

Chapter 9

Catalytic Gasification of Lignocellulosic Biomass

C.V. Pramod and K. Seshan

Abstract Gasification of lignocellulosic biomass has attracted substantial current research interest. Various possible routes to convert biomass to fuels have been explored. In the present chapter, an overview of the gasification processes and their possible products are discussed. Gasification of solid biomass and steam and aqueous-phase reforming is discussed with a special emphasis on supercritical condition operations. The production of synthesis gas from biomass and its contaminants with their permissible limits are covered along with the cleanup and upgrading of the resulting syngas. The chapter ends with conclusions and an outlook for future opportunities and challenges.

Keywords Biomass gasification • Aqueous-phase reforming • Process and catalyst development • Synthesis gas • Fischer-Tropsch

9.1 Introduction

Lignocellulosic biomass is essentially a combination of cellulose, hemicellulose, and lignin. Lignocellulose is abundant and is available from different sources such as woody, nonwoody, and organic wastes. Composition of the lignocellulosic biomass depends on the material that it originates from, and biomass that is considered a waste or by-product and does not compete with the food supply is a possible source for renewable fuels and chemicals. Three conceivable approaches for the conversion of biomass are fast pyrolysis liquefaction (moderate temperature, ~500 °C, with short residence times, < 1 s), carbonization (~200 °C, 1–12 h), and gasification (>800 °C, 10–20 s).

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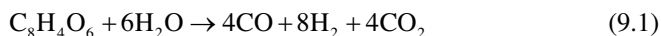
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Pyrolysis aims at producing a bio-oil that can be a source of fuels or chemicals, while carbonization results in solid fuels for heat and electricity production.

In general, the term “gasification” is associated with the conversion of solid feedstock, i.e., here lignocellulose, to gaseous products such as CO, CO₂, H₂, CH₄, and higher hydrocarbons. This chapter highlights the gasification of biomass to form synthesis gas (CO + H₂), thereby providing a route to various products such as methanol, dimethyl ether (DME), or H₂. In the gasification step, biomass (whose generic average composition is C₈H₄O₆) undergoes oxidation to give synthesis gas. When water is used as an additional oxygen and hydrogen source, the reaction is termed steam reforming and proceeds according to Eq. 9.1.



Even though gasification of solid biomass is currently attempted, transport logistics and easier handling suggest that liquefied biomass would be a more relevant feed for gasification. Solid biomass can be converted to bio-oil by the pyrolysis process. The oil has the same chemical composition, but higher energy density. Thus, gasification activities in the coming years will revolve around conversion of both solid and liquid biomass-based feedstocks.

Over the last many years, a tremendous amount of expertise has been established in the gasification of solid (coal) and liquid (fossil oil) feedstocks. Logically, know-how and experience in these areas are often applied to biomass gasification for first attempt experiments based on past experience in the area of coal/fossil oil gasification. Certainly, biomass gasification, even though more complex, can learn from past activities on coal/oil gasification. In this context, a brief description of the developments in the area of coal gasification is relevant and given below.

9.1.1 Background on Coal/Fossil Oil Gasification

A considerable coal gasification industry existed in Europe already around 1850. In those early days, the gas was used for lighting, industrial heating, and as feed for the internal combustion engine (power generation). Air, steam, and carbon dioxide were all oxidants for the gasification. A real breakthrough in the technology was the Siemens gasifier (1861). The Siemens gasifier was the first continuous process which had spatially separated combustion and gasification sections. All early gasifiers were air-blown fixed-bed reactors with a maximum temperature in the gasification zone of about 900 °C. Winkler introduced the first alternative to the fixed-bed gasifier in 1926 by developing a low-temperature fluidized bed gasifier. The advantages of a fluidized bed over a fixed-bed gasifier were claimed to be the ability to accept all types of coal, especially smaller-sized coal, and allow for more ash removal flexibility.

The availability of oxygen on a plant scale (Linde process) and advances made in the manufacturing of high-pressure vessels set off the development of

high-pressure oxygen-blown gasification. The Lurgi dry-ash (1936) process was the first oxygen-blown moving-bed gasifier. Like the Siemens gasifier, the Lurgi gasifier was operated at temperatures below 1000 °C in order to prevent ash melting. This system is, though in slightly modified form, still in operation today (e.g., by SASOL). In 1938, the Koppers-Totzek entrained-flow gasifier came into commercial operation. The Koppers-Totzek gasifier produced synthesis gas containing no tars and methane on a continuous basis at ca. 1850 °C and atmospheric pressure from oxygen-entrained coal. At the end of the 1940s and the early 1950s, Texaco, Lurgi, and Shell all developed technologies for the production of the synthesis gas by oil gasification. These were entrained-flow reactors with top-mounted burners (atomizers) in the down flow. Operating pressures and temperatures were up to 80 bar and in the range of 1250–1500 °C, respectively. Currently, most oil gasifiers are part of a refinery and are used for poly-generation of power, H₂/synthesis gas mixtures, and steam. In the early 1970s, coal gasification became attractive again as a result of the oil crisis. It was again Texaco and Shell (together with Krupp-Koppers) that developed entrained-flow high-pressure (20–70 bar) and high-temperature (>1400 °C) coal gasification.

Two points from these developments are significant and relevant for the current situation. No catalyst was/is used in commercial coal or oil gasifiers so far; thus, catalyst development for biomass-based gasification needs new, dedicated, smart efforts. On the positive side, experience and infrastructure (even facilities) availability can be taken advantage of to minimize development time and process costs.

9.1.2 Biomass Gasification: Early Developments

Early developments in sustainable energy occurred around the World War II when a large part of the cars and trucks were powered by gas produced from built-in wood and waste gasifiers. In that time Germany started to produce Fischer-Tropsch diesel from wood-derived synthesis gas. These developments were motivated by the scarcity of liquid fuels and to attain independence from imported oil. After the war, the interest in bio-based fuels rapidly declined because of the increasing availability of cheap crude oil. The oil crisis in the 1970s caused a small revival, but it was more due to the increasing awareness of the environmental problems of using fossil fuels that put biomass gasification back on the map.

In the 1970s, against the background of a foreseen natural gas shortage, research into catalytic gasification of coal for the production of synthetic natural gas (SNG) was started. The Exxon CCG (catalytic coal gasification) process reached the demonstration phase but was abandoned and did not become commercialized due to several issues such as (i) the discovery of new gas fields, (ii) difficulty in the recovery of the potassium used as catalyst from the ash, and (iii) the overall economics of the process [1].

9.1.3 Types of Gasification Processes and Products

In the beginning biomass gasification was primarily placed in combination with heat and power generation. At present, production of liquid fuels and chemicals via synthesis gas is also regarded as an interesting route. Developments in the coal and oil industry so far have led to three typical gasifiers, viz., fixed-bed, fluid bed, and entrained-flow reactors. From the extensions of these archetypes and combinations of them, several derived systems were developed such as slugging fixed beds, circulating fluid beds, high-temperature fluid beds, twin reactors with separate zones for reduction and oxidation, etc. These gasifiers are listed in Fig. 9.1. For a complete and detailed overview of coal and oil gasification, readers are referred to “Gasification Processes” by Higman and van der Burgt [2].

Gasifiers are operated below 950 °C (low-temperature gasifiers) to generate the so-called fuel gas consisting of CO, H₂, CO₂, H₂O, C_xH_y, C_xH_yO_z, tars, and N₂ (in the case of air-blown gasification). This gas mixture needs extensive conditioning (toward synthesis gas) and cleaning before it can be used as feed for the production of fuels and chemicals. Tars are the Achilles heel of this technology, as these polycyclic components cause fouling (condensation) problems in downstream units. Operation above 1300 °C (high-temperature gasifiers) can result in a relatively cleaner synthesis gas (CO, H₂, CO₂, H₂O). Intermediate gasification temperatures of 950–1300 °C are not favorable because the ashes in the feed become partly molten, a situation that is almost impossible to handle in a reactor (see Fig. 9.1). Both fuel gas and synthesis gas need extensive cleaning (removal of S, N, Cl, alkalis, tars) before entering a catalytic conversion step to make fuels and/or chemicals.

