (Lignocel). HZSM-5, silicalite and Al-MCM-41 were used as the catalyst. The effects of catalytic upgrading on the bio-oils derived from the pretreated and untreated biomass samples were similar in terms of the product yield and bio-oil composition. On the other hand, the concentration of phenols increased considerably when the bio-oil obtained from the pyrolysis of the hydrothermally pretreated biomass was upgraded over the less acidic silicalite and Al-MCM-41 catalysts. Because pretreated biomass has a higher lignin content than untreated biomass, it produced more phenolic compounds upon catalytic pyrolysis over the less acidic catalysts.

The catalytic pyrolysis of various waste wood materials was also studied. The catalytic pyrolysis of a waste wood composite (waste melamine-coated chipboard) was reported [29]. Lewis acids ($AlCl_3$, $TiCl_4$, and $FeCl_3$), bases (NaOH and KOH) and basic salts (Na_2CO_3 and K_2CO_3) were applied to the catalytic pyrolysis of waste melamine-coated chipboard. A fixed-bed reactor was used at temperatures ranging from 400-700 °C and a reactor residence time of 1 h. Among the Lewis acids, catalytic pyrolysis over $FeCl_3$ resulted in a lower gas yield than that of non-catalytic pyrolysis. This also led to a higher oil yield than those obtained with $AlCl_3$ and $TiCl_4$. The basic catalysts reduced the solid residue yield at all temperatures tested by promoting gasification. Phenolics were the main products under all conditions tested. The Lewis acid catalysts enhanced the production of aldehydes. On the other hand, the detailed mechanisms for the pyrolysis reactions over these catalysts were not examined, highlighting the need for a follow-up study. Kim et al. [30] performed the catalytic pyrolysis of waste wood chip over mesopo-

rous catalysts, such as meso-MFI and Al-MCM-48. The acid properties affected the composition of the product oil significantly. The upgrading performance of the hierarchical meso-MFI was better than that of Al-MCM-48 owing to its stronger ability for deoxygenation. Meso-MFI also showed high selectivity toward valuable aromatic compounds.

HZSM-5, HBeta, Ga/HZSM-5 and SBA-15 catalysts were also used for the catalytic pyrolysis of waste particle board [31,32]. HZSM-5, Ga/HZSM-5 and HBeta were effective for the production of hydrocarbons including aromatics, whereas Al-SBA-15 led to the highest yield of high-value-added products, such as phenolics and furans.

Although a range of nano metal oxides have been used for catalytic reactions, their application to the catalytic pyrolysis of biomass is infrequent. Lu et al. [33] carried out the catalytic pyrolysis of poplar wood over six different nano metal oxides: nano MgO, CaO, TiO_2, Fe_2O_3, NiO and ZnO. These catalysts showed different catalytic selectivity towards the pyrolytic products. For example, CaO suppressed the production of phenols and anhydrosugars and removed acids, but enhanced the formation of cyclopentanones, hydrocarbons and light compounds. On the other hand, further investigation on the detailed mechanism will be needed to better understand the role of nano metal oxides in catalytic pyrolysis.

