Chapter 5
Catalysts in Thermochemical Biomass Conversion

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5.1 Thermochemical Biomass Conversion

Thermochemical biomass conversion methods can be divided into three main groups as combustion, gasification and Pyrolysis (Fig. 5.1). Combustion is thermal conversion of organic matter with an oxidant to produce mainly carbon dioxide and water. Combustion of biomass is the most direct and technically easiest process. However, the overall efficiency of generating heat from biomass energy is low. Gasification of biomass provides power generation for the technical applications needing energy. The process generates valuable gaseous products (CO, CO_2, H_2O, CH_4, C_2–C_6) and char depending on the design and operating conditions of the gasification reactor. Pyrolysis is thermal heating of the materials in the absence of oxygen, which results in the production of three categories: gases, pyrolytic oil and char [1–3]. Pyrolytic oil, also known as "tar or bio-oil", cannot be used as transportation fuels directly due to the high oxygen (40–50 wt%) and water contents (15–30 wt%) and also low H/C ratios. However, pyrolytic oil is viscous, corrosive, relatively unstable and chemically very complex [4–6].

The main advantages of these methods for biomass conversion over other conversion methods such as biochemical conversion technologies are the feedstock used. All plant-based residues can be converted into value-added products such as transportation fuels (diesel), hydrogen, methane, syngas and chemicals [7]. However, the undesirable products like alkali compounds and the cost of cleaning the gaseous products and drying of biomass are the major problems. There are many attempts such as catalyst usage, co-firing of biomass with coal in order to improve product quality and the optimization of the experimental conditions.

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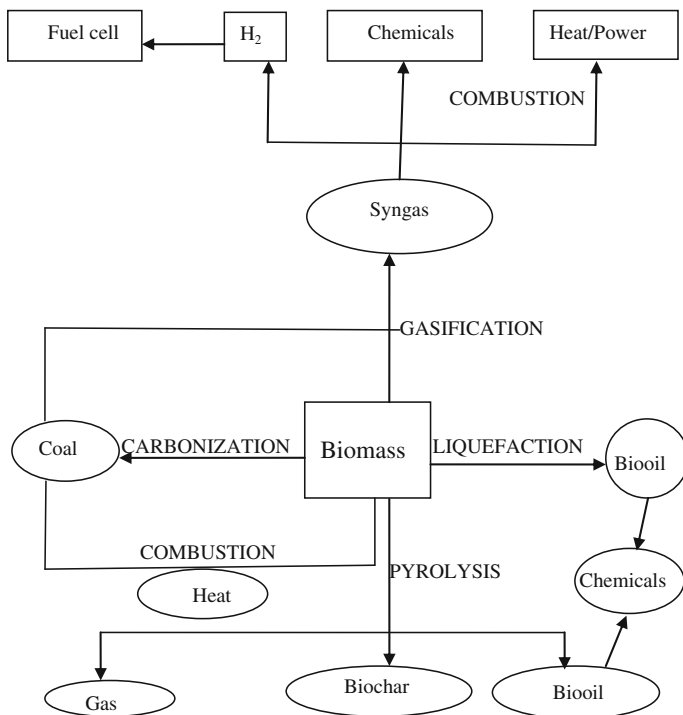Beşevler-Ankara 06100, Turkey
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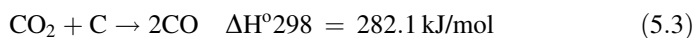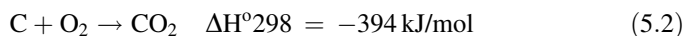**Fig. 5.1** Main routes for thermal biomass conversion

This chapter chiefly deals with the role of catalysts during thermochemical biomass conversion since usage of different types of catalysts for this conversion leads to the tar and oxygen removal, increasing calorific value of the products and reduction in the amount of undesirable contaminants. The effects of new types of nanocatalysts together with known types of catalysts on the process conditions and the product quality will also be discussed.

