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Biomass Gasification in Supercritical Water – A Review

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Biomass Gasification in Supercritical Water – A Review

Prabir Basu and Vichuda Mettanant

Abstract

Supercritical water possesses a number of important characteristics that make it suitable for oxidation, synthesis and gasification reactions. It is especially advantageous for very wet biomass whose gasification in this medium avoids the large expense of energy required for drying. Although the process is in laboratory scale it has a great potential for production of hydrogen and other gases from biomass. This paper reviews the present state of the art and summarizes major observations arrived at in small scale laboratory flow and batch reactors. Effects of operating parameters like, pressure, temperature, etc., on the yield and conversion are discussed. Catalysts appear to play an important role in increasing the conversion rate and decreasing the reaction temperature for gasification. Heat recovery from the product stream holds key to making the gasification process auto-thermal. Heat exchanger efficiency, therefore, plays an important role in this process. Several investigators have used the equilibrium model and exergy analysis for thermodynamic analysis of supercritical gasification plants. Energy efficiency of such a plant could be around 50%.

KEYWORDS: SCW, gasification, biomass, review, exergy analysis

INTRODUCTION

Biomass is a promising renewable energy resource. The availability of biomass in the world is 220 billion oven-dry ton per year or 4 500 EJ (10^{18} J) (WEC, 2004). It is world's largest and most sustainable energy resource. Increasing the amount of energy produced from biomass, one can reduce the fossil fuel consumption, and thereby bring in three important benefits:

1. Reduced net release of greenhouse gases to the atmosphere;
2. Conserve the finite resource of fossil fuel by substituting it with renewable biomass;
3. Reduced dependence on imported fossil fuels for many countries.

Converting biomass to fuel gases can improve its utilization as the gases can be used for the following purposes:

1. Supply feedstock for some chemical industries
2. Synthesis of some gases into liquid fuels
3. Generation of electricity through diesel engine, steam turbine, gas turbine and fuel cell
4. Delivery of thermal energy to metallurgical furnaces.

Liquid fuels, synthesized from biomass, can substitute fossil fuels for transportation. Presently, a sizeable amount of transport fuel is produced commercially from biomass using following methods:

- Fermentation of starch (from corn, sugar cane etc.) to ethanol
- Transesterification of fatty acid (from soy, canola etc.) to bio diesel.

Such substitution of fossil fuels with biomass has, however, a major criticism on the ground that present processes use food cereals as the feedstock instead of non-food ligno-cellulose biomass. This approach is straining the supply of food grains, and thereby raising their price. The other criticism of ethanol production from starch is that the net energy balance considering the entire production cycle (crop production, transportation, process etc.) is marginally positive to marginally negative varying between +30% to -10% (Johnson, 2006), which means that the energy required to produce ethanol can be higher than energy produced.

High moisture content is a major problem of biomass (Table 1). Biomass, in general, contains more moisture than solid fossil fuels. It is especially very high for some biomass like water hyacinth (*Eichhornia Crassipes*), and sewage that could have moisture content exceeding 90 wt% (Xu et al., 1996, ECN, 2007). Direct combustion would require drying of the biomass, but the energy spent in evaporating water from such biomass is so large that the net energy production could be negative. For example, the net energy production of raw sewage is (-) 1700 kJ/kg wet basis (Leible et al, 2006). Therefore, direct use of biomass as an energy source through burning is not practical in all cases.

Table 1. Moisture content of some biomass

| Biomass type | Moisture (% wet basis) |
|----------------|------------------------|
| Wheat straw | 8-20 |
| Sawdust | 25-55 |
| RDF pellet | 25-35 |
| Wood bark | 30-60 |
| Corn stalk | 40-60 |
| Rice straw | 50-80 |
| Food waste | 70 |
| Cattle manure | 88 |
| Water hyacinth | 95.3 |

Low energy density of biomass is another shortcoming of biomass. For example, lower heating value (LHV) of rice husk is 14 987 kJ/kg (dry ash free basis), while that of natural gas is 38 047 kJ/kg on the same basis (ECN, 2007). This increases the transportation and handling cost and thus, a direct utilization of such biomass for energy production becomes unattractive.

Gasification can help increase the energy density and facilitate its handling reducing the transportation cost. For converting biomass into fuel gases, followings means are available:

- Thermal gasification
- Pyrolysis
- Anaerobic digestion
- Supercritical water gasification (SCWG)

Except for the options of anaerobic digestion and supercritical water gasification, the total energy conversion efficiency reduces as the moisture content of the biomass feed increases. This is due to the increasing amount of energy consumed in drying the fuel. Supercritical water gasification does not require drying as the water serves as hydrogen donor and a reaction medium. Thus the drying problem is largely avoided in SCWG.

The conversion efficiency of thermal gasification is generally higher than other options, but above a fuel moisture content of 31%, the conversion efficiency of thermal gasification falls below that of supercritical water gasification (Yoshida et al., 2003). The conversion efficiency of anaerobic digestion route (30.5%) is insensitive to the moisture content in biomass, but its efficiency is well below that of SCWG (Table 2).

Table 2. A comparison of energy conversion efficiency of different options for biomass conversion. (Data collected from Yoshida et al., 2003)

| Moisture content in feed | 5% | 31% | 55% | 75% |
|----------------------------------|----------------------------------|-----|-----|-----|
| Biomass conversion means | Energy conversion efficiency (%) | | | |
| Thermal gasification | 61 | 55 | 47 | 27 |
| Pyrolysis | 57 | 53 | 45 | 27 |
| Liquefaction | 39 | 37 | 36 | 34 |
| Anaerobic digestion | 31 | 31 | 31 | 31 |
| Supercritical water gasification | 55 | 55 | 55 | 55 |

Supercritical water gasification thus offers a good option for gasification of high moisture biomass. This process is however, relatively new. Only a limited amount of research has been carried out in small scale laboratory units. In view of its high potential, extensive research and development is necessary in the near term. The present paper lays the ground of further research by providing a broad review of the present state of the art.

The paper briefly outlines the properties of supercritical water and different process based on these properties. The review is divided into two broad sections. The first section discusses the SCW gasification process including kinetics and parametric study of SCWG, while the second section reviews the thermodynamic analysis of the SCWG system.

Properties of supercritical water

Water above its critical temperature, 374.1°C, and critical pressure, 22.1 MPa is known as ‘Supercritical water’ (SCW) (Wagner and Prass, 2002). Water below the critical temperature, 374.1°C but at a pressure above its saturation pressure is referred to as ‘Subcritical water’. Below its saturation pressure and critical temperature water is called ‘Subcritical steam’. Similarly, below the critical pressure, water will be called subcritical steam even if its temperature is above the critical temperature. Figure 1 illustrates this definition.

Above the critical pressure, instead of having a ‘boiling point’ like at subcritical pressure, water would have a ‘pseudo-critical’ temperature, where water experiences a transition from liquid like to gas like behavior. The pseudo critical temperatures for a given supercritical pressure can be estimated within above and on the critical pressure by the relation given below. This relation is valid up to 80MPa (Malhotra, 2006).

$$\frac{T_{sc}}{T_c} = \left(\frac{P}{P_c} \right)^F \quad (1)$$

Where,

$$T_{sc} > T_c, P > P_c$$

$$F = 0.1248 + 0.01424 \left(\frac{P}{P_c} \right) - 0.0026 \left(\frac{P}{P_c} \right)^2$$

At the upper right corner of Figure 1 the shaded area indicates the supercritical region of water. Water at atmospheric pressure (subcritical water), when heated above its saturation temperature undergoes phase change from liquid to vapor with a sharp and large change in density (958 kg/m^3 at 99°C to 0.55 kg/m^3 at 124°C , at 0.1 MPa).

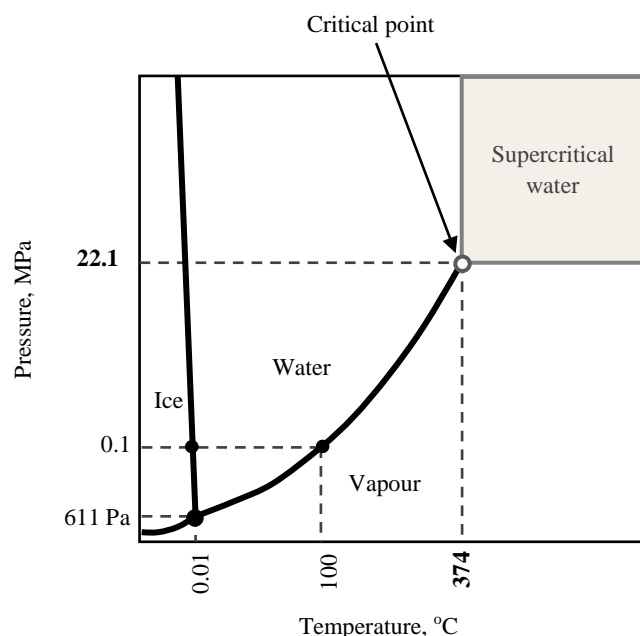


Figure 1 Schematic phase diagram of water.

Above the critical pressure the density change in water is gentle and modest across its 'pseudo-critical' temperature, where a transition from liquid-like to vapor-like state takes place. For example, at a supercritical pressure of 25 MPa , the density of water reduces from 630 kg/m^3 at 350°C to 170 kg/m^3 at 400°C . (Wagner and Prass, 2002) without a jump as one would expect when the water at subcritical pressure is heated beyond its boiling point.

Above the critical pressure one avoids the conventional phase change through boiling. As such, the additional energy (heat of vaporization) required for phase change in subcritical pressure is not needed. This property is significant especially for recovering heat from SCW through a heat exchanger. In a heat exchanger the temperature difference between the two streams is the driving force. Without latent heat energy transfer without changing in temperature is diminished. This makes the

efficiency of a heat exchanger increases. Thereby, a large part of the heat for heating up water to the operating temperature for SCWG process (600°C) can be recovered.

Density, viscosity and dielectric constant are three main properties that influence the gasification of biomass. Supercritical water is well suited for gasification on account of its favorable values for all these three properties, and as such these are discussed briefly below.

Water at supercritical state possesses gas-like viscosity and liquid-like density properties. The gas-like low viscosity provides better mass transfer. The liquid-like density promotes better solvation property.

