



Review

Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review

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ABSTRACT

A current aim of society is to produce fuels from non-food biomass and catalysis is central to achieving this aim. Catalytic steam-reforming of biomass gives synthesis gas and this can be further transformed to give transport fuels using catalysis. Biofuels and fuel additives can also be obtained by catalytic upgrading of bio-oil produced by non-catalytic pyrolysis of biomass. This upgrading can be performed by low temperature esterification with alcohols (followed by water separation) or by high temperature gasification, cracking or hydrotreating processes. Upgraded bio-oil can also be obtained by pyrolysis of biomass in the presence of catalysts. This review considers recent trends in the chemistry of these processes for biofuel production and the catalysts used.

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1. Introduction

With the development of society, the consumption of fuels is increasing continuously and is likely to double between 2000 and 2050 [1]. At the same time, there is a gradual decrease in the known reserves of fossil fuel feedstocks. This decrease is coupled with an increase in the emissions of greenhouse gases, mainly CO₂, these being responsible for global warming. Hence there is a need to develop methods to decrease the total global greenhouse gas emissions and this has led to an increasing interest in the use of biofuels. The CO₂ evolved during utilisation of biofuels is consumed during photosynthesis for plant growth and so it does not contribute to the problem of greenhouse gas emissions. The targets set by the European Union renewable roadmap indicate that every EU member state should substitute 10% of its fuels by biofuels by 2020 [2]. This implies that a substantial research programme should be performed in order to reach this target.

Currently, biofuels are produced mainly from biomass suitable for food, using the so-called “First Generation” technologies; this is at a time when some part of the Earth’s population is suffering from hunger. The so-called “Second Generation” technologies for the production of fuels allow the use of a wide range of non-food “cellulosic” biomass feedstocks. These include agricultural residues (e.g. forest, straw, bagasse, corn stover), wastes (e.g. paper, cardboard, manures, sawmill residues) and specially grown energy crops (e.g. miscanthus, willow, switchgrass) [3–5].

Cellulosic biomass normally consists of the biopolymeric species: cellulose, hemicellulose and lignin, in the proportions 35–50%, 15–25% and 15–30%, respectively. This biomass may be converted by hydrolysis or thermochemical routes. Enzymatic hydrolysis of biomass to ethanol is normally slow [6]. Acidic hydrolysis gives levulinic acid, formic acid, furfural and char [3,7]. The ligneous char obtained in acidic hydrolysis as a by-product can be used for heat and power generation. Biomass hydrolysis to give levulinic acid followed by catalytic conversion to give fuel additives has recently been discussed intensively [3,6–9].

Two main approaches in thermochemical conversion of biomass are gasification or pyrolysis (Fig. 1). Gasification gives synthesis gas which may then either be further processed to give Fischer–Tropsch diesel fuel or purified to give hydrogen as product. Bio-oil is a liquid product of the pyrolysis of biomass and it can then be converted catalytically to give smaller molecules that are suitable for use as fuels or fuel additives. Bridgwater [10] has indicated that pyrolysis and gasification should be considered as complementary rather than competitive. The advantage of the thermochemical approach is that all the biomass is converted, including the lignin. The dis-

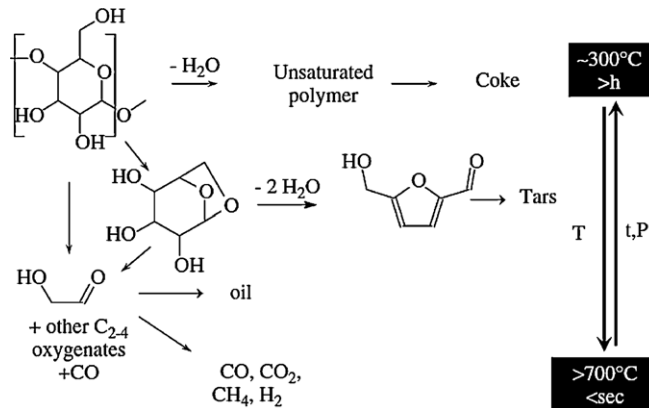


Fig. 2. Pyrolysis of carbohydrates. Adapted from Lange [1].

advantage is that heating to high temperatures is energy intensive. The products of pyrolysis, bio-oils, are more complex than the products of acidic hydrolysis in relation to further conversion to fuels. It is important that when compared to the hydrolysis route, the pyrolysis route gives quite similar carbon yields of products [6,11].

Several reviews [5,6,12–19] have discussed different aspects of the production of fuel additives via thermochemical/catalytic transformation of biomass and biomass pyrolysis liquids. We have previously reviewed work on catalytic biomass gasification to give synthesis gas [20]. The present review, after a brief mention of biomass pyrolysis processes, the catalytic pyrolysis of biomass and recent trends in gasification, discusses some modern trends in the catalytic conversion of biomass pyrolysis liquids, emphasis being placed on the chemistry of these processes and the effects of catalyst composition. Four main approaches to bio-oil upgrading to give fuel additives are discussed: gasification to synthesis gas, hydrotreating, cracking and esterification.

2. Pyrolysis of biomass

2.1. Non-catalytic pyrolysis of biomass

Pyrolysis is performed in the absence of air. During the heating of the biomass, gas, liquid and char are formed in proportions that depend on the mode of pyrolysis and the type of pyrolysis system used. Hemicellulose decomposes between 250 and 400 °C and gives up to 20 wt.% of char upon heating to 720 °C; cellulose requires slightly higher temperatures, 310–430 °C, and gives about 8 wt.% of char; and lignin decomposes at 300–530 °C, yielding about 55 wt.% of char [21]. The pyrolysis of carbohydrates is shown schematically in Fig. 2 [1]. At low temperatures, carbohydrates depolymerise to give smaller units. Dehydration takes place at about 300 °C, yielding unsaturated polymers and char. At yet higher temperatures, extensive rupture of C–C and C–H bonds takes place, giving C_{2–4} oxygenates and the products of gasification: CO, CO₂, H₂ and CH₄.

Bridgwater [22,23] has classified the different modes of pyrolysis as shown in Table 1. All the products of biomass pyrolysis are valuable and can be used. The most interesting product is pyrolysis

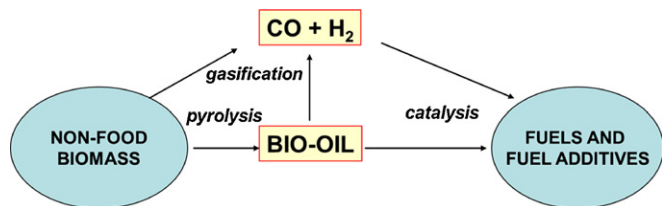


Fig. 1. Thermochemical/catalytic approaches for transformation of non-food biomass to fuel additives.

Table 1
Modes of pyrolysis.

Mode of pyrolysis	Temperature/°C	Residence time	Yields/%		
			Liquid	Char	Gas
Slow	400	Very long	30 (70% water)	35	35
Intermediate	500	Moderate (10–20 s)	50 (50% water)	25	25
Fast	500	Short (<2 s)	75 (25% water)	12	13
Gasification	800	Long	5	10	85

Adapted from Bridgwater [22,23].

oil as it can be converted to fuel additives in a wide variety of ways. The yield of pyrolysis oil under optimised fast pyrolysis conditions may reach 70–80%. It should be noted that this liquid includes up to 25% of water. Slow pyrolysis gives considerably higher concentrations of water. At lower temperatures and with longer residence times, the yield of pyrolysis oil decreases while char is formed in higher amounts. High temperatures lead to the formation of gases.

Pyrolysis of biomass may proceed through radical or catalytic mechanisms. Different salts and acids present in biomass and formed during pyrolysis may affect the reactions taking place at increased temperatures [12].

2.2. Bio-oil (pyrolysis oil)

Piskorz [24] has pointed out that the formation of a considerable amount of liquid products during vacuum pyrolysis of biomass was first reported by Klason as early as in 1914. Nevertheless, the first plant for energy applications of biomass pyrolysis was constructed by the DynaMotive Energy System Corporation in Canada in 2005 [25]; at present, this is producing Bio-Oil+, a liquid product that can be used in place of heating oil, natural gas or propane. A new plant has been constructed recently by this company to convert 200 tonnes of dry biomass per day [26]. The projected cost of the fuel is as low as \$2 per gallon [27]. The Ensyn Corporation has commissioned a smaller plant that transforms 100 tonnes of dry wood per day [28]. BTG has constructed a plant that converts 50 tonnes of biomass per day in Malaysia and is now designing a plant that is 2.5 times larger [29].

