A review on the upgrading of bio-oil based on separation

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Abstract The development of bio-based liquid fuel is important for the substitution of transport fuels. Fast pyrolysis can efficiently convert solid biomass wastes into bio-oil. However, its poor properties limit its high-quality utilization and therefore upgrading is required. Because of the complicated composition, upgrading bio-oil by a single technique faces many problems, such as low conversion efficiency and severe catalyst deactivation. These problems can be largely overcome by graded upgrading based on separation, in which bio-oil is first separated into several fractions and then these fractions are upgraded by different techniques. This paper is a review of the current states in the upgrading of bio-oil fractions obtained from water extraction and vacuum or molecular distillation. The corresponding upgrading techniques include esterification, steam reforming, catalytic cracking, and hydrodeoxygenation. For each upgrading technique, the corresponding conversion behaviors and mechanisms of typical model compounds in bio-oil fractions are first outlined, and then the applications of this technique in actual bio-oil fraction upgrading are introduced. The graded upgrading of bio-oil based on separation will have more potential and become more economical if various separation techniques, upgrading methods, and the extraction of valuable chemicals can be combined.

Keywords Biomass; Pyrolysis; Bio-oil; Upgrading; Separation

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1 Introduction

Biomass, a unique renewable carbon source, has attracted worldwide attention, due to the shortage of traditional fossil fuels, environmental pollution, and CO_2 emissions. Since most biomass has low contents of sulfur and nitrogen, the emissions of SO_x and NO_x are not severe during its utilization. Moreover, by integrating biomass growth in the whole life cycle, CO_2 emission can be regarded as neutral for biomass utilization.

Biomass can be directly used for combustion or converted into gas, liquid, and solid fuels by thermochemical processes. Fast pyrolysis is an important thermochemical technology for biomass conversion, in which biomass is rapidly heated in the absence of air, with a short residence time and a medium reaction temperature in the range of 450—650 ℃ [1]. The aim is to produce liquid bio-oil, with a yield as high as 70—75 wt% [2]. Meanwhile, some gas and char are also produced.

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Bio-oil is viscous and appears dark-brown, and it has high water and oxygen contents, leading to a low heating value. Meanwhile, the pH of bio-oil is low, and the viscosity of bio-oil is higher than those of gasoline or diesel. Analysis of the chemical composition of bio-oil by gas chromatography-mass spectrometry has revealed that it can be composed of more than 300 oxygenated compounds, including acids, ketones, phenols, aldehydes, sugars, esters, alcohols, and some other components [1—3]. In addition, bio-oil also contains some high-molecular-weight compounds that cannot be detected by gas chromatography, such as polymeric sugars and phenolic oligomers (pyrolytic lignin) [4].

Due to its low heating value and high acidity, bio-oil cannot be directly used as a transport fuel, but it is commonly used as the power fuel in boilers and kilns. Researchers at BTG Biomass Technology Group BV and Dynamotive have used bio-oil as a boiler fuel [5, 6]. Additionally, researchers have also tried to use bio-oil in diesel engines and gas turbines. Tests of bio-oil combustion in diesel engines showed that because of its high water content, the ignition of bio-oil was difficult and therefore diesel had to be used for auxiliary ignition; meanwhile, the acidity of bio-oil would also cause the corrosion of nozzles and combustors [7—9]. Consequently, device modification would be necessary for bio-oil combustion in gas turbines [10].

Therefore, the upgrading of bio-oil is required to enable its high-grade utilization. The common bio-oil upgrading technologies include catalytic cracking, steam reforming, hydrodeoxygenation, and esterification [11—13]. As shown in Figure 1, steam reforming produces hydrogen and cracking generates aromatic hydrocarbons, both of which are usually performed as heterogeneous gas—solid (reactant—catalyst) processes in fixed-bed or fluidized-bed reactors. Hydrodeoxygenation for aliphatic hydrocarbon generation can be carried out in a slurry reactor for either heterogeneous liquid-solid (reactant-catalyst) or homogeneous liquid-liquid (reactant-catalyst) reactions, or in a fixed-bed reactor for heterogeneous gas-solid (reactant-catalyst) reaction. Esterification is aimed at ester fuel production, for which a slurry reactor is often used.

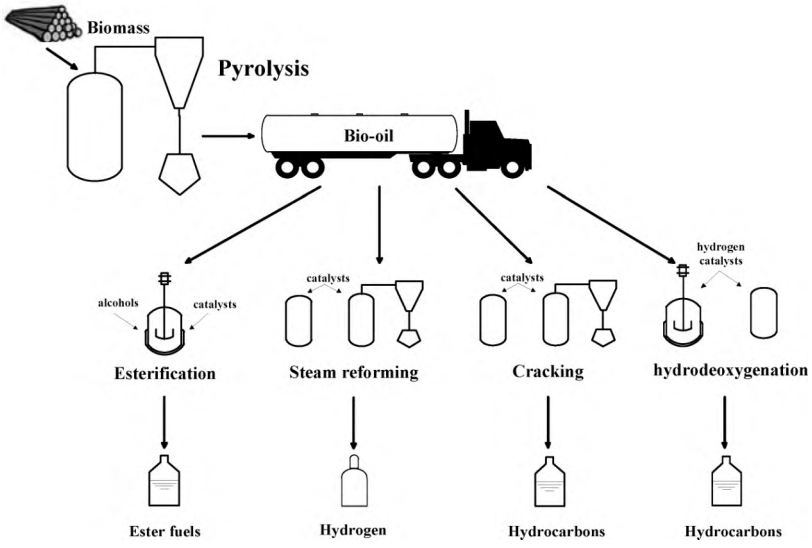

Figure 1 Upgrading techniques for bio-oil.

Although bio-oil can be upgraded by the aforementioned techniques, its direct upgrading by a single technique faces many problems, such as low conversion efficiency and severe catalyst deactivation. Low-molecular-weight compounds in bio-oil, such as acids, hydroxyketones and monophenols, show relatively high reactivity in steam reforming and cracking processes [14, 15]. Otherwise, the high-molecular-weight compounds in bio-oil, especially phenolic oligomers, are not active in these processes and tend to form coke, leading to catalyst deactivation and reactor blockage [16]. Ben *et al*. [17] have shown that such high-molecular-weight phenolic oligomers are more suitable for hydrodeoxygenation processes under a high reaction pressure. However, most acids and ketones in bio-oil may be converted into gaseous alkanes

through hydrodeoxygenation, which lowers the desired liquid hydrocarbon yield and increases the hydrogen consumption [18]. In addition, esterification processes are more effective in the conversion of carboxylic acids.

Consequently, bio-oil needs to be pre-separated in order to enrich some specific components, and the obtained fractions can then be upgraded by different techniques, thus promoting the integral conversion efficiency and economy [19]. This review concerns the current states in the upgrading of bio-oil fractions obtained from water extraction, and vacuum or molecular distillation.

2 Separation pre-treatment for bio-oil

Bio-oil has a complex composition with wide distributions in both polarity and boiling point. Common bio-oil separation methods include solvent extraction, distillation, and column chromatography [20]. Solvent extraction and column chromatography are based on the different polarities of the components, whereas separation by distillation is based on the difference in boiling points or mean molecular free paths of the components. Form the viewpoint of industrialization, solvent extraction and distillation are considered to be of greater potential.

2.1 Solvent extraction

According to their polarities, the components in bio-oil can be roughly divided into two groups: the pyrolytic products of cellulose and hemicellulose, such as acids, hydroxyketones, aldehydes, and some sugars, which are polar compounds owing to the presence of hydroxyl, carboxyl, and aldehyde groups; and the pyrolytic products of lignin, which include weakly polar phenols and their oligomers (pyrolytic lignin). Therefore, based on the principle of similarity and intermiscibility, components with different polarities can be separated by solvent extraction.

The commonly used solvents for extraction include water, esters, alkanes, ethers, ketones, and so on. Taking the recovery efficiencies of solvents and operating costs into consideration, bio-oil separation by organic solvent extraction is usually only applied in the fine analysis of components. In the chemical analysis of bio-oil by Oasmaa *et al*. [21], *n*-hexane was firstly used to extract the soluble compounds, then the residue was separated by adding water to obtain the water-soluble and water-insoluble fractions, and the water-soluble fraction was further separated by dichloromethane/diethyl ether extraction. It was found that the fraction extracted by the combination of dichloromethane/diethyl ether mainly contained aldehydes, ketones, and some degradation products of lignin, whereas the water-insoluble fraction mainly comprised pyrolytic lignin. Similar studies have also been performed by other researchers using several organic solvents to implement multi-extraction of bio-oil for chemical analysis [22, 23].

Normally, water is preferred as the solvent for extraction, because it is inexpensive and easily available. In addition, the water-soluble fraction (aqueous fraction) and water-insoluble fraction (organic fraction) to some extent meet the requirements of subsequent graded upgrading. Crude bio-oil has a water content of 15—30 wt% and appears homogenous. When the water content increases beyond 50 wt%, phase separation occurs [24]. The upper phase is the aqueous fraction while the lower phase is the organic fraction. Vitasari *et al*. [25] found that for water/bio-oil weight ratios in the range of 0.3—0.9, the water content in the obtained aqueous fraction was 50—70 wt%. When the water/bio-oil ratio was increased, more water-soluble components were extracted and the recovery efficiency reached 80—90%.