5.2 Types of Catalysts in the Thermochemical Biomass Conversion

5.2.1 Known Catalyst Types for Biomass Gasification

5.2.1.1 The Synthesis Gas

The main product of biomass gasification is the synthesis gas. The synthesis gas is produced in the presence of steam. The following reactions are observed during biomass gasification.

$$C + H_2O \rightarrow CO + H_2 (syngas) \quad \Delta H^o 298 = 323.1 \, kJ/mol \quad (5.1)$$

$$C + O_2 \rightarrow CO_2 \quad \Delta H^o 298 = -394 \, kJ/mol \quad (5.2)$$

$$CO_2 + C \rightarrow 2CO \quad \Delta H^o 298 = 282.1 \, kJ/mol \quad (5.3)$$

The first reaction, between carbon and steam, is strongly endothermic, producing carbon monoxide (CO) and hydrogen (H_2). When the coke bed has cooled to a temperature at which the endothermic reaction can no longer proceed, the steam is then replaced by a blast of air.

The reactions (5.2) and (5.3) take place, producing an exothermic reaction—forming initially carbon dioxide—raising the temperature of the coke bed—followed by the second endothermic reaction, in which the latter is converted to CO. The overall reaction is exothermic, forming "producer gas". Steam can then be re-injected, then air etc., to give an endless series of cycles until the coke is finally consumed. Producer gas has a much lower energy value, relative to syngas, primarily due to dilution with atmospheric nitrogen. Pure oxygen can be substituted for air to avoid the dilution effect, producing gas of much higher calorific value.

The synthesis gas can be used for power/heat generation or further transformed into diesel range hydrocarbons by Fischer–Tropsch synthesis. Since products of synthesis gas conversion by the Fischer–Tropsch reaction contain olefins and oxygenates, there is considerable interest in combining a Fischer–Tropsch metal, such as Fe, Co or Ru, with ZSM-5 to form a bifunctional catalyst. These catalysts exhibit improved selectivity for a gasoline-range product, and synthesis gas can be converted to gasoline-range hydrocarbons in one step.

5.2.1.2 Dolomite and Olivine

$MgCO_3CaCO_3$ (Dolomite) is a magnesium ore widely used in biomass gasification since the tar content of the produced gases during the biomass conversion process is significantly reduced in the presence of Dolomite [8–10]. In addition, this catalyst is relatively inexpensive and disposable, so it is possible to use it in bed reactors as primary catalysts as well as in secondary, downstream reactors. The studies related to the catalytic effect of dolomite during biomass gasification are mainly focused on reformation of higher molecular weight hydrocarbons (tar). Steam gasification of biomass in the presence of dolomite leads to the efficient removal of coke formed on the catalyst surface and thus product selectivity is significantly enhanced. On the other hand, olivine [$(Mg,Fe)_2SiO_4$], another effective catalyst for biomass gasification, is also an attractive material regarding stability in fluidized bed reactors [11] due to its attrition resistance. Olivines also possess very low surface areas (about 0.4 $m^2 \, g^{-1}$), normally being an order of magnitude less than those of dolomites. The advantages of both catalysts are their low price and high attrition resistance. However, olivines and dolomites have higher calcination temperatures and this restricts the effective use of both catalysts.

In fact, calcination of both materials leads to several unwanted phenomena such as losing tar conversion activity and catalyst stability, reducing surface area, etc.

5.2.1.3 Alkali Metal Catalysts

Alkali metals such as lithium, sodium, potassium, rubidium, cesium can be used directly as catalysts in the form of alkali metal carbonates or supported on other materials such as alumina and silica. Alkali salts are mixed directly with the biomass as it is fed into the gasifier. Addition of alkali metals to biomass can also be achieved by impregnation. These metals are highly reactive. Alkali metals as catalysts lead to an enhancement for the biomass gasification reactions, especially for the char formation reactions.

Alkali metals could act as promoters present in commercial steam-reforming catalysts by enhancing the gasification reaction of carbon intermediates deposited on the catalyst surface [8]. But, the major disadvantages of these catalysts are their loss of activity due to particle agglomeration. In addition, 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. Alkali metal catalysts are also active as secondary catalysts. Potassium carbonate supported on alumina is more resistant to carbon deposition although not as active as nickel [8].

