

Application of Biomass to Hydrogen and Syngas Production

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Today there is a worldwide interest in the use of biomass as an environmental friendly renewable energy source. The depletion of fossil oil reserves, constant uncertainties as far as price is concerned, unsecured supplies, and environmental pollution are among the many energy problems, when the use of fossil fuels are considered. Greenhouse effect and its consequences on climate change is one of the drawbacks resulting from the extensive use of this kind of fuels. These problems require the development of new alternative fuels such as biofuels. In this way, the biomass appears as an attractive source for the production of fuels and chemicals due to its versatility, renewable nature and low environmental impacts. The available energy production processes from biomass can, roughly, be divided into two general categories, to know: thermochemical and biological processes. Pyrolysis, gasification, reforming and combustion are the four thermochemical processes and direct biophotolysis, indirect biophotolysis, biological water–gas shift reaction, photo-fermentation and dark-fermentation are the five biological processes. Alternative thermochemical via (pyrolysis and gasification) can be practically applied to produce hydrogen and syngas from many types of renewable feedstock and deserve special attention. Bearing this in mind, this paper gives an overview of these technologies for hydrogen and syngas production from biomass.

1. Introduction

Today there is a worldwide interest in the use of biomass as an environmental friendly renewable energy source. Many concerns point out to the need to use of renewable feedstock, composing the energetic matrix and replacing as much as possible the fossil fuels; among them could be mentioned the depletion of fossil oil reserves, constant uncertainties as far as price is concerned, unsecured supplies, and environmental pollution. Greenhouse effect and its consequences on climate change is one of the drawbacks resulting from the extensive use of this kind of fuels. These problems require the development of new alternative fuels such as biofuels. Biomass is a potential energy resource and there are several pathways (e.g. physical, thermal, chemical, and biological conversion) to generate energy from biomass. By the preceding methods, biomass could be converted to heat, electricity, solid fuels (coal), liquid fuels (bio-oil, methanol and ethanol) and gas fuels (hydrogen and syngas), respectively (Chang et al., 2011). In the near term, biomass is the most likely renewable organic substitute to petroleum. Biomass is a renewable material containing appreciable quantities of hydrogen, oxygen and carbon. It is available from a wide range of sources such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (i.e. switch grass), waste paper, corn, and many more. For hydrogen and syngas productions, the current biomass technologies include: pyrolysis, gasification, reforming (the most studied by researchers worldwide) and combustion. A brief description of these processes to hydrogen and syngas productions will be given here, based on the work of Ahmed and Gupta (2011). The pyrolysis of biomass without catalyst is a very simple and a cheap method for energy conversion. Pyrolysis is also a previous step to other thermo conversion processes, such as combustion and gasification. Valuable gases, such as hydrogen and monoxide carbon, can also be generated by pyrolysis. These gases can be useful, among other applications, in chemical synthesis and high efficiency combustion systems such as fuel cells. Gasification is an old thermo-chemical conversion technology with a change of the chemical structure of the biomass at 500– 900 °C in

the presence of a gasifying agent (for instance air, oxygen, steam, CO₂, or mixtures of these components) that enables the promotion of steam reforming reactions and thus, consist on another method of producing a hydrogen rich gas from biomass. Gasification is a thermo-chemical process for destruction of feedstock (i.e. biomass, lignocellulosic residues, agriculture waste, refuse derived fuel and organic wastes) to produce energy carrier. The production of hydrogen or syngas is another promising use of biomass. Products of high added value such as hydrogen or syngas can be produced from the thermochemical processes of biomass. Hydrogen has been considered the most suitable alternative for future energy, aiming to reduce the dependence on fossil fuels and carbon based emissions. The largest consumption of hydrogen includes the synthesis of ammonia and methanol, upgrading the heavy hydrocarbons and (iron) ore reduction. As the growing concerns on reductions the greenhouse gas emissions in response to the Kyoto Protocol, finding alternative routes for the production of hydrogen is of interest of economist, environmentist and engineers. Hydrogen production is the first step associated with hydrogen economy. Hydrogen is currently produced from hydrocarbon reforming (i.e., the natural gas and petroleum) and electrolysis processes. Because the hydrogen deficiency, an integrated process in which hydrogen can be supplied from waste and residual (e.g., glycerol from biodiesel) is considered the only economically viable approach to operate a biorefinery.