In the bio-oil aqueous fraction, the contents of acids, hydroxyketones and hydroxyaldehydes are relatively high. Vitasari *et al*. [25] observed that hydroxyacetaldehyde, acetic acid, and hydroxyacetone could be enriched in the aqueous fraction with contents of 4.1 wt%, 4.1 wt% and 2.7 wt% (wet basis), respectively. In the aqueous fraction obtained by Valle *et al*. [26], the contents of acetic acid and hydroxyacetone reached 19.1 wt% and 8.7 wt% (dry basis), while the content of hydroxyacetaldehyde was only 1.8 wt%. Another major chemical family in the bio-oil aqueous fraction comprises water-soluble sugars, such as levoglucosan and some other monosaccharides and oligosaccharides [27]. The contents of levoglucosan and hexose in the aqueous fraction obtained by Valle *et al*. [26] reached 19.6 wt% and

2.7 wt%(dry basis), respectively. Significant amounts of levoglucosan and other sugars in the aqueous fraction were also detected by Vispute *et al*. [4]. It is worth noting that some monophenols, especially polyhydroxy-monophenols, are also present in the aqueous fraction, because their chemical structures consist of hydrophilic phenolic hydroxyl group(s) and only one hydrophobic benzene ring [27]. Valle *et al*. [26] found that the total content of phenols in the aqueous fraction reached 13.4 wt% and a relatively high content of catechol was also observed by Vispute *et al*. [4].

The bio-oil organic fraction is mainly composed of phenols, including monophenols and phenolic oligomers (pyrolytic lignin). In the characterization of lauan bio-oil by Wang *et al*. [28], it was found that among the monophenols, the content of guaiacol was obviously higher than those of phenol and catechol; this could be attributed to the presence of the methoxyl group, which lowered its solubility in water. Meanwhile, the obtained pyrolytic lignin showed a wide distribution in polymerization degree and an average molecular weight higher than 1000 g/mol. Similarly, a series of phenolic oligomers in the organic fraction was also observed by Mullen and Boateng [29].

2.2 Distillation

Distillation is widely used in the separation of crude oil in the petrochemical industry. Traditional distillation is operated based on the difference in boiling points of components. Researchers have attempted bio-oil separation by atmospheric distillation. However, bio-oil is thermally sensitive, and polymerization reactions of its ketones, aldehydes, and phenols tend to occur upon heating. Therefore, during the atmospheric distillation of bio-oil, it was observed that boiling of the sample started at a temperature below 100℃, but ended at 250—280℃, and the residue yield was 35—50 wt% [2].

In view of the poor atmospheric distillation behavior of bio-oil, vacuum distillation has been used to improve the distilling efficiency and to circumvent polymerization reactions. Lu *et al*. [30] compared the atmospheric distillation and vacuum distillation of bio-oil: in atmospheric distillation, boiling of the bio-oil began at about 80℃ and ended at 250℃, with a residue yield of 32.1 wt%; in vacuum distillation, volatiles started to be distilled out at temperatures below 50℃ and a lower residue yield of 27.5 wt% was obtained at 65℃. The vacuum distillation of bio-oil by Zhang *et al*. [31] showed that low-molecular-weight compounds, such as formic acid, acetic acid, and hydroxyacetone, could be efficiently distilled out.

In addition to vacuum distillation, Wang *et al*. [32, 33] firstly introduced molecular distillation into bio-oil separation. In contrast to the principle of traditional distillation, molecular distillation is performed based on the difference in mean free paths of molecular thermal motions, as shown in Figure 2. When the

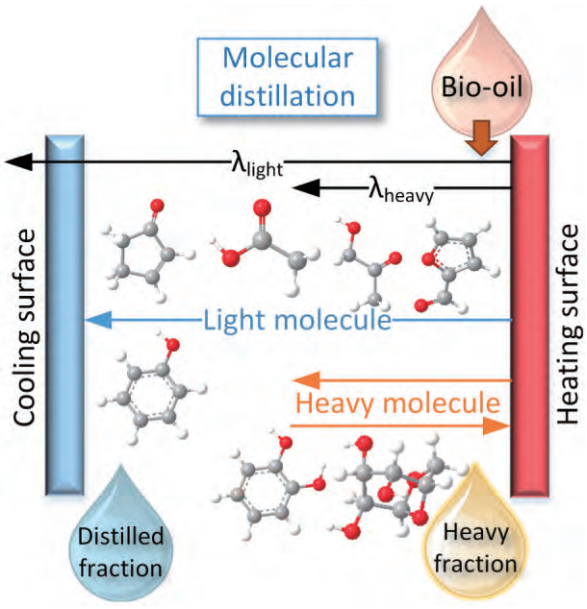

Figure 2 Schematic diagram of molecular distillation.

mixture is heated, molecules with sufficient energy can escape from the heating surface. In this case, if the mean free paths of some compounds are longer than the distance between the heating surface and the cooling surface, they can be cooled and condensed; or they cannot reach the cooling surface and return to the heating surface. As a result, the molecules are effectively separated at temperatures much lower than their boiling points. Molecular distillation has the advantages of low operation temperature, short heating time and high separation efficiency. Therefore, it is suitable for the separation of thermally sensitive bio-oil.

Wang *et al*. [33] carried out a systematic study of bio-oil molecular distillation. The yields of fractions at 60 Pa and different temperatures are shown in Table 1. It was found that the total yield of the distilled fraction could reach 85 wt%. In addition, no obvious coking (polymerization) was observed.

Table 1 Yields of bio-oil fractions by molecular distillation [33]

Distillation temperature (℃)	Condensation temperature (℃)	Pressure (Pa)	Bio-oil (g)	Recovery ratio (%)	Fraction I		Fraction II		Fraction III	
					Weight (g)	Yield (%)	Weight (g)	Yield (%)	Weight (g)	Yield (%)
70	20	60	156.2	97.65	080.0	50.0	10.8	06.75	65.4	40.9
100	20	60	197.0	97.55	102.2	50.6	23.7	11.75	71.1	35.2
130	20	60	181.6	98.20	117.0	63.2	35.8	19.4	28.8	15.6

The compositions of these fractions are shown in Figure 3. The light fraction mainly contained acids and ketones and the middle fraction contained more phenols and sugars; the enrichment of phenols and sugars in the heavy fraction was obvious [34, 35]. These distributions of compounds are related to their molecular sizes. Meanwhile, the operation conditions also affected the distillation performance. It was found that both increasing the temperature and reducing the pressure could promote the distilling out of high-molecular-weight compounds [36]. In addition, multiple molecular distillation of bio-oil has also been conducted, and four distinct fractions were obtained [37].

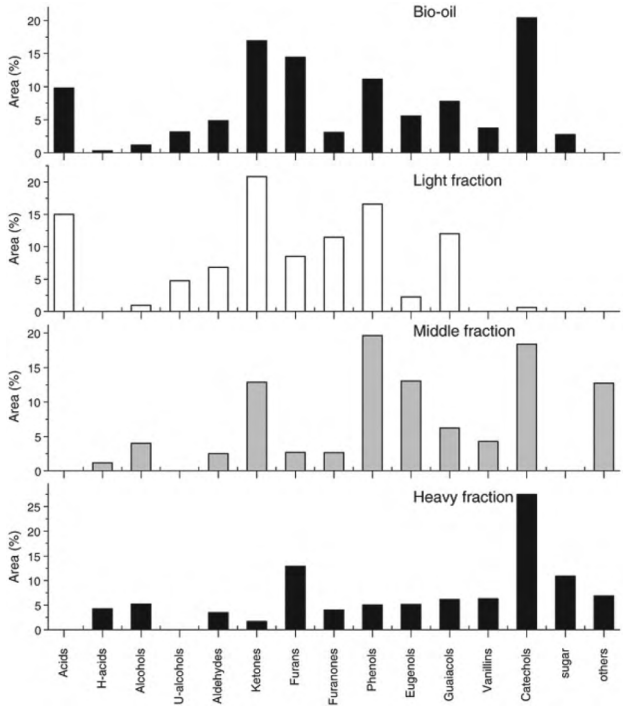

Figure 3 Compositions of bio-oil fractions by molecular distillation [33].

2.3 Graded upgrading based on separation

Because of their relatively low boiling points and high reactivities, the low-molecular-weight acids,

hydroxyketones and hydroxyaldehydes in the bio-oil aqueous fraction are all suitable for heterogeneous gas-solid processes. Although some monophenols and sugars still remain, the bio-oil aqueous fraction exhibits better performance in catalytic cracking and steam reforming than crude bio-oil. For the phenolic organic fraction, application of a liquid-solid hydrodeoxygenation process can overcome the difficulty in evaporation due to the high boiling points of the components. Moreover, hydrodeoxygenation reactions can achieve the depolymerization of phenolic oligomers, saturation of unsaturated bonds and further deoxygenation to produce liquid alkanes. In a report submitted to the Department of Energy of the U. S. by the UOP Company and Pacific Northwest National Laboratory, a technical route was proposed: bio-oil aqueous fraction was used for steam reforming to produce hydrogen, which was used as the feedstock for hydrodeoxygenation of the organic fraction to produce liquid fuels [38]. Wright *et al*. [39] calculated the economy of this technical route, and Dang *et al*. [40] performed a life-cycle analysis, both of which confirmed its feasibility.