Bio-oil may consist of more than 300 organic compounds. It is an easily transportable source of chemicals and it has energy content higher than that of biomass. Another advantage is that it is cleaner than biomass. van Rossum et al. [30] have reported that some impurities of the original biomass such as minerals and metals are left in the char. This is quite important, both from an environmental point of view and in relation to the post-treatment of the bio-oil. This post-treatment often involves a number of catalytic processes, each of which might suffer from poisoning of the catalyst by impurities such as alkali metals and compounds containing sulphur or nitrogen. As compared to petroleum, bio-oil generally contains less sulphur, but may contain more nitrogen and chlorine.

Crude bio-oil can be used as a fuel additive for some boilers and engines [16,31]. The problems associated with its use are its immiscibility with petrofuels and its low heating value as compared with petrofuels. Emulsifiers must be added to make it possible to use bio-oil as a fuel additive in these devices. This increases the cost of these materials.

Table 2 compares some of the properties of bio-oil with those of conventional transport fuels. Bio-oil contains some heavy aromatic compounds and this contrasts with gasoline and diesel which comprise of mixtures of hydrocarbons with relatively low carbon chain lengths of 5–10 and 12–20, respectively. The H/C ratio in bio-oil is in the range 1.2–1.4 and this is closer to that of aromatics than to that of alkanes. The O/C ratio in bio-oil is high (0.5) as this liquid contains significant quantities of water and oxygen-containing groups. The consequence of high level of oxygen is that bio-oil is not suffi-

ciently stable and is also corrosive and immiscible with petrofuels. Transport fuels may contain only a limited quantity of oxygen in order that their use will provide sufficient energy efficiency. Hence, upgrading of bio-oil is necessary in order that suitable transport fuels are obtained. Thus, the main objectives of bio-oil upgrading are the removal of oxygen (i.e. deoxygenation) and the cracking of the large aromatic structures to give smaller ones. It is desirable that the upgrading process gives a product with lower amounts of water and oxygen as well as decreased acidity and viscosity and a higher heating value. There are four main catalytic approaches to transform bio-oil to fuel additives: gasification, hydrotreating, cracking and esterification. Pyrolysis can be also performed in the presence of catalysts, bringing about simultaneous pyrolysis of the biomass and upgrading of the product.

2.3. Catalytic pyrolysis of biomass

Zeolites with different porous structure (Table 3) have frequently been used for catalytic biomass pyrolysis and bio-oil upgrading. ZSM-5 zeolites are known catalysts for catalytic cracking and they have been used more often than other zeolites for the cracking of biomass and bio-oil. Gayubo et al. [32] explained the choice of this zeolite by suggesting that it provides a suitable compromise between activity, shape selectivity to C_{12} hydrocarbons, limited deactivation by coke, and high thermal stability.

Samolada et al. [33] have used ZSM-5 zeolites as catalysts for pyrolysis of biomass and found that introduction of these to a reactor used for non-catalytic biomass pyrolysis led to a decrease of the concentration of liquid products and to an increase of the quantity of gaseous products. This might be expected as the application of catalysts gives cracking, leading to a decrease of the molecular weight of the product molecules.

Aho et al. [34] have compared non-catalytic (using a reactor with added quartz sand) and catalytic pyrolysis of pine chips in the presence of different zeolites in a fluidized bed reactor (Table 3). They observed a decrease of the organic fraction in the pyrolysis oil obtained in the experiments using the catalysts and showed that ZSM-5 zeolite gave the highest yield of organic fraction in pyrolysis oil as compared with β -, Y- and mordenite zeolites ($SiO_2/Al_2O_3 = 12$ –25). The formation of acids was lower with ZSM-5, but the formation of ketones was higher than over the other zeolites. Polyaromatic hydrocarbons were detected with zeolites, but none was observed when only quartz sand was added to the reactor. In accordance with the data of Aho et al. [34], French and Czernik [35] have demonstrated that ZSM-5, with and without additives (Ni, Ga, Co and Fe), gave better deoxygenation of biomass than did

Table 2
Some features of bio-oil, gasoline and diesel.

	Bio-oil	Gasoline	Diesel
Carbon chain length	Up to 100	5–10 branched alkanes, aromatics	12–20 linear alkanes
H/C ratio	1.2–1.4	1–2	~2
O/C ratio	0.5	0	0

Table 3

The yield of products (wt.%) from the pyrolysis of pine chips over different zeolites at 450 °C.

	Quartz sand	β -zeolite	Y zeolite	Mordenite zeolite	ZSM-5 zeolite
SiO ₂ /Al ₂ O ₃ ratio	–	25	12	20	23
Pore size/nm	–	0.76 × 0.64, 0.55 × 0.55	0.74 and 1.18	0.70 × 0.65	0.52 × 0.57, 0.53 × 0.56
Organic fraction in pyrolysis oil	27.3	15.1	9.0	17.6	20.7
Water	5.4	13.9	16.7	14.4	13.0
Char and coke	15.3	21.6	23.2	19.9	14.2
Gas	52.0	49.5	51.1	48.1	52.1

Adapted from Aho et al. [34].

Table 4The yield of products (wt.%) from the pyrolysis of pine chips over β -zeolites with different SiO₂/Al₂O₃ content at 450 °C.

SiO ₂ /Al ₂ O ₃ ratio	Concentration of Brønsted acid sites at 450 °C/ μ mol/g	Organic fraction of bio-oil	Water	Char and coke	Gas
25	125	15.8	13.1	21.7	49.4
300	23	17	9.5	20.1	53.4

Adapted from Aho et al. [36].

different large pore zeolites. They obtained a maximum yield of 16 wt.% of hydrocarbon products, including 3.5 wt.% of toluene.

Aho et al. [36] have also studied the effect of the acidity of β -zeolite on the properties of the bio-oil formed by catalytic pyrolysis (Table 4). They reported that an increase in the acidity of the zeolite (decrease of the SiO₂/Al₂O₃ ratio) gave a decrease in the yield of the organic fraction of the pyrolysis oil and that there was concurrently an increase in the water and polyaromatic hydrocarbons yields. However, as can be seen from the data of Table 4, the effect of the concentration of Brønsted acidic sites, although noticeable, is small. Hence, it seems that additional work on this subject is needed.

Bridgwater [12] has pointed out that an important step in the reactions of hydrocarbons over zeolites is aromatization. Huber and Corma [4] noticed that this aromatization may proceed via the Diels–Alder reaction in which olefins obtained by cracking combine with each other, forming cyclic and aromatic compounds (Fig. 3).

Carlson et al. [18] have compared the composition of the bio-oil after fast pyrolysis of cellulose, cellobiose, glucose and xylitol mixed with different catalysts. They reported that the highest yield of aromatics (30% carbon yield) was shown in the case of a ZSM-5 zeolite (Si/Al = 60) as compared to β - and Y-zeolites (Si/Al = 50), silicalite and silica-alumina (Si/Al = 8). The ZSM-5 zeolite gave higher molecular weight aromatics than did the Y- and β -zeolites. Brønsted acid sites were needed for the production of aromatics. The pore structure was also important. The authors indicated that aromatics production from bio-oil is a shape selective reaction in which the selectivity is a function of both the structure and the nature of active sites of the catalysts. However, as these authors pointed out, the content of aromatics in gasoline sold in the U.S. is limited to 25 vol.% while the benzene content is limited to 0.8 vol.% because of its carcinogenic properties. Further limit for benzene of 0.62 vol.% is planned by 2011 [37]. Thus, the alkylation of benzene [38] and/or hydrogenation of aromatics (see Section 4) in the bio-oil are needed when such molecules are present in high concentrations.