The catalytic pyrolysis of lignocellulosic biomass under microwave irradiation has also been studied. Bu et al. [34] examined the catalytic pyrolysis of Douglas fir over activated carbon and microwave irradiation. A very high concentration of phenolics (66.9%) in the bio-oil was obtained, which was attributed to the decomposition of lignin. On the other hand, the concentration of esters in the bio-oil was quite high (42.2%) when Zn powder was used as the catalyst. They argued that phenolics and esters can be separated from the bio-oil to be used as feedstock in the chemical industry. Zhang et al. [35] evaluated the microwave-catalytic pyrolysis of aspen pellets over molecular sieve-based catalysts and zirconium-based catalysts. The molecular sieve-based catalysts included MS (Molecular sieve) 4A, Fe_2O_3/MS 4A, CoO/MS 4A, NiO/MS 4A, MgO/MS 4A, PtO/MS 4A, Al_2O_3/MS 4A, La_2O_3/MS 4A, Cl^-/MS 3A, SO_4^{2-}/MS 3A, Na_2O/MS 3A, CaO/MS 3A, and K_2O/MS 3A. The zirconium-based catalysts included CoO/ZrO_2, NiO/ZrO_2, La_2O_3/ZrO_2, NiO-CaO/ZrO_2, Cl^-/ZrO_2, SO_4^{2-}/ZrO_2, Na_2O/ZrO_2, CaO/ZrO_2, and MgO/ZrO_2. Among these catalysts, only Cl^-/ZrO_2 and SO_4^{2-}/ZrO_2 changed the composition of the product bio-oil significantly. 1,1-dimethoxyhexane was the main product of the catalytic pyrolysis over Cl^-/ZrO_2 or SO_4^{2-}/ZrO_2. As research on the microwave-catalytic pyrolysis is in its initial stages, further studies using a range of catalyst systems will be needed to determine its potential.

2. Herbaceous Biomass

Herbaceous biomass, like woody biomass, is a type of lignocellulosic biomass. The production of bio-oil from various herbaceous biomass materials has been reported. Compared to woody biomass, however, research on the pyrolysis of herbaceous biomass is normally conducted on laboratory scale. Therefore, bench-scale or pilot-scale studies will be needed in the future.

Mochizuki et al. [36] examined the catalytic pyrolysis of two types of jatropha residues generated in the Philippines and Thailand, and cryptmeria over USY zeolites. Both jatropha residues showed high potential for the production of aromatics with low-silica USY zeolite (SiO_2/Al_2O_3=10), whereas the production of aromatics from

cryptmeria was insignificant.

Park et al. [37] conducted the catalytic pyrolysis of miscanthus, and listed the catalysts that exhibited high selectivity toward phenols and aromatics. They reported that the acidity and pore size of the catalyst as well as the presence of Pt in the catalyst affected the property of bio-oil produced considerably. For example, mesoporous Al-MCM-41, Al-MCM-48 and meso-MFI were more effective in the production of phenolics, whereas HZSM-5 and Meso-MFI with strong acidity showed higher selectivity toward aromatics. The presence of Pt on HZSM-5 and Meso-MFI promoted cracking, dehydrogenation, deoxygenation and aromatization.

From the catalytic slow pyrolysis of Onopordum acanthium L. over a sepiolite catalyst, Gerçel et al. [38] reported that a 10 wt% sepiolite catalyst enhanced the yield of bio-oil from 18.5% to 27.3%. Pütün [39] examined the catalytic pyrolysis of cotton seed over different amounts of MgO to produce bio-oil containing hydrocarbons in the diesel range (C_{10}-C_{16}).

Wang [40] et al. conducted the catalytic pyrolysis of Manchurian ash (Fraxinus mandshurica Rupr.) sawdust over four different zeolite catalysts (HZSM-5, H-, USY, and Na-Y). The Y-type catalysts were most effective in promoting the formation of isoalkanes and aromatics while inhibiting the production of aldehydes, acids and ethers.

Jeon et al. [41] upgraded the bio-oil derived from waste rice husk using meso-MFI and Pt/meso-MFI catalysts. The catalytic cracking of heavy phenols resulted in a reduced heavy phenol content and an increased light phenols and aromatics content. The increase in aromatic content by catalytic upgrading was attributed to the strong Brønsted acid sites and the shape selectivity of the Meso-MFI catalyst. The Pt-loaded meso-MFI catalyst showed even higher activity for deoxygenation and the production of aromatics.