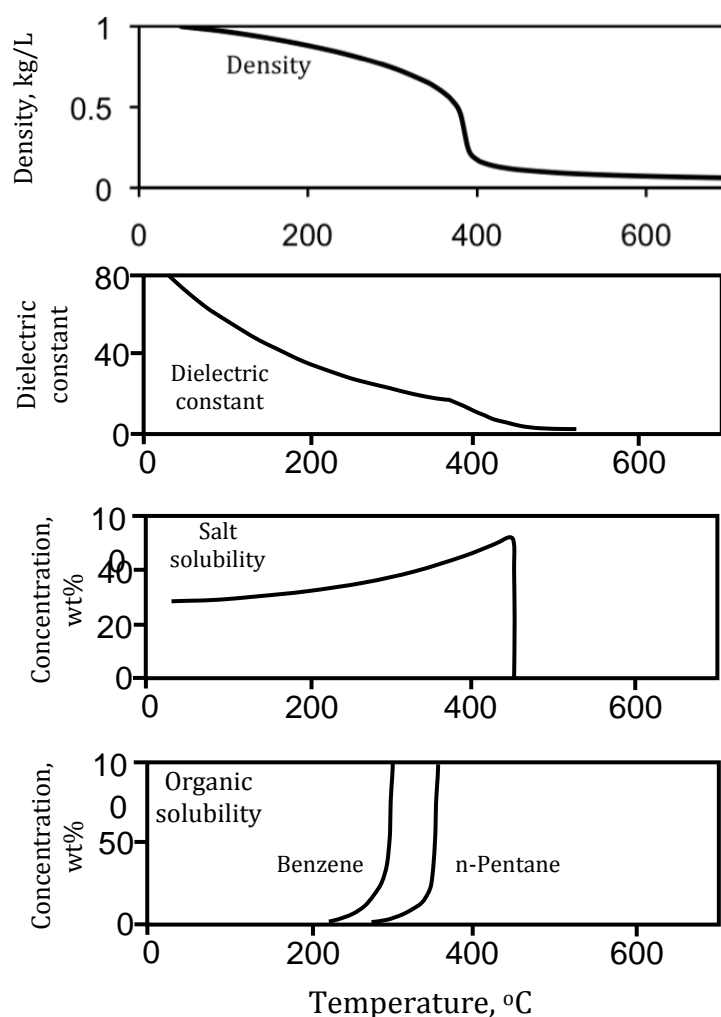


Figure 2. Properties of water at 25.3 MPa. (Yesodharan, 2002)

The dielectric constant of SCW is very low. For example, at 25 MPa, the dielectric constant of water drops from 80 at ambient temperature down to 2 at about 450°C (Figure 2). There is a large difference in density between these two conditions. One implication of the density change is that when density decreases, the number of hydrogen bond drops, and their strength is weakened, which is manifested by the drop in dielectric constant (Marrone et al., 2007). This makes water a highly polar solvent at ambient temperature (or at subcritical condition), and a non-polar solvent in the supercritical region.

SCW is, thus, a good solvent for non-polar organic compounds like benzene, n-pentane and others, which has very low solubility at subcritical condition. This solvent property will allow organic compounds including ligno-cellulosic materials to readily dissolve in supercritical water, and therefore break the inter-phase boundary during the gasification. Once dissolved, supercritical water will efficiently break cellulose bonds resulting in rapid formation of gaseous products. These properties make SCW a better reaction medium in which mixing is fast and organic materials dissolve well (Yesodharan, 2002).

Gases like CO₂, CH₄, H₂, N₂ and air are completely miscible in supercritical water (Japas and Frank, 1985a and 1985b, Trodheide and Franck, 1963, Seward and Frank, 1981, Krader and Frank, 1987). The polar inorganic compounds like, KCl, NaCl, CaSO₄ etc., which have high solubility in subcritical water shows very low solubility in supercritical water. Thus it is relatively easy to separate them from the product. This allows the product of SCWG to leave the system free from the salt. The more details are available in Peterson et al. (2008b).

Supercritical water is characterized by its high ion product, which implies high [H⁺] or [OH⁻] concentration in supercritical water. This allows SCW act like an acid or base catalyst in the reactions. Many organic chemicals that do not react in water without the presence of strong acid or base catalyst may readily react under the hydrothermal condition of SCW.

Certain reactions that are catalyzed by protons or hydroxyl ions could take place in water near its critical conditions without any addition of acid or base catalyst (Buhler et al., 2002). Here water provides the protons and hydroxyl ions catalysts due to its enhanced self-dissociation near the critical point. Thus water serves as a reaction medium, solvent as well as a catalyst. Savage (1999) and An et al., (1997) presented excellent reviews of such reactions.

The characteristics of supercritical water may be summarized as follows:

1. Density of SCW lies between that of water and steam vapor
2. SCW dissolves most gases (Japas and Frank, 1985a)

Ion product is another interesting characteristic of water. It is the product of [H⁺] and [OH⁻] ions in the substance. This has effect on a) acid or base catalyzed reaction, b) ability to solubilize salt and c) corrosion. At 25 MPa, the ion product of water at ambient temperature is 10⁻¹⁴ and increases to a maximum

at 10^{-11} at around 200-300°C, but when the temperature increases further above 550°C, the ion product drops below 10^{-23} (mol/kg)² (Marrone et al., 2007). Ion product affects the ability of SCW to solubilize inorganic salts. Most ionic substances such as inorganic salts are soluble in subcritical water, but are nearly insoluble in typical conditions of SCW gasifiers (Figure 2). Corrosion, which is another practical issue of gasification, could occur in a SCW system due to its high density, high temperature, and high aggressive ion concentration (e.g., acidic) (Marrone and Hong, 2008).

The self-dissociation property of water near its critical point allows it to serve also as a catalyst for many decomposition reactions like in glycerol etc. (Antal et al., 1985 and Ramayya, 1987). Near the critical temperature the ionic product of water being high, many reactions can be catalyzed by the $[H^+]$ or $[OH^-]$ ions in the water.

Besides the attractive features like high mass transfer and high solubility for organic compounds and gases, SCW shows a sharp rise in specific heat followed by a drop near its pseudo-critical temperature. This combined with moderate continuous drop in density results in a large increase (8 to 13 kW/m²K) in heat transfer coefficient followed by a drop to about 2 kW/m²K (Shang et al., 2008). This drop in heat transfer coefficient still offers values more than what is expected in subcritical steam (Furusawa et al., 2007).

Supercritical gasification (SCWG) is an excellent means for extraction of energy from biomass. By tuning temperature or pressure, one can change the characteristics of SCW, which in turn change the reaction chemistry and kinetics producing desired products at desired concentrations. Due to the unique properties of SCW, thermodynamic equilibrium and high chemical reaction rates are possible. SCWG allows high solid conversion (over 99%) and high hydrogen concentration in the product gas (up to 50%) with suppression of char and tar formation (Calzavara et al., 2005).

Additionally, the gas produced can be stored or utilized at high pressure obviating the need for the additional expense of gas-compression.

The following section will discuss the process of supercritical water based gasification (SCWG) in more details including the effects of design and operating conditions, kinetics as well as thermodynamic modeling and analysis.

Supercritical water based processes

Gasification medium in thermal gasification is generally an oxygen deficient gas like steam, carbon dioxide. In supercritical water gasification the reaction medium is water above its critical temperature and pressure. Such water is recognized as an excellent medium for several other processes as below:

1. Supercritical water oxidation

2. Supercritical water synthesis
3. Supercritical water for thermal power generation
4. Supercritical water gasification

Present review concerns supercritical water gasification alone, but a brief description of the other three options may be relevant here.

Supercritical water oxidation

The process of supercritical water oxidation (SCWO) is well developed, and is currently being implemented in commercial units (Yesodharan, 2002). Here, supercritical water helps oxidize hazardous or toxic chemicals. For many toxic and hazardous wastes like chemical warfare agents, the alternative for a safe disposal is rather limited. Deep well injection, open burning, and incineration are either restricted or completely unavailable in many areas and have become costly where they are still options.

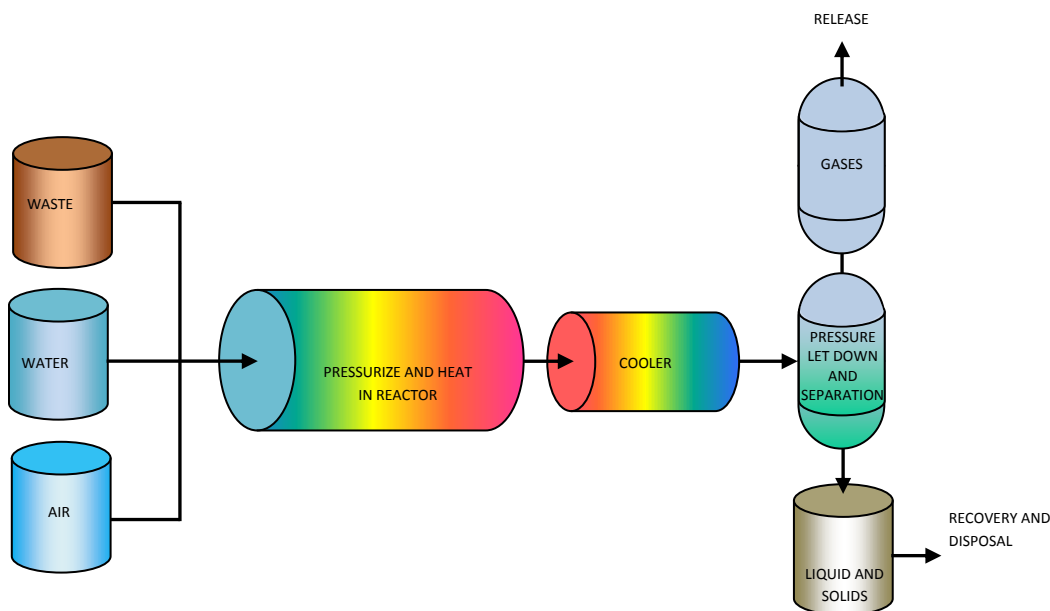


Figure 3. Process diagram of supercritical water oxidation process for destruction of hazardous process (General atomics, 2008).