Biomass gasification is basically the same technology as coal when solid biomass is used. In this context, liquefied biomass (bio-oil) should take ideas from oil gasification. Gasification processes for biomass need to take into account very wet feedstocks. Differences between biomass and coal are (i) the oxygen content of biomass (~40 wt%), (ii) the differences in ash (mineral) composition, and (iii) the reactivity. The differences in reactivity become clear when analyzing the main gas-

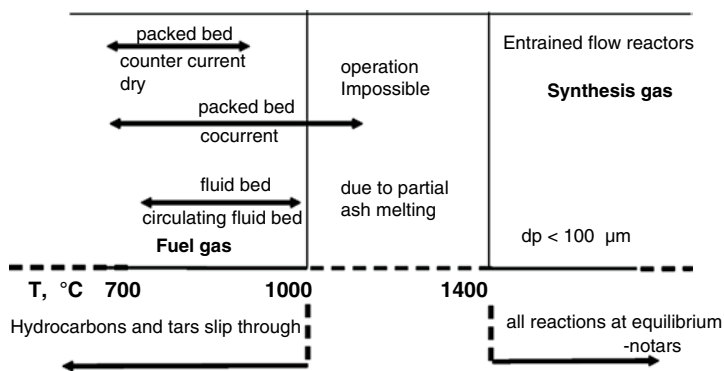


Fig. 9.1 Typical gasifiers developed and their temperature regimes of operation

producing step: in coal gasification, gas is produced by the heterogeneous reaction of solid carbon with H_2O and/or CO_2 , while for a solid biomass, the majority of the gas comes directly from depolymerization or devolatilization reactions of the feedstock. Complete reviews on biomass gasification and the associated problems are those of A. A. C. M. Beenackers et al. and Maniatis et al. [3, 4]. As in the case of coal/biomass combined liquefaction route, gasification route also can benefit from co-feeding opportunities.

9.1.4 Scope and Focus of the Chapter

The production routes of liquid biofuels via gasification are all through the synthesis gas (see Fig. 9.2). Synthesis gas can be produced either from solid biomass, liquefied biomass, or even aqueous streams containing low amounts (<20 wt%) of dissolved organics. The last can come from paper or food industries or even from pyrolysis liquefaction of biomass. In all the cases, the target is to produce synthesis gas which can further be used for conversion to fuels and chemicals. In case hydrogen is the desired product, an additional water-gas shift conversion ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is required [5]. Synthesis gas is currently almost exclusively made from methane [6], steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$) being the most applied route. Catalysts are mandatory for this conversion to be able to operate at lower temperatures (<900 °C).

Accordingly, most of the current biomass gasification routes take their origin, especially with respect to catalyst selection, from methane steam reforming catalyst developments. The critical issue in the case of steam reforming of lignocellulosic feedstocks is the formation of tars which cause severe catalyst deactivation. Thus, the design of catalysts that can operate under these conditions is critical.

In this chapter we will focus on the catalyst developments that are relevant to low-temperature catalytic gasification/steam reforming of (i) solid lignocellulosic biomass, (ii) liquefied lignocellulosic wood (e.g., pyrolysis oil), and (iii) aqueous biomass streams (aqueous-phase reforming (APR)). One typical case, i.e., the steam

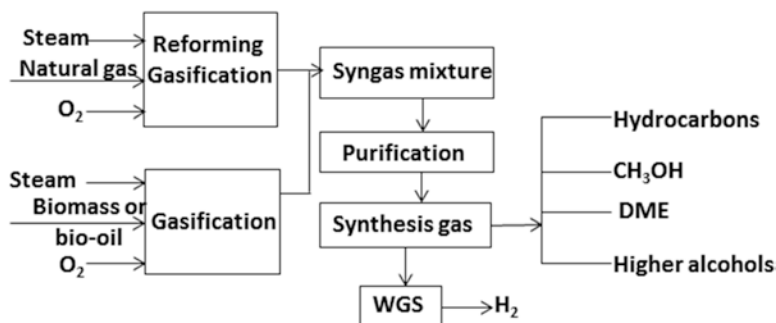


Fig. 9.2 Production of liquid fuels from natural gas and biomass

reforming of glycerol, a currently available waste by-product from biodiesel production, is presented. Finally catalytic cleaning of the thus made synthesis gas from tars, S, N, and Cl and future issues to produce fuels and chemicals are presented.

9.2 Catalytic Gasification of Lignocellulosic Biomass

Catalytic gasification deals with the application of catalysts inside the gasifier. Catalytic gasifiers typically operate below 850 °C. The reasons for applying catalysts inside the gasifier are typically (i) to reduce the conditioning and cleaning cost of the fuel gas by lowering the tar and hydrocarbon content and (ii) producing directly synthesis gas at a low temperature. Producing synthesis gas at a lower temperature decreases the costs significantly and allows smaller-scale synthesis gas production. In contrast, synthesis gas by entrained-flow gasification is reported to be economically feasible only at scales around 1 GW because of the need for an oxygen plant.

9.2.1 Catalytic Gasification of Solid Lignocellulosic Biomass

Catalysts are mostly considered for reactors of the fluid bed family, i.e., bubbling fluidized beds and circulating fluidized beds. Note that here both the feedstock and the catalyst are solids so that the catalyst only acts on the produced gases and vapors. Most of the research to date has been focused on tar removal and hydrocarbon conversion to CO/H₂. Sutton et al. [6] elaborated the criteria for a biomass gasification catalyst to be (i) effective to gasify/remove tars, (ii) capable of reforming methane, (iii) resistant to deactivation by coke/oligomer deposition and sintering, (iv) easy to regenerate, (v) robust (mechanically strong), and most importantly (vi) cheap. Dedicated efforts to develop catalysts for biomass gasification are still in early stages, and the strategy until now has been to use (i) “off-the-shelf,” commercial, and hence relatively expensive methane steam reforming catalysts or (ii) cheaper materials, e.g., dolomite-based clays and alkali salts (Na, K, chlorides) [6].

Dolomite CaMg(CO₃)₂ [7, 8] has gained the most attention as it is very cheap and easy to apply. It is applied either inside the gasifier to promote direct tar cracking or separately in a bed downstream of the gasifier. Although it can convert tars to a large extent, it is more often used as a tar reducer, i.e., as a guard material, allowing the usage of not only more active but also more sensitive catalysts downstream [9]. Dolomite is however not able to effectively convert methane and also suffers from attrition instability [8, 10]. Olivine (transition metal silicates) [10, 11] is much more resistant to attrition than dolomite but with a somewhat lower activity for tar destruction. One of the problems often encountered is the loss of catalyst in the ash, making it difficult to recover and reuse. Catalyst deactivation, catalyst makeup, and fluidization problems still need research attention before these dolomite and olivine catalysts can be effectively applied.

Alumina-supported nickel catalysts have been used in the industry for naphtha and natural gas reforming for many years, and it was therefore also logical to test them for biomass gasification applications. Several Ni-based catalysts have been investigated in fluidized beds, but they suffered from rapid deactivation, which was ascribed to carbon fouling. The current status of catalysis in solid biomass gasifiers is that they can lower the tar and the higher hydrocarbon content of the gas, which lowers the load on downstream tar removal and reforming units. There are, however, still operational problems.

Tars and hydrocarbons are therefore still dealt with predominantly downstream of the gasifier, and the status of catalysis inside gasifiers with solid biomass feeds will continue to be similar and may not change significantly anymore. This also holds true for pressurized low-temperature solid biomass gasifiers. At higher pressures, thermodynamics favor methane formation. Thus, one option for pressurized gasifiers is catalyzing the methanation reaction. At pressure above 40 bar ca. 65 %, the heating value of biomass-derived gas is present in the form of methane. Catalyzing the methanation reaction can be done with very simple (natural) catalysts like alkali [Marshall, 1981]. Methane-rich gas can be blended in the grid or can be further upgraded and pressurized to compressed natural gas (CNG) which is being used as an automotive fuel.

The design of stable catalysts for the efficient gasification of biomass should take into account the ability of the catalysts to depolymerize deposits because suppressing oligomerization is nearly impossible as it occurs on almost any surface. One possibility is to remove the coke/deposits, which deactivate the catalysts otherwise, via gasification with steam. For this, high activity reforming catalysts need to be developed, the idea being that the coke-forming precursors are also gasified and catalyst stability is improved [12]. The rate-limiting step in steam reforming is normally the activation of water [13]. Thus, new catalyst (metal/support) combinations that maximize availability of activated water on the catalyst to help gasification of also coke oligomers are essential [12]. Another option is to carry out gasification in the presence of steam and/or oxygen just as in the case of typical autothermal reforming. The role of oxygen in this case is to help to combust coke/oligomer deposits and keep the catalytic sites clean. However, the catalyst should selectively combust coke and not CO or H₂. This is certainly both a catalyst and reactor design issue.