Compared with water extraction, vacuum distillation and molecular distillation can leave sugars with high boiling points in the residual fraction, and thus the obtained distilled fraction is rendered more suitable than the aqueous fraction for gas-solid processes such as steam reforming and catalytic cracking. In view of the characteristics of the obtained fractions, Wang *et al*. [1, 32] proposed a graded upgrading route of bio-oil based on molecular distillation. As shown in Figure 4, the light fraction rich in acids and ketones could be subjected to esterification, cracking and steam reforming; the middle fraction containing acids and ketones as well as some phenols could be subjected to catalytic cracking, steam reforming and hydrodeoxygenation; and the heavy fraction with high contents of polymeric sugars and phenolic oligomers could be subjected to hydrodeoxygenation. In addition, some valuable chemicals, such as sugars and phenols, could also be extracted from the heavy fraction.

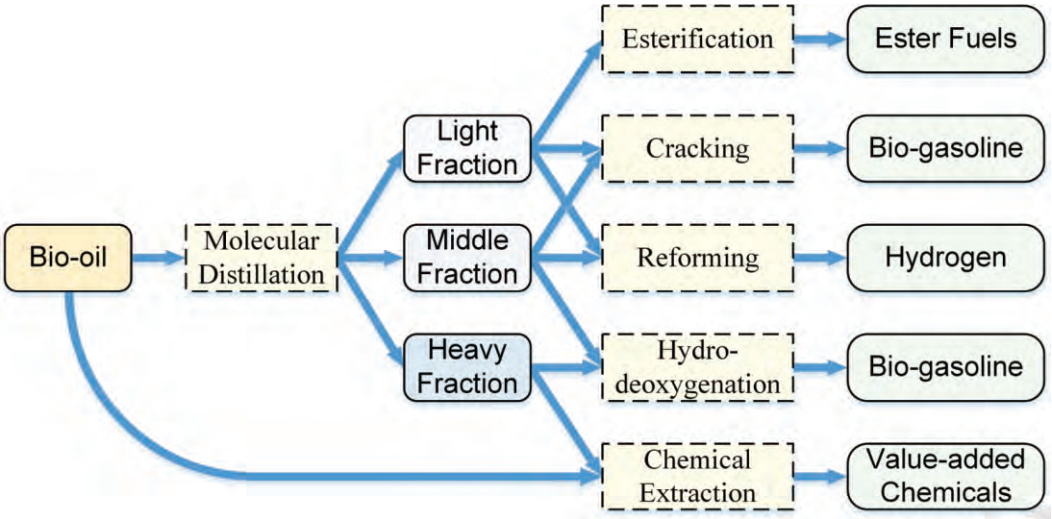

Figure 4 Graded upgrading of bio-oil based on molecular distillation.

In the following discussion, different bio-oil upgrading technologies and their application to the aforementioned fractions are reviewed. The upgrading behaviors and mechanisms of typical model compounds in these fractions are also illustrated to better understand the upgrading performances of the fractions.

3 Steam reforming for hydrogen production

Hydrogen can be produced by the steam reforming of bio-oil, which is regarded as a promising upgrading route [41], and it can also be used as the hydrogen supply for other upgrading processes, such as hydrogenation, hydrocracking, and hydroesterification. Steam reforming is normally accompanied by water gas shift reaction and methanation, as shown in Eqs. (1)—(3) [42].

Reforming: $C_nH_mO_p+(n-p)H_2O\rightarrow nCO+(n-p+m/2)H_2$ (1)

Water Gas Shift: $CO+H_2O\rightarrow CO_2+H_2$ (2)

Methanation: $CO+3H_2\rightarrow CH_4+H_2O$ (3)

3.1 Steam reforming of bio-oil model compounds

Bio-oil is a mixture of hundreds of components, including a variety of oxygenated compounds, such as carboxylic acids, aldehydes, ketones, alcohols, and phenols [43, 44]. Direct steam reforming of crude bio-oil would lead to severe catalyst deactivation [45]. Therefore, it is common to investigate the reforming behavior of some typical chemical compounds in bio-oil. Alcohols, phenols, acids, and ketones are considered to be suitable for steam reforming. Accordingly, ethanol, acetic acid, phenol, and hydroxyacetone have frequently been selected as typical model compounds [42, 46, 47]. Numerous catalysts have also been studied and developed to achieve a high conversion rate of bio-oil and a high selectivity for hydrogen, comprising different active metals (Rh, Pt, Pd, Ni, Co, Cu, Fe, etc.) [48—50], supports (Al_2O_3, SiO_2, SBA-15, etc.) [51—55] and promoters (K, Mg, Ca, La, Y, etc.) [56, 57].

3.1.1 Steam reforming of acetic acid

Steam reforming of acetic acid has been investigated over Pt/ZrO_2 as catalyst and a corresponding mechanism was proposed [58]. The first step was identified as dissociative adsorption of CH_3COOH to form CH_3COO^* or CH_3CO^* species on the Pt surface. The formed CH_3COO^* and CH_3CO^* species could then decompose to CO, CO_2, and CH_x, although no specific surface reactions were proposed for the decomposition reactions. CH_x could either polymerize to form a carbon layer on the catalyst or react with OH from the support to produce carbon oxides and H_2 [58]. Dehydration to CH_2CO and ketonization to CH_3COCH_3 proved to be undesirable reactions, since they were found to produce coke precursors and thereby lead to coke deposition [42].

Later, a more detailed reaction mechanism over Co, Ni, and Pd catalysts was proposed on the basis of density functional theory (DFT) calculations [46, 59—61]. According to the calculated reaction barriers for various bond scissions, the most probable pathway on a Co surface is $CH_3COOH^*\rightarrow CH_3CO^*\rightarrow CH_2CO^*\rightarrow CH_2^*\rightarrow CH^*$, and the rate-determining step is CH_3CO dehydrogenation, as shown in the red line pathway in Figure 5 [59]. Besides, the most probable pathway on the Pd surface was identified as $CH_3COOH^*\rightarrow CH_3CO^*\rightarrow CH_3^*+CO^*$ [60], whereas it was predicted as $CH_3COOH^*\rightarrow CH_3COO^*\rightarrow CH_3CO^*\rightarrow CH_3C^*\rightarrow CH_3^*\rightarrow CH_2^*\rightarrow CH^*$ over the Ni catalyst [61]. It can be seen that acetic acid would go through different pathways over different active metals.

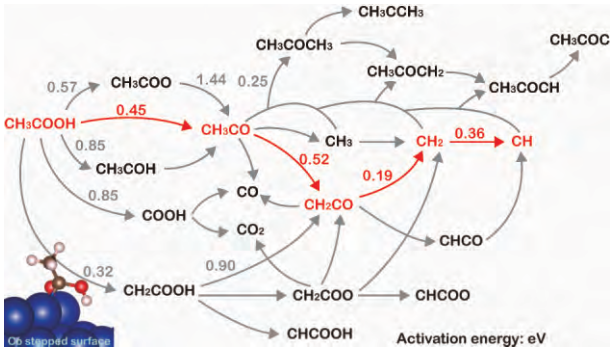

Figure 5 Scheme of possible acetic acid decomposition networks [59].

Steam reforming of acetic acid led to near-complete conversion to hydrogen over 17% $Ni/La_2O_3/Al_2O_3$ catalyst at above 700℃ [52], and a 5% $Ru/MgO/Al_2O_3$ catalyst performed better by maintaining 100% conversion and hydrogen selectivity for 35 h, whereby the modification effects of La_2O_3 and MgO were confirmed [62]. Later, Iwasa *et al*. [63] modified Ni catalysts with various alkali metals and studied the steam reforming behavior of acetic acid at a relatively low temperature of 450℃ and a steam-to-carbon (S/C) ratio of 3.3. The results showed that 1.0 wt% K promoted the reduction of Ni species, doubled the

acetic acid conversion to 94%, and increased the H_2 concentration to 6.6% compared with the alkali-metal-free Ni catalyst. Wang *et al*. [64] selected special coal ash as a catalyst support and achieved a phenol conversion of 83.5% with an H_2 yield of 79.1% at 700℃ and an S/C ratio of 9.2. Notably, the large amount of alkali and alkaline-earth metals in the specific coal ash favored water adsorption, which contributed to gas production, and Fe functioned in the reforming reaction to produce hydrogen. In particular, the function of Fe was further confirmed, and a coal-ash-supported Ni—Fe catalyst was found to perform better than previously studied Ni catalysts [65].

3.1.2 Steam reforming of other compounds

Steam reforming of ethanol has been extensively studied for catalyst improvement and delineating reaction routes [66—70]. Vizcaíno *et al*. [71] investigated the ethanol steaming reforming behavior over a Cu—Ni catalyst and proposed a scheme of the reaction routes. Ethanol was considered to first undergo dehydrogenation or dehydration to produce acetaldehyde or ethylene, respectively, which was also found by Chen *et al*. [68]. The formed acetaldehyde would further undergo decarbonylation to generate CH_4 and CO, followed by the production of H_2 and CO_2 through steam reforming. Ethylene could be converted into carbon deposited on the catalyst, or H_2 production through reacting with steam. Based on experimental studies and DFT calculations, Wang *et al*. [72] further designed a stable Ni/CeO_2 catalyst and calculated the elementary reactions. An optimal pathway for ethanol reforming on the surface of a Ni catalyst was proposed as: $CH_3CH_2OH^* \rightarrow CH_3CH_2O^* + H^* \rightarrow CH_3CH_2^* + O^* \rightarrow CH_3C^* + 2H^* \rightarrow CH_3^* + C^*$.