SCWO takes advantage of the unique properties exhibited by water when used above its critical point, 374°C and 22.1 MPa. The organic content of the waste feed is quickly and efficiently converted to carbon dioxide, water, and salts with negligible production of carbon monoxide, NO_x , or SO_x . SCWO exhibits unparalleled environmental compliance capabilities, without the need of a pollution-abatement system. The higher operating pressure, relative to alternative

destruction processes such as incineration, results in a very compact unit design with high throughput capability (General atomics, 2008). General Atomics of USA, Chematur of UK, Hanwha Chemical of Korea and Mitsubishi Heavy Industries of Japan. (Marone et al., 2007) are amongst companies who offer commercial plants. Figure 3 presents a schematic of the process.

Supercritical water synthesis

Synthesis in supercritical water (SCWS) is a relatively new application of supercritical water process. For environmental and safety concerns, traditional but hazardous solvents such as methylene chloride or benzene is to be replaced with SCW as a solvent in synthesis reactions. The main aim is to synthesize a potentially valuable chemical, which is formed as an intermediate in the destruction of a more complex feed (Marrone et al., 2007). Many hydration, dehydration as well as hydrolysis reactions take place in supercritical water without additional support materials, such as acids or bases, with high selectivity and with high space-time yields (Krammer et al., 1999). SCWS is found to be capable of producing a wide variety of nano particles of metals/metal oxides and mixed metal alloys; including TiO_2 , CeO_2 , Silver, CuO , YAG, InO_2 , CdS and ZrO_2 through hydrothermal synthesis. Interest in this area is rising rapidly (Rangappa et al., 2007).

Supercritical water for thermal power generation

Here the thermodynamic property of supercritical water is exploited to generate electricity from fossil or biomass fuels. Supercritical water works as the working fluid in a Rankine cycle plant. High temperature and pressure of the fluid allows a steam turbine to produce electricity at a much higher efficiency (Basu et al., 2000). Fairly large number of thermal power plants are in current operation and its use is increasing in view of lower pollution and lower electricity generation cost (Butler and Basu, 2007).

Supercritical water gasification

This is the subject of the present reviews, and therefore it is described in details in the next section.

Supercritical water gasification process

In SCW gasification, supercritical water helps break (cleavage) large molecules of biomass into smaller molecules like CO , H_2 , CH_4 , CO_2 etc. The water provides the reaction medium as well as the hydrogen necessary for the hydrolysis reaction.

The overall reaction is endothermic or slightly exothermic. One of the major characteristics of gasification in SCW is that if carried out properly, the char production is minimal, and it is the observation that sparked the initial interest in supercritical gasification (Amin et al., 1975).

The process of supercritical water gasification (SCWG) is explained in Figure 4 by means of a typical process flow diagram. A supercritical gasifier necessarily requires the feedstock and the water to be pressurized to the required high supercritical pressure. To overcome the problem of pumping fibrous solids against such a high pressure the biomass could be made into pumpable slurry. The pumpable slurry of biomass is prepared in a feed tank by mixing ground biomass in water with an appropriate emulsifying agent. A high-pressure slurry pump then pumps the slurried feedstock to the reactor. The pressurized water passes first through a heat exchanger where it is preheated by utilizing the heat from the hot product leaving the reactor then biomass is injected into the reactor. This heat alone is not sufficient to heat the feed water to the required reactor entry temperature. So, it is further heated in an externally heated preheater before entering the gasifier reactor.

After gasification, the product gas would pass through a cooler that delivers the heat to pre-heating the feedstock. The product is further cooled down in an externally cooled heat exchanger, and then it goes to a gas-liquid separator. The gas mixture might go through further purification equipment such as scrubber and or pressure-swing adsorption unit if necessary. The liquid fraction of the product is collected from the high-pressure gas-liquid separator while the gas fraction could go to the pressure swing absorber. A pressure-reducing valve decreases the pressure of the liquid further before it enters a low-pressure gas-liquid separator (Figure 4).

This is just one of many potential process flow diagrams one can adapt for supercritical water gasification. The option would depend on the desired product-mix, design reactor temperature and chosen means of preheating the feed and separation of product constituents.

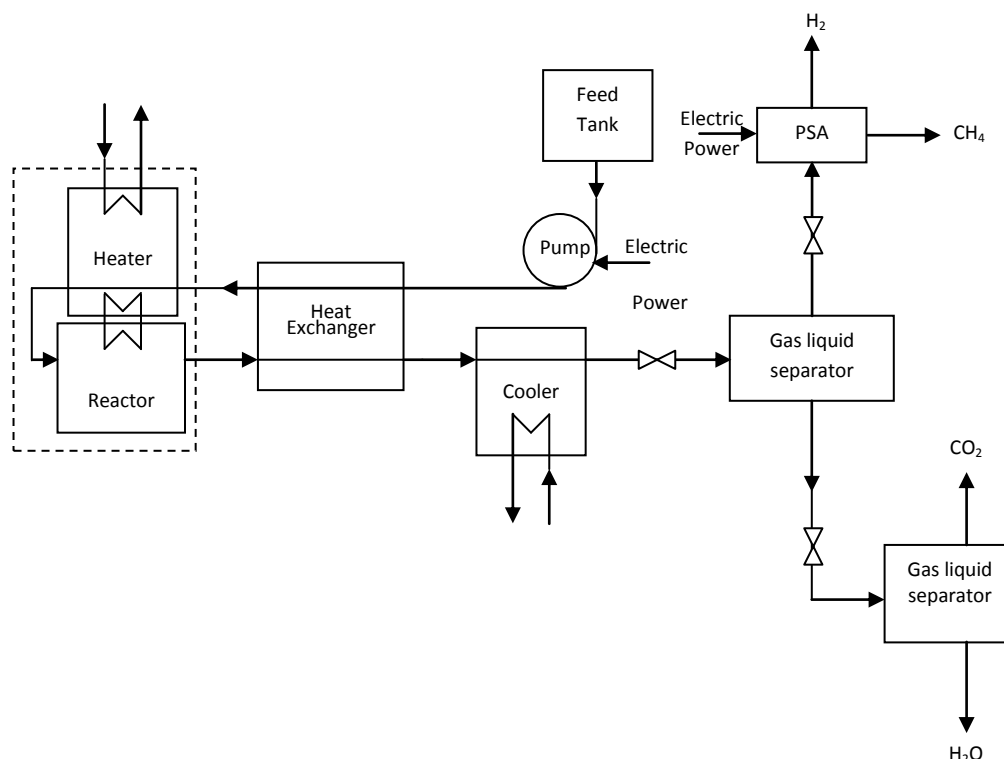


Figure 4. Supercritical water gasification process

Economic viability

Supercritical water gasification is still in very early stage of development. Very little information on its commercial viability is available at the moment. Yoshida et al. (2003) compared the efficiency and carbon dioxide emissions between various methods of biomass energy conversion to determine the energy flow from biomass resources to electricity, automotive fuels and heat. The supercritical gasification combined cycle is the most efficient option for high moisture content biomass. They also examined the option of operation of SCWG with fuel cells and found that it would be optimal when the relative cost of fuel cell decreases. Supercritical water gasification is evaluated to be more advantageous over biomethanation, but the cost of gas production is still high (Matsumura, 2002). To improve efficiency of SCWG, studies of its kinetics, effect of operating parameters and thermodynamic analysis of the process are necessary.

Current status of commercialized

Research efforts in SCWG have been active since 1970's (Matsumura et al., 2005). Several research laboratories including Forschungszentrum Karlsruhe in Germany, University of Twente in the Netherlands, De L'Aquila University in Italy and Selcuk University in Turkey, Pacific Northwest National Laboratory and University of Hawaii in USA, National Institute for Resources and Environment as well as many universities in Japan, State Key Laboratory of Multiphase Flow in Power Engineering in China and Advanced Institute of Science and Technology in Korea are working in this field (Calzavara et al., 2005, Lu et al., 2006, Lee et al., 2002). Research results from many of these laboratories are reviewed and discussed in this paper.

Commercial application of SCWG is still awaited. The pilot plant VERENA (experimental facility for exploitation of agricultural matter) is one of the largest SCWG in operation with a capacity of 100 kg/h, capable of operating to 28 MPa, 660°C (Boukris et al., 2005). One collaborative European project (WINEGAS, 2002) is working on supercritical water gasification of wine grape waste at 300 bar and 600°C using a bench scale unit (20 kW_{th}) to produce a hydrogen rich clean fuel gas with the final objective to design a 1 MW demonstration plant. The production of hydrogen from biomass through SCWG has been confirmed in the Verena unit. (Boukris et al., 2005)

As mentioned above, SCWG is still in an embryo stage. Experimental work is generally limited to very small (few millimeter diameter) bench scale reactors. Matsumura et al. (2005) presented a good review of reactors used by different researchers.

KINETICS AND PARAMETRIC STUDY OF BIOMASS GASIFICATION IN SCW

The gasification in supercritical water is affected by a large number of parameters including, reaction temperature, solid concentration, pressure, catalyst etc. For a rational design a comprehensive understanding of the effects of these parameters is necessary. The following section presents a brief review of the kinetics and parametric study of biomass gasification in SCW.

Kinetics

Amongst three major constituents of biomass, cellulose, hemicellulose and lignin, the first one has been studied most extensively. A simplified picture of the reaction pathways of liquefaction and/or gasification for the main constituents of the biomass, i.e., cellulose, is discussed first (Figure 5). After that a discussion of

the other two constituents and mixture of individual constituents would be presented.

Figure 5 presents the simplified reaction pathways of liquefaction and/or gasification for the main constituent of the biomass, i.e., cellulose after Kruse et al. (2003).

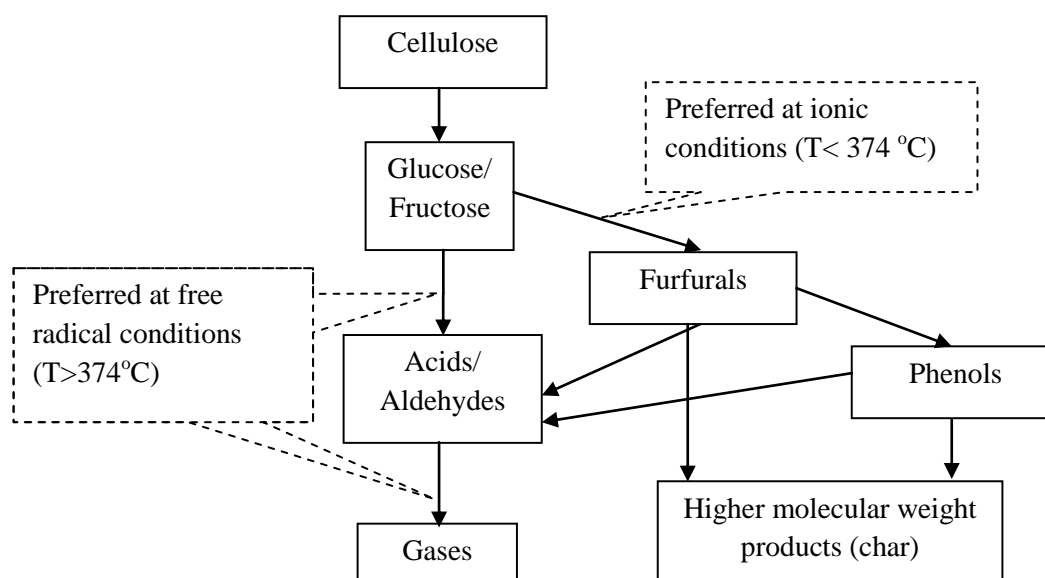


Figure 5. Main reaction pathways for cellulose liquefaction and/or gasification (Lu et al., 2006).