9.2.2 Catalytic Gasification of Liquefied Lignocellulosic Biomass

Advantages of converting bioliquids rather than solid biomass are that a liquid with a high volumetric energy density is used, which is easier to handle, store, and transport, and contains less contaminants (S, Cl, N, alkalis, metals) than the biomass it is derived from. The latter (i.e., a lower contaminant concentration) is a specific advantage when using dedicated catalysts in the gasification process because of their detrimental influence on catalyst activity and stability.

Czernik et al. [14] initiated research on gasifying/reforming a bioliquid, namely, pyrolysis oil. They started research on model compounds and the water-soluble fraction of pyrolysis oil. Using a commercial nickel-based naphtha steam reforming catalyst (designed for fixed-bed operation) in a fluidized bed at ca. 850 °C and 1 bar, the water-soluble fraction of pyrolysis oil was reformed with a H₂ selectivity of 80 %. Over the run for 90 hours, the methane concentration increased and saturated at 2.5 vol.%, which indicated loss of catalyst activity. The applied steam over carbon ratio of 7 is too high to suit process economics. It was found that the application of fixed-bed catalysts in a fluidized bed led to attrition losses that were economically unacceptable.

A new fluidized bed catalyst has been developed which is able to handle the whole pyrolysis oil [15]. Special attention was given to the attrition resistance of the support. Aluminas containing MgO, SiO₂, and K₂O were found to have attrition rates as low as 0.01 wt%/h. However, in pyrolysis oil reforming tests, it was found that these catalysts still suffer from deactivation leading to methane slip [16]. van Rossum et al. [1] studied the gasification of the whole pyrolysis oil for synthesis gas production. First they applied a single fluidized bed with commercial steam reforming catalysts. This system suffered from activity loss which was ascribed mainly to the attrition and sintering of the catalyst. They proposed and tested a staged reactor consisting of an inert fluidized bed of sand particles in which the pyrolysis oil was atomized followed by a fixed catalytic bed for the gasification/reforming of vapors and gases [1]. In their two-stage concept, no additional steam was used; the process used only the water present in the pyrolysis oil.

Figure 9.3 shows the gas production as a function of time for this staged system where both beds were kept at around 800 °C. No methane production was found after six consecutive experiments (including burn-off reactivation cycles), using the same catalyst which lasted 10 h of actual gasification time in a single long-duration run (11 h). For a commercial application, this would need to be much longer, and further dedicated development work is required. The produced synthesis gas has a H₂/CO ratio of 2.3 (see Fig. 9.3), which is ideal for Fischer-Tropsch synthesis. Further, van Rossum et al. [17] reported the option of applying different temperatures in the fluidized bed and the catalytic fixed bed. It turned out that with a fluidized bed (oil atomizer) temperature of 500 °C and a catalyst bed temperature of 680 °C, a hydrogen-rich synthesis gas could be produced containing only a small amount of methane. This temperature difference opens up the opportunities for heat integration. Two strategies are under consideration for the development of catalysts, depending on the type of work, i.e., research (fundamental) or development (applied). They are (i) “off-the-shelf” catalysts developed for steam reforming of hydrocarbons used for bio-oil reforming or (ii) establish novel catalyst design principles based on studies of reforming typical oxygenates present in bio-oils.

Dedicated catalysts for the reforming oxygenated compounds were investigated by Rioche et al. [18], Takanabe et al. [13], and Basagiannis et al. [19]. These studies indicated that the steam reforming activity depends not only on the metal but also on the support used. This is because the water which is a reactant needs to be activated on the support oxide which enhances steam reforming activity. Takanabe

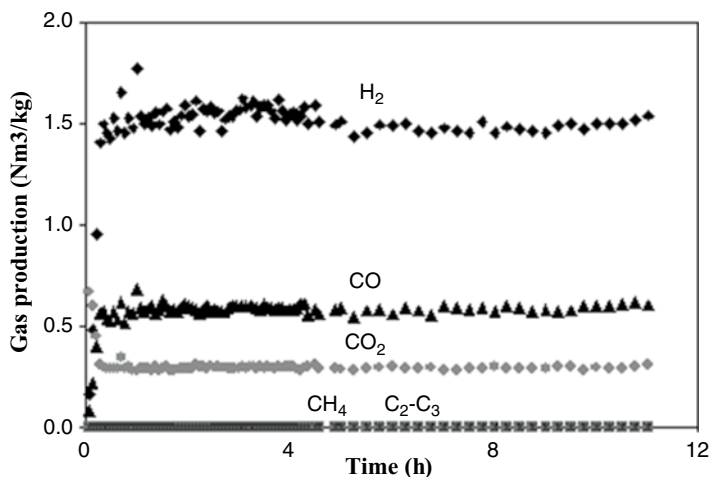


Fig. 9.3 Results of catalytic gasification of pyrolysis oil. Staged reactor concept at ~ 800 °C, 1 bar [1]

Table 9.1 Steam reforming of acetic acid over supported Pt catalysts [20]

Catalyst (0.5 wt% Pt)	Specific surface area (m^2g^{-1})	H/Pt ^a	TOF H ₂ on the perimeter (s^{-1})	
			Per accessible Pt	Per Pt on the perimeter
Pt/ZrO ₂ ^a	20	0.84	17	39
Pt/ γ -Al ₂ O ₃	111	0.99	14	28
Pt/MgO	20	0.18	3	27
Pt/ α -Al ₂ O ₃	4	0.58	5	16
Pt/SiO ₂	369	0.41	4	15

Reaction conditions: 452 °C, GHSV = 1,600,000 h⁻¹, H₂O/C = 5

et al. performed steam reforming of acetic acid [20] over Pt on various supports like ZrO₂, γ -Al₂O₃, MgO, α -Al₂O₃, and SiO₂, and the activity data is presented in Table 9.1.

The results show that the catalytic activity per Pt atom (TOF) is varying when different supports are used. Thus design of catalysts should also take into account the role of oxide support in the catalysts. These Pt-based catalysts deactivate severely due to coke formation via typical oligomerization/condensation reactions (see Fig. 9.4), which most of the oxygenates undergo. Hence, in the figure, all the routes marked by crosses need to be avoided or taken care of.

Two ways of achieving this are to (i) combust the coke and regenerate the catalyst or (ii) enhance steam reforming activity by choosing a proper metal support combination. Periodic regeneration is possible (Fig. 9.5), but the periods of catalyst stability are too small to be economically feasible. Development of a stable steam reforming catalyst is going to be very difficult as tar/oligomer formation is inevitable and only an autothermal type operation will help. Addition of trace amounts of

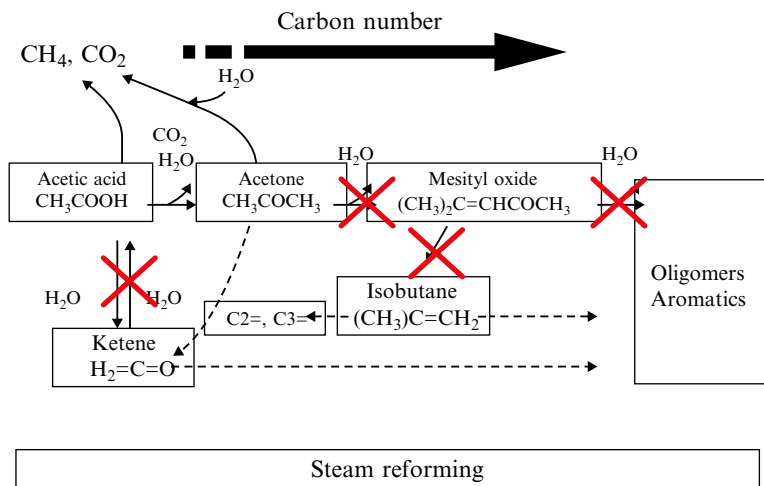


Fig. 9.4 Pathways for oligomer/coke formation

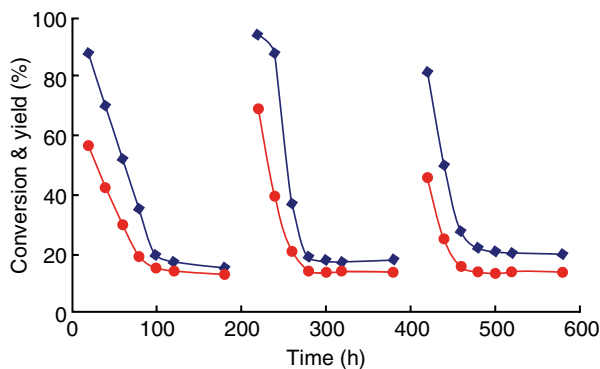


Fig. 9.5 Pt/ZrO₂ catalyst regeneration and recovery of activity. (◆) CO conversions and (●) H₂ yields (reaction conditions: 602 °C, H₂O/C=5, GHSV=160,000 h⁻¹)

oxygen to the steam reforming stream will help in situ combustion of coke as it formed and keep the catalyst stable. But as Pt-based catalysts are good combustion catalysts, it is important that the oxygen added does not combust product CO or H₂. This needs development.