Syngas is a vital building block for the petrochemical industry. Syngas produced from biomass pyrolysis and gasification is an important intermediate for synthesis of large numbers of industrial products. Examples include ammonia synthesis and hydrocarbons using the Fischer-Tropsch synthesis. Syngas is also a raw material of methanol (Li, 2013). Nowadays, syngas is mainly produced by gasification of natural gas, coal, and occasionally from heavy oil residues (Dalai et al., 2009). Thus, maximizing the syngas yield from biomass will largely promote the biomass utilization with high efficiency. Bio-automotive fuels and chemicals can be produced from high-quality syngas (mainly H₂ and CO) which is obtained by thermochemical processes with or without catalyst of biomass and wastes (Skoulou and Zabaniotou, 2013). This may be carried out energy efficiently and environmentally by integration with existing agricultural and forest industries, energy industry or chemical industry in a concept of biorefinery. This paper aims to give an overview of methods of hydrogen and syngas productions from biomass and their potential of development.

2. Biomass supply energy and Fuel processing

Currently, there is a wide variety of biomass resources available to be converted into energy. Ni et al. (2006) classified this biomass into four general categories: (i) Energy crops: herbaceous energy crops, woody energy crops, industrial crops, agricultural crops and aquatic crops. (ii) Agricultural residues and waste: crop waste and animal waste. (iii) Forestry waste and residues: mill wood waste, logging residues, trees and shrub residues. (iv) Industrial and municipal wastes: municipal solid waste (MSW), sewage sludge and industry waste. Pyrolysis, gasification, reforming and combustion are the four thermochemical processes to produce syngas and hydrogen from biomass. Direct biophotolysis, indirect biophotolysis, biological water-gas shift reaction, photo-fermentation and dark-fermentation are the five biological processes. Combustion is the direct burning of biomass in air to convert the biomass chemical energy into heat, mechanical power or electricity, using equipment such as stoves, furnaces, boilers or steam turbines, respectively. According to Ni et al. (2006), the combustion process is not suitable for hydrogen production due to low energy efficiency (10–30 %) and the pollutant emissions are the by-products. Fuel processing technologies convert hydrogen containing waste material such as biomass, crude glycerol into a hydrogen rich stream. Currently, syngas and hydrogen are produced from several sources biomass and different thermo-chemical processes (pyrolysis, gasification, steam reforming, partial oxidation, combustion). The choice of the most suitable one is not easy and this presents perhaps a significant challenge to process development for some feedstock. Bearing this in mind, steam reforming will also be discussed.

3. Pyrolysis versus Gasification

According to Zhou et al. (2008), the pyrolysis process at low temperatures (673 – 873 K) is formed of liquid and gaseous products are formed from high temperature (1023 K). Gasification is a process related to pyrolysis, and the most significant difference between the two processes is that the gasification occurs in the presence of oxygen in the form of air or steam. Gases and liquids produced in the pyrolysis and gasification processes can be used as energy, as heat and electricity or chemicals production. For example, gases with high contents of CO and H₂ can be a source of syngas (used for production of methanol and / or ethanol) or H₂ (used in fuel cells) (Baumlin et al., 2006).

According to Arni et al. (2010), pyrolysis is a thermal process in which biomass is converted into gas, liquid, and solid in the absence of air. The solid product is rich in coal and ash, and has several applications. The tar (liquid) consists of condensable hydrocarbon pyrolysis process, consisting of a very complex mixture of oxygenated hydrocarbons and water, and can be used as a substitute for fuel oil in many static applications such as in boilers, and constitutes an important source of chemicals. The gas is non-condensable fraction of the pyrolysis process, consisting mainly of H₂, CO, CO₂, CH₄ and other low molecular weight hydrocarbons, and is used as fuel gas. On the other hand, the gasification process can be defined as a process of partial combustion; it uses an amount of air lesser than the stoichiometrically necessary. The gaseous product is obtained consisting of hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂), comprising the syngas. Unlike pyrolysis, gasification occurs in the presence of oxygen in the form of air, pure oxygen or steam and it is not necessary to use carrier gas (Baumlin et al., 2006). Biomass can be converted to hydrogen and syngas by pyrolysis and gasification process, and biomass gasifiers have been designed in various configurations (Table 1).