Lignin is the most difficult component of biomass to convert. Thring et al. [39] have reported that it is possible to convert lignin to

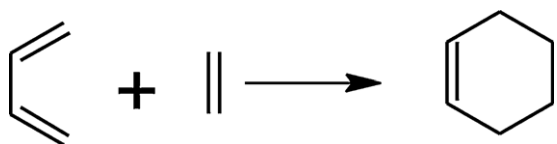
a liquid product consisting mainly of aromatic hydrocarbons (benzene, toluene and xylene, with toluene dominating) with yields of up to 90% using a ZSM-5 catalyst (Si/Al = 56) at temperatures from 500 to 650 °C. The liquid mixture obtained possessed a high octane number and the gaseous product contained C₁–C₅ hydrocarbons, CO and CO₂. These authors suggest that the mechanism involves the initial formation of olefins which then undergo further cyclization, oligomerization and alkylation reactions due to the presence of strong acid sites; this is in accordance with the ideas put forward by Huber and Corma [4]. Jackson et al. [40] have also reported the formation of 46.7% of simple aromatics and 46.2% of naphthalenic ring compounds from lignin using a ZSM-5 zeolite at 600 °C. The same authors found that a Co/Mo/Al₂O₃ catalyst gave a liquid product containing 21% aromatics, 4% naphthalenics and 75% oxygenated aromatics.

It is well known that coke is formed on many catalysts under the reaction conditions used for catalytic pyrolysis and that this leads to deactivation. Carlson et al. [18] have shown that coke formation can be minimised by using high heating rates of the biomass with the catalyst, high catalyst to feed ratios and proper catalyst selection. Aho et al. [34] have studied the nature of the coke formed on different zeolites by dissolving the zeolite in hydrofluoric acid and then dissolving the coke in dichloromethane. The coke content was highest using Y-zeolites, probably because of the presence of large pores. These authors showed that the coke formed consisted mostly of linear long-chain alkanes and alkenes, ranging from C₁₀ to C₂₈. The number of carbon atoms in the chain was even (10, 12, 14, etc.). The coke formed on Y-zeolite and ZSM-5 contained also branched C₁₈, C₂₀, C₂₂ alkanes and a linear C₃₀ alkene. The same authors [34,36] found that regeneration of the deactivated catalysts was possible in air at high temperatures.

MCM-41 materials possess high surface areas (>1000 m² g^{−1}), moderate acidity and a hexagonal array of uniform mesopores, the size of which can be tailored in the range 1.4–10 nm. Lapas and co-workers have studied Al-MCM-41 materials undoped [41] and doped by Cu, Fe and Zn [42,43] in the catalytic pyrolysis of wood biomass using a fixed-bed pyrolysis system. All the catalysts provided an increase in the concentration of phenolic compounds; these products could be important in the chemical industry in relation to the production of adhesives, but the phenols could also be hydrodeoxygenated to give aromatics and cyclohexanes for fuel applications [44–46]. Iliopoulou et al. [41] found that high Si/Al ratio (lower acidity) materials had a positive effect on liquid product yields and composition while lower Si/Al ratios led to an increase in the yields of gas and coke. Samolada et al. [33] have reported that Al-MCM-41 catalyst effectively removed acids from the bio-oil; however, this catalyst possessed only low hydrothermal stability (leading to dealumination) as compared to ZSM-5.

Yourgun and Simsek [47] have studied the effect of the alumina addition on the pyrolysis of miscanthus grass. They showed that the content of aliphatic and aromatic hydrocarbons was increased as compared with non-catalytic pyrolysis; however, the oxygen content in the product was still high.

Wang et al. [48] have performed catalytic pyrolysis of pine, Alaskan spruce and tropical lauan biomass in a fluidized bed reac-

**Fig. 3.** Diels–Alder reaction.

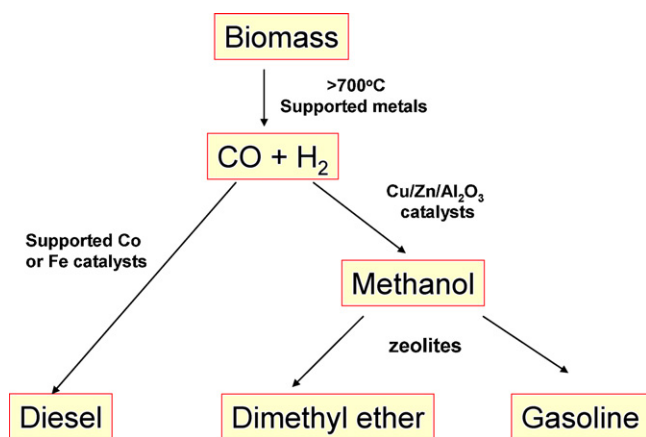


Fig. 4. Scheme showing the use of biomass gasification to give fuels.

tor and in the presence of hydrogen and a sulphided CoMo/Al₂O₃ catalyst. The composition of products at 863 K was quite similar, independent of the type of the biomass used. This was ascribed to the similar chemical composition of the feedstocks. The yield of light aromatics in all cases was about 6%. As compared to the sulphided CoMo/Al₂O₃ catalyst, a NiMo/Al₂O₃ catalyst gave a high selectivity to methane.

Lin et al. [49] used CaO as a catalyst for the pyrolysis of white pine biomass. They showed that the oxygen content in the bio-oil obtained and the contents of formic and acetic acids were lower than those in the bio-oil obtained by pyrolysis of the same biomass material without a catalyst.

Thus, we can conclude that the use of catalysts in biomass pyrolysis changes the composition of the products. The acidic properties and pore structures of the catalysts determine the products obtained. ZSM-5 zeolites are the most promising as they give an organic liquid mixture with large proportion of aromatics which could be used as a fuel. The chemistry of some processes involved in catalytic biomass pyrolysis are discussed further in relation to bio-oil conversion (Sections 4 and 5) since bio-oil can be considered as a mixture of the type of intermediates likely to be found in the biomass pyrolysis process.

3. Gasification of biomass and bio-oil

3.1. Gasification reactions

Gasification of biomass and bio-oil gives synthesis gas and this can be used for power/heat generation or further transformed to diesel range hydrocarbons by Fischer–Tropsch synthesis with Co or Fe catalysts [50] or to dimethyl ether or gasoline range hydrocarbons via methanol formation over Cu based catalysts [51,52] (Fig. 4). Gasification of biomass and bio-oil is normally performed in the presence of steam and the process depends on the occurrence of the steam-reforming reactions.

Small amounts of oxygen can also be added to the gas feed to enable the heat of the resultant exothermic oxidation reactions to drive the endothermic steam-reforming reaction. This oxygen may also lead to a decrease of catalyst deactivation by burning some of the coke formed. Synthesis gas formation often demands high temperatures (over 700 °C) and is performed over supported metals [53–56]. The advantage of biomass with respect to coal in the gasification process is that it already contains oxygen and this leads to gasification at lower temperatures. van Rossum et al. [30] have reported that the process can be performed without a catalyst at temperatures higher than 1250 °C yielding tar and methane free synthesis gas with composition corresponding to the equilibrium.

These temperatures can be probably attained under autothermal conditions; however, catalysts allow decreasing the temperature and equipment cost [30]. They may also remove tar and methane as well as adjust the H₂/CO ratio to give a synthesis gas suitable for Fischer–Tropsch or methanol synthesis (Fig. 4) via the water-gas shift reaction (1):



This reaction is a critical reaction in gasification processes [57].

The main problems in catalytic processes for bio-oil conversion are similar to those of catalytic biomass gasification [20]: the formation of condensable organic compounds (tars) and methane as well as catalyst deactivation. The formation of tar may block the process equipment. Hence, the catalyst used for gasification should effectively convert any tar to synthesis gas. van Rossum et al. [30] and Valle et al. [53] have reported that better results could be obtained with a two-unit system. Thermal cracking of bio-oil was performed in the first stage (reactor) without a catalyst [53] or with a sand fluidized bed [30] to decrease coke formation on the catalyst placed in the second reactor. Rennard et al. [58] used different staged approaches for poplar bio-oil conversion in order to increase the hydrogen yield and decrease coke formation. It was noticed that co-processing of bio-oil with methanol or methane improved the reactor operation stability.

Czernik et al. [54] have indicated that the most important parameters of steam reforming of bio-oils are the temperature as well as the steam to carbon and catalyst to feed ratios. High steam concentrations lead to effective coke removal from the catalyst surface and improve heat and mass transfer. At the same time Xu et al. [59] have noticed that higher steam to carbon ratio will increase the cost of producing hydrogen from bio-oil. The design of the reactor is also quite important. A fluidized bed approach looks favourable; however, the catalyst for such an application should be resistant to attrition. Lan et al. [60] have reported that the carbon deposition content obtained from the fluidized bed reactor was lower than that from the fixed bed reactor at the same reaction temperature. The maximum H₂ yield obtained in the fluidized bed was 7% higher than that in the fixed bed.