3. Algae

Although the pyrolysis of aquatic and marine biomass, such as algae, has attracted particularly strong attention [42], reports on their catalytic pyrolysis are rare compared to lignocellulosic biomass or other land biomass. Algae bio-oil has a higher heating value than the bio-oil from lignocellulosic biomass. Therefore, its catalytic upgrading is very important for the production of high-quality fuel. Research on the catalytic pyrolysis of algae, compared to that of woody biomass, is also limited to catalyst screening. In particular, most studies focused on the pyrolysis of microalgae. Therefore, more studies on the pyrolysis of macroalgae will be needed. Research on scaling-up the catalytic pyrolysis of algae for the mass production of bio-oil and the removal of nitrogen compounds included in the product oil will also be needed. The following gives a summary of the most recent studies on the catalytic pyrolysis of algae.

Thangalazhy-Gopakumar et al. [43] performed the catalytic pyrolysis of chlorella vulgaris, a type of fresh water green alga, over HZSM-5. They reported that the carbon yield of aromatic compounds increased from 0.9 to 25.8 wt% by catalytic upgrading with a catalyst-to-biomass ratio of 9 : 1, indicating the high selectivity of HZSM-5 toward aromatics in the catalytic pyrolysis of algae.

Yang et al. [44] examined the catalytic pyrolysis of Nannochloropsis sp. over HZSM-5. HZSM-5 effectively removed a variety of polar functional groups, while promoting the production of aromatic compounds. The heating value of the alga-derived bio-oil was reported to be higher than that from lignocellulosic biomass.

Lee et al. [45] addressed the catalytic pyrolysis of a marine alga, *Laminaria japonica*, over two mesoporous catalysts: meso-MFI and Al-MCM-48. Meso-MFI was more effective in deoxygenation and aromatization than Al-MCM-48. The lower catalytic activity of Al-MCM-48 was attributed to its weak acidity.

4. Other Biomass

As pyrolysis can be performed on any biomass materials, the pyrolysis of organic waste, if it is generated in large quantities, will not only reduce the waste disposal cost but also increase the economic value of the waste materials. Recently, Kim et al. [46], Park et al. [47] and Heo et al. [48] evaluated the catalytic pyrolysis of oil fractions separated from food waste leachate in different seasons over a range of microporous and mesoporous zeolite catalysts. The effect of acidity was found to be particularly important. HZSM-5, Meso-MFI and Beta with strong acid sites mainly produced hydrocarbons in the gasoline range, whereas Al-MCM-41 and Al-SBA-15 with weak acid sites showed high selectivity toward oxygenates and diesel-range hydrocarbons.

CATALYTIC DEOXYGENATION OF TRIGLYCERIDES

Biodiesel from the transesterification of triglycerides has some disadvantages from the viewpoint of fuel specifications. First, biodiesel has a lower heating value. The calorific value of biodiesel is approximately 33 MJ/L, which is 9% lower than that of petroleum-based diesel. Second, biodiesel has storage problems due to acid corrosion [49,50], which require additional investment for the establishment of an independent fuel storage and supply system for biodiesel. All these disadvantages were attributed mainly to oxygen atoms incorporated in biodiesel [49].

1. Production of Hydrocarbon Based Fuels by Hydrodeoxygenation

To remove these oxygen atoms, HDO was proposed and developed. Fig. 4 compares the concept of HDO with transesterification when triglycerides are used as reactants. The biodiesel (fatty acid methyl ester) produced by transesterification preserved oxygen atoms in the form of carboxylic groups. On the other hand, HDO mainly removed the oxygen in triglycerides in the form of H_2O by hydrogenation. As the HDO process converted triglycerides to pure hydrocarbon, hydrogenated biodiesel by HDO is expected to be compatible with the existing fuel storage and supply system. This section addresses HDO using triglycerides as reactants.