Table 1: Pyrolysis and Gasification Process

Process	Biomass	Reactor	Catalytic	Products	Source
Gasification	Glycerol lignocellulosic	withFixed Bed	-	Syngas	Skoulou and Zabaniotou (2013)
Gasification and Pyrolysis	Pine sawdust	Tubular	Nickel	Syngas	Xie et al. (2012)
Gasification	Sawdust	Fluidized Bed	Fe/CaO	-	Huang et al. (2012)
Gasification and Pyrolysis	Rubber	Tubular	-	Hydrogen and Syngas	Ahmed and Gupta (2011)
Gasification	Lignocellulosic materials	Tubular	-	Hydrogen	Chang et al. (2011)
Gasification	Wood	-	-	Syngas	Simone et al. (2011)
Gasification	Glycerol	Fluidized - Bed	-	Syngas	Yoon et al. (2010)
Gasification and Pyrolysis	Food waste	Tubular	-	Syngas	Ahmed and Gupta (2010)
Gasification	Refuse fuels	Fixed Bed	-	Syngas	Dalai et al. (2009)
Gasification and Pyrolysis	Pine sawdust	Fluidized Bed	Dalomite and Nickel	Syngas	Lv et al. (2007)

3.1 Pyrolysis

Pyrolysis is an important process in energy recovery from biomass and also as a previous stage to other processes such as gasification. For about 20 years, there has been considerable interest in liquid production by pyrolysis. Valuable gases, such as H₂ and CO, can also be generated by pyrolysis. These gases can be useful, among other applications, in chemical synthesis and high efficiency combustion systems such as fuel cells. According to Ni et al. (2006), parameters such as: temperature, heating rate, residence time and type of catalyst used are important in the pyrolysis process. In order to increase gaseous products especially hydrogen production, high temperature, high heating rate and long volatile phase residence time are required. Temperature is an important variable in thermal decomposition processes of biomass, significantly influencing the product distribution. Pyrolysis is an endothermic process, and when the reaction temperature decreases, the total gas yield diminishes and the yield to liquid products increases. The same tendencies have also been observed in steam gasification of biomass (Garcia et al., 2001).

According to Ni et al. (2006), pyrolysis can be further classified into slow pyrolysis and fast pyrolysis. Slow pyrolysis is normally not considered for hydrogen production. Fast pyrolysis is a high temperature process, in which the biomass feedstock is heated rapidly in the absence of air, to form vapour and subsequently

condensed to a dark brown mobile bio-liquid. The products of fast pyrolysis can be found in all gas, liquid and solid phases. In particular, the gaseous product is of considerable interest due to its potential as a source of hydrogen fuel. Moreover, this process has advantages as negligible production of toxic oxidised species (e.g. dioxins), less energy consumption and the production of a disposable solid waste (char). Most literature reports focus on pyrolysis using conventional electric resistance heating, which offers a number of advantages and shows excellent potential for treating the biomass. The reactions can be written in the following forms (Equation 1 and 2) (Song et al. 2012 and Ni et al., 2006):



Some works have reported several sources of biomass to produce hydrogen and syngas by pyrolysis (see Table 1), such as agricultural residues, peanut shell, post-consumer wastes such as plastics, trap grease, mixed biomass and synthetic polymers as well as rapeseed. They have been widely tested for pyrolysis for hydrogen production. Ni et al. (2006) reported hydrogen production cost of biomass pyrolysis versus the costs of hydrogen production by electrolysis. The cost estimated the hydrogen production of biomass pyrolysis is in the range of 8.86 US\$/GJ to 15.52 US\$/GJ depending on the facility size and biomass type. For comparison, the costs by wind-electrolysis systems and PV-electrolysis systems are 20.2 US\$/GJ and 41.8 US\$/GJ, respectively. It can be seen, at least for the economical point of view, that biomass pyrolysis is a competitive method for renewable hydrogen production.