A series of Ni catalysts were prepared over γ-Al_2O_3, MgO, and La_2O_3 supports for ethanol steam reforming. It was found that Ni/La_2O_3 showed the best performance and stability, while Ni/γ-Al_2O_3 and Ni/MgO showed lower stability and inferior H_2 selectivity, respectively [69]. The ethanol conversion reached 100% with a hydrogen yield of 98.6% without any catalyst deactivation for 30 h, at an S/C ratio of 9.2 and a reaction temperature of 725℃ [72]. Vizcaíno *et al*. [71] modified Ni catalysts with Cu on γ-Al_2O_3, SiO_2, MCM-41, and ZSM-5 supports. It was found that Ni facilitated hydrogen production, while Cu inhibited CO production as well as coke deposition. Besides, γ-Al_2O_3 favored ethanol dehydration to ethylene at the acid sites, increasing the coke deactivation process. A higher hydrogen selectivity of 79.0%, with a carbon conversion of 95.4%, was achieved over a Cu-Ni/SBA catalyst, due to its smaller metallic crystallite size. Moreover, Li *et al*. [73] tested several preparation methods for Ni/Al_2O_3 catalysts and found that the co-precipitation method gave the best performing catalyst, offering an ethanol conversion of 99% and an H_2 yield of 88%.

Steam reforming of phenols is much more difficult than that of acetic acid, since the benzene ring is more stable and it takes more energy to open it. Much more severe carbon deposition was observed during phenol reforming compared with that of the other model compounds mentioned previously [74]. It has also been reported that the energy barriers for the respective steps of phenol steam reforming are quite high and all steps are endothermic, leading to more difficulty in the dehydrogenation of intermediates and reduced stability of intermediates on the surface [61]. In addition, phenols are not as soluble in water compared to alcohols and acids, and therefore a much higher S/C ratio has frequently been adopted in the steam reforming reaction. In early research, noble metals were utilized [74, 75], and phenol was completely converted into H_2 and CO_x at about 700℃ with an S/C ratio as high as 100 [48]. Constantinou *et al*. [76—78] selected active natural materials, such as calcite, dolomite, and olivine, and found that phenol conversion reached about 30%, with an H_2 selectivity of around 15%, over calcined olivine at 650℃ with an S/C ratio of 54.

Steam reforming of hydroxyacetone is much easier compared with that of acetic acid or phenol [79, 80]. It is frequently selected as a ketone model compound, since acetone is the most important intermediate in the acetic acid reforming process and its reforming has been studied during acetic acid reforming investigations [81]. Ramos *et al*. [82] selected hydroxyacetone to study the effects of La and Co promotion on the performance of Ni—Al catalysts. It was found that La in Ni—Al catalysts increased the CH_4, CO_2, C_2, and total gas yields, such that carbon conversion was more than 90% at 650℃ with an S/C ratio of 4.6, whereas Ni—Co—Al catalysts gave a lower carbon conversion of only about 80%.

Wang *et al*. [80] improved conventional Ni/Al_2O_3 catalyst by utilizing nano-Al_2O_3 and carried out the catalytic reforming of three typical bio-oil model compounds, namely phenol, acetic acid, and hydroxyacetone. A uniform structure contributed to a better distribution of the active metal on the catalyst support. Thus, the newly developed catalyst showed superior performance in terms of activity and stability. The conversions of phenol, acetic acid, and hydroxyacetone reached 84%, 98%, and 99%, and the corresponding hydrogen yields were 69%, 87%, and 97%, respectively, at 700℃, such that the conversion of hydroxyacetone to hydrogen was almost complete. The corresponding decomposition and reforming pathways of hydroxyacetone on an Ni(111) surface were elucidated through DFT calculations. By comparing the activation energies and reaction enthalpies for various elementary reactions, the most probable pathway was identified as $CH_3COCH_2OH^* \rightarrow CH_3COCH_2O^* \rightarrow CH_3COCHO^* \rightarrow CH_3COCO^* \rightarrow CH_3CO^* \rightarrow CH_3C+CH_3^* \rightarrow CH_2^* \rightarrow CH^*$, as shown in Figure 6 [61]. Furthermore, CH^* and CH_3C^* were identified as two key carbon precursors in catalytic steam reforming reactions. Specifically, CH_3^* can be easily reformed to CO^* through CH^*, whereas CH_3C^* is stable and tends to be regenerated according to $CH_3C^* \rightarrow CH_3COH^* \rightarrow CH_3CO^* \rightarrow CH_3C^*$.

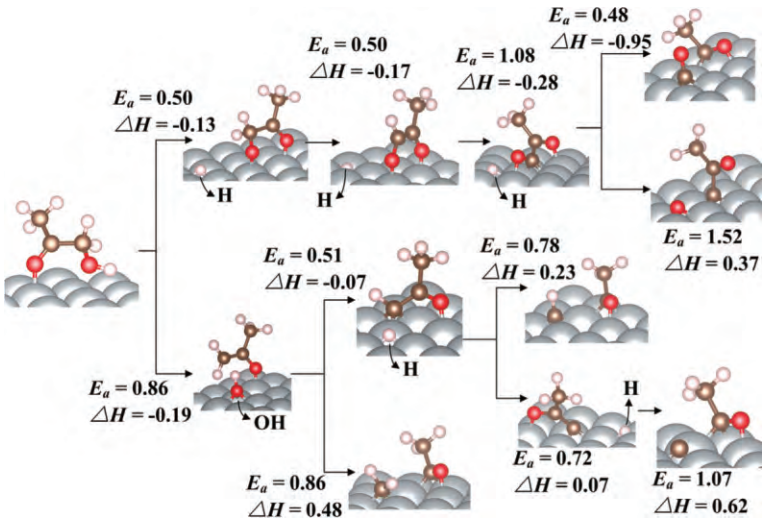

Figure 6 The most active pathway of hydroxyacetone decomposition [61].

3.2 Steam reforming of bio-oil fraction

Bio-oil steam reforming at high temperatures faces similar problems as mentioned above, in that the catalyst activity tends to be severely inhibited by high-molecular-weight compounds such as sugars and oligomeric phenols in crude bio-oil [83]. Therefore, bio-oil has frequently been pre-treated by adding water to obtain an aqueous phase [56, 84—89] or by gathering active volatiles [90, 91]. In this way, the inactive components in the crude bio-oil, principally pyrolytic lignin, were left behind. However, sugars were still found in the aqueous phase, and the main obstacle for bio-oil aqueous phase reforming was severe carbon deposition and therefore rather short catalyst lifetime.

At >800℃ with an S/C ratio of 4.92, H_2 yield reached 80% in the steam reforming of poplar wood bio-oil aqueous phase, but the reactivity was maintained for no more than 30 min [56]. For pine sawdust bio-oil aqueous phase reforming at an S/C ratio of 7.6, the carbon conversion remained at about 60% with 0.07 g H_2/g organics and the performance lasted for almost 2 h [88]. Furthermore, four bio-oils with various components were tested, and the influences of their major components were investigated. It was found that acetic acid and furfural were responsible for the most important differences, and the former was identified as a compound with low reactivity and low coke formation. In contrast, furfural was found to show a high reactivity and a high tendency to produce coke [87]. As regards catalysts for the aqueous phase steam reforming, five Ni/Al catalysts modified with Ca, Ce, Mg, Mn, and Zn were investigated at 800℃ and an S/C ratio of 3.54. It was found that Ni/Mg—Al showed a higher hydrogen production (56.46%), whereas Ni/Ca—Al showed a lower hydrogen production (46.58%) at both early and

stabilized stages during 4 h tests [92].

As regards the volatile organic components of bio-oils, it was interesting that the electrochemical catalytic reforming performed better in terms of increasing the carbon conversion from 63.2% to 90.6% and the H_2 yield from 55.0% to 87.5% at 400℃ with an S/C ratio of 6.1 [93], since the thermal electrons could promote the dissociation of oxygenated organic molecules in the bio-oil [94]. In addition, an integrative gasification—reforming process was adopted to avoid direct contact between the bio-oil and the reforming catalyst. The results revealed that deactivation of the catalyst was significantly suppressed, and that high activity was maintained for 6 h [95]. For the improvement of reaction process, coal ash was packed in front of nickel-based catalyst, acting as a guard catalyst. The improved reaction system succeeded in effectively converting bio-oil into hydrogen and exhibited high activity, and extending Ni/Al_2O_3 catalyst lifetime from 6 to 8 h [96].

Besides separation through water extraction, bio-oil has also been separated by molecular distillation [97]. The obtained light distilled fraction, which was enriched with water and low-molecular-weight oxygenated compounds, proved to be quite reactive and could easily be converted into the target products [98]. On the basis of this research, Wang *et al*. [61] proposed a new method for bio-oil reforming by utilizing its light distilled fraction. A carbon conversion of 95% and an H_2 yield of 135 mg/(g organics) were achieved, along with high stability for a duration of 11 h. The economic efficiency was also promoted since the distillate was reactive and no extra water addition was needed. The results were presented in Table 2, along with those of some previously reported works.