3.2. Catalysts for direct biomass gasification and clean-up

Sutton et al. [20] have outlined the general criteria for catalysts for gasification and clean-up of the formed gases. The catalysts should effectively remove tars, be capable of reforming methane, be resistant to deactivation, be easy to regenerate, be inexpensive, and have significant strength (as fluidized beds are often used for gasification).

Dolomites, olivines, alumina, alkali metals salts and supported metal catalysts have all been used as catalysts for gasification of biomass and clean-up. Dolomites are cheap, natural minerals comprising of a mixture of magnesium and calcium carbonates that decompose to oxides at high temperatures. These minerals may also contain alumina and iron oxide and the iron can play an important role in relation to catalytic activity [20]. The dolomites are often included as a guard bed after a biomass reactor to decrease the tar content by transforming tar molecules to gases. However, all these catalysts suffer from deactivation.

Another mineral which may have applications in gasification of tars is olivine. Olivine is a mixture of magnesium and iron silicates and can be represented by the formula (Mg,Fe)₂SiO₄. The catalytic activity of olivine has been attributed to the presence of Fe. As compared to dolomites, this mineral is much more attrition resistant and this allows it to be used in fluidized catalytic beds. The olivines also possess very low surface areas (about 0.4 m² g^{−1} [61,62]), normally being an order of magnitude less than those of dolomites. Calcination of the olivines as well as of the dolomites is

needed for high activity. Devi et al. [61] have shown that calcination at 900 °C for 10 h was optimal. The calcined dolomite demonstrated higher activity in the conversion of tars than did calcined olivine. Thus, the tar conversion over dolomite at 850 °C was 56% while that over olivine was only 16%. Similarly, Corella et al. [63] have indicated that a dolomite was 1.4 times more active than an olivine, but that dolomite possessed lower attrition resistance, generating 4–6 times more particulates or dust. In contrast, Rauch et al. [64] have shown that two different olivines had better activity in toluene reforming than did a dolomite, magnetite or iron ore and this has led to utilisation of olivine as catalyst in the Guessing Biomass Conversion Plant.

Alkali salts can be added directly to biomass as catalysts, for example, by impregnation or dry mixing. Alkali cations may decrease both the tar and methane contents in the products. However, the recovery of the alkali metals appears to be difficult. Ashes often contain high concentrations of alkali metals and these can also be added to biomass. However, their applications in fluidized bed reactors should be approached carefully as the ashes may lead to the agglomeration of particles.

Matsuoka et al. [65,66] have reported that alumina and iron/alumina catalysts can also be used to decrease the amount of tar formed in the gasification of wood chips at 500–700 °C. The tar captured in the alumina can subsequently be reformed with steam to give synthesis gas. The addition of iron promoted hydrogen formation. This was assigned to the interaction of steam with the reduced iron.

Nickel catalysts have frequently been investigated for gasification of biomass and bio-oil because of their comparatively low price and high activity. They are normally used in a supported form. Recently, Richardson et al. [67] demonstrated that in situ generation of supported Ni nanoparticles could be performed using wood biomass impregnated with Ni nitrate. During the wood impregnation step, the numerous oxygenated groups present in the wood act as adsorption sites for metal cations in the aqueous medium, yielding very high dispersion of the metal precursor throughout the wood matrix. During pyrolysis, an amorphous $Ni_xO_yH_z$ phase is formed which is reduced to Ni metal at temperatures below 500 °C. Ni nanoparticles with different sizes ranging from 2 to 4 nm were obtained, the size depending on both the nickel loading in the wood sample and the final pyrolysis temperature.

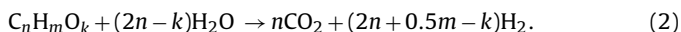
Ni catalysts serve not only for the removal of tars and methane but also for the adjustment of the synthesis gas composition by means of water-gas shift reaction. Unfortunately, Ni catalysts often suffer from deactivation by sintering and/or coke deposition.

Combined application of nickel catalysts and dolomite guard beds looks promising [20]. Even more interesting is the use of a dolomite as a catalyst support for Ni. Wang et al. [68] reported that no deactivation of such a catalyst was found after 60 h of operation. Similarly, Ni/olivine catalysts have previously been studied in different reactions related to biomass conversion by the group of Kiennemann [69–71]. Coke deposition on these catalysts was found negligible [72,73]. These catalysts showed excellent results in pilot scale biomass gasification units and showed no deactivation during a 45 h test [74].

3.3. Catalysts for bio-oil gasification

Kechagiopoulos et al. [56] have performed steam reforming of the aqueous phase of bio-oil derived from beech wood and model non-aromatic compounds (acetic acid, acetone, ethylene glycol) over an industrial Sud-Chemie Ni-containing catalyst (20 wt.% Ni/CaAl₂O₄, doped with K) used for naphtha reforming and compared their data with those obtained for non-catalytic steam reforming. The hydrogen yield from the stoichiometric steam-

reforming reaction (2) was about 60% [56]:



The steam reforming of the model compounds selected showed that these could be more effectively reformed, with hydrogen yields up to 90%, at reaction temperatures higher than 600 °C. Coking was found to be a serious problem. These authors argued that acetone was responsible for coking in the case of a mixture of model compounds. The acetone forms ketene and mesityl oxide and these molecules can undergo oligomerization, forming deposits on the catalysts which lead to deactivation.

Czernik et al. [25] have used the same industrial Ni-containing catalyst as well as their own Ni catalysts for steam reforming of whole bio-oil and found that the H₂, CO and CO₂ concentrations did not change much during 18 h on stream at 850 °C; however, the concentration of methane increased with time on stream. The authors suggested that this was due to methanation of the carbon monoxide as well as to thermal cracking of the complex molecules formed from the bio-oil. In these experiments, the hydrogen yield reached 70–80% of the stoichiometric amount; this was better than the yields obtained by Rioche et al. [55] using more expensive noble metals as catalysts. Czernik et al. [54] have also obtained quite similar results for the steam reforming of the water soluble fraction of bio-oil. A water-gas shift reactor inserted after the reforming reactor further increased the hydrogen yield up to 90%.

Medrano et al. [75] have used a fluidized bed reactor to compare the performance of samples of a 28.5 wt.% Ni/Al₂O₃ catalysts modified with Ca and Mg for the steam-reforming of the aqueous fraction of bio-oil and to examine coke deposition on the catalysts. They found that the magnesium-modified catalyst showed the better performance of the catalysts tested, with the higher carbon conversion to gas and a higher hydrogen yield. The calcium-modified catalyst showed a poorer performance, giving higher CO yields and lower H₂ and CO₂ yields.

Wu et al. [76] have performed steam reforming of bio-oil in a two stage reactor over a Ni/MgO catalyst (5.7 wt.% Ni). Dolomite was used in the first stage to decrease the coke deposition on the Ni catalyst. The maximum hydrogen yield (about 60%) was obtained at 900 °C and steam to carbon ratio equal to 16.

Valle et al. [53] have used a 1 wt.% Ni-ZSM-5 catalyst (Si/Al = 30) for the steam reforming of whole bio-oil in the presence of methanol. This catalyst gave high yields of hydrocarbons with more than 18% of non-aromatic C₅ hydrocarbons and 33% of single-ring aromatic hydrocarbons.

Rioche et al. [55] have studied the steam reforming of whole bio-oil as well as various different model compounds (acetic acid, phenol, acetone and ethanol) using a range of 1 wt.% noble metals catalysts (Pt, Rh, Pd) supported on alumina as well as on ceria/zirconia at 740–860 °C. They found that Pt and Rh were both more active than Pd. The alumina-supported catalysts were less active than the ceria/zirconia supported ones. The activities of the catalysts in the conversion of bio-oil and model compounds based on the hydrogen production were in the order: Rh/CeZrO₂ > Pt/CeZrO₂ ~ Rh/Al₂O₃ > Pd/CeZrO₂ > Pt/Al₂O₃ > Pd/Al₂O₃. Both CO and CO₂ were formed during reforming. The CO₂/CO ratio was higher at lower temperatures, probably because of equilibrium in the water-gas shift reaction. Methane was found among the products and its amount was highest when alumina was used as a support. A 9 h experiment with a 5:1 steam/bio-oil ratio demonstrated that a gradual but slow deactivation occurred with the Pt/CeZrO₂ catalyst; however, a hydrogen yield of 50% was maintained. It is interesting to note that the introduction of a small amount of oxygen to the feed decreased the amount of hydrogen obtained and led to severe deactivation of the Pt/CeZrO₂ catalyst, but coke deposition was reduced. Thus, the deactivation was explained by Pt sintering.