The use of catalysts in the thermo-chemical processing of biomass can be an interesting approach for increasing the gas yield by decreasing the amount of liquid. Catalytic pyrolysis occurs at relatively low temperatures (≤ 750 °C) and the catalyst is incorporated in the same reactor where the pyrolysis of biomass is performed. According to Garcia et al. (2001) nickel is the metal most frequently used in catalysts for biomass processing. The catalyst must have appropriate physical and chemical properties, including mechanical strength, because of its use in a fluidized bed. The thermal stability of the active phase is also very important. Ni/Al coprecipitated catalysts combine these characteristics. The calcination and reduction conditions of the catalyst impact on the gas yield of the catalytic pyrolysis of biomass.

The catalytic pyrolysis is important to reduce the tar formed during pyrolysis process. The use of dolomite or nickel oxide as catalysts in biomass pyrolysis had been attracted much attention, because it was inexpensive and abundant and it could significantly reduce the tar content of the product gas (Lin, 2013). Zang et al. (2009) investigated non-catalyst and catalytic fast pyrolysis of corncob in a fluidized bed reactor and the results showed that the optimal conditions for liquid yield (56.8 %) were for a pyrolysis temperature of 550 °C, gas flow rate of 3.4 L/min, static bed height of 10 cm and particle size of 1.0–2.0 mm. The presence of the catalyst increased the yields of non-condensable gas, water and coke, while decreased the liquid and char yields.

3.2 Biomass Gasification

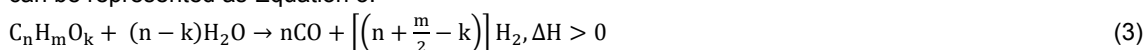
Biomass gasification is a renewable alternative that has the potential to decrease CO₂ emissions. However, efficient energy and resource utilization is essential. Previous works had shown that biomass is most cost-effectively used for heating purposes or electricity generation. But to increase the overall efficiency, biomass gasification could be integrated in industrial processes. The gasification is an old thermo-chemical conversion technology with a change of the chemical structure of the biomass at 800 – 1000 °C in the presence of a gasifying agent (for instance air, oxygen, steam, CO₂, or mixtures of these components) enables the promotion of steam reforming reactions and thus it consists another method of producing a H₂ rich gas from biomass. Gasification is a thermochemical process for destruction of feedstocks (i.e. biomass, lignocellulosic residues, agriculture waste, refuse derived fuel and organic wastes) to produce energy carrier. Air has been widely used as the oxygen source for gasification. There are several researches that discussed the performance of biomass gasification process with/without air and steam (Table 1). However, this technology with steam requires additional energy cost for increasing the temperature of supplementary steam. Due to the economic viewpoint, it was gained attention on the low temperature biomass gasification with air and steam. Since the steam gasification reaction is an endothermic reaction, air is also used to reduce the energy cost by partial oxidation (exothermic reaction) reaction of biomass (Chang et al., 2011). The gasification process is applicable to biomass having moisture content lesser than 35 %. Direct gasification (or autothermal gasification) occurs when the oxidant gasification agent partially oxidises the feedstock and provides the heat for the process. Low temperature direct gasification (below 900 °C) can be carried out in a fixed bed, a fluidized bed (FB) or a circulating fluidised bed (CFB), and high temperature direct gasification (over 1300 °C) in an entrained flow gasifier. (Song et al. 2012).

