



Green Gasification Technology for Wet Biomass

Chong, W. H., Leong, J. W., Yoong, J. H., Mohd. Halim Shah, I.*

Department of Chemical & Environmental Engineering, Faculty of Engineering,
Universiti Putra Malaysia, Serdang, Selangor, Malaysia, 43400

*E-mail: mshalim@eng.upm.edu.my

Abstract

The world now is facing two energy related threats which are lack of sustainable, secure and affordable energy supplies and the environmental damage acquired in producing and consuming ever-increasing amount of energy. In the first decade of the twenty-first century, increasing energy prices reminds us that an affordable energy plays an important role in economic growth and human development. To overcome the abovementioned problem, we cannot continue much longer to consume finite reserves of fossil fuels, the use of which contributes to global warming. Preferably, the world should move towards more sustainable energy sources such as wind energy, solar energy and biomass. However, the abovementioned challenges may not be met solely by introduction of sustainable energy forms. We also need to use energy more efficiently. Developing and introducing more efficient energy conversion technologies is therefore important, for fossil fuels as well as renewable fuels. This assignment addresses the question how biomass may be used more efficiently and economically than it is being used today. Wider use of biomass, a clean and renewable feedstock may extend the lifetime of our fossil fuels resources and alleviate global warming problems. Another advantage of using of biomass as a source of energy is to make developed countries less interdependent on oil-exporting countries, and thereby reduce political tension. Furthermore, the economies of agricultural regions growing energy crops benefit as new jobs are created.

Keywords: energy, gasification, sustainable, wet biomass

1. Introduction

There are several issues related to the sustainability of Malaysia's energy developments. First aspect is the sustainability with respect to the use of indigenous fossil energy resources. If energy consumption continues to increase, those resources will be depleted all too soon and Malaysia will become highly dependent on imported energy as demonstrated in the section above. Furthermore, the continued efforts to make the Malaysian industries competitive on international markets will be negatively affected by the slow energy efficiency improvements that take place for its industries compared to other countries. In the future, energy costs will have to reflect international energy prices to a higher degree because of the increased dependence on imported energy. Therefore, the national energy policy focuses on sustainable development of energy resources, greater utilization and adequate electricity generating capacity of gas and renewable energy and supporting industries that produce energy related products and services (Pusat Tenaga Malaysia, 2006). Renewable energy resources available in Malaysia are biomass, solar, mini-hydropower, municipal waste and biogas.

Almost 60% of the land area of the country is dominated by natural forest and 15% is shared by agricultural cultivation which means that there is a great potential the development of biomass energy. The Ministry of Energy, Water and Communications (MECW) stated that the most important renewable energy sources in Malaysia are biomass and solar

Biomass is a very general term which comprises all organic matter that originates from photosynthesis. It is not a well-defined and often inhomogeneous feedstock, whose composition may vary depending on origin, physical location, age, season and other factors. Biomass types include many types of wood, plants, vegetable oils, green waste, and materials such as manure and sewage sludge. These biofuels differ in many aspects, such as their availability, cost, suitability as a gasifier fuel, and also in their acceptance by the public.

a. Availability of Biomass in Malaysia

Biomass is available in Malaysia in a vast abundant. More than 70 million tons of biomass is collected every year (Sumathi *et al.*, 2008). The climate in Malaysia, which has high sunlight intensity and high rainfall

allowed biomass to be produced throughout the year. Malaysia, as the one of the world largest palm oil producers, making palm oil industry contributes the highest fraction, which is 85.5% of the total biomass.

b. Thermal Conversion Processes of Biomass

Figure 1 shows us the thermal conversion processes which are available for the thermal treatment of biomass and the products gain from the respective processes. Thermal conversion processes can be considered in three main categories which are combustion, gasification and pyrolysis (Belgiorno *et al.*, 2002).