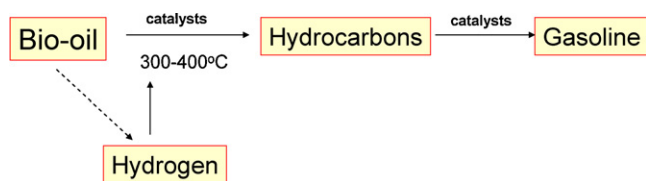


Fig. 5. Scheme of bio-oil upgrading via hydrodeoxygenation.

Rioche et al. [55] and Czernik et al. [54] have noted the importance of the bifunctional properties of the catalysts used for the conversion of bio-oil to synthesis gas. They suggested that the ceria/zirconia support leads to improved steam activation and that metallic particles are involved in the activation of organic molecules.

It can thus be concluded that the use of noble metal catalysts gives good hydrogen yields in bio-oil steam reforming; however, these catalysts are expensive. Ni catalysts are promising and not expensive catalysts for bio-oil and biomass gasification, but further work is needed to optimise the formulation of the catalysts: the Ni content, the average Ni particle size, the catalyst support and the concentrations and type of doping additives. Ni catalysts have been widely studied for the steam reforming of acetic acid, an important component of bio-oil [77–79]. Supports based on magnesia and ceria-zirconia look promising for the creation of effective catalysts for tar and methane removal from synthesis gas.

4. Hydrotreating of bio-oil

4.1. Hydrotreating reactions

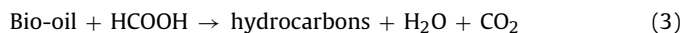
Hydrotreating (hydrodeoxygenation, HDO) (Fig. 5) eliminates oxygen in the form of water; however, CO₂ can be also formed. For this elimination, catalysts and hydrogen are necessary. Bridgwater [13] has reported that hydrodeoxygenation gives hydrocarbons with a maximum stoichiometric yield of 56–58% by weight of liquid bio-oil. Hydrodeoxygenation consists of a family of reactions such as hydrogenation, cracking and decarboxylation. Cracking and hydrogenation are the rate-determining steps [17].

Hydrogen is relatively expensive. Huber et al. [5] have indicated that the price of hydrogen produced from biomass is \$1.1–2.0 kg^{−1}, being slightly higher than the market price of hydrogen of \$0.7–1.4 kg^{−1}. Cheaper hydrogen is available at petroleum refineries. Despite the fact that hydrogen can also be produced from bio-oil and biomass by steam reforming, hydrodeoxygenation is sometimes considered as an unattractive process [14]. Another drawback of hydrodeoxygenation is the necessity of high pressures (70–200 bar). Additionally, 20–30% of the carbon content of the biomass is removed to the gas phase and catalyst deactivation takes place.

Partial hydrotreating of bio-oil to give a suitable fuel is also possible [12]. Such an approach has been adopted by the DynaMotive Energy Systems Corporation, which has developed a hydrotreating process involving limited use of hydrogen [80]. Venderbosch

et al. [81] and Vispute et al. [82] have reported that mild hydrogenation at temperatures lower 500 K is very useful for stabilisation of the bio-oil before further transformation to fuel additives.

Interesting results have also been obtained using hydrogen donor compounds instead of hydrogen. Elliott [17] has reported that performing bio-oil upgrading in the presence of a hydrogen-donor solvent leads to improvement of the product and that less deactivation of the catalyst was observed in this case. The hydrogen donor compounds used can be by-products of biomass conversion processes. For example, formic acid may be obtained together with levulinic acid from the hydrolysis of biomass [3]. The formic acid can then react with an oxygen-containing bio-oil according to reaction (3):



Appropriate catalysts normally based on noble metals, Ni or Cu that are active in hydrogen transfer reactions should be used for this reaction [83,84]. Barth and co-workers [85,86] have reported that formic acid may depolymerise lignin at about 400 °C, leading to a hydrogen-rich oxygen-depleted product with a preponderance of aliphatic hydrocarbon structures (Fig. 6). They did not use any specially introduced catalyst but suggested that the stainless-steel walls of the reactor probably acted as a catalyst.

Several groups [5,13,17,53] have proposed the use of a dual-reactor process for bio-oil hydrodeoxygenation. In the first stage, unstable compounds in the bio-oil are transformed thermally at about 270 °C without a catalyst to give a mixture of coke and more stable compounds which then are transformed in the second reactor with the hydrotreating catalyst. The consumption of hydrogen in the first step is small [13]. Using a dual reactor process decreases polymerization of the bio-oil and deactivation of the catalyst in the second reactor.

Elliott [17] and Laurent and Delmon [87] have outlined the reactivity of different organic compounds with respect to hydrogen over CoMo and NiMo sulphided catalysts (Fig. 7). Olefins, aldehydes and ketones can easily be reduced by H₂ at temperatures as low as 150–200 °C. Ketonic groups are hydrogenated to CH₂ groups [87]. Alcohols react at 250–300 °C by hydrogenation and thermal dehydration to form olefins. Carboxylic and phenolic ethers react at around 300 °C; the carboxylic groups can be transformed to methyl groups, but a parallel decarboxylation reaction may also occur at a comparable rate [87].

Strict environmental standards for aromatics have led catalytic scientists to seek ways to decrease the aromatic content in petrofuels [88]. Hydrogenation of the aromatics has been considered as a possible way to achieve this [89]; however, a decrease of the octane number after the hydrogenation step needs to be taken into account. For example, if toluene has a high research octane number equal to 119, the value for the hydrogenated product, methylcyclohexane, is 73 [88]. Another, problem related to the hydrogenation of aromatics is the increased consumption of expensive hydrogen. Hydrogenation of aromatics over sulphided NiMo and NiW catalysts showed the following trend of activity under moderate reaction conditions: benzene < toluene < p-xylene < m-xylene < o-xylene [90]. This set of results indicates that methyl

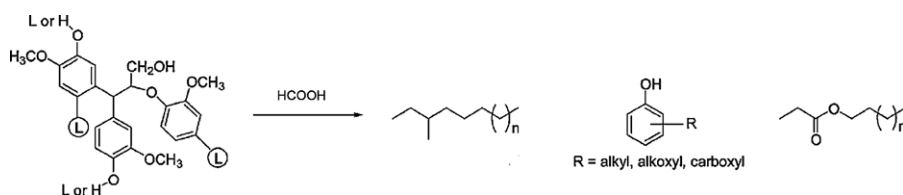


Fig. 6. Scheme showing the formation of products by the pyrolysis of lignin in the presence of formic acid.

Adapted from Gellerstedt et al. [86].

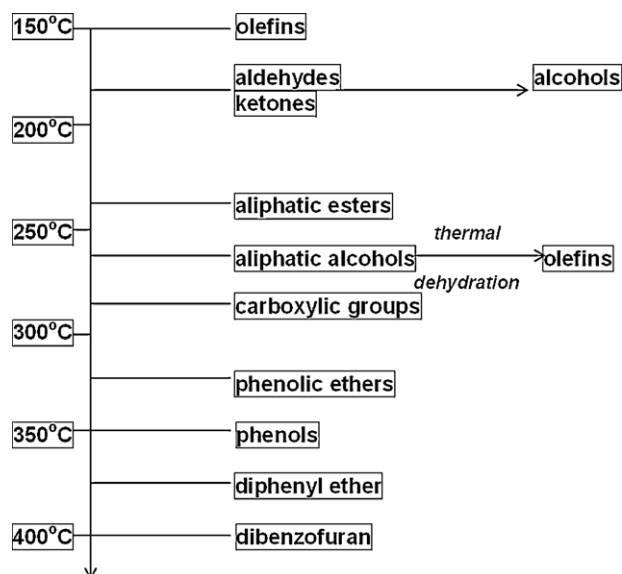


Fig. 7. Reactivity scale of organic compounds under hydrotreatment conditions. Adapted from Elliott [17].

groups enhance the reactivity of the aromatics. It is interesting to note that the hydrogenation reaction over noble metal catalysts exhibits a reverse trend [89]. Sanati et al. [89] have argued that the presence of methyl substituents on the benzene ring stabilizes the adsorbed π -complex with a resultant increase of the activation energy for the hydrogenation reaction.