Alternatively, steam reforming activity can be enhanced by choosing components like Ni, alkali, and La that help to activate water and can improve the stability. This is shown in Fig. 9.6. Addition of La also helps to prevent sintering and loss of catalyst surface area and activity [21]. However, all these catalysts will have a limited lifetime, and continuous removal of coke is essential. In our view catalytic gasification of bioliquids is however still a feasible process, as it uncouples the locations of biomass availability and processing/demand and allows for small-scale syn-

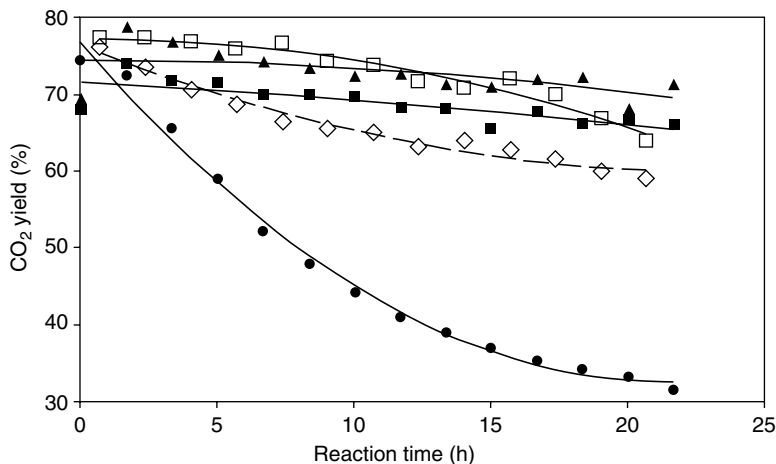


Fig. 9.6 CO₂ yield vs. time on stream for the steam reforming of acetic acid over (●) 3.5%Ni/ZrO₂, (□) 3.5%Ni/La-ZrO₂, (◇) 3.5%Ni/K-ZrO₂, (▲) 3.5%Ni/K-La-ZrO₂, (■) commercial (reaction conditions: 700 °C, H₂O/C=5, GHSV =240,000 h⁻¹)

thesis gas (with a good H₂/CO ratio) production at reasonable costs (mild temperature and no pure oxygen needed). The process has a high production rate (residence times of seconds are enough). Proof of principle is established and now process developments should follow. Catalyst development should focus on mechanical strength and stability.

9.2.3 Gasification of Aqueous Biomass Streams

Depending on the water content, biomass is classified as solid (<20 % water) or aqueous biomass which contains more than 80 % of water. These aqueous biomass streams originate from various bio/organic wastes from industries for food, paper, etc. These can also be seen as possible feedstocks for the production of synthesis gas. The conversion of this aqueous biomass into high heating value products such as hydrogen, synthesis gas, and methane using conventional reforming processes at lower pressures is energy intensive due to the need for the evaporation of water. Dumesic and coworkers tackled this problem by developing the so-called aqueous-phase reforming (APR) process [22–24] in which water is kept in the liquid phase by applying elevated pressures. The concept was demonstrated for reforming of diluted oxygenate feeds at mild temperatures in pressurized liquid water (225–265 °C, 29–56 bar) over supported metal catalysts. The phase diagram of water is shown in Fig. 9.7, which shows the pressures required to keep the hot water in the liquid phase.

Dumesic et al. reported the thermal dependence of the standard Gibbs free energy for the water-gas shift and ethylene glycol reforming reactions in liquid and vapor

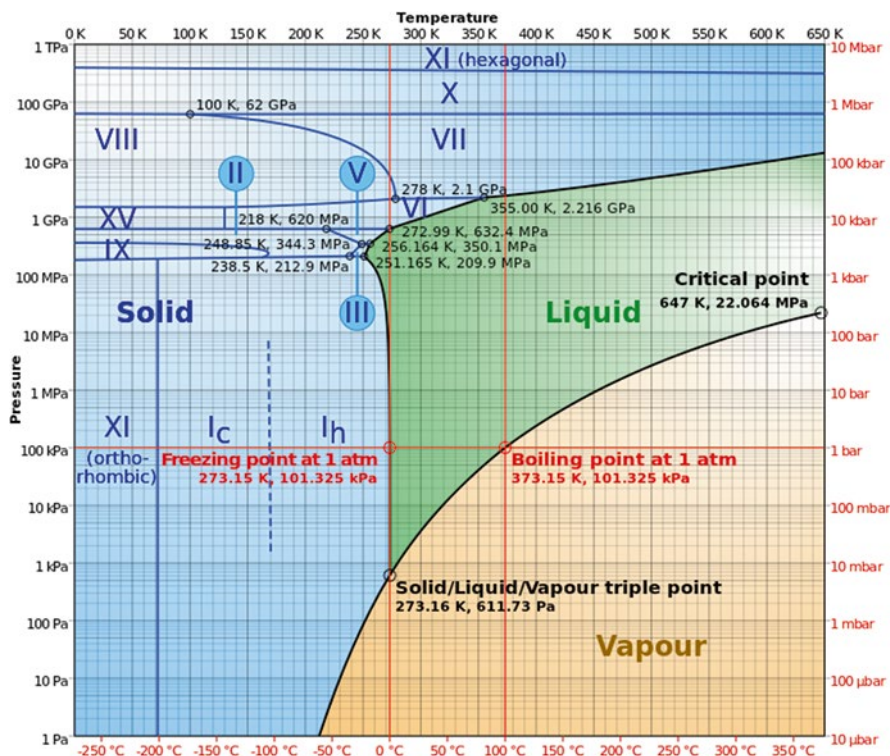


Fig. 9.7 Phase diagram of water (Source: Wikimedia Commons)

phase as shown in Fig. 9.8. The Gibbs free energy of the water-gas shift reaction in liquid phase was reported to be negative and temperature independent in the range 300–650 K (27–375 °C). In the case of the vapor-phase water-gas shift reaction, the reaction becomes less favorable at higher temperatures. The reforming of ethylene glycol in liquid phase compared to vapor phase becomes more favorable beyond 450 K (175 °C). The advantages of APR are (i) there is no need of evaporation of the water and (ii) the water-gas shift activity and reforming are more favored in liquid phase than in vapor phase at temperatures above 175 °C.