Table 2 Comparison with some well-reported works [61]

Feedstock	Reactor	Catalyst	T (℃)	S/C	G_{Cl} HSV (h^{-1})	C_{H2} (mol%)	H_2 yield (mg g^{-1} organics)	Stability (h)	Reference
MDF. Rice husk[a)]	Fixed bed	Ni/Al_2O_3	700	3.2	1 020	69.4	135	11	[61]
Aq. Beech wood	Fixed bed	C11—NK (Ni based)	700	8.2	300—600	~69	—	5	[99]
Aq. pine[b)]	Fixed bed	$NiCo/MgO—Al_2O_3$	650	7.6	13 000	—	138	2	[86]
Aq. pine	Fixed bed	$NiCu/MgO—Al_2O_3$	650	7.6	13 000	—	93	2	[86]
Aq. Rice hull	Fixed bed	$Ni/CeO_2—ZrO_2$	800	4.9[c)]	—	61.8	—	0.5	
Aq. pine	Fluidized bed	$Ni/La_2O_3—Al_2O_3$	700	12	4 700	71	83.6[d)]	>5	
Aq. pine	Fluidized bed	$Ni/MgO—Al_2O_3$	650	7.6	5 411	67.4	132.8	2	[89]
Aq. pine	Fluidized bed	$Ni/CaO—Al_2O_3$	650	7.6	11 817	60.8	77.4	2	[89]

a) MDF: molecular distillation fraction; b) Aq: aqueous fraction; c) Water/Bio-oil; d) mg g^{-1} bio-oil.

4 Catalytic cracking of bio-oil for hydrocarbon production

Catalytic cracking is an important technique for bio-oil upgrading, which can remove oxygen in the forms of CO, CO_2 and H_2O [102]. Zeolites, such as HZSM-5, silicalite, H-mordenite, H-Y, and so on, have been widely used as catalysts due to their acid sites and special pore structures [103, 104]. With these catalysts, deoxygenation, aromatization, polymerization, isomerization, and alkylation could occur in the process of catalytic cracking [105]. Furthermore, catalytic cracking over zeolite catalysts does not require a hydrogen supply and can thus be performed at atmospheric pressure, resulting in lower operational costs compared with hydrotreatment [41]. However, the effective hydrogen-to-carbon ratio ($(H/C)_{eff} = (H—2\times O)/C$) of bio-oil is quite low [102], and therefore the obtained hydrocarbon yields are not satisfactory. Severe coke deposition may also be observed during the cracking process [41].

4.1 Catalytic cracking of typical model compounds

Due to the complexity of bio-oil, some typical model compounds have been chosen to investigate its cracking behavior. Adjaye *et al*. [105] studied the catalytic cracking behavior of propanoic acid, 4-methylcyclohexanol, 2-methylcyclopentanone, methyl acetate, ethoxybenzene, and eugenol over HZSM-5 catalyst. They found that the reactants first participated in primary reactions such as cracking and deoxygenation to generate hydrocarbon gases, followed by oligomerization and aromatization to produce

olefin oligomers and aromatics. Besides, isomerization and polymerization could also occur, and thus some aliphatic hydrocarbons and coke were generated. More liquid hydrocarbons (>40% in the products at > 370℃) were obtained in the conversions of 4-methylcyclohexanol and 2-methylcyclopentanone because the aromatization of hydrocarbon gases dominated. However, polymerization and isomerization were the main reactions in the conversion of ethoxybenzene and eugenol, leading to low yields of liquid hydrocarbons (ranging from 1.2 to 3.1 wt% at 370 and 410℃). Similar differences in reactivity among different chemical families were also found in the work of Gayubo *et al*. [14, 106]. Aliphatic alcohols showed superior reactivity in the cracking process, and ketones were still easily converted though they were less active than alcohols, with the production of olefins, paraffins and aromatic hydrocarbons. As regards other model compounds, acids gave rise to ketones as the primary product and thus their transformation was more difficult. Phenols and aldehydes showed quite low reactivity in conversion to hydrocarbons, and severe coke formation could be observed. Significant catalyst deactivation with the addition of phenols was also observed by Gracça *et al*. [107]. Wang *et al*. [108] revealed that the presence of phenol could contribute to the rapid formation of heterocyclic or polymeric aromatic compounds, which may block the pores of the catalyst and lead to its deactivation.

Furans are also typically found in bio-oil, and their catalytic cracking behavior over HZSM-5 has been studied by Cheng *et al*. [109] and Carlson *et al*. [110]. At 450℃, furan was found to be primarily transformed into benzofuran, whereas the product distribution was more selective towards aromatic hydrocarbons, especially benzene and toluene, in the temperature range from 450 to 600℃. At 650℃, olefins became the dominant products and their carbon selectivity was comparable to that of aromatic hydrocarbons. However, coke was extensively deposited on the catalyst surface, which caused the yields of aromatic hydrocarbons and olefins to decrease dramatically within the first 30 min of time on-stream. A similar product distribution was also identified in the catalytic cracking of furfural over HZSM-5 and the carbon selectivities for benzofuran and aromatics were maximized at 400 and 500℃, respectively [111]. A high tendency for coke formation was observed by Gayubo *et al*. [112] when furfural was introduced. As regards catalytic cracking of sugars, Haniff and Dao [113] investigated the conversions of D-glucose, fructose, and their derivatives over HZSM-5 in a fixed-bed reactor. They found that the hydrocarbon yield was as low as 2.2 wt% and the coke yield amazingly reached 65.1 wt% with a feedstock of 20.3 wt% glucose in water solution. Besides, furans were detected as reaction intermediates. Correspondingly, Carlson *et al*. [114] also indicated that coke was generated through intermediate furan polymers in the catalytic cracking of glucose over HZSM-5.

According to the aforementioned results, some components of bio-oil could be efficiently converted into hydrocarbons; however, large amounts of compounds with low $(H/C)_{eff}$ or high molecular weight were responsible for severe coke formation during the bio-oil catalytic cracking. The tendency for coke formation may be concluded in the order: alcohols<ketones<acids, aldehydes or furans<monophenols<sugars or phenolic oligomers.

4.2 Improvement of catalytic cracking performance

Several effective methods have been proposed to restrict coke formation and to improve the conversion efficiency in the catalytic cracking of bio-oil and its model compounds, such as co-cracking with hydrogen-rich reactants, introduction of mild hydrogenation prior to cracking, and the modification of catalysts.

4.2.1 Co-cracking with hydrogen-rich reactants

Aliphatic alcohols, such as methanol and ethanol, have high $(H/C)_{eff}$. Meanwhile, they are well miscible with bio-oil components. Therefore, they are ideal co-reactants to take part in the catalytic cracking together with bio-oil. Mentzel *et al*. [115] investigated the co-cracking behaviors of bio-oil model compounds with methanol and found that the catalyst lifetime was efficiently improved as the blend ratio of methanol was increased. In the conversion of glucose, the coke yield decreased sharply from 65.1 wt% to 33.3 wt% when 30% of methanol was added to the aqueous solution [113]. Wang *et al*. [116—119] studied the co-cracking performances of hydroxyacetone, cyclopentanone, and acetic acid, respectively, with ethanol over HZSM-5 in a fixed-bed reactor. The experimental results showed that these three

substrates were each completely converted, and the selectivities for the oil phase reached 31.9, 35.2, and 33.4 wt%, respectively, with a blend ratio of ethanol of 70 wt%.

In addition to alcohols, other hydrogen-rich feedstocks, such as gasoil and long residue, may also be used as co-reactants. Gracça *et al*. [107, 120, 121] carried out a series of experiments on the co-cracking of bio-oil model compounds and gasoil (and its model compound) in a fixed-fluidized-bed reactor. They revealed that the introduction of gasoil reduced the coke yield and enhanced the generation of fuel gas, and gasoline. High gasoline yields of 33.4 wt% and 35.9 wt% were detected when acetic acid and hydroxyacetone were co-cracked with gasoil over an industrial fluid-catalytic-cracking equilibrium catalyst. Besides, the addition of long residue was also shown to improve the cracking process and to reduce coke yield from more than 20 wt% to about 6 wt% [122].