Vispute et al. [82] have proposed an integrated approach for upgrading of bio-oil. In the first step, hydrogenation of the oxygen containing species in bio-oil with hydrogen to give polyols and alcohols was performed using Ru/C and Pt/C catalysts at low temperatures, 398 and 523 K, respectively. The mixture obtained was then transformed with a ZSM-5 zeolite at higher temperatures to give a mixture of light olefins and aromatic hydrocarbons. The composition of the products could be adjusted by changing the degree of hydrogenation at the first step.

Hence, the upgrading of a bio-oil by hydrodeoxygenation leads to a product with a decreased content of carbonyl and olefinic compounds; some hydrogenation of aromatic compounds also takes place [17]. The content of oxygen can be decreased to as low as 2–5 wt.%. Huber et al. [5] have reported that the octane number of a bio-oil that had been upgraded by hydrodeoxygenation was 72–77, a value which is still lower than that of gasoline. The hydrocarbons formed by bio-oil upgrading can therefore be used for some applications but not directly as a transport fuel. This is because their composition approximates to that of naphtha and so additional refining is necessary to obtain a suitable gasoline [13]. This refining can be performed using catalytic alkylation, reforming, isomerization and other reactions. The naphtha-type hydrocarbons formed during upgrading can be mixed with a petroleum-based feedstock for refining.

4.2. Catalysts for bio-oil hydrotreating

Conventional supported sulphided CoMo and NiMo catalysts used for the hydrotreating (desulphurization) process also provide good results for bio-oil upgrading via hydrotreating. The known advantage of the sulphided catalysts is resistance to any sulphur-containing compounds that may present in feedstock; the concentrations of these will be much less in bio-oil than in oil-based raw materials. Elliott [17] has noted that deoxygenation with NiMo catalysts was more effective than that with CoMo and that the sul-

Table 5

Properties of the raw and hydrotreated bio-oil.

Properties	Density/ kg m ⁻³	Heating value/ MJ kg ⁻¹	C/wt.%	H/wt.%	O/wt.%	N/wt.%
Raw oil phase of bio-oil	1.12	21.3	60.4	6.9	31.8	0.9
Bio-oil hydrotreated over sulphided CoMoP catalyst	0.93	41.4	87.7	8.9	3	0.4

Adapted from Zhang et al. [93].

phided form of the catalysts was more active than the oxide form. He also reported that no sulphur removal occurred from these catalysts during the process; however, sulphur removal could not be excluded at longer times on stream.

Elliott [17] has also mentioned that a copper chromite catalyst was less active for hydrodeoxygenation than the sulphided CoMo and NiMo catalysts. An undoped Ni catalyst possessed activity similar to that of the sulphided catalysts but it gave higher gas yields and required more hydrogen. NiW was not effective in oxygen removal. Centeno et al. [91] compared the activities of carbon- and alumina-supported CoMo and NiMo catalysts for hydrodeoxygenation of model compounds containing carbonyl, carboxyl and methoxy groups. They found that the alumina-supported catalysts were three times more active than those supported on carbon. However, it should be recognised that operation in gas mixtures with high water contents may lead to destruction of the support since gamma and delta aluminas are not generally stable in water environments at temperatures higher than 350 °C [17], transforming to the hydroxide (boehmite). Hence, supports that are more stable in steam could be of interest in the further development of suitable catalysts.

Rocha et al. [92] have hydrotreated bio-oil over a colloidal Fe sulphide (FeS) and found that it became more aromatic in character. An increase of hydrogen pressure decreased the extent of aromatization and lowered the yields of char.

Zhang et al. [93] have hydrotreated a mixture of the oil phase of a bio-oil with tetraline over a sulphided CoMoP catalyst supported on alumina (Table 5). The content of oxygen in the mixture decreased by one order of magnitude. The density of the bio-oil decreased and the heating value doubled as a result of oxygen removal.

Elliott [17] has reported that supported precious metals had higher activities than the sulphided CoMo, NiMo and NiW catalysts examined. Catalysts containing Pt, Rh or Ru supported on alumina and also Raney nickel materials were very active in upgrading a slow pyrolysis oil. All of these materials gave higher concentrations of gaseous products than a Pd-based catalyst. The use of a carbon support in place of alumina also led to higher gas production [91].

Wildschut et al. [94] have studied bio-oil hydrotreatment in the presence of Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C, and Pd/C catalysts with 5 wt.% of metal at 250–350 °C, and have compared the results with those obtained with typical hydrotreatment catalysts (sulphided NiMo/Al₂O₃ and CoMo/Al₂O₃). They demonstrated that the Ru/C catalyst possessed a superior activity with respect to the oil yield and deoxygenation level (up to 90%). The heating value of the upgraded bio-oil increased by a factor of two (up to 40 MJ kg⁻¹).

Fisk et al. [95] have treated a synthetic bio-oil in an autoclave at 350 °C over different catalysts containing 1 wt.% of Pt. Hydrogen was generated from light oxygenates present in bio-oil by steam reforming reaction. A Pt/Al₂O₃ catalyst was found to be most effective in deoxygenation. The oxygen content in the bio-oil decreased from 41.4 wt.% to 5 wt.%. Catalysts based on zirconia, ceria or titania were considerably less effective.

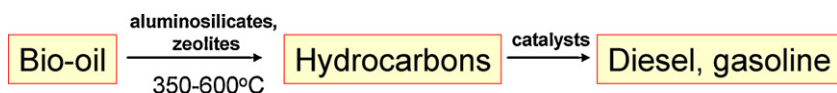


Fig. 8. Scheme of bio-oil upgrading via cracking.

Aromatics can be partially hydrogenated over some metallic catalysts under the conditions of bio-oil hydrogenation and the order of catalytic activity for benzene was reported as follows: Rh > Ru > Pt > Pd > Ni > Co [89,96]. Additionally, noble metal catalysts based on acidic supports such as SiO₂-Al₂O₃ showed higher activities in hydrogenation of aromatics than those supported on Al₂O₃ [97,98]. The enhanced activity was attributed to a reaction between spilled-over hydrogen and aromatics molecules adsorbed on the oxide surface in the metal-support interfacial region.

Hence, considerable research has been done on hydrogenation of model compounds leading to understanding of the reactions taking place during bio-oil hydrotreating. Noble metal catalysts are the most active in bio-oil hydrotreating; however, sulphided CoMo and NiMo catalysts can also be used effectively. Bio-oil contains many compounds such as acids and alcohols which may participate in bio-oil upgrading as hydrogen donors. This will decrease the consumption of expensive molecular hydrogen.

5. Cracking and decarboxylation of bio-oil

5.1. Cracking and decarboxylation reactions

Another approach to deoxygenation of bio-oil is catalytic cracking (Fig. 8). Catalytic cracking is normally performed over solid acid catalysts such as aluminosilicates and zeolites. This approach does not require added hydrogen and oxygen is eliminated in the form of water and CO₂. As compared to hydrotreating, cracking gives a higher value transport fuel product because of higher aromatic content [12]. However, the yields are lower and the amount of coke formed is relatively high. The yields obtained in the process reach 50–60% of the theoretical maximum. The liquid product obtained by cracking as the product obtained by hydrotreating demands further refining to produce gasoline or diesel hydrocarbons.

The catalytic reactions of model compounds over the cracking catalysts have been investigated. This gave some hints concerning the reasons of deactivation and led to the process development. Thus, Gayubo et al. [99,100] have studied the transformation of different organic compounds typical of a bio-oil over a ZSM-5 zeolite (Si/Al = 24). They showed [99] that alcohols could easily be converted to olefins by means of dehydration and that these could be transformed to paraffins at temperatures higher than 350 °C. Phenol and 2-methoxyphenol had low reactivity for hydrocarbons formation; deposition of a coke formed thermally by condensation of 2-methoxyphenol was noticeable. This coke blocked the catalyst bed.