It shows two parallel paths of conversion. The one on the left is through free radical reaction, preferred at supercritical condition (high temperature and or low pressure), while the one on the right is ionic reaction, preferred at subcritical condition (lower temperature and or higher pressure) (Buhler et al., 2002, Matsumura et al., 2005, Lu et al., 2006). As gases are typical products of the free radical reactions the formation of gaseous products occurs at higher temperatures (above critical temperature) (Buhler et al., 2002). The sequential steps of the gasification reaction may be described as below:

1. Rapid hydrolysis of cellulose to glucose and/or fructose occurs. Sugar (water-soluble) takes place first at around 200°C . No gas, oil or char is produced at this stage (Minowa et al., 1995 and 1998).
2. Thereafter, the process is followed by two competing parallel reactions.
 - a) Decomposition of the sugar into short chain aldehyde and organic acids
 - b) Dehydration and ring closure to furfural derivatives and phenols. Here furfural and phenols represent the tar.

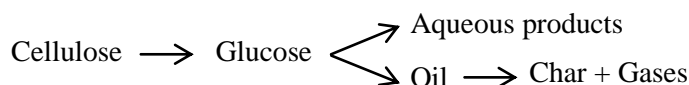
The first reaction path is ionic, preferred in subcritical water, while the second one is free-radical type, which is preferred in supercritical water.

3. Short chain aldehyde and acid react to form gases. Furfural and phenols could also decompose into gases in SCW, but this reaction is slower than the decomposition of the glucose.
4. Furfural and phenols could also produce char or coke.

At supercritical conditions ($T > 374.1^{\circ}\text{C}$), the pathway on the left in Figure 5 becomes more important and the gas yield increases. The density of water at supercritical state is lower than that at subcritical conditions. This inhibits ionic reactions in SCW, but favors free-radical reactions, which are necessary to form gases such as H_2 or CH_4 (Kruse and Gawlik, 2003).

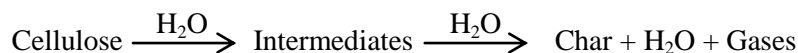
It may be noted that the intermediate decomposition products are dissolved in SCW as a result of its high solvent power for organic compounds. It allowed faster reaction while minimizing the formation of tar or char (Kruse et al., 2003).

Minowa et al. (1998) proposed an alternative model similar to that of pyrolysis for conversion in high pressure water.



According to this model, hydrolysis of cellulose begins between $200\text{--}220^{\circ}\text{C}$ producing water-soluble products like glucose and oligomer. Above 240°C , the formation of non-glucose compounds, oil and gases starts. Cellulose is entirely decomposed above 280°C , and the conversion of glucose is complete above 300°C (Minowa et al., 1998).

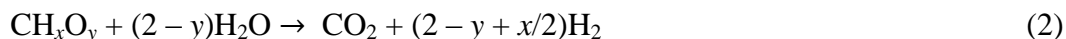
Varhegyi et al. (1993) proposed the following model for water-catalyzed decomposition of biomass in high-pressure water. They also suggested that at low temperature ($> 200^{\circ}\text{C}$), hydrolysis is the primary step.



In the above description of cellulose gasification reaction it may be remembered that cellulose from different biomass sources may have varying crystalline and chemical structures. As such their degradation could also be different.

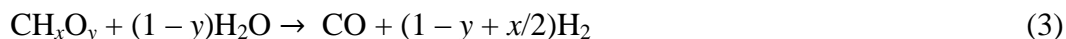
Chemical reactions

The overall chemical reaction for biomass gasification to hydrogen in supercritical water (SCW) can be represented by the following simplified reaction (Guo et al., 2007), which is endothermic in nature.



Behind this overall reaction three major competing intermediate reactions can occur during the gasification of biomass in supercritical water (Guo et al., 2007):

Steam reforming:



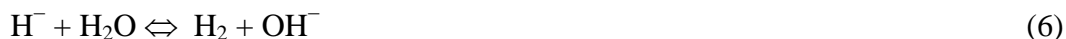
Water-gas shift:



Penninger and Rep (2006) described the mechanism of water gas shift reaction in supercritical water as below. In supercritical condition the ionic dissociation of water takes place releasing OH^- ions. The reaction between CO and OH^- produces formate anion (HCOO^-), according to equation below:



The formate anion decomposes into CO_2 and hydride anion (H^-), which in turn interacts with water, forming H_2 and OH^- by electron transfer (Penninger and Rep, 2006).



Methanation:



Due to the desire product of SCWG is H_2 therefore water-gas shift reaction should be dominant and methanation should be restrained. High reaction temperature can provide this effect (more details are provided in “Effect of reaction temperature” section). More specifically for the gasification of cellulose and glucose, the overall reactions are (Hao et al., 2003):

Cellulose:



Glucose:



Kinetic rate

For determination of the kinetics of biomass gasification in SCW, several investigators like Jesus et al. (2006a and 2006b) used tubular-flow reactors. It can be viewed as an ideal plug-flow reactor when it satisfies the criteria:

$$\text{Pe} = \frac{ud}{D} \rightarrow \infty \quad (10)$$

When the length of the reactor is more than 100 times of its diameter, the axial dispersion coefficient (D) approaches zero. Then the Peclet number (Pe) tends to infinity and the above condition for ideal plug-flow reactor is satisfied. For ideal plug-flow, the reaction is modeled as (Jesus et al., 2006a and 2006b):

$$\frac{dX_C}{d\tau} = -\frac{r_C}{C_{C0}} \quad (11)$$

Experimental data of Jesus et al. (2006a and 2006b) on corn silage confirms this equation. The gasification yield of corn silage increases linearly with residence time of the feed in the reactor.

Lee et al. (2002) and Blasi et al. (2007) used irreversible, first-order, Arrhenius type reaction rate under the assumption that reactor operates at isothermal and isobaric conditions. This assumption gives $-r_C = K C_C$. Equation (11) can be rearranged to:

$$\tau = C_{C0} \int_0^{X_C} \frac{dX_C}{-r_C} \quad (12)$$

$$\text{Where } X_C = \frac{C_{C0} - C_C}{C_{C0}}$$

The residence time, τ , and conversion, X_C , being known from experiments the reaction rate constant, K can be estimated from:

$$K = -\frac{\ln(1 - X_C)}{\tau} \quad (13)$$

Assuming the reactions to be Arrhenius type, the reaction rate constant, K may be written as:

$$-r_C = K C_C = A \exp(-E/RT) C_C \quad (14)$$

Table 3 lists values of the parameters of reaction rate constant collected by different researchers for gasification of glucose (a model biomass compound) in SCW. The parameter includes values for the pre-exponential factor, A , and activation energy, E , for gas production, tar production, glucose conversion, chemical oxygen demand destruction, (COD), and destruction of total organic carbon (TOC) in waste-water. The total reaction of biomass conversion is divided into reactions for individual species and the reaction rate is determined for them. The data of Matsumura et al. (2006) was collected at 25 MPa, 400-600°C in presence of activated charcoal catalysts.

Table 3. Pre-exponential factor and activation energy

| | Pre-exponential factor (s ⁻¹), A | Activation energy (kJ/mol), E | Source |
|-----------------------------------|--|---------------------------------|------------------------|
| Gas production from glucose | 99 600 | 89.4 | Matsumura et al., 2006 |
| Tar production from glucose | 19.4 | 36.0 | Matsumura et al., 2006 |
| Glucose conversion | $10^{3.09 \pm 0.26}$ | 67.6 ± 3.9 | Lee et al., 2002 |
| COD destruction | $10^{2.95 \pm 0.23}$ | 71.0 ± 3.9 | Lee et al., 2002 |
| Destruction of TOC in waste water | 897 ± 29 | 75.7 ± 22 | Blasi et al., 2007 |

Buhler et al. (2002) found non-Arrhenius type behavior of degradation of glycerol in the temperature range of 350-475°C and pressure range of 25-45 MPa. They developed a model based on free radical and ionic reactions to explain their experimental results. It showed a preference of free radical reactions at higher temperatures ($>T_c$) and lower densities (lower pressure but $>P_c$) and ionic reactions at lower temperature ($<T_c$) and higher densities (higher pressure).

Summarized of assumed first-order Arrhenius plot of glucose and cellulose degradation from others literatures are also available in Peterson et al. (2008a).

Effect of design and operating parameters on gasification

Supercritical water gasification is a relatively new field of research. It has not been explored fully. So far, the following parameters have been identified as ones influencing gasification of biomass in SCW:

1. Reaction temperature
2. Reaction pressure
3. Residence time
4. Heating rate
5. Feed concentration
6. Biomass type
7. Size of biomass particles
8. Reactor design
9. Reactor geometry
10. Reactor material type
11. Carbon build up on reactor wall
12. Catalyst

Data presented here are mostly from small batch reactors, and many are based on a model biomass like glucose.

To discuss the effect of design and operating parameters on gasification it is important to define what is meant by gasifier performance. The performance of a gasifier is evaluated in terms of several indices. Most important of them are: gasification efficiency, carbon efficiency, and yield of specific products.

Gasification efficiency (GE) is defined as the percentage of biomass converted into gas (Basu, 2006). Carbon efficiency (CE) is the ratio of carbon in fuel converted into gases. The yield of different gases is measured primarily in terms of their percentage in the product gas as well as the amount of product gas produced per unit feed. These indices would be used to discuss the performance of a gasifier.