4.2.2 The introduction of mild hydrogenation prior to cracking

Long-term cracking processes are still hampered by severe coke formation because of the quite low $(H/C)_{eff}$ of bio-oil. To circumvent the consequent rapid catalyst deactivation, mild hydrogenation can be introduced prior to catalytic cracking. Vispute *et al*. [4] carried out the catalytic hydrogenation of crude bio-oil, followed by catalytic cracking of the liquid products. It was found that only 21% of the available carbon was converted into olefins and aromatic hydrocarbons if fed directly into the reactor without hydrotreatment, with a high carbon selectivity for coke of 49.5%. With hydrotreatment, the selectivities for the target products (olefins and aromatic hydrocarbons) and coke were measured as 32.6% and 34.6%, respectively. A mild hydrogenation process for bio-oil model compounds was studied by Chen *et al*. [123]. Their results showed that phenols, acids, and aldehydes were efficiently converted, and a high-quality pretreated bio-oil fraction, ready for subsequent upgrading, was thereby obtained. The corresponding reaction pathway is shown in Figure 7. Thereafter, Wang *et al*. [124] compared the catalytic performances of a single-stage cracking and a two-stage continuous hydrogenation-cracking process. It was found that the introduction of mild hydrogenation greatly improved the reactivity and the stability of the subsequent cracking reaction. In a single-stage cracking process, a dark-brown oil phase and a light-yellow aqueous phase were obtained (Figure 8(a), (b)), and the selectivity for the oil phase was only 23—28 wt%. When mild hydrogenation was introduced, a light-yellow oil phase and a clear aqueous phase were collected (Figure 8(c), (d)), with the selectivity for the oil phase increasing to 40 wt% within 8 h. The improved upgrading process was more amenable to continuous operation and hence more practical.

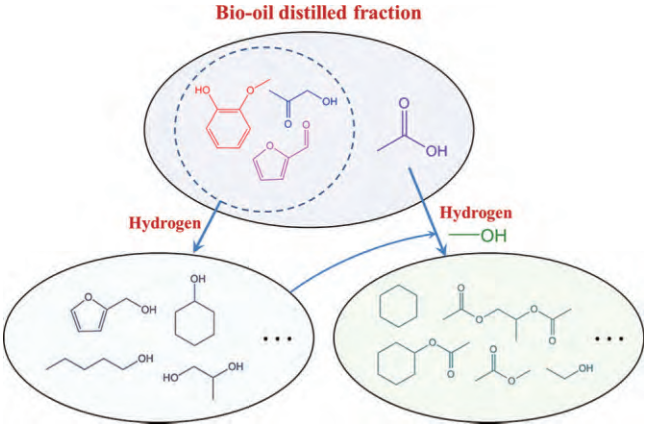

Figure 7 Reaction pathways of the acid-rich fraction of bio-oil [123].

4.2.3 Modification of catalysts

Several studies by different groups have shown that HZSM-5 exhibits superior catalytic performance [125—127]. However, the stability and reactivity of HZSM-5 still need improvement. Recently, some metal-oxide-modified catalysts have been developed to improve the conversion efficiency and catalyst stability.

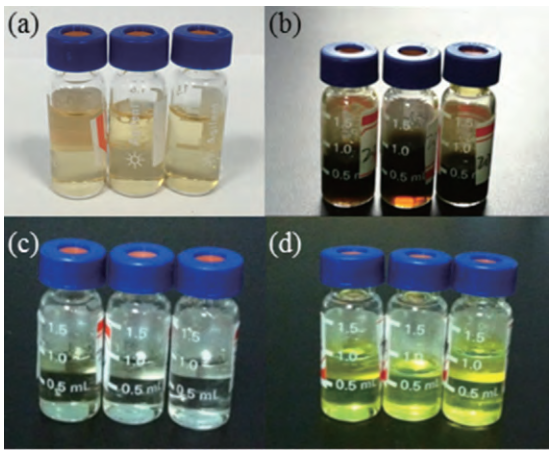

Figure 8 Photographs of liquid products: the aqueous (a) and oil (b) phases obtained from the single-stage cracking process, and the aqueous (c) and oil (d) phases obtained from the two-stage hydrogenation-cracking process.

Mg- and La-modified HZSM-5 have been used to produce olefins in the catalytic cracking of bio-oil and its model compounds [128, 129]. With the addition of Mg and La, medium acidity sites of the catalysts were moderately increased, which significantly enhanced the selectivity for light olefins and suppressed coke deposition on the catalyst surface. Zinc cations were introduced into HZSM-5 due to their capacity for hydrogen atom transfer [130], which plays an important role in aromatization [131]. As a result, Zn-modified HZSM-5 has commonly been used to promote the formation of aromatic hydrocarbons [108, 111, 132]. In addition, Ga_2O_3 may be loaded onto HZSM-5 to enhance its property for aromatization reaction, enabling gaseous hydrocarbons to be converted into aromatic hydrocarbons [133]. When the Ga_2O_3 loading was increased from 0 to 15%, the selectivity for the oil phase increased from 31.5 to 39.2 wt%, and the selectivity for C_3H_8 and C_4H_8 decreased significantly. The reaction mechanism over Ga_2O_3/HZSM-5 is depicted in Figure 9. The Ga_2O_3/HZSM-5 catalyst facilitated the aromatization of light olefin intermediates to produce aromatic hydrocarbons. Due to the enhancement of light olefin aromatization, surplus hydrogen was produced. Some of this surplus hydrogen could participate in the initial deoxygenation of reactants, thereby promoting the formation of light olefin intermediates and further benefitting the aromatization reaction, leaving more carbon in the oil phase. Therefore, it was observed that the selectivity for the oil phase increased significantly. In addition, it was also found that Ga_2O_3/HZSM-5 showed superior catalytic performance over some other metal-oxide-modified HZSM-5 catalysts, such as ZnO/HZSM-5 and CuO/HZSM-5, especially in the presence of phenols [108]. Besides, transition metals such as Ni and Co have been used to modify zeolite catalysts to obtain better catalytic performance in terms of higher hydrocarbon yield, higher efficiency of oxygen removal, and less coke deposition [134, 135].

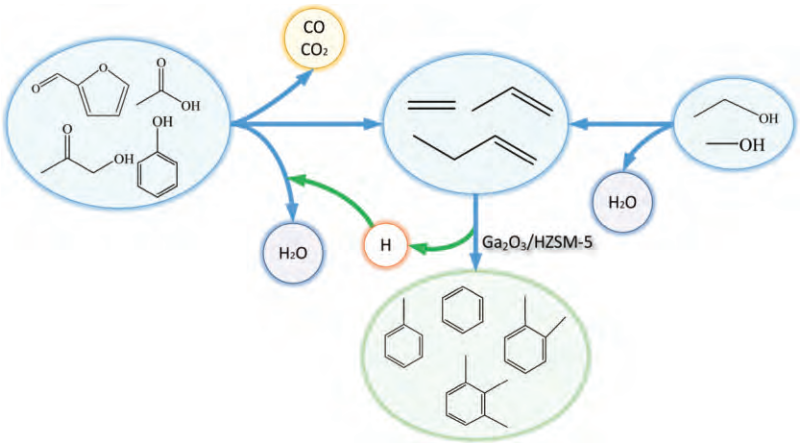

Figure 9 Reaction mechanism over Ga_2O_3/HZSM-5 [133].

4.3 Catalytic cracking of bio-oil fractions for hydrocarbon production

4.3.1 Catalytic cracking of water-soluble bio-oil

Crude bio-oil contains high-molecular-weight phenolic oligomers and sugars, which are responsible for severe coke formation in the catalytic cracking process. Therefore, pre-separation, by water extraction, molecular distillation, etc., is necessary to remove high-molecular-weight compounds.

Polar compounds, such as acids, ketones, aldehydes, monophenols, and sugars, containing polyhydroxy groups, can readily be enriched in the aqueous phase. However, some less polar compounds with high molecular weight, such as pyrolytic lignin, are poorly water-soluble. Therefore, water extraction can be used to separate phenolic oligomers from bio-oil and to enrich some low-molecular-weight compounds with relatively high reactivity in the water-soluble bio-oil fractions. Vispute *et al*. [4] selected the water-soluble bio-oil fraction (obtained by mixing bio-oil and water in a weight ratio of 1 ∶ 4) as a sample, and found that a lower coke selectivity of 32.3% was achieved compared with that from crude bio-oil (49.5%). When hydrotreatment was introduced prior to catalytic cracking of the water-soluble bio-oil fraction, the coke selectivity was further decreased to only 12.6%. Gong *et al*. [129] investigated the production of light olefins by the catalytic cracking of water-soluble bio-oil over a La-modified zeolite. The bio-oil was almost completely converted, and a maximum yield of 0.28 ± 0.02 kg olefins per kg bio-oil was obtained. Vispute *et al*. [4] and Zhang *et al*. [136] also studied the catalytic cracking of water-soluble bio-oil in a fixed-bed reactor. Compared with crude bio-oil, more compounds were identified in the water-soluble bio-oil, in which sugars and catechol were enriched [136]. For the catalytic cracking of water-soluble fractions, the carbon selectivity for aromatics and olefins increased to 26.7% and the carbon selectivity for coke was reduced to 32.3%, compared with 21.0% and 49.5%, respectively, for crude bio-oil [4]. Although water extraction can efficiently remove phenolic oligomers, large amounts of sugars still remained in the water-soluble bio-oil, which lead to severe coke formation.

4.3.2 Catalytic cracking of bio-oil molecular distilled fraction

Following molecular distillation, acids and ketones are enriched in the distilled fraction (DF), while sugars and phenolic oligomers remain in the residual fraction [37]. Thus, the DF is suitable to be subjected to catalytic cracking for hydrocarbon production. Wang *et al*. [98] carried out experiments on the co-cracking characteristics of the bio-oil DF and ethanol in a fixed-bed reactor. The DF had a low water content of 20.7 wt% after vacuum distillation. Under the condition of 400℃ and 2 MPa, a high yield of oil phase, 25.9 wt%, and a low coke yield of 3.2 wt% were achieved by the co-cracking of DF and ethanol with a mass ratio of 2 ∶ 3. The oil phase had a high hydrocarbon content of 98.3%, mainly in the form of C_7—C_9 aromatic hydrocarbons (Figure 10).