Combustion processes are chemical oxidation processes where the organic fraction of the waste is fully oxidized at high temperatures to form carbon dioxide, water vapour, small quantities of acid gases, environmentally significant amounts of organic compounds and particulate matter that contains some heavy metals. Heat exchanger can recover the heat from the hot gases in order to generate the steam and electricity. However, the gases formed must be cleaned so as to be essentially pollutant-free. The combustion process is relatively simple to understand.

After the waste is brought to the site, it is then fed into the incinerator. High temperature flames (2400°F) inside the incinerator chambers burn the waste in either one stage or in multiple stages. Ash is produced which as the waste is burned, which is collected for later disposal in a landfill (Holland, 1999). Table 1 shows the advantages and disadvantages of waste combustion with energy recovery.

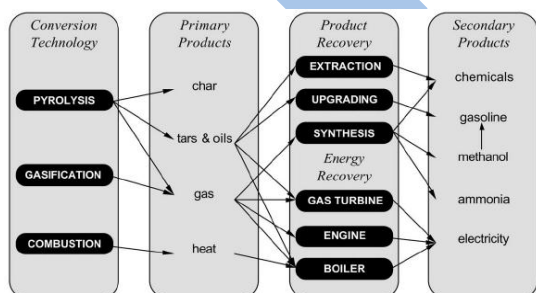


Figure 1. Thermal Conversion Process and Products (Belgiorno *et al.*, 2002).

Generally, gasification can be defined as the thermo-chemical conversion of a solid or liquid carbon-based material (feedstock) into a combustible gaseous product (syngas) by the supply of a gasification agent (another

gaseous compound) (Belgiorno *et al.*, 2002). The organic fraction of the waste is broken down by heat alone or partial combustion to form combustible gas contains CO_2 , CO , H_2 , CH_4 , H_2O , and trace amounts of higher hydrocarbons, inert gases present in the gasification agent, various contaminants such as small char particles, ash and tars.

Table 1. Advantages and disadvantages of combustion.

Advantages	Disadvantages
i. Reduce volumes of waste up to 90% and the weight of waste by 70%	i. Produce fly ash and air pollution control residue that are special wastes
ii. Convert a large proportion of the calorific value of waste into usable energy	ii. Negative public perceptions lead to planning problems
iii. Reduce demand for landfill and other waste management capacity	iii. Potential for polluting gaseous and liquid emissions (e.g. carbon dioxide and dioxins) to atmosphere
iv. Stabilize putrescible waste such as ash, reducing the potential of leachate and landfill gas production at landfills	iv. Changes in calorific value of the waste cause changes in the operational costs
v. Produce suitable residues for recycling	v. Potential for dust and odor problems during storage of waste prior to incineration
vi. More effective energy recovery than anaerobic digestion and landfill gas	vi. Require high water usage
	vii. Inhibit waste minimization and recycling

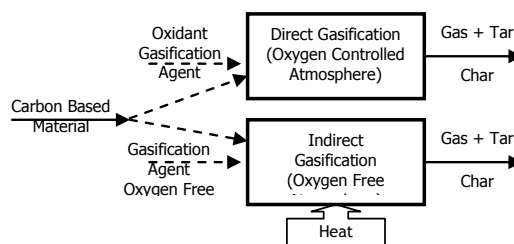


Figure 2. Gasification and pyrolysis processes (Belgiorno *et al.*, 2002).

From Figure 2, we can know that, direct gasification occurs when an oxidant gasification agent is used to partially oxidize the feedstock. In this case, the oxidation reactions supply the energy to keep the temperature of the process up. It is called indirect gasification and needs an external

energy source, if the process does not occur with an oxidizing agent. Steam is the most commonly used indirect gasification agent because it is easily produced and increases the hydrogen content of the combustible gas.

The three major output fractions resulting from the gasification process are a combustible gas, a liquid fraction (tar) and a char consisting of almost pure carbon plus inert material originally present in the feedstock. The basic advantage to gasification technology is it is not incineration. Thus, it can be perceived as a cleaner process. A summary of the advantages and disadvantages of gasification is presented in Table 2.