The same group [100] has studied the transformation of acetone and indicated that its transformation over acidic catalysts takes place via isobutene, further yielding olefins and aromatics (Fig. 9). Gayubo et al. [100] have also shown that the conversion

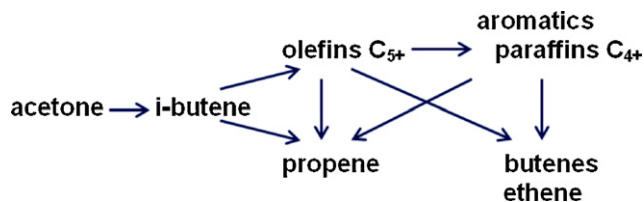
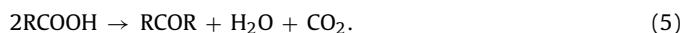


Fig. 9. Scheme showing the transformation of acetone over ZSM-5. Adapted from Gayubo et al. [100].

of acetaldehyde to hydrocarbons is low and that this conversion is accompanied by deactivation of the catalysts as a result of coke deposition. They attributed this to the ability of the acetaldehyde to oligomerize to form trimethyltrioxane. This thermal degradation caused operating problems in the reactor and so prior removal of acetaldehyde is advisable; this could be performed in a dual reactor system discussed below.

The same authors [100] have shown that the catalytic transformation of acetic acid took place by decarboxylation and, to a lesser degree, through dehydration. Acetic acid may also give acetaldehyde, giving rise to the problems outlined above. Generation of coke from acetic acid was more significant than that with alcohols. Increase of the water content in the mixture led to decreased coke formation.

Transformation of acids present in bio-oil to hydrocarbons and ketones may improve the product obtained. Acids can be converted via direct decarboxylation (4) or decarboxylative ketonization (5) at temperatures < 400 °C:



Typical catalysts for decarboxylation based on MgO, ZnO, CeO₂, MnO₂ and ZrO₂ [101–106] have not been studied widely for bio-oil upgrading up to now. These catalysts may be sensitive to the presence of carbon dioxide [107], water [107,108] and different organic compounds [102,108]. However, Deng et al. [102] have reported that water and phenols have small effects on the conversion of acetic acid over ceria/alumina catalysts, while furfural demonstrated a strong inhibition effect on the ketonization reaction. Rajadurai [108] has found that isopropanol and the product of the reaction, acetone, inhibit ketonization of acetic acid over a Zn/Cr/Fe oxide.

For both cracking and hydrodeoxygenation of bio-oil, it is preferable to use a dual reactor system [5]. As mentioned above, the thermal reactions of bio-oil take place in the first reactor without a catalyst. This gives rise to less coking and deactivation of the catalyst in the second reactor. In spite of the use of two reactors, the process still suffers severely from deactivation. Thus, the use of a fluid catalytic cracking (FCC) approach, widely used in petrochemistry, could be considered [4].

5.2. Catalysts for cracking and decarboxylation of bio-oil

Zeolites (Table 3) are often used as catalysts to improve the product from biomass pyrolysis. The zeolites contain a suitable porous structure and possess the acidic properties necessary for the cracking of large polymeric molecules as well as oxygenates formed from the biomass.

Adjaye and Bakhshi [109,110] have compared the activities for the catalytic cracking of bio-oil of various different zeolite materials containing silica and alumina with those of silicalite and silica-alumina. The yields of hydrocarbons were found to be: 27.9 wt.% with ZSM-5 (SiO₂/Al₂O₃ = 56); 14.1 wt.% with Y-zeolite (SiO₂/Al₂O₃ = 6); 4.4 wt.% with mordenite (SiO₂/Al₂O₃ = 14); 5 wt.% with silicalite; and 13.2 wt.% with silica-alumina (SiO₂/Al₂O₃ = 0.79). Whereas ZSM-5 and mordenite produced a higher proportion of aromatic than aliphatic hydrocarbons, Y-zeolite, silicalite and silica-alumina produced more aliphatic than aromatic hydrocarbons. The liquid aliphatic

hydrocarbon fractions consisted mostly of alkylated cyclopentene, cyclopropane, pentane and hexene. The overall performance of the catalysts in bio-oil conversion followed the order: ZSM-5 > mordenite > Y-zeolite, silica-alumina, silicalite.

Vitolo et al. [111] have compared the conversion of bio-oil using ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50\text{--}80$) and Y-zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$). They found that the maximum conversion of raw bio-oil to upgraded bio-oil, with a minimum conversion to char, occurred at 450°C . The quantity of gas and coke increased with increasing temperature. Of the two materials, the Y-zeolite produced a smaller amount of upgraded bio-oil, but more coke. Vitolo et al. [111] have also observed a higher oil fraction yield at lower residence times and found that this corresponded to an increased fraction of oxygenated functional groups and a significant reduction of coke formation. The upgraded oil showed a much improved heating value and the authors attributed this to the decrease of the concentration of oxygenated functional groups in the product.

Pattiya et al. [112] have studied pyrolysis of a cassava rhizome using ZSM-5 ($\text{Si}/\text{Al} = 50$), Al-MCM-41, Al-MSU-F and alumina-stabilised ceria; these were separated from the biomass by a plug of quartz wool in the reactor. Thus, the bio-oil vapours formed could be cracked over the catalyst before cooling. The catalysts improved the initial viscosity and heating values of the liquid product. The ZSM-5 catalyst was the most effective in the production of aromatic hydrocarbons from the bio-oil. However, with the exception of ceria-alumina, which is known decarboxylation catalyst, the catalysts increased the amount of acetic acid in the upgraded bio-oil, thus increasing the corrosiveness of the product.

Gayubo et al. [32,99,100] have studied the interaction of different compounds present in bio-oil with a ZSM-5 zeolite ($\text{Si}/\text{Al} = 24$) in the presence of water. At temperatures lower than 450°C , dealumination and irreversible deactivation of the zeolite were avoided; however, dealumination took place at higher temperatures [32], but this was not accompanied by pore blockage. Valle et al. [113] have reported recently that utilisation of a ZSM-5 catalyst with high Si/Al ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) and the modification of ZSM-5 zeolites with low Si/Al ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) by incorporating Ni (1 wt.%) are suitable strategies for obtaining hydrothermally stable catalysts. They also have noticed that the acidity of the catalyst should be moderate in order to decrease carbon deposition and deactivation.

Samolada et al. [114] have used FCC catalysts based on Re and USY (Ultra-stable Y) zeolite to obtain bio-gasoline from bio-oil and compared the composition of the bio-gasoline obtained with that of FCC gasoline. The bio-gasoline contained lower concentrations of olefins and naphthenes, while the total aromatic content was higher.

Lu et al. [115] have studied bio-oil pyrolysis over titania-based materials. They showed that a $\text{ZrO}_2\text{--TiO}_2$ catalyst was more effective in reducing phenols, acids and sugars than were TiO_2 (anatase) and TiO_2 (rutile). Upgrading of bio-oil over these catalysts also led to increase of hydrocarbons, linear ketones and cyclopentanones.

Nokkosmaki et al. [116] have applied zinc oxide as a catalyst for bio-oil upgrading. This ZnO , containing basic surface sites, can be considered as a decarboxylation catalyst. The authors found that the zinc oxide was a mild catalyst and that the liquid yields were not substantially reduced; further, it had no effect on the water insoluble fraction derived from lignin of the bio-oil. The upgraded oil showed an improved stability as compared with the untreated one. However, the authors observed a deactivation of the catalyst similar to that found with acidic zeolites.

Lu et al. [117] have studied MgO , CaO , TiO_2 , Fe_2O_3 , NiO and ZnO in the catalytic upgrading of bio-oil from poplar wood. They reported that the CaO catalyst was better than the ZnO catalyst because it could more effectively remove acids from the bio-oil. All these catalysts (except of NiO) reduced the formation of heavy

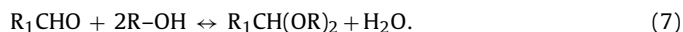
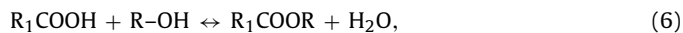
products such as anhydrosugars and phenols and increased the formation of hydrocarbons and cyclopentanones. Unfortunately, no BET surface areas or other characterisations of these catalysts were presented.

Therefore, as with catalytic biomass pyrolysis, ZSM-5 zeolites are the most promising in the catalytic cracking of bio-oil; however, these catalysts suffer under certain conditions from deactivation by coke deposition and dealumination. Basic decarboxylation catalysts have been less studied in bio-oil upgrading.