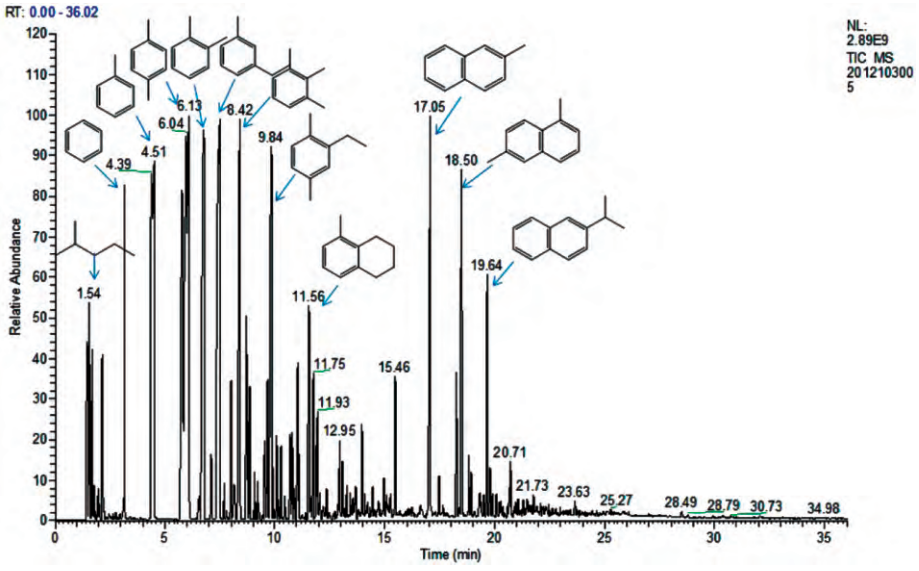

Figure 10 GC—MS chromatogram of the oil phase (2∶3 DF/ethanol, 400℃, and 2 MPa) [98].

5 Catalytic esterification

Bio-oil exhibits strong corrosiveness, especially at high temperatures [2, 137], because of its high content of carboxylic acids. Thus, investment and operational costs will be greatly increased if bio-oil is directly applied in certain high-temperature processes, such as catalytic cracking and steam reforming. Carboxylic acids in bio-oil can be converted into the corresponding esters by catalytic esterification, and this will also improve the stability of the bio-oil during storage and transportation prior to subsequent upgrading [138]. The esterification can be catalyzed by acids. The formation of a strongly protonated acid intermediate is followed by nucleophilic attack from the alcohol, and subsequent dehydration yields the corresponding ester [139].

Although conventional homogeneous acid catalysts such as H_2SO_4 exhibit high reactivity, strong corrosiveness and the production of voluminous aqueous waste limit their utilization. Solid acid catalysts have been widely used for catalytic esterification of bio-oil, such as sulfated zirconia [140—142], zeolites [143, 144], heteropoly acids (HPAs) [145—148], ion-exchange resins [149], carbon-based solid acid catalysts [150, 151], and so on. In addition, the use of solid base catalysts and ionic liquid catalysts has also been reported [152, 153].

5.1 Catalytic esterification of bio-oil model compounds

Some researchers have focused on the catalytic esterification of model compounds to investigate the performances of different catalysts. Yu *et al*. [141] explored the esterification behavior of acetic acid and ethanol in a 2∶1 molar ratio over Yb_2O_3/Al_2O_3-promoted SO_4^{2-}/ZrO_2 in a batch reactor. The yield of ethyl acetate reached a maximum of 86.60% after 150 min at 87℃. The experimental results showed that the addition of Yb_2O_3 and Al_2O_3 could promote the esterification activity and suppress catalyst deactivation caused by surface sulfur loss by solvation. Zhang *et al*. [152] performed the esterification of bio-oil over solid acid and base catalysts, and found that $SiO_2/TiO_2—SO_4^{2-}$ showed higher catalytic activity than $K_2CO_3/Al_2O_3—NaOH$. Over the acid catalyst, carboxylic acids reacted with alcohols to produce not only esters but also acetals by nucleophilic addition. In addition to esterification, isomerization could also occur over the base catalyst. HPAs possess unique strong Brønsted acid sites; however, they have relatively low surface area and low reactivity. Mesoporous silica can be used as a high-surface-area support to overcome this issue. Liu *et al*. [145] reported that SBA-15 loaded HPA ($H_3PW_{12}O_{40}$) was effective for the reaction of acetic acid and butanol, and a high yield of *n*-butyl acetate with 100% selectivity was achieved at 87℃. MCM-41-supported HPA has also been applied in the gas-phase esterification of acetic acid and 1-butanol, and in the liquid-phase esterification of hexanoic acid and 1-propanol. MCM-41-supported HPA exhibited a higher activity than that of pure HPA [148]. Besides, a carbon-based catalyst, sulfated graphene (G—SO_3H), has been used in the esterification of acetic acid with cyclohexanol and 1-butanol [150]. This catalyst maintained high reactivity after being recycled five times.

5.2 Catalytic esterification of bio-oil fractions

Bio-oil can be separated into two fractions by distillation. Li *et al*. [154, 155] carried out catalytic esterification of bio-oil fractions in supercritical methanol, and a distilled fraction was obtained at 110℃ and 9 kPa. The experimental results showed that supercritical conditions (250℃, 1.5 MPa H_2 for low-boiling fraction; 290℃, 2 MPa H_2 for high-boiling fraction) could greatly facilitate the esterification process. All of the acids in the distilled fraction could be converted, even without a catalyst, within a reaction time of 6 h.

Guo *et al*. [156] obtained a distilled fraction by molecular distillation and investigated its esterification behavior over a La-modified solid acid catalyst. After esterification, the content of carboxylic acids decreased from 18.39% to 2.70%, and the content of esters significantly increased from 0.72% to 31.17%. The compositions of the distilled and upgraded fractions are shown in Figure 11. Besides, ketones with unsaturated C=C bonds could be converted into saturated products, greatly improving the stability of the bio-oil.

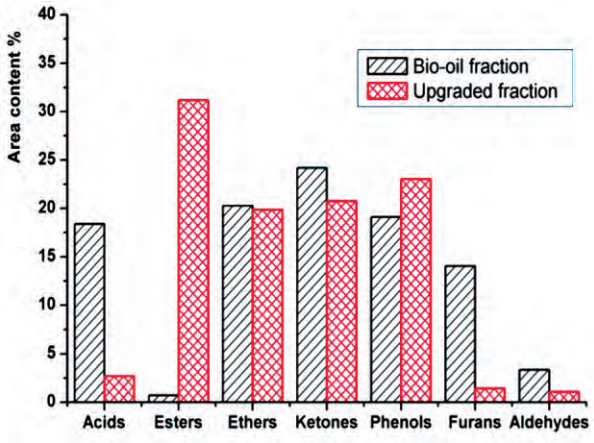

Figure 11 Compositions of the DF and the upgraded fraction [156].

6 Hydrodeoxygenation

Bio-oil hydro-processing can be divided into two types, namely mild hydrogenation and hydrodeoxygenation. As mentioned above, mild hydrogenation is usually operated at low reaction temperatures and pressures, and is aimed at the saturation of some unsaturated functional groups, such that unsaturated oxygenated compounds are mainly converted into saturated alcohols [4]. Therefore, mild hydrogenation is often used for bio-oil stabilization [123, 157]. Hydrodeoxygenation can bring about the deoxygenation of oxygenated compounds and the hydrogenolysis (hydrocracking and depolymerization) of polymeric sugars and phenolic oligomers. Consequently, liquid alkanes in the gasoline or diesel range are generated. Considering the high oxygen content of bio-oil, the difficulty in achieving depolymerization, and the high boiling points of some components, a liquid—solid hydrodeoxygenation process in slurry reactor is favored [158, 159]. Nevertheless, some studies on gas—solid hydrodeoxygenation processes in a fixed-bed reactor have also been reported [160, 161].

6.1 Hydrodeoxygenation behavior of typical model compounds

For some bio-oil components containing unsaturated oxygenated functional groups, such as acids, ketones, and aldehydes, their hydrogenation (saturation) first occurs during the hydrodeoxygenation process. The ketones and aldehydes in bio-oil may be efficiently hydrogenated to alcohols under mild conditions [123]. However, the hydrogenation of acids is relatively difficult. Elliott and Hart [162] found that the conversion of acetic acid required a higher reaction temperature and a longer reaction time than that of furfural; moreover, the acetic acid was only partially hydrogenated while some decomposing to produce CH_4 and CO_2. Chen *et al*. [123] observed that the appropriate hydrogenation temperature for acetic acid was higher than that for ketone. According to the study of Grange *et al*. [163], the activation energy for ketone hydrogenation was much lower than those for acid and phenol hydrogenations. Elliott [164] concluded that the requisite hydrogenation temperatures for different compound classes were in the following order: olefins (C=C) < ketones and aldehydes < carboxylic acids < phenols, reflecting their different reactivities. Although the hydrogenation of acids is more difficult than that of ketones and aldehydes, all three compound types could nevertheless be hydrogenated under relatively mild conditions, which can be attributed to the feedstocks and catalysts [4, 123, 157]. The alcohols produced by the hydrogenation of acids, ketones, and aldehydes can subsequently be subjected to hydrodeoxygenation to produce gaseous alkanes [102]. Ardiyanti *et al*. [18] found that the yield of gaseous products reached 9% with a C_2—C_3 hydrocarbon content of 20%—30%. Mercader *et al*. [122] also observed a C_2—C_3 hydrocarbon content of >20% in the gaseous products from bio-oil hydrodeoxygenation.