Effect of reaction temperature

Reaction temperature is perhaps the most important parameter that influences the performance of a SCW gasifier. It has a significant effect on the specific yield of gasification especially in absence of catalyst (Guo et al, 2007). In fact, the gasification process in pressurized water may be divided into three groups depending on the primary product of gasification (Table 4) (Peterson et al., 2008a).

Table 4. Division of hydrothermal reaction by temperature of reaction

| Temperature range | Catalyst use | Product yield |
|---|----------------|--|
| High temperature ($>500^{\circ}\text{C}$) | No catalyst* | Hydrogen rich gas |
| Medium temperature (T_c to 500°C) | With catalysts | Methane rich gas |
| Low temperature ($<T_c$) | With catalysts | Other gases from smaller organic molecules |

*No-catalysts may be used if needed, T_c – critical temperature

High temperature processes (500°C - 800°C) are thermodynamically less efficient than low temperature ones. Also, external energy may be needed to sustain the process. Guo et al. (2007) showed that in the case of equilibrium calculation and SCWG of lignin 650°C and 725°C are the maximum reaction temperatures required, respectively. The temperature higher than these are unnecessary due to further increase in temperature does not affect the increasing of product gas. However the temperature to reach equilibrium depends on reaction conditions such as biomass concentration and heating rate.

Low temperature (200 - 300°C) processes are more efficient in this respect, but the uncatalyzed gasification in this temperature is difficult to achieve. So, use of catalyst becomes essential for low temperature processes. For methane production equilibrium calculations show that lower temperature (374 - 500°C) gives higher yield. Due to the reaction of complete conversion of biomass to hydrogen is endothermic while the reaction that completely converts biomass to methane is slightly exothermic. According to the Le Chatelier principle, the formation of methane increase at lower temperature (Kruse 2008).

The gaseous yield of gasification depends on chemical reactions involved and their rate. The product gas composition would be governed by the chemical equilibrium of the reactions involved. The kinetic rate of any Arrhenius type equation increases with temperature (Jesus et al., 2006a and 2006b). Equation (14), developed for SCW gasification also predicts that the reaction rate constant increases with temperature. So, the overall gasification yield is higher and its rate of increase with time also increases with temperatures.

Several investigators (Hao et al., 2003, Lu et al., 2006, Schmieder et al., 2000) studied the effect of temperature on gasification yield from both model-biomass (glucose) and real biomass like fruit shell etc.

Results with glucose as model biomass

Following section presents data based on glucose conversion in SCW. In general, the gasification efficiency increases as reactor temperature increases.

These effects are qualitatively similar at different pressures. Figure 6 shows variations in composition of the gasification products against reactor temperature for glucose at 28 MPa (Lee et al., 2002). Hydrogen and carbon dioxide yield increases with temperature. Carbon monoxide composition increases with temperature at low temperature, but after reach a maximum, the CO composition drops rapidly. Figure 6 also shows that the gasification efficiencies for conversion of carbon, hydrogen, and oxygen increase with the reaction temperature.

Here, the gasification efficiencies are percentage of the total moles of C, H

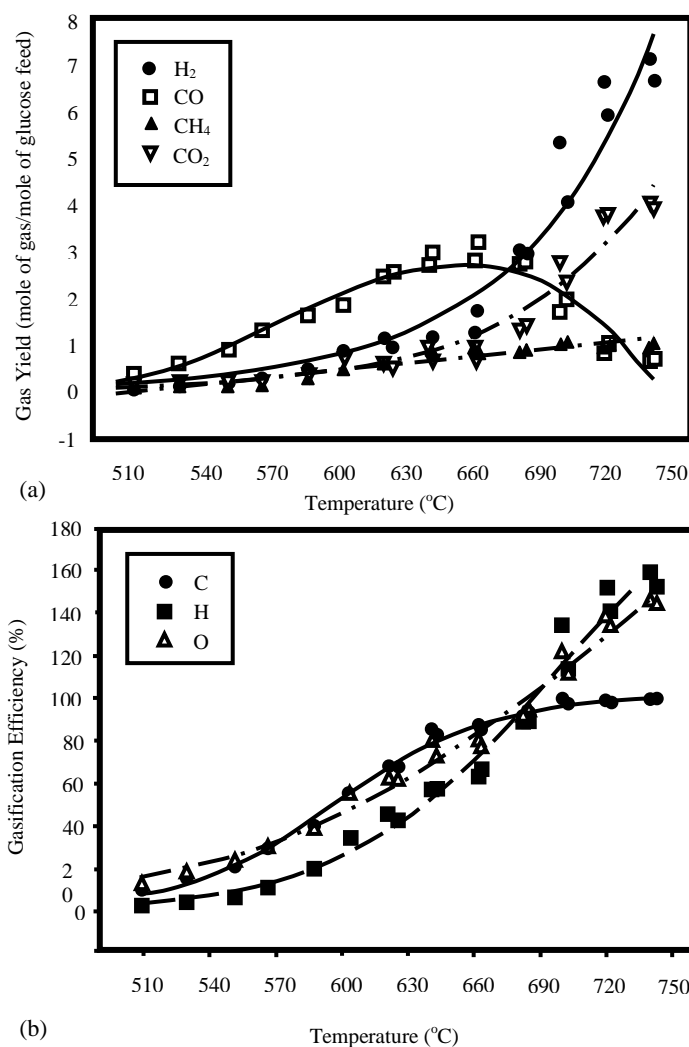


Figure 6. Effect of temperature on glucose gasification in SCW: (a) gas yields, (b) gasification efficiencies (Lee et al., 2002).

or O atom in gaseous products per moles of C, H or O atom of glucose feed. Carbon gasification efficiency reaches 100% at 700 °C representing complete conversion of glucose to product gas. The gasification efficiency of Hydrogen is interestingly higher than 100%. This is possible here because the supercritical water contributed some of the hydrogen in the product gas. Thus it confirms that SCW serves as both a hydrogen source as well as a solvent for glucose gasification.

A very large effect of temperature was noted by Hao et al. (2003) at 25 MPa. A 30% increase in reaction temperature (500 to 650 °C) resulted in a 167% increase in the carbon efficiency (CE), and more than 300% increase in the gasification efficiency

(GE). The hydrogen production increased by 46%, but CO reduced by 74%. Lee et al.'s (2002) result showed both hydrogen and CO to increase with temperature but beyond 660°C, the CO yield dropped below that of H₂.

Xu et al. (1996) obtained results similar to this but their CO yield started decreasing at a lower temperature. This may be due to their use of activated charcoal as catalyst, while others used none.

Lee et al. (2002) inferred that at temperatures of 510-660°C a significant fraction of the glucose is converted to carbon monoxide and remain stable. At temperature above 660°C, carbon monoxide and other intermediate products are converted to hydrogen. To explain the effect of temperature, they proposed the following mechanism for glucose conversion in SCW. Glucose is first broken down into several water-soluble intermediates that could undergo steam-reforming reaction producing CO:

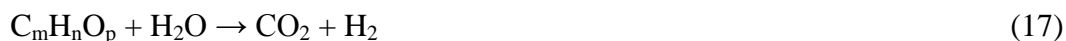


Biomass \rightarrow water-soluble intermediate \rightarrow gases

The CO produced then undergoes water gas shift reaction forming additional hydrogen.



At low temperatures the reaction (15) is faster than reaction (16). So, more CO is produced than that is converted into hydrogen. But at higher temperatures reaction (16) is very fast resulting in a net reduction in CO and increase in hydrogen. Some of the intermediates also undergo reaction producing hydrogen and carbon dioxide.



Reactions (16) and (17) contributed to the increase in carbon dioxide and hydrogen yield with the rise in temperatures observed in experiments.

Lignin is an important refractory component of biomass. For lignin gasification (1.5 wt% lignin in water, without catalyst), Guo et al. (2007) observed carbon conversion efficiency, (CE) increased from 30% at 500°C to 41%, at 650°C. Above 700°C the conversion could well approach 100% for 3 wt% lignin in water. The hydrogen yield and gasification efficiency (GE) also increased with temperature in the same way. This led Guo et al. (2007) to suggest a temperature of 700°C or higher is necessary for complete gasification of lignin.

Methane is another important product of SCW gasification. As shown in Table 4, its yield could be high in the intermediate temperature range of 374-500°C, but use of catalyst is necessary. Figure 6 shows that its yield, though low in absence of catalyst. Methane is very stable in SCW, and is not converted into any smaller molecules (Lee et al., 2002).

Results with real biomass

The effect of reaction temperature on the gasification of real feedstock is similar to that of the model biomass. For gasification of wood sawdust in SCW, Lu et al. (2006) noted more than 10% increase in GE, and CE when temperature increased from 600°C to 650°C. The yield of H₂, CO₂, and CH₄ also increased with temperature in their experiments at 30 MPa.

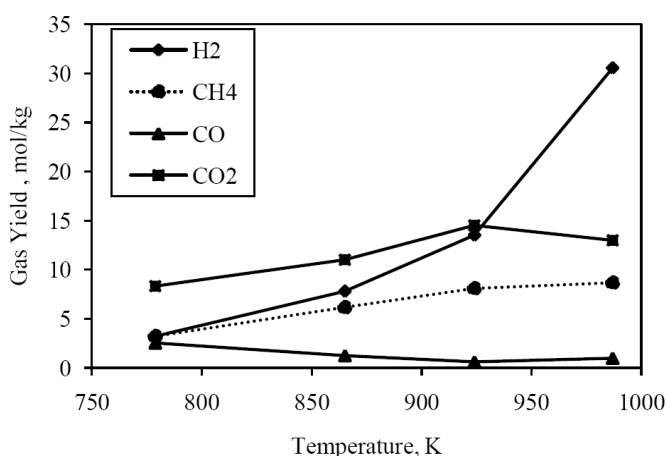


Figure 7. Effects of temperature on gas yield from SCWG of rice husk at 32 MPa, 2 wt% biomass concentration and 60 min residence time.

SCW gasification of clover grass showed a strong dependence of the gas yield on the temperature. The fractional gasification yield increased from 0.62 to 0.88 and the carbon concentration of the liquid residue (TC) decreased from 1017 to 333 ppm as the temperature rose from 625-700°C.