Cortright et al. [22] showed that aqueous-phase reforming (APR) of dilute biomass-based oxygenate streams (glucose, alcohols such as ethylene glycol, methanol, etc.) at low temperatures (<265 °C) and medium pressures (25–50 bars) offers a possibility to convert them into a hydrogen-rich gas containing CO₂ and trace amounts of CO and alkanes. A reaction network was suggested by Dumesic et al. and is shown in Fig. 9.9. The oxygenated hydrocarbon undergoes dehydrogenation and adsorption on the catalyst surface. The intermediate formed can further react through two pathways. The desired pathway to form hydrogen involves C-C cleavage, which results in H₂ gas and adsorbed CO. Hydrogen yields can be further increased by the water-gas shift reaction (CO + H₂O → CO₂ + H₂). The undesired pathway involves cleavage of the C-O bond leading to species such as acids and

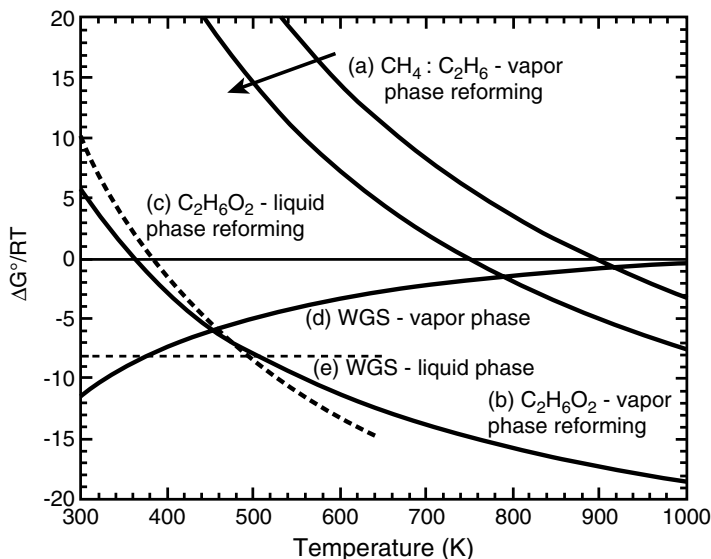


Fig. 9.8 Thermodynamic calculations for the steam reforming and WGS in vapor and liquid phase for ethylene glycol. Values for CH_4 and C_2H_6 are given for comparison (Reprinted from Ref. [25], Copyright 2003, with permission from Elsevier)

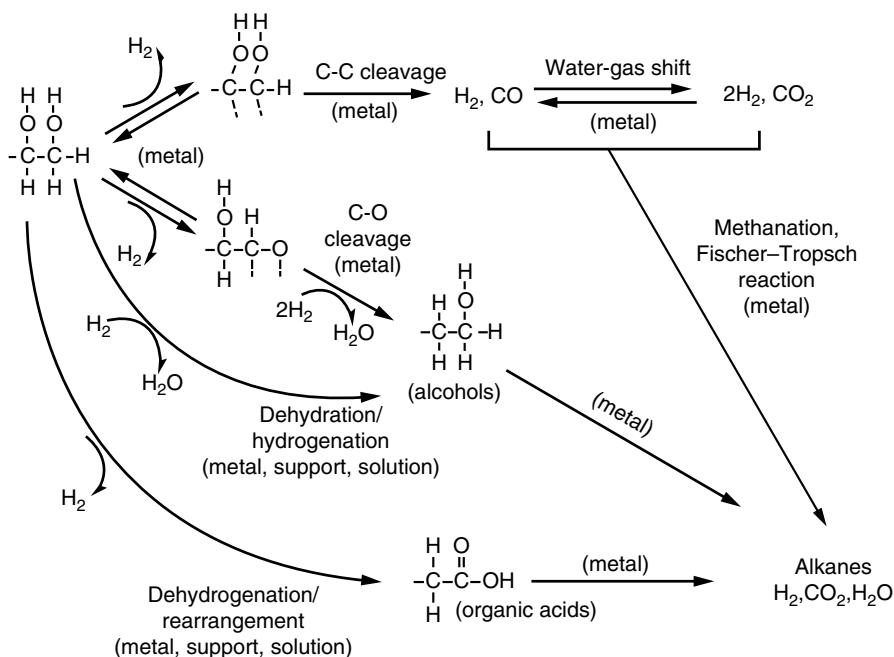


Fig. 9.9 Reaction pathways for production of H_2 by reactions of oxygenated hydrocarbons with water (*asterisk* represents a surface metal site) (Reprinted by permission from Macmillan Publishers Ltd: Ref. [22], Copyright 2002)

alcohols that further undergo sequential reforming to produce alkanes. Other pathways leading to undesired products include dehydration which leads to vinyl alcohols thereby producing mono alcohols on further hydrogenation. Direct hydrogenation of CO_x can also lead to the formation of CH_4 or even higher alkanes through the Fischer-Tropsch process.

Pt/ Al_2O_3 catalyst gave the highest hydrogen yields, but the catalyst was not very stable. The process is interesting because (i) it avoids the need to evaporate water and oxygenates as in a gas-phase reforming, thus leading to savings in energy, (ii) the higher water pressures allow for high WGS conversions producing hydrogen gas with trace amounts of CO (<1000 ppm), and (iii) it gives a single-step conversion to hydrogen. Low temperature and higher pressures also favor hydrogenation of oxygenates and give methane or higher alkanes.

The CO content of the gas depends on the ability of the catalyst to affect the WGS. This can be manipulated by adding a second component to Pt catalysts. WGS activity is determined by the catalyst's ability to adsorb and activate CO. Pt-Ru/C which is a weak WGS catalyst gives H_2/CO ratio of 1.3, and Pt-Re which is a much better WGS catalyst gives H_2/CO ratio of 2 [26]. The latter composition is also suitable for a FT feed ($\text{CO} + 2 \text{H}_2 \rightarrow -[\text{CH}_2]_n + \text{H}_2\text{O}$). Pt-Re catalysts when supported on carbon are also reasonably stable (50 h). Issues that are still open are (i) selectivities to methane and alkanes and (ii) the cost of the process.

When the water is present as a liquid in the reforming process, it is considered as aqueous-phase reforming. If the high temperatures and high pressures are maintained, then water goes into its supercritical state and the reforming of biomass at this condition is generally termed as gasification in hot compressed water. This process ($T=250\text{--}700\text{ }^\circ\text{C}$, $P>200\text{ bar}$) is considered as another promising technique to convert such wet biomass streams to a gas that is rich in either hydrogen or methane depending on the operating conditions and applied catalysis. For this process heat exchange between the reactor effluent and the feed stream is essential, which requires operation at high pressures [27]. Without catalysis the process suffers from incomplete conversion and an uncontrollable gas distribution [28, 27]. Below, gasification in hot compressed water is discussed for low (250–400 °C) and high (>550 °C) temperature, separately.

9.2.3.1 Low-Temperature Steam Reforming of Aqueous Wastes

In the last century, Pacific Northwest National Laboratory (USA) developed a catalytic process for the destruction of organic waste at ca. 350 °C while producing a methane-rich gas [29–31]. Tests were carried out at laboratory and pilot scale focusing on both catalyst and process development. Ruthenium on rutile titania, ruthenium on carbon, and stabilized nickel catalysts showed the highest activity and the best stability. With these catalysts, nearly 100 % gasification of model components (1–10 wt% in water) was achieved, while without catalyst the extent of gasification was very limited at this temperature. The gas produced consisted of nearly only CH_4 and CO_2 , as dictated by the overall thermodynamic equilibrium.

The catalytic process was carried out in a series of fixed-bed reactors. When using feedstock with the tendency to produce char/coke, a continuous stirred-tank reactor (CSTR) was required before the fixed bed to soften the feed and to prevent the buildup of solids. Pilot plant runs using complex feeds such as potato waste and manure were carried out. The required liquid hourly space velocity (LHSV) was in the range of 1.5–3.5 $\text{Nm}^3_{\text{feed}}/\text{m}^3_{\text{cat}}/\text{h}$. For a waste disposal process, these LHSVs are acceptable, but for the production of gaseous energy carriers from biomass, the activity is rather low.

Waldner et al. [32] reported high extents of gasification and equilibrium methane yield from concentrated (up to 30 wt%) wood sawdust slurries using Raney nickel as catalyst at 400 °C. For complete gasification, a 90-min reaction time was required in their batch reactor. Nevertheless, how the catalysts enhance the extent of gasification at these low temperatures has not been completely clarified. Either they accelerate the rate of the gasification reaction relative to the rate of polycondensation/polymerization reactions, or they are able to gasify the formed polymers or a combination of both. Obviously, these catalysts catalyze all gas-phase component reactions because good agreement was found between the observed gas composition and the gas composition dictated by thermodynamic equilibrium. Reported problems with respect to the catalysts are poisoning through trace components such as sulfur, magnesium, and calcium and the growth of the active metal crystals during operation (sintering). In order to get a handle on catalyst requirements, often studies with single components have been carried with the sole aim of designing stable and efficient catalysts.