Table 2. Advantages and Disadvantages of Gasification (Forth and Van, 2004)

Advantages	Disadvantages
i. Not incineration	i. Requires waste pre-treatment to remove non-organic waste and homogenize the material
ii. Efficient energy production through combustion of gases	ii. Residuals could be hazardous
iii. High temperatures can make the process flexible to other waste streams	iii. System is sensitive to non-organic feedstock
iv. Recycling can be enhanced by up-front separation	iv. More expensive than other proven technologies

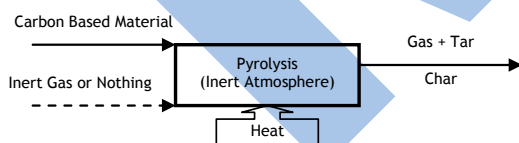


Figure 3. Pyrolysis processes (Belgiorno *et al.*, 2002).

Pyrolysis is the thermal processing of waste in the complete absence of oxygen. The pyrolysis process produces carbon, gases as well as oil which are further combusted in the secondary chamber. Quite often, pyrolysis systems are used interchangeably as gasification systems. However, scientifically they are totally different process. Pyrolysis is an indirect gasification process with inert gases as the gasification agent as shown in Figure 3. The advantages

and disadvantages might be summarized best as shown in Table 3.

Table 3. Advantages and Disadvantages of Pyrolysis (Forth and Van, 2004).

Advantages	Disadvantages
i. Potential for significant waste diversion - as much as 90 percent	i. Unproven technology
ii. Potential for producing quantities of usable gas, fuel oil, and fuels, as well as front-end recovery products	ii. Problems in scaling up from very small applications to full-scale
	iii. High projected capital and operating costs

2. Biomass Gasification

Gasification involves the production of a gaseous fuel by partial oxidation of a solid fuel. The gasification of coal and biomass began in about 1800 and by about 1850 gas light for streets was commonplace. Before the construction of natural gas pipelines, there were many "gasworks" serving larger town and cities in Europe and the US. During the petroleum shortages of World War II, almost a million gasifiers were used to run cars, trucks, and buses using primarily wood as a fuel. These gasifiers were mothballed after the return to peace and the availability of inexpensive petroleum fuels. However, the oil crisis in the 1970's and 1980's has inspired continued research and development of coal gasifiers. Since the 1990's, concerns about global warming shifted the focus to biomass as a gasifier fuel (Stassen *et al.*, 2002).

Due to its higher efficiency, it is desirable that gasification becomes increasingly applied in future rather than direct combustion. Gaseous fuels can be easily distributed for domestic and industrial use, used in electricity producing devices such as engines, gas turbines and fuel cells, or for chemical synthesis of liquid fuels and chemicals. Several types of gasifiers have been developed; an overview is shown in Figure 4. These gasifiers have different hydrodynamics (especially the way in which the solid fuel and the gasification agent are contacted), gasification agents (air, oxygen and/or steam) and operating conditions such as temperature and pressure. The most important types are fixed-bed gasifiers, operated in counter-current, co-current or cross-current mode, fluidized bed gasifiers and entrained flow gasifiers (Stassen *et al.*, 2002).

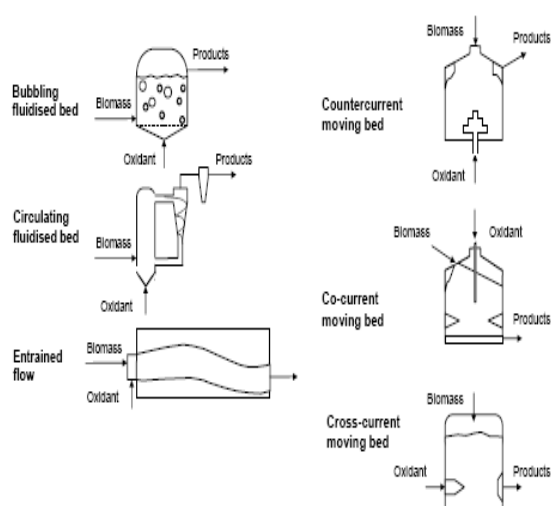


Figure 4. Overview of gasifier types (Stassen *et al.*, 2002).