6. Esterification of bio-oil

6.1. Esterification reactions

A series of different reactions take place in bio-oil at room temperature, moving the mixture towards an equilibrium mixture, leading to a deterioration of the bio-oil properties. The main reactions occurring are polymerization and condensation. Diebold and Czernik [118] have reported that small concentrations of alcohols (<10%) can be used for bio-oil stabilization. The addition of ethanol or methanol drastically reduced the ageing rate of the bio-oil, as shown by an increase of viscosity in time. For methanol, which was the more effective, the rate was reduced by a factor of nearly 20 times. This improvement of the bio-oil properties probably takes place because of the reactions of the added alcohols with the acids and aldehydes present in the bio-oil: ester formation from the acids (6) and acetal formation from the aldehydes (7):



Both reactions are catalysed by acids present in the bio-oil. The reactions are reversible and the removal of water may give higher concentrations of products.

Mahfud et al. [119] and Zhang et al. [120] have considered esterification as an approach to obtaining an upgraded bio-oil. Reactions (6) and (7) are carried out over acid catalysts under mild conditions ($50\text{--}80^\circ\text{C}$), the product water being separated afterwards using distillation [119,120] or adsorption on a zeolite [121]. Generally, the presence of high concentrations of water in bio-oil is a serious problem because the heating values of the products containing water are lower than those without it and the water content in raw bio-oils is considerable (Table 1). Water has to be removed and that is easier from an ester-containing mixture than from the original acidic mixture because of the lower level of hydrogen bonding. Thus, a separate step of water removal should be considered.

Biomass-derived alcohols such as ethanol and butanol can be used for the esterification process. Both can be obtained by fermentation of materials from renewable resources. The advantage of using butanol is that its boiling point is higher than that of water, leading to easier water removal from the mixture.

Mahfud et al. [119] have compared the reactivity with bio-oil of different high boiling-point alcohols such as butanol, ethylene glycol and 2-ethylhexyl alcohol. Butanol gave an acceptable product but 2-ethylhexyl alcohol was not useful for such applications as the product obtained gave solids after standing at room temperature for one day. Further, ethylene glycol led to a product with high viscosity that was not acceptable.

6.2. Catalysts for esterification

Sulphuric acid is often used as a catalyst for esterification. However, it is corrosive and is difficult to separate it from the products. Further, there is an environmental concern regarding the use of liquid acids leading to requirement that they must be neutralised or regenerated after the upgrading step. Solid acid catalysts are eas-

Table 6
Characteristics of raw bio-oil and bio-oil upgraded by esterification with ethanol.

	Density/ kg m ⁻³	pH	H ₂ O content/%	Heating value/ MJ kg ⁻¹	Dynamic viscosity at 20 °C/mm ² s ⁻¹
Raw bio-oil	1.24	2.60	29.8	15.8	120.7
Bio-oil upgraded with SiO ₂ /TiO ₂ - SO ₄	0.96	1.12	13.6	23.9	5.2
Bio-oil upgraded with K ₂ CO ₃ /Al ₂ O ₃ - NaOH	0.97	5.93	12.4	24.0	6.1

Adapted from Zhang et al. [120].

ier to separate from the products; they possess high acidity and can sometimes be used at lower temperatures than H₂SO₄ [122]. Solid acid catalysts are non-inflammable, non-toxic and environmentally friendly. According to Okuhara [123], about 200 industrial processes are performed at present using solid acid catalysts in place of conventional acids. However, there are likely to be problems due to catalyst deactivation and limited access of some of the reactants to the active sites of typical porous solid acids. The high molecular weight hydrocarbons present in the bio-oil may block the active sites and pores of the catalysts.

Mahfud et al. [119] have demonstrated that the activity in esterifying of bio-oil with butanol over the solid acid Nafion SAC 13 was lower than that in the presence of sulphuric acid. However, they noted that the concentration of surface acid sites in Nafion in these experiments was considerably lower than the concentration of protons in the acidic solution. The concentration of water in bio-oil after upgrading using Nafion and H₂SO₄ dropped from 32% to 9 and 5%, respectively. The density of the upgraded bio-oil decreased from 1.17 kg L⁻¹ to 0.95 and 0.96 kg L⁻¹, the kinematic viscosity decreased from 17 mm² s⁻¹ to 7 and 7.6 mm² s⁻¹ and the heating value increased from 20.6 MJ kg⁻¹ to 28.7 and 27.7 MJ kg⁻¹, respectively.

Zhang et al. [120] have esterified bio-oil with ethanol over a solid acid catalyst, SiO₂/TiO₂-SO₄, and a solid base catalyst, K₂CO₃/Al₂O₃-NaOH. They found that both these materials improved the properties of the bio-oil (Table 6). This improvement led to a decrease of the bio-oil density and the water content as well as to an increase of the heating value in accordance with the data of Mahfud et al. [119], who used butanol and the Nafion catalyst. Additionally, a GC-MS analysis of the bio-oil upgraded over the solid acid catalyst demonstrated that the concentration of esters as compared to the raw bio-oil increased by a factor of twenty. Isomerization of some of the components of the bio-oil also took place.

Xu et al. [124] have obtained quite similar results with different solid acid catalysts (SO₄²⁻/M_xO_y, M = Sn, Ti, Zr). The activity of the sulphated zirconia catalyst was the highest among those studied.

Tang et al. [125] have reported recently on the utilisation of a Pd/SO₄²⁻/ZrO₂/SBA-15 catalyst for bio-oil upgrading in supercritical ethanol. The reaction was performed under a hydrogen atmosphere at 280 °C. The catalyst was expected to demonstrate promising properties in simultaneous hydrotreatment, esterification and cracking. The concentrations of aldehydes and ketones in the upgraded bio-oil decreased considerably. Most of the acids were converted to esters. At the same time, more volatile products were produced from the high molecular weight compounds. However, the high ethanol to bio-oil ratio of 3:1 used in this work masked any improvement of the physical properties of the bio-oil.

Hence, esterification over solid acidic catalysts can be used as a method for bio-oil upgrading, the reaction allowing a decrease of water content in the product and an increase in heating value. Acidic sulphated zirconia looks the most promising in this process.

7. Summary

Bio-oil obtained by fast pyrolysis is a transportable intermediate which can be used for the production of fuel additives. The price of bio-oil was estimated in 2004 as being 10–100% higher than that of fossil fuels [31,126]. Upgrading of this intermediate by decreasing the water and oxygen content is necessary. An upgraded product can be obtained by applying catalysts in the pyrolysis of biomass. Gasification of biomass and bio-oil to give synthesis gas followed by Fischer–Tropsch synthesis of diesel can also be used effectively. The problems associated with catalytic bio-oil gasification are the same as for the catalytic gasification of biomass – catalyst deactivation by coking, tar and methane formation – all of which could be decreased by using optimised catalysts. Catalytic hydrotreating can give a product with a high heating value; however expensive hydrogen and high pressures are needed. Thus, utilisation of organic compounds such as formic acid as hydrogen donors for hydrotreating looks promising. Generally, bio-oil contains already different hydrogen donors which may provide hydrogen for deoxygenation of biomass derived intermediates. Catalytic cracking of bio-oil decreases effectively the level of oxygenates in the bio-oil and gives a higher value product than hydrotreating. However, improved yields might be expected for this process. Esterification can give a significant improvement of the chemical and physical properties of bio-oil; however, the process consumes valuable alcohols and demands water separation.

The majority of the processes for bio-oil upgrading include several stages and the catalysts used for these all suffer from deactivation. Deactivation is often caused by coke deposition. The coke, which may block the active sites of the catalysts, may originate from oxygenated compounds such as acetic acid, acetaldehyde or acetone as well as from different phenols and complex aromatics. Sintering of metallic particles in metal-based catalysts and dealumination of zeolites in the presence of water should be prevented. Careful tuning of the acid–base properties and porosity of a catalyst is necessary. Optimisation of reaction conditions and the mode of operation of the process are also of great importance. Therefore, the production of transport fuels from bio-oil involves complicated catalytic processes, all of which could be attractive in the future, especially with any oil price increase.

The synthesis of higher value oxygen-containing chemicals from biomass could be more profitable than the synthesis of fuels [1]. The well-established reason for this is that biomass intermediates already contain oxygen, but in the case of petrochemical intermediates (hydrocarbons), oxygen has to be inserted to obtain oxygen-containing compounds. At present, phenols, vanillin, hydroxyacetaldehyde, levoglucosan derivatives, acetic and formic acids can all be manufactured from bio-oil [13,31].

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