9.2.3.2 Aqueous-Phase Reforming of Model Compounds

The typical model compounds formed during the APR of ethylene glycol or sorbitol which are being part of the biowaste or the by-products of bioconversion are ethanol, methanol, and acetic acid. Steam reforming of ethanol and methanol is intensively studied, and the catalyst systems are well established. Acetic acid is one of the important by-products of the bioconversion that has been under study. APR experiment conducted for acetic acid at 275 °C and 200 bar on Pt/Al₂O₃ and Pt-Ni/Al₂O₃ is shown in Fig. 9.10. Initial conversion levels of ± 50 % were obtained. However, the conversion decreased rapidly with time for both Pt and Pt-Ni catalyst. Both the catalysts lost all activity after 3 h on stream with final conversion levels (~ 5 %) being similar to the reforming experiment without a catalyst. Deactivation of the catalyst with acetic acid is commonly observed in reforming reactions [33]. Raman spectroscopy was used to characterize the spent Pt catalysts used in the reforming of acetic acid at room temperature in air.

The spectrum obtained was depicted in Fig. 9.11, which revealed the presence of the Boehmite structure of Al₂O₃ in Pt/Al₂O₃ catalyst owing to five sharp bands between 65 and 4000 cm^{-1} (362,494,672,3076 and 3212 cm^{-1}). The difference in the hydroxyl groups and the cause of deactivation of the catalyst were further investigated by FT-IR spectroscopy. An FT-IR spectrum was recorded at room temperature

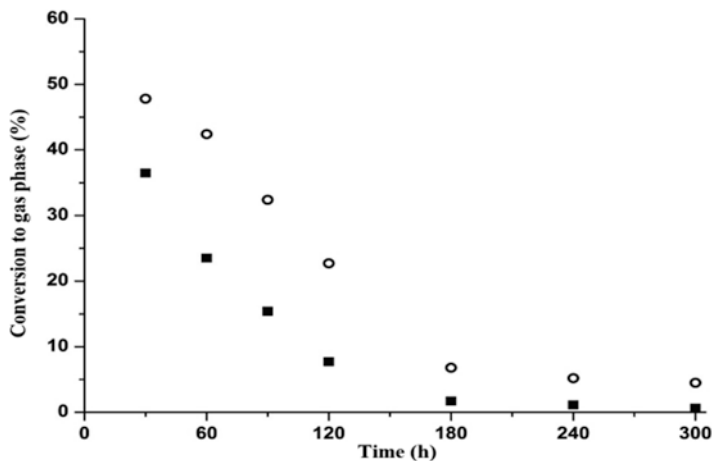


Fig. 9.10 Reforming of acetic acid over Pt catalysts for the conversion to gas phase at 275 °C and 200 bar. ○ 1.5 wt% Pt/Al₂O₃ ■ 1.15–0.35 wt% Pt-Ni/Al₂O₃

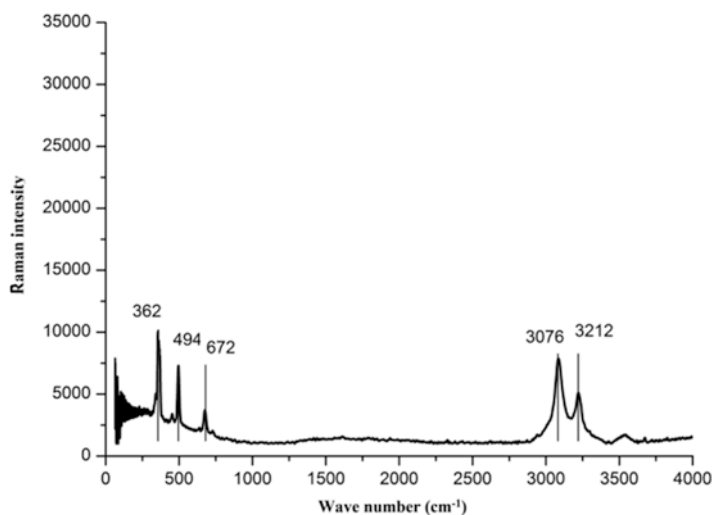


Fig. 9.11 Raman spectra of spent 1.5 wt% Pt/Al₂O₃ used for reforming of acetic acid at 275 °C and 200 bar

in air in the wave number range of 2400–1000 cm⁻¹ and normalized for sample weight shown in Fig. 9.12. The spectrum shows the presence of three strong bands which are located at one in the region 1000–1200 cm⁻¹ due to lattice vibration and two other bands at 1975 and 2112 cm⁻¹ which have been suggested to originate from the complex Al-O-H zigzag structures in Boehmite [34]. These results indicate the presence of a highly hydroxylated type of Boehmite structure in the catalyst that is responsible for deactivation.

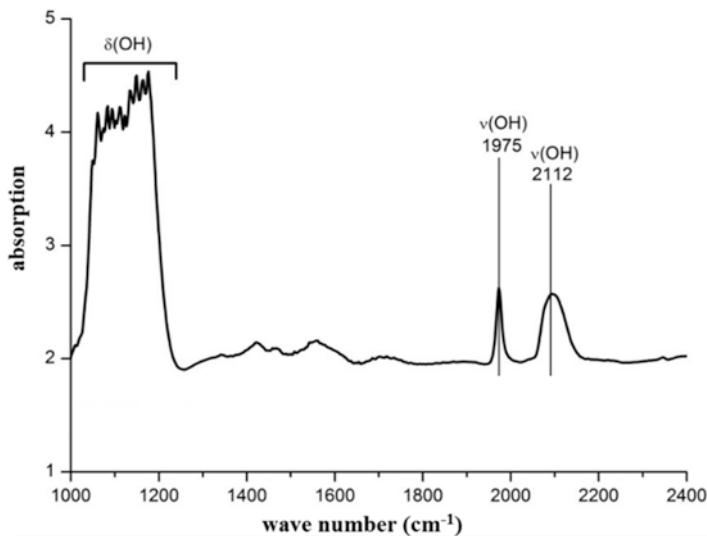


Fig. 9.12 FT-IR spectra of spent 1.5 wt% Pt/Al₂O₃ used for reforming of acetic acid at 275 °C and 200 bar

To strengthen the evidence, the catalyst was also characterized by TEM technique and the resulting image is shown in Fig. 9.13. The Pt particles and the lattice distances of the Al₂O₃ are clearly visible. The Al₂O₃ lattice distance is measured from the image is 0.7 nm. The Pt particle is covered by a layer that shows the same lattice distances of 0.7 nm as alumina, indicating that the Pt is covered by alumina. Hence, the Pt sites are covered by hydroxylated alumina layer which is causing deactivation of the catalyst.

A further general problem in the near- and supercritical region is that it enhances leaching of the catalytic active phases and degeneration of the support. However, hot compressed water is a good solvent for most organic chemicals and thus especially useful to keep coke precursors dissolved. Further, if coke is formed on the surface of the catalysts, the high H₂O concentration helps in keeping it clean via gasification. In accordance with that, it was found that coke formation on the catalyst surface is a minor problem.

Huber et al. and Cortright et al. reported interesting catalysis for the production of hydrogen-rich gas from small oxygenated hydrocarbons using Raney nickel promoted by Tin [22] and Pt [35], respectively, at around 230 °C. They were able to decrease the methane formation rate via C-O bond cleavage and methanization (hydrogenation) while maintaining the high rates of C-C bond cleavage and water-gas shift for hydrogen production. High hydrogen yields were obtained for methanol, ethylene glycol, and glycerol. However, with sorbitol and glucose as feedstock, already significant amount of methane was also being produced next to hydrogen. Though in an embryonic stage, the methodology of decelerating methane producing reactions at catalytic sites while keeping a high rate of catalytic hydrogen produc-