In terms of the catalyst, HDO also has an advantage. The biodiesel production process has been established and mainly commercialized using homogeneous catalysts, such as sodium hydroxide
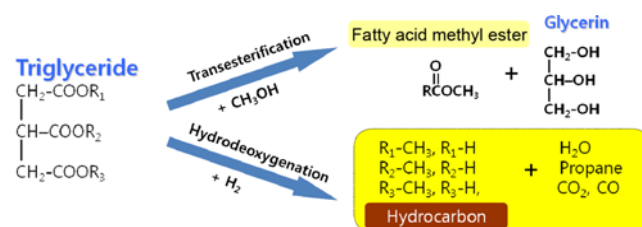

Fig. 4. Comparison of reaction pathways and products between transesterification and hydrodeoxygenation of triglyceride.

and potassium hydroxide dissolved in methanol. Homogeneous catalysts are difficult to separate from the product mixture. Therefore, considerable amounts of polluted water were created to remove the basic catalyst from the biodiesel product. On the other hand, the catalysts used in the HDO process originate mainly from those of hydrodesulfurization (HDS) with minor optimization. Because the process and catalysts for HDS were already well-established for the continuous production of petroleum-based diesel with a low sulfur concentration, the recently established HDO process based on the HDS process is expected to be promising. Owing to these advantages, many companies have tried to commercialize the HDO process. In particular, many refinery companies, such as Neste Oil, Petrobras, SK-Innovation, and UOP/Eni, have focused on the development of HDO because they already have HDS facilities and the corresponding catalysts. Among them, Neste Oil carried out pioneering work for commercialization [51]. Neste Oil produced hydrogenated biodiesel (HBD) commercially called "NexBTL". UOP/

Eni also used the HDO process and produced HBD called "Green Diesel" [52,53]. Although other refineries, such as Petrobras and SK-Innovation did not commercialize HBD, they already used the HDO process and considered commercialization. In addition to refineries, Dynamic Fuels, a joint venture between Syntroleum Corporation and Tyson Foods located in Geismar, Louisiana, began the commercial production of HDB with a production capacity of 75,000,000 gallon/year [54]. Non-foods, such as animal fats, vegetable oil, tall oil and greases, were used as the feedstock for HDB production. In addition to hydrotreating, isomerization and standard fraction steps were combined to enhance the value of the product by the co-production of jet fuel.

In addition to the efforts for the commercialization of HBD by HDO, many studies examined the reaction mechanism of HDO. Huber et al., at the University of Massachusetts-Amherst, examined the possibility of the simultaneous treatment of vegetable oil and heavy vacuum oil (co-processing) in conventional HDS equip-
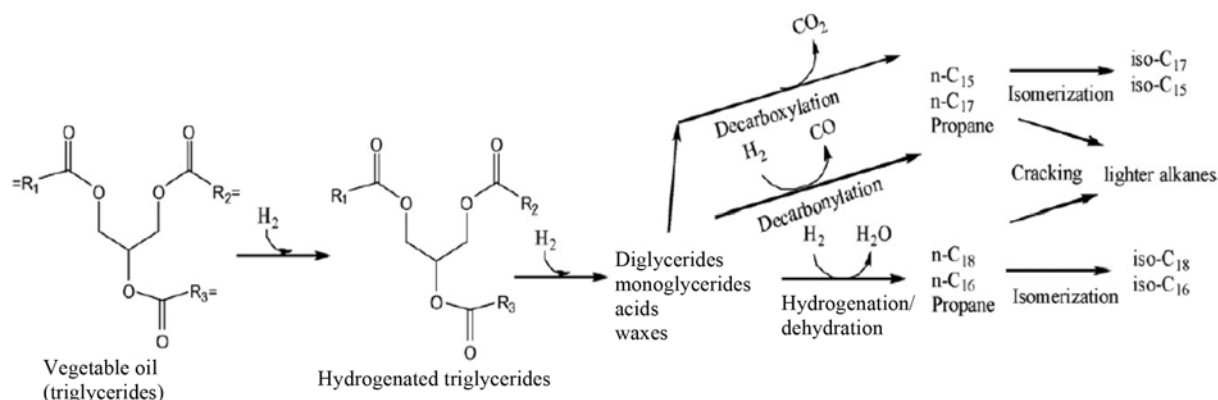