According to previous studies, the addition of Na_2CO_3 enhances the catalytic gasification of rice straw compared with nickel catalyst and significantly increases the formation of gas, and the catalytic activity of single salts in steam gasification depends on the gasification temperature, with the following order of activity: $K_2CO_3 > Ni(NO_3)_2 > K_2SO_4 > Ba(NO_3)_2 > FeSO_4$ [12].

Better interaction between feedstock and catalyst should be provided to get the enhanced performance of the catalyst. Impregnation has many advantages over mixing directly. Mudge et al. studied the catalytic steam gasification of wood using alkali carbonates and naturally occurring minerals, which were either impregnated or mixed with the biomass. They reported that the impregnation decreased particle agglomeration [13].

According to Hallen et al. the presence of Na_2CO_3, K_2CO_3 or $CsCO_3$ as catalyst in biomass steam gasification decreased the carbon conversion degree to gas. However, an increase in the rate and total amount of gas produced was observed. The presence of a catalyst increased the char yield during the volatilization stage but then decreased the char yield during the second stage of the gasification process. [14].

5.2.1.4 Nickel-Based Catalysts

Nickel-based catalysts have been widely used for syngas production in the petrochemical industry. These types of catalysts are very effective for the catalytic hot gas cleanup during biomass gasification. Elimination of tar is also accomplished

by Ni-based catalysts with a high rate. The mechanism of tar elimination can be summarized as follows [15]. Adsorption of hydrocarbons (C1–C7) and water onto the nickel surface is the first step in tar removal. Then, the OH radicals migrate to the metal sites at suitable temperatures and this leads to the oxidation of the intermediate hydrocarbon fragments and surface carbon to $CO + H_2$.

High tar levels on the generated gases lead to coke deposition on the nickel surface and deactivation occurs restricting the routine use of the catalyst. Regeneration of the catalysts might have a positive effect on removal of coke.

Simell et al. investigated the effect of different process parameters on sulfur poisoning of nickel catalysts in tar (toluene), ammonia and methane decomposition [16]. Removing sulfur from the gas mixture leads to the recovered catalyst activity for tar removal. Not only sulfur, but also chlorine and alkali metals might show a poisoning effect.

Ni-based catalysts have also been used for the production of hydrogen-rich product gas as proposed by Wang et al. [17]. They produced significant amounts of hydrogen from acetic acid and hydroxyacetaldehyde in the presence of a Ni-based catalyst. In addition, noble metal catalysts such as Ru, Pt and Rh are considered to be the most important catalysts in hot gas cleaning processes. They are highly effective to remove tar and to help improve the content of syngas. However, they are more expensive than nickel-based catalysts.

For example, nickel-based catalysts were reported as very effective for tar conversion in the secondary reactor at around 700–800°C, resulting in about 98% tar removal from product gas [18]. Asadullah et al. [19] used Rh/CeO_2/M (M5 SiO_2, Al_2O_3, and ZrO_2) type catalysts with various compositions for the gasification of cellulose in a fluidized bed reactor at 500–700°C. Compared with the conventional nickel and dolomite catalysts and other compositions of Rh/CeO_2 catalyst, Rh/CeO_2/ SiO_2 with 35% CeO_2 was found to be the best catalyst with respect to the carbon conversion to gas and product distribution. Addition of steam contributed to the complete conversion of cellulose to gas even at 600°C. Moreover, although they directly used the catalyst in the primary reactor, tar formation was not observed. This is an encouraging result because even if the use of catalyst in the primary reactor offers the benefit of simplification of the overall process, there are very few studies focusing on the direct use of catalysts in the primary bed due to severe catalyst deactivation. Ni-based catalysts are regarded as popular and also very effective for hot gas cleaning [20]. The recent advancement of nanocatalysts has made it possibleto upgrade the produced syngas and to reduce the tar formation in gasification of biomass. In a direct gasification of sawdust, Li et al. [21] used nano-Ni catalyst (NiO/ g-Al_2O_3), and demonstrated that their catalyst can significantly improve the quality of the produced gas and meanwhile efficiently eliminate the tar generation.