Hydrogen and syngas production from biomass through thermochemical conversion, gasification in particular, have been widely studied. According to Chang et al. (2011), the temperature is the most influential factor for gasification, and increasing the temperature, resulted in increase in gas yield and more hydrogen production. Particle size is another factor that affects the gasification process, therefore carbon conversion efficiency and hydrogen yield increase with decreasing particle size. The optimization of gasification temperature is around 830 °C and steam to biomass ratio of 0.6-0.7 (w/w). Xie et al. (2012) studied syngas production by two-stage method of biomass catalytic pyrolysis and gasification. The results illustrated that higher temperature was needed in the gasification process (850 °C) than in the pyrolysis process (750 °C) to maximize syngas yield, and the maximum syngas yield could achieve up to 3.29 N m³/kg biomass (dry wt.), much higher than previous studies. Gao et al. (2012) investigated hydrogen production from biomass gasification with porous ceramic reforming. The results indicated that the hydrogen yield increased from 33.17 to 44.26 (g H₂)/(kg biomass) with the reactor temperature increase. The H₂ concentration of production gas in oxygen gasification (oxygen as gasifying agent) was much higher than that in air gasification (air as gasifying agent). The hydrogen yields in air and oxygen gasification varied in the range of 25.05 - 29.58 and 25.68 - 51.29 (g H₂)/(kg biomass), respectively. Nipattummakul et al. (2012) investigated syngas production from steam gasification of oil palm trunk waste and it was observed that the high initial syngas flow rate is mainly attributed to the pyrolysis of volatile matter from the oil palm sample. Almost 50 % of the syngas is produced during the first 5 min. The results showed that there is over 60 % increase in hydrogen production with steam gasification as compared to that with pyrolysis. The increase in steam flow rate reduced the time duration of gasification, and promoted steam reforming reactions to result in increased hydrogen yield. Increase in steam flow rate provided negligible effect on the apparent thermal efficiency. Lv et al. (2007) studied catalytic gasification of pine sawdust and the maximum gas yield reached 2.41 N m³/kg biomass at 850 °C.

4. Steam reforming

Currently, the most widely way used to produce hydrogen and syngas is the catalytic reforming of hydrocarbons, a process that involves the breaking of H-C and C-C bonds.

The process of steam reforming is performed at lower temperatures (150 to 700 °C) in the presence of catalysts, and these are divided into two groups: non-precious metals (Ni) and precious metals of Group VIII (Platinum - Pt or Rhodium - Rh). Most studies are using Nickel (Ni) supported on Alumina (α -Al₂O₃) (Holladay et al., 2009). The nature of the metal components has a significant influence on performance and distribution of gaseous products. In steam reforming is important to control the formation of coke, or coke formed deactivates the catalyst. The steam reformation of organic compounds such as biomass is one of the most widely used processes for hydrogen production. In this process, the substrate is reacted with steam in presence of a catalyst to produce hydrogen, carbon dioxide and carbon monoxide (Adhikari et al., 2009). The catalysts are mainly used to increase the reaction rate and selectivity of hydrogen. This process is highly endothermic and the low pressure favours the selectivity to hydrogen. The main reactions can be represented as Equation 3.



The reform process involves mainly the breakdown of hydrocarbons in the presence of water (equation 3) and the reaction of water with carbon monoxide formed, known as the reaction of water-gas shift, producing carbon dioxide and hydrogen as Equation 4. Moreover, the methanation of carbon monoxide (equation 5) (Adhikari et al., 2009).



5. Conclusion

In order to decrease the dependence on fossil fuels, there is a wide variety of research being pursued in the development of hydrogen and syngas productions from renewable resources such as biomass. Biomass is potentially a reliable energy resource for hydrogen production. Biomass is renewable, abundant and easy to use. Over the life cycle, net CO₂ emission is nearly zero due to the photosynthesis of green plants. The thermochemical pyrolysis and gasification hydrogen and syngas production methods are economically viable and will become competitive with the conventional natural gas reforming method. And the cost estimated the hydrogen production of biomass pyrolysis is more competitive than the costs by electrolysis systems. It can be seen that biomass pyrolysis is a competitive method for renewable

hydrogen production. With further development of these technologies, biomass will play an important role in the development of sustainable hydrogen economy.

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