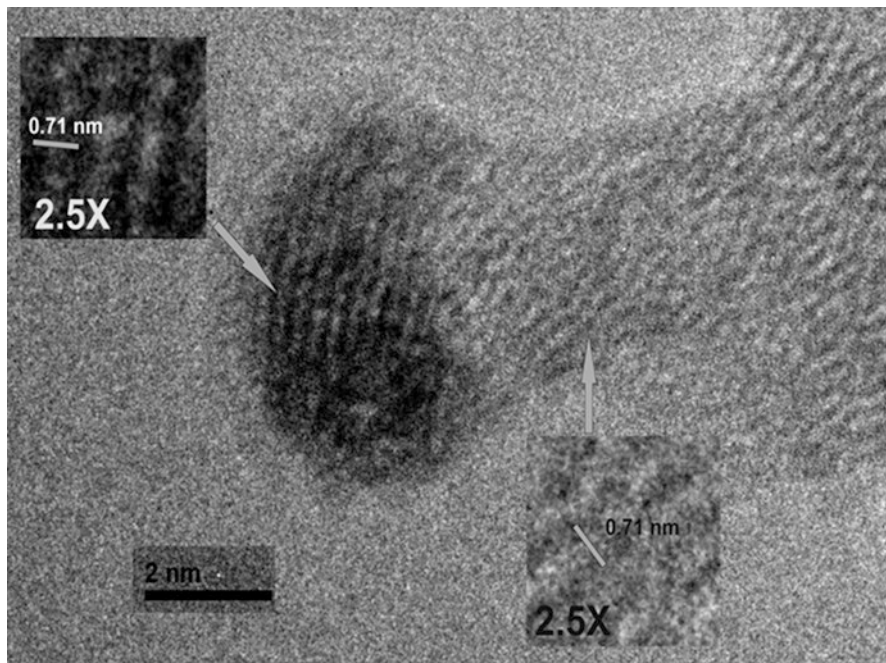
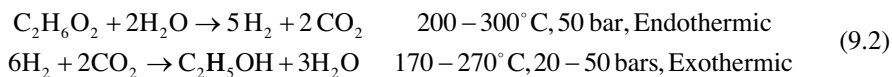


Fig. 9.13 TEM image of Pt particle covered with alumina

tion seems promising to produce hydrogen-rich gas at conditions for which overall chemical equilibrium dictates methane-rich gas, viz., at subcritical temperature and at the combination of high temperature and high concentration of organics. In this concept, it will be important to decrease homogeneous reactions to undesired by-products (oil/char/ CH_4) and to increase the reaction rate and catalyst stability against leaching. This is quite a challenge for both catalyst and reactor design. In the case of catalysts with a high WGS activity, the product gas from a typical hot compressed reforming is not suitable as synthesis gas for FT but can be used for alcohol synthesis, although this is still in the research phase (Eq. 9.2).



Reaction temperatures for the catalytic synthesis of alcohols are low, typically below 300°C alcohols, and higher pressures are favorable for equilibrium alcohol yields. This raises a variety of possibilities. The design of catalysts to work directly in hot compressed water to give methanol/higher alcohols directly from CO_2/H_2 obtained during reforming would be exciting and challenging at the same time. Figure 9.14 summarizes the various product routes.

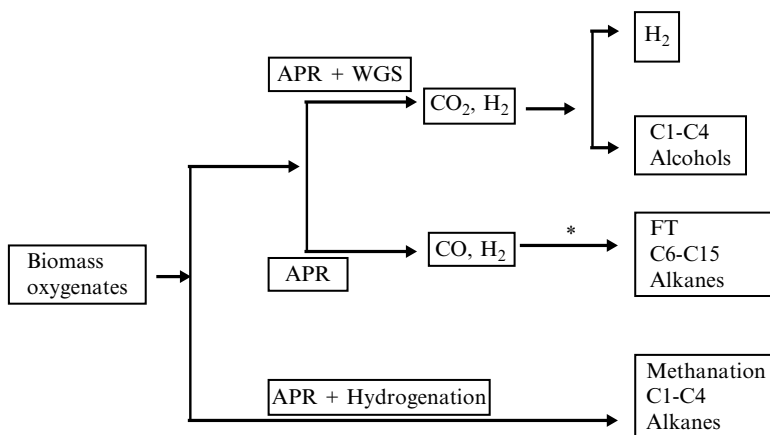


Fig. 9.14 Aqueous-phase reforming (APR) routes: * gas cleaning (S, Cl, tars very critical)

9.2.3.3 High-Temperature Catalytic Steam Gasification

For high temperatures (>500 °C), alkalis have been proposed as catalysts [6]. Alkalis promote the water-gas shift and methanation reactions leading to more hydrogen or methane production and a carbon monoxide lean gas. The studies on whether or not alkalis enhance the extent of gasification are contradictory [36, 27]. Recovery of alkalis from the process may be a problem, because alkalis hardly dissolve in supercritical water. Antal et al. [37] reported that leading the effluent over a fixed bed of activated carbon derived from coconut increased the extent of gasification from 0.7 to 1.0. Despite the successful use of this activated carbon as a catalyst on laboratory scale, it may not be the catalyst finally selected for the process. Two important reasons are (i) neither the catalytic activity nor its decline is understood and (ii) the rate of coal (carbon) gasification is slow but certainly not zero leading to consumption of the catalyst. Kersten et al. [27] used Ru/TiO₂ and found complete gasification of glucose (1–17 wt% solutions) at 600 °C and ca. 60 s residence time. The produced gas was at chemical equilibrium. The reaction is much faster at 600 °C compared to 350 °C, which is beneficial for the size of the reactor. However, no information is yet available concerning the stability of catalysts in the high-temperature-range supercritical water.

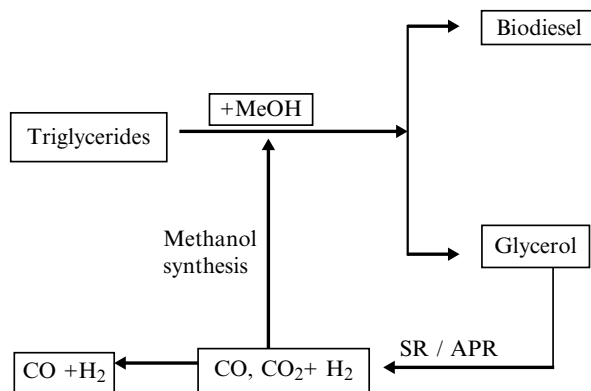
9.2.3.4 Catalytic Gasification of Glycerol as Feedstock By-Product from Biodiesel Production

Biodiesel produced from esterification will not survive in the long run as an option even when considering both algae and plant oil as sources of triglycerides. This has also to do with the large volumes of diesel consumption compared to the availability of triglycerides. However, this activity will continue in the short future especially to

meet urgent legislative requirements because there is an appreciable amount of biodiesel produced currently. As a result there is a glut of glycerol available in the market due to the methanol-triglyceride esterification activities. Prices of glycerol have dropped from around 80 c/lb by more than 50 % between 2005 and 2006. There are therefore efforts to use glycerol as a feedstock for fuels. The possibilities are shown in Fig. 9.15. There are quite a few challenges that need to be addressed for an efficient conversion (steam reforming (SR) or aqueous-phase reforming (APR)) of glycerol. Critical issues are the high boiling point (290 °C) and thermal instability of glycerol (APR is therefore more appropriate). Dehydration of glycerol is also facile and leads to olefins, ethylene, and propylene, which deactivate catalyst via coke formation. Decomposition of glycerol to methane is also favorable under steam reforming conditions and loss of H₂/syngas, which leads to selectivity issues that are to be solved. Additionally, glycerol from esterification also contains impurities such as alkalis, which can deactivate downstream catalysts.

Catalyst development is currently attempted in many laboratories. Bimetallic catalysts based on Pt-Re showed encouraging results [38]. Hirai et al. demonstrated a highly efficient 3 wt% Ru/Y₂O₃ catalyst for glycerol steam reforming in the gas phase which showed high activity in the long run, being resistant to deactivation via carbon deposition [39]. Rossum et al. used hybrid steam reforming concept which involves the prereforming stage to utilize the crude glycerol for reforming over commercial catalysts [40]. Ortiz et al. managed to achieve high yields of H₂ with less energy requirements with complete conversion of glycerol under supercritical conditions [4]. Co-gasification of crude glycerol and hardwood chips, in a downdraft gasifier, was another promising option for utilizing crude glycerol. The loading amount of crude glycerol had significant influence on CO and CH₄ concentration, while having no effect on H₂ and CO₂ yield. The study suggested that the co-gasification could perform well in downdraft gasifiers with hardwood chips mixing with liquid crude glycerol up to 20 wt% [3]. Rodríguez et al. identified a stable Ni-Ce composite catalyst for the reforming of glycerol to produce H₂ with nearly absence of CO and CH₄ [41]. Franchini et al. studied perovskite-type mixed oxides for the steam reforming of glycerol to produce H₂-rich product [42]. The effect of

Fig. 9.15 Integration of glycerol by-product as feedstock



Re promotion to carbon-supported Pt and Ru catalysts in the APR of glycerol has been well documented by Ciftci et al. [43]. The economic evaluation of the APR of glycerol studied by Rodolfo et al. indicated that nickel catalysts supported on alumina or zirconium oxide are a promising and competitive technology for hydrogen production [44]. Aqueous-phase reforming is still in the research phase, and a high-temperature process is more plausible. Issues still pending are coke formation, methane formation, and impurities. Further, alkali impurities present in glycerol have a negative impact on the catalyst. Purification is not difficult but pure glycerol is more expensive. A commercial breakthrough mandates catalysts that take all these factors into consideration and commercial processes can be expected in the next couple of years [45, 46].