2.1 Technical Suitability of Biomass for Gasification

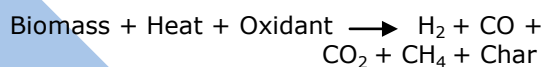
Biomass gasifiers are considered omnivorous and flexible towards the feedstock that is to be processed. A wide range of biomass sources, such as traditional agricultural crops, dedicated energy crops, residues from agriculture and forestry as well as organic wastes can be gasified. This is generally regarded as a real advantage, because it means that the most available and usually economically most attractive feedstock can be selected. However, the question is whether all the biomass types can be converted with comparable efficiencies. These biomass types differ in chemical composition, heating value, ash and moisture content.

The Phyllis database, maintained by the Energy research Centre of the Netherlands (2004), provides information about these properties. Comparison of the various types of biomass listed in Phyllis shows that the higher heating value of biomass does not vary much (standard deviations of 4-7%) and lies generally in the range of 19-21 MJ/kg. Contrarily, variations in moisture content and ash content are especially large (standard deviations of 50-120%). Evaporation of moisture in a thermal processing apparatus reduces the energy efficiency, although this problem is less severe if waste heat is available for pre-drying. Furthermore, the processing and disposal of large amounts of ash poses problems. Therefore, other technologies are more suitable for the wet streams, such as anaerobic digestion and supercritical water gasification (Goudriaan *et al.*, 2001).

2.2 Types of Biomass Gasification

a. Biomass Conversion via Conventional Gasification

Gasification is the conversion of carbonaceous fuel to a gaseous product with a useable heating value. Biomass can be gasified into combustible gas mixture by partial oxidation at high temperature, typically in the range of 800-900°C. Synthesis gas or syngas consisting of hydrogen and carbon monoxide are produced in varying ratios (Higman and Maarten, 2003). This conversion process can be expressed as:



The major difference between pyrolysis and gasification is that the latter process is carried out in the presence of oxygen. The oxidant used can be pure oxygen, air or steam. Besides, gasification aims to produce gaseous products while pyrolysis aims to produce bio-oils and charcoal. Gasification is applicable to biomass with moisture content less than 35% (Ni *et al.*, 2006). In a gasifier, the carbonaceous material undergoes several different processes (Saxena *et al.*, 2008):

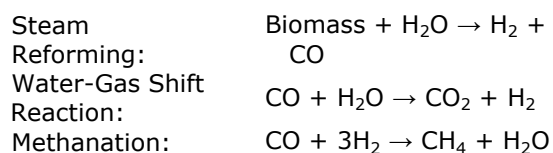
- i. The pyrolysis (or devolatilisation) process occurs as the carbonaceous particle heats up. Volatiles are released and char is produced.
- ii. The combustion process occurs as the volatile products and some of the char reacts with oxygen to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. Letting C represent a carbon-containing organic compound, the basic reaction here is $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$.
- iii. The gasification process occurs as the char reacts with carbon dioxide and steam to produce carbon monoxide and hydrogen, via the reaction $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$.
- iv. In addition, the reversible gas phase water gas shift reaction reaches equilibrium very fast at the temperatures in a gasifier. This balances the concentrations of carbon monoxide, steam, carbon dioxide and hydrogen. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$.