Demirbas (2004) studied a wide range of real biomass over a relatively short temperature range, but clearly noticed the dominant effect of temperature on the gas yield. In the case of cotton cocoon shell, the effect of temperature is similar to that of glucose. The present authors studied the effect of temperatures (770-990K) on gasification of rice husk. The details of experimental setup were mentioned in Basu et al. (2009). They noted (Figure 7) yield of hydrogen increases with temperature while that of CO decreases. Demirbas (2004) noted an opposite (increasing) trend for CO in lower temperature range (650-750K). This is expected from equilibrium calculations (Lu et al., 2007).

Jesus et al. (2006a), also noted a strong influence of temperature on the gas yield in their studies on the gasification of corn starch in SCW. The gasification yield rose from 41% to 92% with the temperature increasing from 550 to 700°C, which resulted in a strong reduction in total carbon in effluent. Another experiment (Jesus et al., 2006a) on

Using results of this biomass, Demirbas (2004) developed a correlation between hydrogen yield (YH) and temperature (T). The related correlation coefficient (r) is high for all runs.

$$\text{For almond shell:} \quad YH = 0.0661T + 36.350, \quad r = 0.9988, \quad (18)$$

$$\text{For cotton cocoon shell:} \quad YH = 0.0517T + 27.700, \quad r = 0.9947, \quad (19)$$

$$\text{For hazelnut shell:} \quad YH = 0.0484T + 26.083, \quad r = 0.9948, \quad (20)$$

$$\text{For sunflower shell:} \quad YH = 0.0564T + 30.550, \quad r = 0.9990, \quad (21)$$

$$\text{For walnut shell:} \quad YH = 0.0440T + 23.567, \quad r = 0.9941, \quad (22)$$

Waste-water, another type of biomass, also showed similar effect of temperature on their gasification (Blasi et al., 2007). The gas yield increases while the TOC decreases with increasing temperature. Difference in residence time did not change this trend much.

Tar yield

Tar yield (in the liquid effluent) is another aspect of SCW gasification affected by the temperature. During hydrothermal gasification at low temperatures ($T < T_c$) a rather high yield of furfural ($C_5H_4O_2$) and low gas production is noticed (Matsumura et al., 2005). Tar yield, in this context, is defined as grams of tar in the liquid effluent/grams of organic feed. At low temperature ($<600^\circ\text{C}$) the liquid effluent became yellowish and a thin layer of a dark brown, oil-like tar is observed in the liquid product, but when the temperature rose to 650°C , clear water was produced (Xu et al., 1996, Hao et al., 2003). Lee et al. (2002) found that the color of the liquid product was almost red at 510°C and varied to dark brown, orange, yellow as the temperature increased up to 600°C . The liquid product became clear at 680°C .

Total organic carbon (TOC) and chemical oxygen demand (COD) in the liquid effluent are used as quantitative measures of the tar. TOC value indicates organic carbon remaining in liquid effluent which is not converted to gas. The COD concentration can also be used as an alternative indicator to represent the concentration of total organic compounds when only glucose and pure water were used in the gasification because its reaction intermediates in the liquid product were unique materials affecting the COD analysis (Lee et al., 2002). Higher tar requires higher oxygen for total decomposition of the organic compound. Lee et al. (2002) took chemical oxygen demand (COD) as a measure of the tar in the liquid effluent. They noted that at higher temperature ($>700^\circ\text{C}$) the decomposition of glucose and destruction of COD increased and thereby reach 100% conversion.

Xu et al. (1996) also noted the effect of temperature on the tar yield, which decreased from 1.3% to 0.1% when temperature increases from 500 to 600°C.

At low temperature (~600°C) Lu et al. (2006) observed yellowish liquid and tar while gasifying sawdust. The reduced total organic carbon (TOC) in liquid residue confirmed this result. They also noted that the amount of TOC in liquid at 650°C is much lower than TOC at 600°C.

Above discussions show that the effect of temperature is significant particularly in the temperature range of 500-700°C range (Peterson et al., 2008a), and is observed under all conditions, i.e. different pressure, without catalyst, different type of feedstock and different residence time. In summary, total gas yield increases with temperature while TOC in liquid product reduces with it. The yield of hydrogen, carbon dioxide is higher at high temperature, and they are particularly high in supercritical water in the vicinity of 600°C (Peterson et al., 2008a).

Effect of reaction pressure

The effect of pressure on biomass gasification in SCW is somewhat complex. Buhler et al. (2002) noted that the rate of free radical reaction (Figure 5) decrease with pressure due to the 'cage effect', while that of the ionic reactions increases with pressure because of higher ionic products at higher densities. The density dependence of these two types of reactions is opposed to each other.

Gasification efficiency (GE) and concentration of hydrogen and carbon dioxide in the product gas increase with increasing pressure at 500°C but opposite

effects are found at 650°C when glucose is gasified (Hao et al., 2003).

Lu et al. (2006) found a modest effect of pressure on the hydrogen yield (H_2 increased from 15 to 17 mol/kg when pressure increased from 17 to 30 MPa), but they explained the increase in conversion with pressured in details. They cited a number of factors contributing to this. Over a wider range of pressure GE and carbon efficiency (CE) seem to be independent of

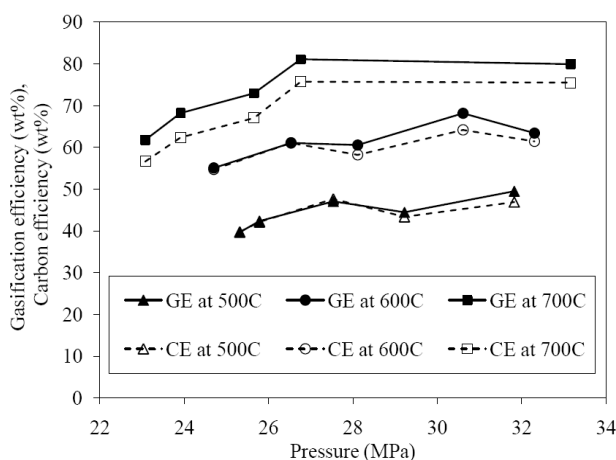


Figure 8. Effect of pressure on GE and CE of SCWG of rice husk at 2 wt% biomass concentration and 60 min residence time

pressure. The trends are clearer at high pressure. The yield of hydrogen shows a modest increase while that of carbon dioxide is less clear.

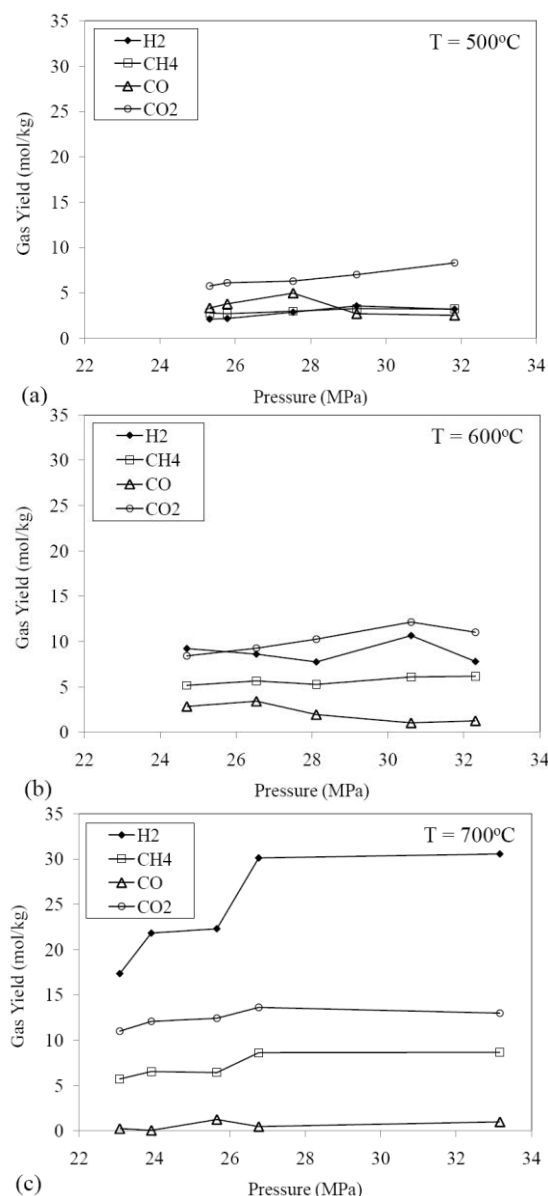


Figure 9. Effects of pressure on gas yield of SCWG of rice husk at 2 wt% biomass concentration and 60 min residence time: a) 500°C, b) 600°C, c) 700°C

The experimental data of Demirbas (2004), in contrast, show more distinct increase of H₂ as well as CO, while CO₂ decreased with pressure. Based on the data on almond shell, cotton cocoon shell, hazelnut shell, sunflower shell and walnut shell, Demirbas (2004) developed several correlations. One of the reasons of such different results could be because these data were come from a batch reactor as opposed to flow reactors used by other.

Figures 8 and 9 show the effect of pressure on gas yield, gasification efficiency and carbon efficiency at 500°C, 600°C and 700°C from SCWG of rice husk in a batch reactor from the results of the present authors. The details of the batch reactor are in Basu et al. (2009). The effect of pressure on GE, CE and H₂ yield appears to be more pronounced at higher temperatures.

When pressure increases, the ion concentration of SCW increases the hydrolysis rate. With increase in pressure, the density, dielectric constant and ion product increase. At high pressure ion reaction is more dominant than free radical reaction. Above factor gives enhance hydrolysis.

When pressure increases, there is a modest but some increase in the viscosity of water (Bett and Cappi, 1965). This make diffusion

of the reactant molecules to each other is difficult. The rate of fission-type reactions such as decomposition reaction reduces. However, isolating of reactant molecules prevents solute-solute reactions but promotes solute-solvent reactions such as water-gas shift reaction (Lu et al., 2006).

Effect of residence time

The reactor residence time is defined here as the reactor volume divided by volumetric flow rate of water at the reactor temperature and pressure. Most of the work reviewed here show that residence time has an important effect at the beginning, i.e. the conversion of biomass increases with residence time but after reaching a 'certain time' it does not change much. This time is however, is not unique. It depends on many factors including reaction temperature, biomass type and reactor vessel.