9.3 Biomass-Derived Synthesis Gas Contaminants and Their Cleanup/Conditioning

Synthesis gas cleanup and conditioning is an important obstacle in the commercialization of biomass gasification technologies. Synthesis gas derived from the gasification of biomass contains a variety of components which are potentially harmful for the efficient and stable performance of catalysts employed for downstream conversions to fuel components. Even the components like Hg, As, Se, Cd, metal carbonyls, etc. are mentioned, making it complex. Table 9.2 shows the list of contaminants and their concentration levels in a poplar wood-derived synthesis gas [43].

Synthesis gas cleanup is practiced for a long time, but the arrival of various catalytic downstream steps for further conversion to fuels makes the demand on synthesis gas specs stringent. A recently published report [38] gives an exhaustive analysis of a multicomponent cleanup of synthesis gas.

Technology already exists for sulfur removal. Scrubber separation (ZnO, Ni, etc.) and hydrodesulphurization (HDS) are commercially possible. Existing HDS capabilities (NEBULA, BASF, Haldor Topsoe) can bring S levels to single digit ppms, but at considerable cost. However, chlorine levels are rather high and provide an even greater challenge. The best option for chlorine, ammonia, and metal contaminants is dedicated sorption processes (ZnO, Pd is used for Cl removal in alcohol synthesis).

Table 9.2 Typical contaminant concentrations in weight % in synthesis gas produced from poplar wood

Contaminant	Weight (%)
Ash	1.33
N (NH ₃ , + HCN)	0.47
S (H ₂ S+COS)	0.01–0.1
Alkalis	0.1
Cl (HCl)	0.1
Tars	~0.1

The presence of tar is the most critical issue while considering synthesis gas cleanup/conditioning. Tar reforming catalysts have not demonstrated that they can clean and condition raw synthesis gas. Conventional methods for tar removal such as thermal cracking, catalytic cracking, or scrubbing will not be sufficient to bring down the tar contents from ~1000 ppm (see Table 9.2) to typically required levels of <2 ppm so that downstream catalysts are not affected. Hot gas cleaning using catalysts which oxidize tar with steam or oxygen will be required. Almost all available catalyst metals have been tested to meet the strict quality standards for downstream fuel or chemical synthesis catalysts, but a commercial breakthrough is still pending for a comprehensive solution that can deal with all types of tars present in various biomass (waste also)-based synthesis gas streams. For example, BTG (Netherlands) has developed the catalytic, reverse flow tar cracking (RFTC) reactor for conversion of tar in producer gas using a commercial Ni catalyst [39]. Besides tar, light hydrocarbons and ammonia are also almost completely removed. Tar removal levels of ~99 % are however still not enough to protect downstream catalysts, as, e.g., Cu catalyst used in alcohol synthesis or Co used in the FT process deactivate at ppb levels of tars.

Supercritical fluids (e.g., water) have excellent coke/oligomer dissolution capabilities, and a combination of steam gasification under supercritical or near-SC conditions may be necessary to bring tar levels down to the required extent. This is still an open issue and requires extensive catalysis and process developments. To summarize, there are general solutions and dedicated cleanup strategies need to be developed depending on the downstream catalysts that see the synthesis gas feed.

9.4 Overview on Synthesis Gas Upgrading to Fuel/Fuel Blends and Catalysis Involved

Generation of synthesis gas from biomass-based feedstocks offers a variety of short-range/time solutions. First of all, synthesis gas conversion to fuels is established technology, e.g., (i) synthesis gas to diesel (Shell, Sasol, ExxonMobil), (ii) synthesis gas to methanol and middle distillates (Shell), (iii) synthesis gas to hydrogen by water-gas shift (JM) for fuel cell and other applications, etc. Thus, synthesis gas generated from biomass can be added on to the large-scale streams of synthesis gas from fossil hydrocarbons (natural gas, naphtha) and thereby help to meet immediate targets set by legislation for sustainability of fuels (e.g., 20 % renewable for the EU area by 2020). There are also efforts ongoing to convert synthesis gas to a variety of other fuel blends, e.g., higher alcohols, DME, gasoline, etc., thus providing even more opportunities. There is no biomass equivalent to kerosene, and synthesis via synthesis gas is the only route to sustainable kerosene. A combination of gasification/steam reforming and water-gas shift can be applied to fine-tune H₂/CO content of synthesis gas as to make it suitable for further fuel synthesis.

H₂ is produced from the purified synthesis gas using iron oxide as a catalyst at high temperature (300–500 °C). A low-temperature (200 °C) reaction is possible with Cu/ZnO catalysts; however, they require a clean feed gas. Pressure swing adsorption [45] is operated to obtain pure H₂. Methanol synthesis is one of the more important applications of synthesis gas. Methanol is used as an intermediate fuel and also used in the transesterification of vegetable oils to produce biodiesel. It can be produced predominantly using Cu/ZnO/Al₂O₃ catalyst in a temperature range of 225–275 °C. Methanol can then be converted into dimethyl ether (DME) [47]. Higher alcohols can also be synthesized from synthesis gas through a series of exothermic reactions. Hydrocarbons, normally dominated by methane along with short paraffins and olefins, are the side reaction products.

9.5 Outlook and Recommendations

Biomass can be seen as an important feedstock for the production of various chemicals and fuels. Various sequential developments were observed in the gasification process and technology. In the oil and coal industry, high-temperature (>1300 °C) entrained-flow gasifiers are used to produce synthesis gas. There are no insurmountable barriers foreseen to adapt these gasifiers to biomass or to co-feed biomass and fossil feedstock. In fact, this is already practiced in commercial and demonstration facilities. If for some reason entrained-flow operation is not possible, e.g., because there is not enough biomass available to balance the capital costs of an oxygen plant, catalytic gasification of biomass at low temperature is a promising technology. An opportunity for catalytic biomass gasifiers is the integration with GTL plants: natural gas- and biomass-based synthesis gas are then blended and fed to the FT unit.

However, the development of catalytic biomass gasifiers that take in solid biomass is in our opinion a dead end for synthesis gas production. Four decades of research has led to no more than a fuel gas with reduced tar and higher hydrocarbon content. There are just too many fundamental and practical problems just as the catalyst-biomass contact, catalyst poisoning by coke and nonorganic contaminants, and catalyst sintering, attrition, and entrainment. Upgrading of fuel gas (from solid biomass feed) has to be done in downstream equipment which makes this route costly. Recently, some interesting work has been reported on the gasification/reforming of bioliquids (e.g., pyrolysis oil and glycerol). In this route, the liquid is evaporated and the vapors are fed over slightly modified standard reform catalysts. Though these processes are in an embryonic stage of development, they are promising, because they do not require oxygen, operate at low temperature (1–30 bar, 350–800 °C), and produce a synthesis gas very suitable for FT synthesis and alcohol synthesis. Gasification in hot compressed water (50–300 bar, 250–600 °C) is also a promising technique as it can dissolve coke precursors. Here methane or hydrogen-rich gas is produced in combination with CO₂. This gas cannot be used for FT, but is suitable for alcohol production. The hydrogen can be used for hydrogenation in

routes involving the production of biofuels via upgrading of bioliquids. In this way a refinery scheme can be created in which the water fraction of bioliquid is used to generate hydrogen (via gasification) for hydrogenation of the oil fraction.

Even though continuous progress is seen in the biomass conversion to various useful fuels and chemicals via gasification, there is still a need for R&D to focus on some aspects such as selection/development of improved catalysts for solid biomass gasifiers with mechanical strength and attrition reduction. Bioliquid gasification should enter the process development stage now and keep the autothermal operation and long-duration catalyst stability in view. Gasification in hot compressed water can be done by considering following improvements: (i) operation under fouling and poisoning conditions, (ii) increasing the reaction rate by at least an order of magnitude, (iii) hydrogen production at high temperature and more concentrated feeds (>10 wt% organics), and (iv) stable catalyst support materials.

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