In gasification, solid fuels except ashes are completely converted into gaseous products with different composition. Therefore, gasification process is a preferred method

for conversion of biomass to produce energy due to its high efficiencies and the production of cleaner gaseous fuel (Saxena *et al.*, 2008). However, there are some problems deals with biomass gasification. The unwanted tar produced from the process may cause the formation of tar aerosol and polymerization to a more complex structure, which are not favourable for hydrogen production. Besides, the formation of ash may cause deposition, sintering, slagging, fouling and agglomeration (Ni *et al.*, 2006).

b. Gasification of Biomass in Supercritical Water

The main purpose of supercritical water gasification is to produce hydrogen from wet biomass at relatively lower temperature compared to conventional gasification process (Kruse, 2008). Supercritical water exists at pressure higher than 22MPa and temperature above 374°C. There is no distinct phase change at supercritical condition and at all times there is only one phase present (Cengel and Boles, 2006). Below the critical point, liquid water could not be utilized in reaction with biomass feedstock since it is immiscible with organic substances. On the other hand, the dielectric constant of supercritical water is in the range of 2 to 30 and 80 for water at ambient condition. The reduced dielectric constant combined with a considerably diminished number of hydrogen bonds causes that hot compressed water behaves like an organic solvent. Therefore, supercritical water is completely miscible with the organic substances as well as gases due to the above mentioned characteristics (Lu *et al.*, 2006). In gasification reaction, the biomass under severe conditions is decomposed at a high efficiency rate into small molecules of gases in few minutes. Gaseous mixture of hydrogen, carbon dioxide, carbon monoxide, methane and other compounds are obtained from the reaction (Ni *et al.*, 2006). The biomass gasification in supercritical water is complex process due to the multiple reactions that occur simultaneously. However, three main reactions are identified, which are steam reforming, methanation and water gas shift reaction (Aurand, 2001).



During steam reforming, the biomass reacts with water at its supercritical condition to produce gaseous mixture of hydrogen and carbon monoxide. The carbon monoxide produced from steam reforming reaction will undergo an inorganic chemical reaction known as water-gas shift reaction with water to produce hydrogen and carbon dioxide. The carbon monoxide produced in steam reforming reaction cause the equilibrium of water-gas shift reaction to shift to the right hand side, hence producing more hydrogen. Methanation occurred in the last reaction where carbon monoxide reacts with hydrogen in the earlier reaction to form methane and water as its final product (Aurand, 2001).

3. Supercritical Water Gasification

3.1 Chemistry of Supercritical Water

Supercritical water possesses properties very different from those of liquid water. The dielectric constant of supercritical water is much lower and the number of hydrogen bonds is much lower and almost entirely disrupted so that water molecules lose the ordering responsible of many of liquid water's characteristics properties. As a result, supercritical water behaves like many organic solvents so that organic compounds have complete miscibility with supercritical water. Moreover, gases are also miscible in supercritical water, thus a supercritical water reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under conventional conditions (Hong *et al.*, 1996).

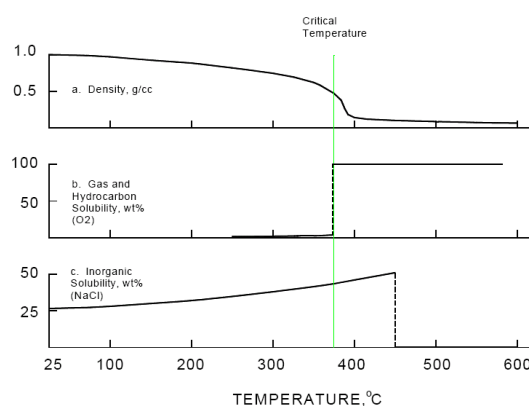


Figure 5. Characteristics of water as a function of temperature (Hong *et.al*, 1996). a. Density, b. Solubility of nonpolar organics and permanent gases.

Figure 5 summarizes the density and typical solubility behaviour of water as a function of temperature. $C + \frac{1}{2} O_2 \rightarrow CO$

3.2 Advantages of Supercritical Water Gasification

There are several advantages to gasify biomass in supercritical water. This approach is a promising method to convert wet biomass and waste stream. When the biomass with moisture content, above 35%, it is claimed better to gasify the biomass in supercritical water (Ni *et al.*, 2006). Thus, pretreatment of the biomass feedstock such as drying can be avoided and eventually prevented the cost related to that process. Study shows oil palm biomass is suitable for supercritical water gasification process in order to produce hydrogen due to its high energy and moisture content. Secondly, supercritical water gasification is preferred due to its high hydrogen yield and minimum formation of tars and chars. The unique properties of hot compressed water promote ionic reaction pathways over radical routes, leading to less char formation.