Recently, phenols and their oligomers have become the most attractive research topics in hydrodeoxygenation, because their hydrodeoxygenation products, such as C_{6+} cycloalkanes and their

derivatives as well as some cyclitols, are the main components in the upgraded bio-oil obtained by hydrodeoxygenation. Mortensen *et al*. [165] tested a series of catalysts for the hydrogenation of phenol, the active components of which were metal oxides (MnO, WO_3, MoO_3, V_2O_5, and CuO) and metals (Ni, Cu, Ru, Pd, Pt, Co, and Fe), and the supports included SiO_2, Al_2O_3, CeO_2, ZrO_2, and carbon. It was found that Ni/ZrO_2 exhibited the highest catalytic activity for phenol hydrodeoxygenation; the corresponding conversion of phenol reached 100% and the selectivity for hexane was close to 80%. Two reaction pathways were proposed to explain the hydrodeoxygenation mechanism of phenol, namely hydrogenation (HYD) and direct deoxygenation (DDO) [166—168]: in HYD, the benzene ring of phenol is first hydrogenated to produce the cyclic ketone and then cyclitol, which finally undergoes hydrodeoxygenation to form the cycloalkane; in DDO, the phenolic hydroxyl group is first removed to generate the aromatic hydrocarbon, and this is followed by hydrogenation of the benzene to produce the cycloalkane. The selectivity for each hydrodeoxygenation route is strongly related to the catalyst used. It was found that over non-sulfide catalysts, such as Pd, Pt, and Ni, the hydrodeoxygenation of phenols mainly followed the HYD route [169—171], whereas over CoMo sulfide catalysts, the DDO route was favored [166, 167].

In addition to phenol, another typical mono-phenolic compound is guaiacol, with a methoxyl group attached to the benzene ring. Compared to the hydrodeoxygenation of phenol, some other reactions, such as demethylation and dihydroxylation, can occur in the hydrodeoxygenation of guaiacol [172]. Lin *et al*. [173] compared the hydrodeoxygenation behaviors of guaiacol over Rh-based and CoMo sulfide catalysts, and they found that the Rh-based catalyst showed a higher catalytic activity, giving a guaiacol conversion of 100% and a cyclohexane selectivity of about 40%.

Besides monophenols, some phenolic oligomers are found in the organic fraction of bio-oil. For the hydrodeoxygenation of these compounds, depolymerization is also very important. Zhao *et al*. [174] investigated the hydrodepolymerization of different phenolic dimers and the relevant linkage types included both C—O—C and C—C bond linkages. To improve depolymerization, they combined the hydrogenation catalyst Pd/C and the cracking catalyst HZSM-5, and thereby achieved complete conversion of phenolic dimers. Moreover, for the dimers with ether bond linkages, the hydrogenation products were exclusively cyclohexane and methylcyclohexane.

In addition, the hydrodeoxygenation of furan has also been studied, mainly focusing on the conversion route of the furan ring. Kliewer *et al*. [175] found that during the hydrodeoxygenation process, the hydrogenation of C = C bond(s) within the furan ring first occurs to produce dihydrofuran or tetrahydrofuran, which then undergo ring-opening and hydrodeoxygenation reactions to generate light hydrocarbons.

6.2 Hydrodeoxygenation of bio-oil fractions

In current studies on hydrodeoxygenation, crude bio-oil is favored as the feedstock, because most components therein are active in hydrodeoxygenation [158, 159]. However, the low-molecular-weight acids, ketones, and aldehydes in bio-oil will be converted into C_2—C_3 gaseous alkanes instead of the desired liquid hydrocarbons. Moreover, for acids and hydroxyketones with relatively high oxygen contents, the increase in hydrogen consumption is obvious. Therefore, in recent years, some studies have been focused on bio-oil fractions, typically the organic fraction separated by water extraction and the residual fractions obtained by vacuum distillation and molecular distillation. All of the organic fractions have much lower contents of acids, ketones, and aldehydes than the crude bio-oil.

6.2.1 Bio-oil organic fraction from water extraction

Several research groups have proposed that bio-oil should first be separated by water extraction, and that organic fraction could be used for hydrodeoxygenation [38, 39]. A report submitted to the Department of Energy of the U. S. by the UOP company and Pacific Northwest National Laboratory presented the results of hydrodeoxygenation of pyrolytic lignin (organic fraction) [38]: in the study by Pacific Northwest National Laboratory, using a Pd/C catalyst with a reaction pressure of 1900—2000 psi, the yield of liquid products after hydrodeoxygenation was 55.6%, the oxygen content in the liquid was

19.5%, and the integral deoxygenation efficiency was 69%; in the study by UOP (Ni/Mo catalyst, 1900—2000 psi), the yield of liquid products after hydrodeoxygenation was 40.8%, the oxygen content in the liquid was 5.9%, and the integral deoxygenation efficiency was 93%.

The research group at Georgia Institute of Technology studied the liquid-phase hydrodeoxygenation of the water-insoluble (organic) fraction obtained from lignin pyrolysis oil [17, 176]. In view of the coke formation observed during the heating process, they proposed a two-stage hydrodeoxygenation process: the organic fraction was first hydrogenated over Ru/C at 14 MPa and 300℃ for 4 h; thereafter, the hydrogenated liquid product was filtered and the filtrate was used for secondary hydrogenation over Ru/C at 14 MPa and 250℃ for 2 h. The carbon yields of the liquid products in the first and second stages were 35% and 33%, respectively. In the first stage, cleavage of the ether bond (depolymerization) and removal of methoxyl group occurred to produce aromatics, and these compounds underwent further hydrodeoxygenation to produce aliphatic hydrocarbons in the second stage. In a subsequent study, they investigated the influence of different hydrogenation catalysts, and found that a Ru-based catalyst showed the best performance.

Mercader *et al*. [177] performed liquid-phase hydrodeoxygenation of the bio-oil organic fraction over Ru/C for 4 h. It was found that the oxygen content decreased from 31.0% to 13.6% after hydrogenation at 310℃, while $(H/C)_{eff}$ increased from 0.80 to 1.07.

6.2.2 Bio-oil residual fraction from distillation

The residual fractions from bio-oil vacuum distillation and molecular distillation are mainly composed of pyrolytic lignins and sugars, which are suitable for hydrodeoxygenation. Capunitan and Capareda [178] investigated liquid-phase hydrodeoxygenation of the residual fraction from bio-oil vacuum distillation. The tested catalysts were Ru/C and Pd/C, the reaction temperatures were 200 and 300℃, the reaction time was 4 h, and the initial hydrogen pressure was 10 MPa. Their results showed that Ru/C was more favorable than Pd/C for hydrogenation of the residual fraction; the oxygen content in the liquid product was only 7%, and the heating value reached 40.2 MJ/kg.

Schwaiger *et al*. [179] carried out a hydrodeoxygenation study of the residual fraction from molecular distillation in a fixed-bed reactor over a CoMo sulfide catalyst at 12.4 MPa and 300—400℃. After hydrodeoxygenation, aqueous and oil phases were produced in yields of about 30% and 20%, respectively. The oxygen content in the oil phase was below 1% and the hydrogen-to-carbon ratio of the oil phase was about 2. In addition, a time-on-stream test showed that the reaction was stable over a period of 62 h.

7 Conclusion

The complicated composition of bio-oil hampers its direct upgrading; however, this problem can be overcome by graded upgrading based on separation. Water extraction, vacuum distillation, and molecular distillation are all effective in the separation of bio-oil. Aqueous and organic fractions are obtained by water extraction: the aqueous fraction is enriched in acids, hydroxyketones, and aldehydes, as well as some sugars. Hence, it shows better performance than crude bio-oil in steam reforming and catalytic cracking processes. The organic fraction mainly comprises phenolic oligomers, and it can be upgraded by hydrodeoxygenation. Compared with the aqueous fraction, the distilled fractions obtained by vacuum and molecular distillation have narrowed distribution ranges of components and are free from sugars, which makes them more suitable for esterification, steam reforming, catalytic cracking and hydrogenation. The residual fraction is mainly composed of high-molecular-weight compounds, and can thus be used for hydrodeoxygenation and chemical extraction. Graded upgrading based on separation can not only improve the conversion efficiency, but also allows the implementation of some self-supply of feedstock to increase the integral economy, as exemplified by the use of the hydrogen produced by steam reforming of the aqueous fraction (or distilled fraction) for hydrodeoxygenation of the organic fraction (or residual fraction).

In conclusion, the integrated "separation-upgrading" process will be an important trend for bio-oil

upgrading in the future. It will have more potential and become more economical if various separation techniques, upgrading methods, and the extraction of valuable chemicals can be combined in a comprehensive utilization of bio-oil.

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