5.2.2 Catalyst Types for Biomass Pyrolysis

Pyrolysis is the thermal heating of materials in the absence of oxygen, which results in the production of three categories: gases, pyrolytic oil and char [22, 23].
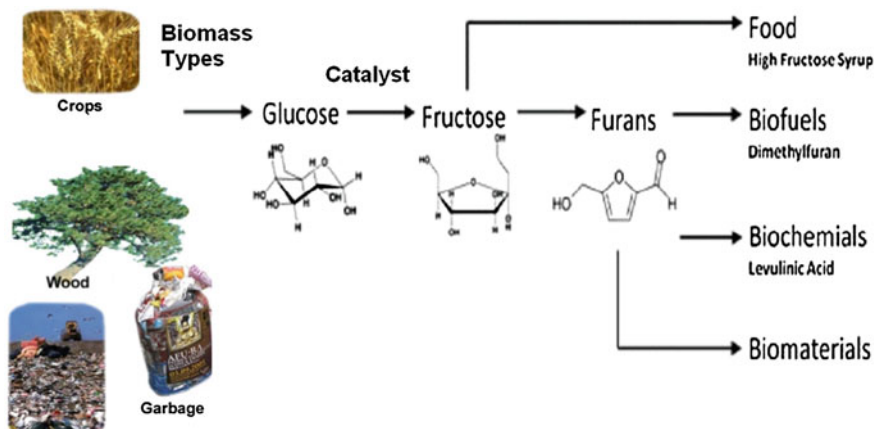
Fig. 5.2 Effect of catalysts on biomass conversion

Pyrolytic oil, also known as "tar or bio-oil", cannot be used as transportation fuels directly due to the high oxygen (40–50 wt%) and water contents (15–30 wt%) and also low H/C ratios. However, pyrolytic oil is viscous, corrosive, relatively unstable and chemically very complex [1, 24–26]. To use bio-oil as a conventional liquid transportation fuel, it must be catalytically upgraded [31]. Catalytic pyrolysis (Fig. 5.2) is an acceptable method for improving the quality of pyrolytic oil such as removal of oxygen, increasing calorific value, lowering the viscosity and improving stability. Many researches have been carried out on upgrading pyrolytic oil in the presence of different catalysts such as HZSM–5, MCM41, Al_2O_3, Al_2O_3/B_2O_3, Na_2CO_3, NaOH, NaCl, Na_2SiO_3, TiO_2, Fe/Cr, etc. [27–30]. Upgrading of the gaseous products from pyrolysis can also be achieved by reacting the vapors directly with a catalyst (in situ pyrolysis).

ZSM-5 is an aluminosilicate zeolite with a high silica and low aluminum content. Its structure is based on channels with intersecting tunnels (Fig. 5.3). The aluminum sites are very acidic. The substitution of Al^{3+} in place of the tetrahedral Si^{4+} silica requires the presence of an added postive charge. When this is H^+, the acidity of the zeolite is very high. The reaction and catalysis chemistry of the ZSM-5 is due to this acidity.

Zeolite catalysts added into the pyrolysis process can convert oxygenated compounds generated by pyrolysis of the biomass into gasoline-range aromatics. Using zeolite catalysts in pyrolysis, Carlson et al. [31] reported that gasoline-range aromatics can be produced from solid biomass feedstock in a single reactor at short residence times (less than 2 minutes) and at intermediate temperatures (400–600°C). In fact, acidity of an ideal catalyst for biomass pyrolysis should be manupilated by various methods such as ion exchange with alkalis. Silica–alumina containing catalysts (weak acids) might also be given as an example.