In 2003, Kruse and Gawlik found that the raw material is totally transformed into hydrogen rich gas without any formation of tars and chars (Yong *et al.*, 2007). Besides, the gases produced by using this method are available at high pressure. Therefore, the expensive compression for storage can be avoided. Only a small volume reactor and low energy for pressurization in storage tank are required (Matsumura *et al.*, 2005). Lastly, it is also found that supercritical water gasification is an economical method to produce hydrogen.

Most of the literature states that the presence of chars and tars in the apparatus when treating biomass, especially real wastes. This phenomenon is usually smaller in supercritical water gasification processes than in low pressure processes, mainly because of the higher amount of water molecules and the specific transport

properties of supercritical water. Even though supercritical water gasification deals with fewer amounts of chars and tars, the drawback has to be carefully considered because of the rather small volume of reactors and tubing. This problem is said to be overcome by the use of catalysts that have the advantage of helping on both the conversion yield and the plugging problem caused by the presence of chars and tars (Matsumura *et al.*, 2005).

3.3 Limiting Factors of Supercritical Water Gasification

Even if the supercritical water gasification process seems to be very efficient, some physical limitations or some technical difficulties are encountered. Some of the other main limitations are corrosion, pressure resistance and hydrogen aging. Corrosion is a limiting factor occurring in high pressure reactors. It has a lot of relevant consequences on the materials that have to be employed to build the reactors. The mechanical constraint caused by high pressure is also a limiting factor.

Indeed, only specific geometries and specific materials can be used because high pressures (over 300 bars) are used in the process. The presence of hydrogen is, as well, a key point because of its influence on the mechanical properties of materials.

3.4 Process Description of Supercritical Water Gasification

The gasification of biomass in supercritical water is accomplished under homogeneous, single phase conditions that provide excellent mixing and high mass and heat transfer rates. This process is chosen since it is known for its cost effectiveness and its environmental friendly means of producing hydrogen and other energetic gaseous fuels. The process route chosen for biomass supercritical water gasification generally consists of six steps and it is summarized in the Figure 6.

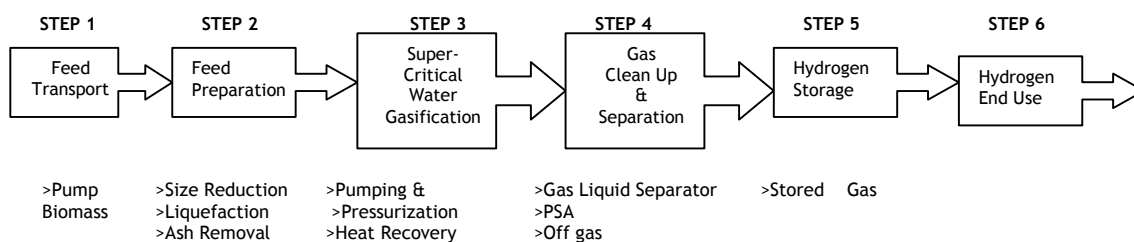
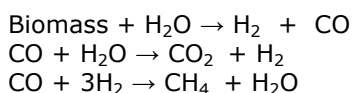


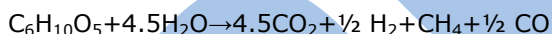
Figure 6. Hydrogen producing step via supercritical water gasification.

In this gasification reaction, the biomass would be under severe conditions of heated water at high temperature and pressure of above 374°C and 22 MPa which will be instantaneously decomposed into small molecules of gases in few minutes, at high efficiency rate.