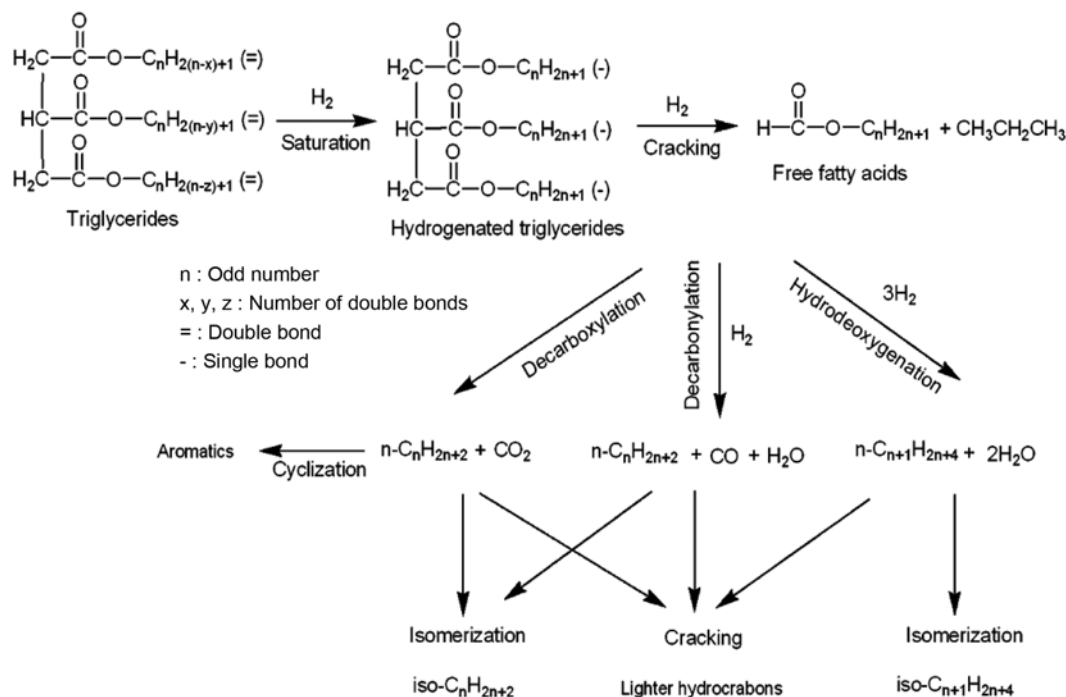Fig. 5. Reaction pathways for conversion of triglycerides to alkanes [21].

Fig. 6. Possible reaction pathways of triglycerides over hydrotreating catalysts [56].

ment with sulfide NiMo/Al$_2$O$_3$. They also examined the reaction pathways for the conversion of vegetable oil (triglycerides) into hydrocarbon. As shown in Fig. 5, the hydrogenation of double bonds in triglyceride was the first step. The removal of oxygen in the form of CO$_2$ (decarboxylation) and H$_2$O (dehydration) occurred in the next step [21,55]. This suggests that the HDO of triglycerides requires a large amount of hydrogen due to the additional hydrogenation of double bonds existing in the triglycerides.

Kim et al., at the Korea Institute of Science and Technology, examined the reaction pathways of HDO depending on the catalysts. Fig. 6 shows that the CoMo-based catalysts promoted isomerization and cracking, and the Ni or Pd-based catalysts enhanced decarboxylation [56]. Several other groups independently examined the reaction mechanism and kinetics of HDO using a series of sulfided CoMo/ Alumina or NiMo/Alumina as catalysts and a range of triglycerides as reactants [57-61].