For batch reactor residence time is the duration of time that reactants stay inside the reactor. The present authors and Williams and Onwudili (2005) conducted experiments in batch reactor to study the effect of various parameters including residence time. Williams and Onwudili (2005) studied the effect of residence time (0-120 min) on gasification efficiency of glucose gasification in SCW at 374°C. The gasification efficiency slight increased and reached 90% after 120 min with a slight decrease in oil yield and an increase in char yield. In the experiments with rice husk at 650°C, 30 MPa and 2wt% biomass concentration (the details of the batch reactor are mentioned in Basu et al., 2009) the present authors found hydrogen yield increased from 7 to 14 mol/kg of biomass feeding when residence time increased from 10 to 40 minutes. No further increase was noted when the residence time increased to 60 minutes.

Jesus et al. (2006a) correlated results of gasification of corn silage at 700°C and 25 MPa, with time and developed a linear relationship between the carbon conversion (Y_C) and the residence time.

$$Y_C = K\tau = 0.11\tau, (R^2 = 1) \quad (23)$$

Hao et al. (2003) studied the effect of residence time on gasification of 0.4 M glucose, 650°C, 25 MPa. When residence time increased from 1.7 to 3.7 minutes, GE increased from 93.6% to 117.6% and CE increased from 77.5% to 98.7%. They found that a minimum of 3.6 minutes resident time was needed for reasonable gasification efficiency. Extending the resident time further one cannot increase the gasification efficiency further. Lee et al. (2002) presented similar results where 0.6 M glucose is gasified in SCW at 28 MPa and 700°C. In their case the minimum residence time was 10.4 s. At longer residence time the yields of all of the gases remained almost constant. However at lower temperature,

600°C, H₂ and CH₄ yields increase with residence time. The yield of CO, on the contrary showed a slight decreasing tendency with increasing residence time.

The yields of H₂, CO₂ and CH₄ increased with residence time (within the range of 9 to 46 second) during the gasification of wood sawdust in SCW at 25 MPa, 650°C (Lu et al., 2006). The CO yield, on the other hand, decreased when residence time increased as was found by Lee et al (2002).

For sawdust the gasification efficiency (GE) and carbon conversion efficiency (CE) increase with increasing residence time but the unconverted TOC in the liquid effluent decreases (Lu et al., 2006). These data suggest that longer residence time is favorable to biomass gasification. Glucose gasification (Lee et al., 2002) shows that at 700°C, for residence time exceeding 14s, the hydrogen yield does not increase further with increasing residence time. But at a lower temperature of 600°C, the gasification yield is lower and it continues to rise within the residence time range of 10-50 s. One can speculate from here that the peak gas yield at a lower temperature might occur at longer residence time. Kato and Matsumura (2003) found that the CE of liquidized cabbage increased with residence time at 200°C but the increase tapered off at around 1200 s.

Effect of heating rate

Former section showed the important influence of the reaction temperature on the gasification in supercritical water (SCW). This section examines how the rate of heating to the reaction temperature might influence the product in SCW as one observes in case of pyrolysis at atmospheric pressure.

High heating rate generally favors biomass gasification process in SCW (Sinag et al., 2004, Lu et al., 2006). Slow heating up leads to the formation of coke/char. One possible explanation for this is the formation of coke at low heating rates. At low heating rate, the biomass-water mixture is gently heated from subcritical temperature to the supercritical temperature. So, the feed spends a finite time at subcritical temperatures in the preheating section of the reactor. As explained in previous section the ionic reaction takes place at low temperatures forming intermediate products, furfurals or other unsaturated compounds. When the reactants reach supercritical temperature, free radical reaction takes over (Matsumura et al., 2005) and these compounds polymerize forming coke/char. The formation of char in turn lowers the carbon conversion. For higher heating rate the time spent in the subcritical region being short the formation of coke/char is reduced and higher conversion is achieved. Matsumura et al. (2006) examined the phenomenon and found that for this reason a lower amount of tar was produced at higher heating rates.

A comparison of results from heating rates 1°C/min and 3°C/min (reaction temperature of 500°C) shows that at the higher heating rate higher yields of hydrogen, methane and carbon dioxide are obtained, but the carbon monoxide

yield is low (Sinag et al., 2004). The yield of CO reduces from 17 mmol/mol of glucose at 1°C/min to 4.5 mmol/mol of glucose at 3°C/min.

The heating rate may also affect the production of tarry materials in supercritical water. In their experiments on conversion of glucose at 25 MPa, 400–600°C, Matsumura et al., (2006) noted that the tar production decreases with temperature due to the formation of furfural (a tar compound). When the heating rate is increased from about 8°C/s to 27°C/s the tar production reduced by 33% and 4% at 600°C and 400°C respectively (Here, the heating rate was increases simply by increasing the heater length, a technique that may be questioned. Additional studies may be necessary to elucidate this point.

Effect of feed concentration

The feedstock of a SCW gasifier comprises mainly solid biomass and water. The concentration of solid in the feedstock has an important effect on the gasification. This could be a major design issue during the commercial application of SCWG. Most of the research carried out to date in laboratory used feed concentration well below what a commercial gasifier would like to use.

Results on gasification of glucose as a model biomass (Hao et al., 2003) show that the percentages of hydrogen and carbon dioxide in the total product gas increases with increasing glucose concentration in the range of 0.1 M to 0.9 M, but carbon monoxide and methane fractions reduces. Gasification efficiency decreases with increasing glucose concentration, and this trend was observed in both 6 mm diameter tubular reactor and in 9 mm diameter tubular reactor. Matsumura et al. (2005) also noted that the yields of H₂, CH₄ and CO₂ decreased when glucose concentration in the feedstock increased but the yield of CO increased.

Experiments with real biomass like wood sawdust and corncob carried out in SCW (Vogel and Waldner, 2006, Lu et al., 2006 and Guo et al., 2007) also showed that at high feed concentration, both gasification efficiency (GE) and carbon conversion efficiency (CE) are lower than those at lower concentration. The yields of H₂, CH₄ and CO₂ decrease with increasing biomass concentration while the yield of CO increases.

When the feed is liquid instead of solid, the effect of feed concentration was found to be similar. Boukis et al. (2006) noted that as the water to methanol (feed) ratio increased from 1 to 10, the methane reduced from 20% to 4% while CO showed a marginal drop. The hydrogen yield increased as water to methanol molar ratio was increased from 68% to 75% vol when water to methanol ratio was increased from 1 to 15. It can be explained by noting that thermal decomposition of methanol produces only 2 mol H₂ per mol of CH₃OH, while the reaction of methanol with water produces 3 mol of H₂ per mol of CH₃OH.

Effect of biomass type

Demirbas (2004) compared results of SCW gasification of five types of fruit shells. Arranged in decreasing order of hydrogen yield the fruit shells are: almond shell, sunflower shell, cotton cocoon shell, hazelnut shell and walnut shell. The results are consistent for all temperature and pressure (650-750 K, 23-48 MPa). The ultimate analysis and compositional analyses show that the yield of hydrogen is related to the hydrogen or cellulose content of biomass. Demirbas (2004) correlated the yields of hydrogen (YH) with the cellulose content (CC) as follows. The correlation coefficients (r) for these are also given alongside the equations for supercritical water extraction of fruit shells in different temperature range:

$$\text{From 293 to 650 K:} \quad YH = 0.0573CC + 3.633, \quad r = 0.9602, \quad (24)$$

$$\text{From 293 to 670 K:} \quad YH = 0.0617CC + 4.426, \quad r = 0.9246, \quad (25)$$

$$\text{From 293 to 690 K:} \quad YH = 0.0653CC + 5.711, \quad r = 0.9037, \quad (26)$$

$$\text{From 293 to 710 K:} \quad YH = 0.0779CC + 6.174, \quad r = 0.9201, \quad (27)$$

$$\text{From 293 to 730 K:} \quad YH = 0.0941CC + 6.399, \quad r = 0.9159, \quad (28)$$

$$\text{From 293 to 750 K:} \quad YH = 0.1132CC + 6.756, \quad r = 0.8915, \quad (29)$$

Lu et al. (2006)'s experiments with rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob, sorghum stalk and wood sawdust suggests that wheat stalk, corn cob and sorghum stalk are easier to gasify than the other biomass, but they found that gas compositions are not distinguishable. The gasification efficiency varies from 60% to 90%, while carbon gasification efficiency is in the range of 50-80%.

Yoshida and Matsumura (2001) studied the effect of three main components of biomass (i.e., cellulose, hemicelluloses, and lignin), and found a similar trend of results. Among them cellulose gives the highest hydrogen yield. The second highest contributor is hemicelluloses (represented by xylan), and the lowest yield is produced from lignin. These researchers suggested that lignin is the key component that affects hydrogen yield. Feedstock containing lignin, i.e., the cellulose-lignin mixture and xylan-lignin mixture, show hydrogen content of the product is lower than their equilibrium values.

If there is no interaction amongst the three biomass components (cellulose, hemicellulose and lignin), the gasification behavior of a mixture can be predicted as an average of the results of single-component gasification weighted by the weight fractions (X_c , X_h , X_l) of each component

$$N_{wa} = N_c X_c + N_x X_x + N_l X_l \quad (30)$$

where N_c , N_h , N_l are yield from cellulose, hemicellulose and lignin respectively.

This equation showed better agreement for CO_2 production than for H_2 and CH_4 yield (Yoshida and Matsumura, 2001). In the case of binary mixtures, Equation 30 indicates a linear dependence of N_{wa} on the weight fraction of a component. In presence of lignin the experimental values deviate from equilibrium values due to a rapid reaction between the lignin and intermediates produced from cellulose and xylan decomposition. This reaction is not a simple hydrogenation of lignin because there is no indication of methane production resulting from the hydrogenation of lignin. On the contrary, there is no interaction between cellulose and xylan. From their experimental results it could be surmised that cellulose or xylan is likely to function as a hydrogen donor to lignin.

Table 5. Composition of ligno-cellulosic biomass and product distribution from SCWG of different biomass feedstock at 500°C; water 140 ml; sample amount 8.3 g (compiled from Yanik et al., 2007)

| Materials | Structural composition (wt%) | | | Potassium (elemental%) | Yield (wt % of biomass) | |
|-----------------|------------------------------|---------------|--------|------------------------|-------------------------|------|
| | Cellulose | Hemicellulose | Lignin | | Gas | Coke |
| Tobacco stalk | 48.5 | 16.2 | 11.1 | 7.5 | 24.7 | 5.5 |
| Cotton stalk | 47.1 | 13.1 | 11.0 | 2.9 | 41.8 | 10.4 |
| Sunflower stalk | 43.1 | 7.4 | 9.7 | 7.9 | 59.2 | 1.9 |
| Oreganum stalk | 33.8 | 10.9 | 9.3 | 5.2 | 39 | 11.3 |

Lignin can be hydrolyzed via cleavage of the ether bonds that are catalyzed by $[\text{H}^+]$ and $[\text{OH}^-]$ or water molecules (Bobleter, 1994). Supercritical water, by virtue of its high ion product ($[\text{H}^+] \times [\text{OH}^-]$), could serve as a good medium for hydrolysis of lignin, but experiments (Fang et al., 2008) found no homogeneous phase in a lignin-SCW system. However, lignin can be completely solubilized in a phenol-SCW mixture, where it could undergo homogeneous hydrolysis and pyrolysis preventing re-polymerization.