Mobile crystalline material (MCM-41) is one of the most used catalysts for the conversion of biomass to value-added products during pyrolysis (Fig. 5.4).
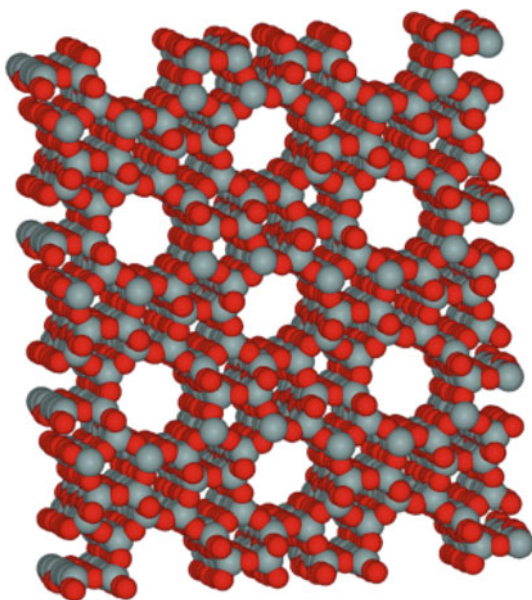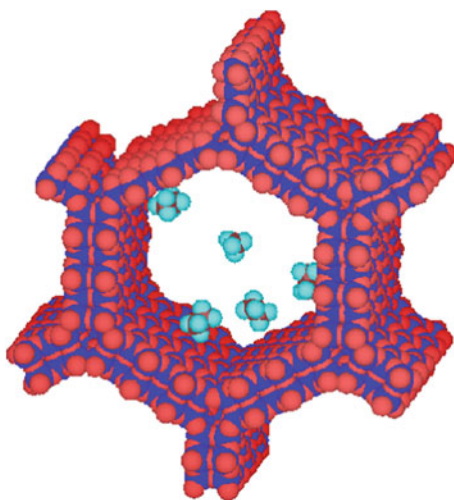
Fig. 5.3 Structure of zeolite
(ZSM-5)

Fig. 5.4 The hexagonal pore
structure of molecular sieve
MCM-41 (*red* oxygen, *blue*
silicon, *light blue* hydrogen,
brown carbon)

Pore size of MCM-41 is relatively narrow and this catalyst has a large surface
area (>1000 m^2 g^{-1}). MCM-41 type mesoporous catalysts converted the pyrolysis
vapors into lower molecular weight products, and hence, more desired bio-oil
properties could be achieved. The catalytic properties of MCM-41 materials can be
significantly improved when specific transition metal cations or metal complexes
are introduced into the structure. Pore enlargement allows the processing of larger
molecules. Different pore sizes were obtained by altering the chain length of the

Table 5.1 Effect of catalysts on the yields during biomass (beech wood) pyrolysis [33]

Catalyst	Total liquids	Organics (Bio-oil)	Water (Bio-oil)	Gases	Coke	Oxygen
Non-catalytic	60.23	38.84	21.4	16.72	–	38.4
Zeolite silicalite	47.58	17.79	30.8	26.70	2.71	23.14
ZSM-5	43.95	9.98	33.97	30.08	2.87	14.21
Al-MCM-41	45.34	15.28	30.06	24.07	7.65	23.07
Al_2O_3	38.71	7.67	31.03	28.18	9.95	26.42

template and by applying a spacer. Due to the activity of the catalysts, the product distribution of pyrolysis vapors changed significantly. In accordance with published reports, higher coke and water formation was observed during the reaction in the presence of the catalysts. The various catalysts showed different influences on the product distribution, and the greatest difference was achieved by using the unmodified Al-MCM-41 catalyst [32].

Stefanidis et al. [33] recently investigated the catalytic activity of Silicalite, ZSM-5, MCM41 and Al_2O_3 for the pyrolysis of beech wood. The results are given in Table 5.1. They found that the use of strongly acidic zeolite H-ZSM-5 leads to a decrease in the total liquid yield (bio-oil) while decreasing the organic phase of bio-oil and increasing its water content, accompanied by an increase of gases and formation of coke on the catalyst.

According to this study, it was found that zeolite silicalite with very low number of acid sites and the mildly acidic Al-MCM-41 induced similar effects with those of H-ZSM-5 but to a less extent, except of the significantly higher coke that was deposited on Al-MCM-41. With regard to the composition of bio-oil, all the catalysts and mostly the strongly acidic H-ZSM-5 zeolite reduced the oxygen content of the organic fraction, mainly by decreasing the concentration of acids, ketones and phenols.