A gaseous mixture of hydrogen, carbon dioxide, carbon monoxide, methane and other compounds is obtained from the reaction (Ni et al., 2006). Basically, there are three main reactions identified during the gasification process under the influence of supercritical water. The three reactions are steam reforming, methanation and water-gas shift reactions (Guo et al., 2007) which are shown as below (Aurand, 2001):



Based on the experimental data, equation below is used to express the biomass conversion reaction in supercritical water where the conversion reaction typically occurs at temperature of 25 MPa and 700°C.

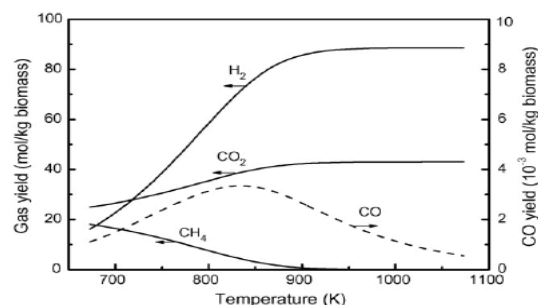
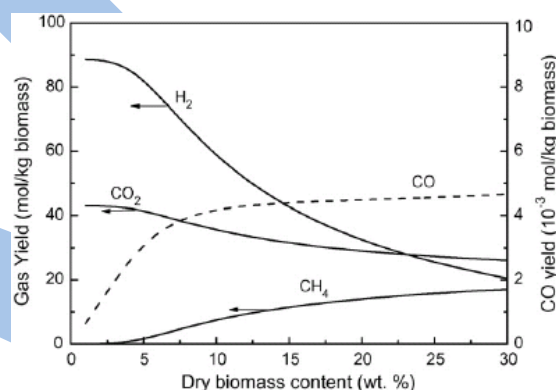


According to the equation, the gas product consists of 55.56% hydrogen, 33.33% CO₂, 7.41% CH₄ and 3.70% CO in mole fraction.

3.5 Thermodynamic Considerations of Supercritical Water Gasification

In 2006, Guo et al. had done a study on biomass gasification in supercritical water. Chemical equilibrium of wood sawdust in supercritical water was predicted. It was found that gasification at high temperature with a feed of low biomass content give higher yield of hydrogen as shown in Figure 7 and 8. It is observed that at relatively low temperatures, catalysis is required and methane rich gases are produced.

At supercritical temperatures, especially with low feedstock concentration, hydrogen rich gases are formed with conventional gasification. Full conversion of biomass into hydrogen becomes difficult and more hydrocarbons are produced when the biomass concentration in water is increasing. Catalysts are needed to improve the conversion (Guo et al., 2007).

**Figure 7.** Equilibrium gas yield as a function of temperature for biomass gasification at 25 MPa with 5 wt% Dry Biomass Content (Guo et al., 2006)**Figure 8.** Equilibrium gas yield in the reactor as a function of dry biomass content for biomass gasification at 25 MPa and 873 K (Guo et al., 2006).

4. Conclusions

As the depletion of world's resource become the serious issue that we may face today, the gasification of biomass in supercritical water may bring us to an answer which solve this main issue we concerned. Biomass which is known as one of the very important energy resources that can be use in order to overcome the energy crisis. In comparing with pyrolysis and combustion, using biomass as the energy source, the gasification process gives the higher rate of efficiency. A gasification process is more environmental friendly because it does not involves the incineration process, which may cause global warming process or exerts harmful stack gaseous to the environment. Since, the production of gasification is gone through the combustion of gaseous, the efficiency is considering higher than the other two options.

Meanwhile, the efficiency of the gasification can even go higher by using supercritical water in the gasification process. The supercritical water which is more miscible exists in high pressure and in a lower temperature, helps to increase the efficiency of the operation process. Since, the operating temperature of the gasification in supercritical water is lower; the gasification in supercritical water process may be conducted in a safer condition and in lower cost comparing to the conventional gasification. Meanwhile, the gasification promises a better efficient in converting wet biomass and waste stream. Hence, by considering this all, we may conclude that the gasification of biomass in supercritical water is more achievable, environmental friendly, feasible, and sustainable method in producing renewable energy resources.

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