Recently, a paper reported by Leherer et al. attracted considerable attention [62]. Most papers dealing with HDO process and catalysts used reagent grade model compounds (stearic acid, oleic acid, etc.) or purified vegetable oils (soybean oil, rapeseed oil). On the other hand, this paper particularly dealt with microalgae oil as a reactant. As microalgae have been reported to have a high yield of triglycerides [19], microalgae oil is considered a promising solution for the stable supply of feedstock in the HDO process for hydrocarbon fuel production. The hydrotreating of crude microalgae oil was performed by 10 wt% Ni/H-Beta as a catalyst at 260 $^\circ$C, 40 bar in a hydrogen environment. The hydrocarbon yield was 78%, which is approaching the theoretical maximum yield of 84%. This suggests that microalgae oil is a potential feedstock for the production of HDB [62].

From the view of the process scheme, two processes (co-processing and stand-alone) were considered in the early stage. Co-processing between heavy vacuum oil from petroleum and triglycerides from biomass has attracted considerable attention because existing facilities in petroleum refineries are expected to reduce the initial investment. However, further studies have shown that trace amounts of contaminants in the triglycerides from a biological origin (phosphorus, sodium, potassium and calcium etc.) deactivated the catalytic performance of the HDO process due to the accumulation of these contaminants on the catalyst. H$_2$O and CO$_2$ produced during HDO also deteriorate the corresponding catalysts [63]. These results suggest that the HDO process using triglycerides from a biological origin should be stand-alone type units that are optimized for particular feedstock conditions.

2. Hydrocarbon Production by Deoxygenation without Hydrogen Consumption

Unlike biodiesel production by transesterification, the HDO process has feedstock flexibility for the production of HBD. As mentioned in the previous section corresponding to Dynamic Fuels, a range of low-grade triglycerides, such as tall oil, grease, animal fats and used frying oils, which are unsuitable for feedstock in the transesterification process, were used freely to produce high quality (high cetane number) hydrocarbon-based fuels. On the other hand, the consumption of huge amounts of hydrogen is unavoidable because hydrogenation of the double bond in the alkyl-chain and oxygen in the carboxylic group occurred simultaneously without specific selectivity. Theoretically, one mole of triglyceride requires more than six

moles of hydrogen. A stable supply of huge amounts of cheap hydrogen might be a disadvantage for the wide-spread use of the HDO process.

To overcome the drawback of HDO, the DO reaction has been studied. Hydrocarbon production with little or no hydrogen might enhance the economic feasibility of DO. Murzin at Avo Akademi University introduced the DO reaction. Murzin et al. first reported the possibility of a DO reaction with palladium catalysts and model reactants in 2005 [64]. Since then, many papers have been published [65-71]. Among the various catalysts, palladium-supported activated carbon (Pd/AC) was selected as an optimized catalyst [65]. Pd/AC showed reasonable catalytic activities for the DO reaction in semi-batch mode with reagent-grade model compounds [66-68]. On the other hand, such an optimized catalyst did not show good catalytic activity in a fixed-bed reactor system. The initial activity was quite high, but the catalytic activity decreased drastically, possibly due to the decrease in surface area and pore blockage by coke deposition [69-71].

Henry Lamb, at North Carolina State University and Diversified Energy, proposed a hydrocarbon production process with the minimum use of hydrogen, called the Centia Process, as shown in Fig. 7. Unlike HDO and DO, hydrolysis is the first step in the Centia Process [reaction pathway (3)] to convert one mole of triglyceride into three moles of free fatty acids (FFAs) and one mole of glycerol. The glycerol separated after the hydrolysis step might be used as a thermal source to operate the entire process. The decarboxylation of FFA is the second step to produce long-chain alkanes by removing oxygen in the form of CO$_2$. Reforming long-chain alkanes into branched alkanes is the final step to enhance the fuel quality. In this process, the decarboxylation step should be effectively realized with the proper catalysts. Lamb et al. mainly performed the DO reaction of FFA with palladium-based catalysts. As reported previously, the double bonds in hydrogenated FFA occurred before decarboxylation. The type of support and carbon number of FFA also affected the change in activity for the DO reaction [72-74].