5.2.3 Nanocatalysts for Biomass Conversion

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysts. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive candidates for use as catalysts. Nanoparticles of metals, semiconductors, oxides and other compounds have been widely used for important chemical reactions.

In recent years, nanomaterials have attracted extensive interest for their unique properties in various fields (such as catalytic, electronic and magnetic properties) in comparison with their bulk counterparts. In view of biomass conversion, nanocatalysts come into view as one of the most promising additives to make fuel combustion complete and fast, decrease ignition time, and therefore produce little or non-toxic by-products. In fact, the large surface areas of nanoscale catalysts as

well as reports on novel chemical reactivity of particles with nanometer dimensions make these materials highly interesting.

Only limited studies are available in the open literature for the application of nano metal oxides in biomass pyrolysis/gasification [34, 35]. Regarding increased relative surface area of the nanomaterials, it is highly expected that nanocatalysts would have a better catalytic activity in enhancing the performance of biomass gasification/pyrolysis. Gökdai et al. found that variation in pyrolysis temperature had a distinct effect on gas evolution in the presence of nano SnO_2 particles [36]. The maximum gas yield in this study was obtained by nano SnO_2—hazelnut shell interaction at 700°C, while the pyrolytic oil yield obtained by nano SnO_2 at 700°C reached its minimum value compared to the other catalysts used. This behavior of nano SnO_2 can be explained by accelerated primary and secondary decomposition reactions of hazelnut shell in the presence of nano SnO_2 due to the size (3–4 nm) and larger external surface area of the nanoparticles as given by Li et al. [34]. This behavior of nano SnO_2 can also be seen by the comparison of the yields obtained by bulk SnO_2. In view of the gaseous products generated, nano SnO_2 showed better performance at higher temperatures among the catalysts used.

Li et al. prepared nano NiO and tested its activity during biomass pyrolysis using a thermogravimetric analyzer [34]. Lu et al. investigated that nano TiO_2 and its modified catalysts were used for experiments and confirmed to have some good catalytic activities [37]. In this study, six nano metal oxides were used as catalysts to test whether they had the capability to upgrade the fuel properties of bio-oil or maximize the formation of some valuable chemicals. The experiments were performed using an analytical Py-GC/MS instrument which allows direct analysis of the pyrolytic products. The catalytic and non-catalytic products were compared to reveal the catalytic capabilities of these catalysts.

Among the six nano metal oxides, CaO was the most effective catalyst in altering the pyrolytic products. It reduced most of the heavy products (anhydrosugars and phenols), and eliminated the acids, while it increased the formation of hydrocarbons and cyclopentanones. Moreover, it increased four light products (acetaldehyde, acetone, 2-butanone and methanol) greatly, which made the catalytic bio-oil a possible raw material for the recovery of these products. ZnO was a mild catalyst because it only slightly altered the distribution of the pyrolytic products. With regard to the other catalysts, they all reduced the linear aldehydes, while they increased the methanol, linear ketones, phenols and cyclopentanones levels. They also reduced the anhydrosugars remarkably, except for NiO. Moreover, the catalysis by Fe_2O_3 was capable of forming various hydrocarbons, but with several PAHs. These catalytic effects suggested a potential for bio-oil quality improvement, due to the enhanced stability promotion due to the reduced aldehyde levels and increased methanol, and the heating value increase by the formation of cyclopentanones and hydrocarbons. In addition, the increased phenol content after catalysis enabled the recovery of the valuable phenols from the catalytic bio-oils. However, none of these catalysts except CaO were able to greatly reduce the acids, which could be a problem for the use of catalytic bio-oils as liquid fuels.

5.3 Conclusion

The sharp increase in the worldwide oil prices will play an important role in the realization of alternative, renewable energy systems such as bio-oil production, syngas generation from biomass in which the types of catalysts play an important role. Although catalytic behaviors of catalysts differing in acid/base properties, metal (Ni, Pt, etc.) content and porous structure on thermal biomass conversion are widely known, it is needed to develop new types of catalysis for biomass conversion in order to improve the quality of products. Nanoparticles with increased surface area are attractive candidates for such applications.

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