Ko et al., at the Korea Institute of Energy Research, also performed the DO reaction without hydrogen consumption. A range of feedstocks, such as reagent grade oleic acid, food-grade soybean oil and microalgal oil obtained by the pyrolysis of microalgae (chlorella *sp.* KR-1), were used as reactants and precious metal catalysts and mixed metal oxide catalysts were used as the catalysts. Unlike
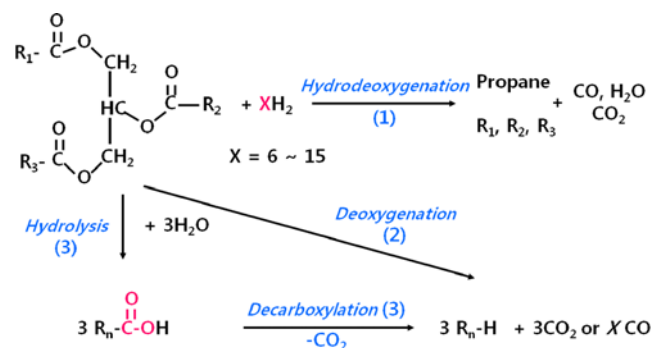

Fig. 7. Reaction pathways for various processes: (1) Hydrodeoxygenation, (2) Deoxygenation, (3) Centia process (hydrolysis+ decarboxylation).

previous reports, platinum-based catalysts showed better DO activity than palladium-based catalysts. The discrepancy between previous results and Ko te al.'s report might be due to the difference in the reaction conditions (reaction temperature and gas environment). This group also reported that mixed metal oxide (MgO+MgAl$_2$O$_4$) obtained from hydrotalcite showed reasonable catalytic activity for DO under the given conditions [75-78].

Recently, Holmes and Wurthmann at the University of Vermont suggested oxidative decarboxylation using a photo-Fenton reagent and applied for a patent. The hydrocarbon production processes mentioned earlier normally carried out reactions at more than 250 °C. However, photo-catalytic decarboxylation can be performed at room temperature. The low reaction temperature might be a strong point, but no specific examples have been published [79]. The homogeneous catalyst used in this photo-catalytic decarboxylation reaction might cause problems during separation of the products and catalysts.

CONCLUSIONS

Atmospheric-pressure catalytic pyrolysis based on cracking reactions is an important method to produce fuel oil from biomass. Studies of catalytic pyrolysis reported from 2010 were reviewed. The catalytic pyrolysis of different types of biomass materials was conducted. The acid properties and pore geometry were reported to be the most important properties of the cracking catalysts. HZSM-5 and meso-MFI, which have many strong acid sites, exhibited high selectivity toward aromatics and gasoline-range hydrocarbons, whereas Al-MCM-41, Al-MCM-48 and Al-SBA-15 exhibited high selectivity for phenols and diesel-range hydrocarbons. An examination of the effects of the process parameters is very important for optimizing the composition of the product. In particular, it is very important to develop methods that prevent catalyst deactivation.

In addition to bio-oil obtained from the pyrolysis of biomass, triglycerides appear to be a promising candidate as a substitute for transportation fuel. Triglycerides were converted successfully to hydrocarbon fuel by HDO. Many papers and patents have been published. Moreover, the HDO process has been developed to the extent of commercialization because most of the catalysts and processes are based mainly on HDS, which is well-established in petroleum refineries. On the other hand, the level of hydrogen consumption should be reduced. To overcome this problem, DO without hydrogen has been proposed and studied since 2005. Precious metal catalysts showed reasonable activity for DO in semi-batch mode, but the catalysts were deactivated by coke deposition. Suitable catalysts for DO should be developed in a further study.

In summary, depending on the biomass material to be pyrolyzed and the final product required, the selection of a stable catalyst, proper reactor configuration and process optimization are essential for the production of high quality bio-fuel.

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