Yoshida and Matsumura (2001) developed equations to estimate the amount and composition of the product gas as a function of lignin content. Nonetheless, in the study of Yanik et al. (2007) although sunflower stalk and

oreganum stalk have similar lignin content (Table 5), the amount of gas obtained from sunflower stalk is 1.5 times more than that of from oreganum stalk (Table 5). Similarly, cotton stalk gives 1.7 times more gas than that of tobacco stalk even their lignin contents are identical (Table 5). These results show that the lignin amount is not the only variable. These confirm that factors other than lignin, cellulose and hemicellulose might have played a greater role in influencing the gasification product of this biomass.

CO yield

Some constituents of the biomass may have catalytic effect on the gasification. For example K_2CO_3 content of the biomass has a catalyzing effect on its gasification resulting in lower carbon monoxide generation. Lu et al. (2006) shows that gasification of glucose without K_2CO_3 gives higher CO content, compared to gasification with K_2CO_3 . Hao et al. (2003) also noted a similar drop in CO with addition of alkali. This was observed for gasification of both sawdust as well as glucose. However, although tobacco stalk and sunflower stalk have similar potassium content (Table 5), the yields and composition of gases obtained from tobacco stalk and sunflower stalk are different from each other (Table 5) (Yanik et al., 2007). In addition to the similarity of potassium content, cellulose content of two biomasses are also similar.

Hydrogen yield

The gasification of corn-cob resulted in the lowest amount of hydrogen yield (2.09 mol H_2 /kg biomass) (Yanik et al., 2007), though it had high amounts of cellulose and hemicellulose. These findings indicate that in the case of real biomass, the gasification reactions are more complex and organic materials other than cellulose, hemicellulose and lignin may have also effect the yield and composition of gas products.

Effect of size of biomass particles

Feed particle size is an important design issue for any gasifier. Finer the required feed-size higher the energy consumption for feed preparation. Though SCWG is yet to enter the commercial phase, some limited studies are available that examined this aspect. Conceptually, since the mass transfer resistance in SCW is less, the particle size may not have a major effect. As most of the work has been done with ideal or model biomass very little information is available on this aspect of SCWG.

Lu et al. (2006) studied the effect of feed size for gasification of rice straw, and found that smaller feed particles resulted in a higher hydrogen yield,

gasification efficiency (GE) and carbon efficiency (CE) during gasification in SCW (Table 6). As additional energy is required for mechanical grinding of biomass to finer particles, an optimal particle size should be found with considering economy and feasibility.

Table 6. Effect of biomass particle size on gasification (Lu et al., 2006)

| Particle size (mm) | Gas yield (mol/kg) | | | | | | GE (%) | CE (%) | TOC (ppm) |
|-----------------------|--------------------|------|-----------------|-----------------|-------------------------------|-------------------------------|-----------|-----------|--------------|
| | H ₂ | CO | CH ₄ | CO ₂ | C ₂ H ₄ | C ₂ H ₆ | | | |
| (0.177-0.42 mm) | 13.74 | 0.11 | 3.31 | 10.47 | 0.27 | 0.43 | 56.51 | 50.20 | 1,455 |
| <0.177 mm | 17.00 | 0.34 | 5.06 | 17.51 | 0.46 | 0.82 | 93.22 | 77.28 | 1,673 |

^a Temperature, 650°C; Pressure, 25 MPa; Residence time, 30s; Feedstock, 2 wt% Rice straw + 2 wt% CMC.

Effect of reactor design

Experimental data reported so far have been generated mainly in following three types of reactor:

1. Batch reactor,
2. Tubular flow reactor and
3. Continuous stirred tank reactor.

The design of the batch reactor is simple but the reaction region in batch reactor is not necessarily isothermal. Several different types of batch reactor have been used.

Hashaiekh et al. (2006) studied the dissolution of willow using a batch-type (diamond-anvil cell). This reactor comprised two diamond separated by an Inconel gasket of 250 micron thick with a 608 micron hole in the centre. This formed a tiny 50 nano-litre reaction volume. More than 95% dissolution of willow was achieved in it. The lignin and hemicellulose in willow were fragmented and dissolved at a temperature as low as 200°C and cellulose dissolved in the 280–320°C temperature range at a pressure of 10 MPa. Hashaiekh et al. (2006) proposed a dissolution mechanism based on this.

The batch reactor has another problem that it is difficult to isolate the different reactions occurring during the heat-up and the cool-down stages. Thus it is not possible to study reaction with very short residence time.

Tubular flow reactor is better suited for reaction analysis in that respect. It provides a continuous gasification with a short residence time, but plugging is a major problem. At high concentration of feedstock, Guo et al. (2007) experienced plugging due to the formation char in the heating section and the buildup of ash inside the reactor. This might be a major hindrance in the application of biomass SCWG in commercial units. Mixing could also be an issue in tubular reactor.

Stirred vessel reactor can overcome these shortcomings due to its excellent mixing and high heating rate. The continuous stirred tank reactor is an integration of autoclave and tubular flow reactor. The biomass can be mixed uniformly in the reactor and heated fairly rapidly. However, the system is more complex and additional energy is required for stirring (Lu et al., 2006, Kruse 2008). Matsumura and Minowa (2004) suggested the potential use of a supercritical water fluidized bed for continuous biomass gasification. In their theoretical study they concluded that a bubbling fluidized bed fluidized by biomass slurry is more appropriate than a fast fluidized bed as it may avoid reactor plugging, but the process is complex and still at the theoretical designing state. Lu et al. (2008) conducted experiment on SCW fluidized bed with a bed diameter of 30 mm and the total length is 915 mm and the reactor plugging problem was not observed. So far, very little work has been done on SCW fluidized bed. In absence of experimental data on fluidized beds it is hard to speculate how such a reactor will behave.

Effect of reactor geometry

Most of the experiments on SCW gasification have been carried out in tiny reactors of few millimeter diameters. Scale up of results from such miniature reactors to several centimeter or even meter diameter reactors may be subjected to a great deal of uncertainties because such small reactors do not show the effect of hydrodynamics, mass transfer and heat transfer inside the reactor. Thus this aspect needs greater attention.

Hao et al. (2003) and Lu et al. (2006) studied the effect of reactor diameter. Two sizes of reactors were used for comparison, one is 6 mm inner diameter and the other is 9 mm inner diameter. The effect of the reactor diameter on the gas yield is not obvious from these studies. The gasification efficiency (GE) reduces with increasing reactor diameter in case of glucose but increases in case of sawdust. The effect of reactor diameter on biomass gasification in supercritical water thus could not be concluded from these results. However, one could speculate that the heat transfer between the feed and the reactor wall might influence the gasification (Lu et al., 2006). Lei et al. (2007) calculated the cumulative degree of thermodynamic perfection (CDP), which is based on exergy and environmental impact. The higher the CDP, the higher the thermodynamics perfection degree of the system is. When the inner diameter of the reaction tube is increased from 3 mm to 9 mm, the CDP is higher. The concept of CDP is described in Lei et al. (2007).

Effect of reactor material type

Vast majority of the experimental data on SCW gasification was derived from very small diameter reactors, which had very large surface to reactor volume ratio. Most of the reactors used metals with catalytic activities and thus the gasification results may have had major influence of the reactor materials.

Antal et al. (2000) found that nickel alloy tubes (i.e., Hastelloy) are not suitable for use in biomass gasification in SCW because of their catalytic effects. Nickel presents in the Hastelloy reactor tube is known to catalyze the gasification. Hastelloy also suffers from severe corrosion. Walls of reactors made of Inconel 625 were also found that catalyzed the water-gas shift reaction (Yu et al., 1993). On the other hand reactors made of 316 steel resulted in rather low gasification due to its low catalytic activity (Boukris et al., 2006).

Another interesting effect of the reactor wall is seen due to the surface treatment of its wall. Boukris et al. (2006) treated the wall surface of their reactor, made of alloy 625, with a solution of hydrogen peroxide (3% wt) at 600°C, 25 MPa for 50 hours. The process oxidized the molybdenum, chromium and nickel on the reactor surface. This pretreatment increased the conversion of methanol from 86% to more than 99% at 600°C. Interestingly, the CO concentration in the product gas decreased from 10-12% to about 1% due to the surface pretreatment.

Chromium, an important component of stainless steel may have a negative effect on the gas yield of biomass gasification. Yanik (2007) found that tannery waste treated with chromium had significantly reduced gas yield compared to that without chromium. This issue needs further exploration in view of its commercial implication.

Effect of carbon buildup on reactor wall

Carbon buildup on reactor walls can induce reactor plugging because the carbon deposited on the wall during a test is a potential promoter for carbon formation in the next gasification experiment. Furthermore, carbon buildup reduces gas yield when the reactor is made of metals that have catalytic effects. Lu et al. (2006) showed that gas yields, gasification efficiency and carbon efficiency were reduced by 3.25 mol/kg, 20.35% and 17.39%, respectively when carbon buildup occurs on the reactor wall compared to when the reactor is clean. Similar results were found in the experiment of Antal et al. (2000). At similar solid loadings, potato wastes (with 9% ash) plugged in one-half the time required by either the corn or the potato-starch gels (with 1% ash).

Effect of catalyst

Data on reactions presented so far have mostly been for non-catalyzed gasification reactions. The present section discusses the influence of addition of different types of catalysts on gasification reactions in SCW. More detailed discussions are available in Elliott (2008), Guan et al. (2008), Xu et al. (1996) and Furusawa et al. (2007).

Catalysts play an important, if not dominant role in biomass conversion in supercritical water. As indicated in “effect of reaction temperature” section the conversion at low temperature ($<500^{\circ}\text{C}$) is so low that use of catalyst in SCW gasifier become essential. The early optimism about very high conversion of biomass in supercritical water could have been tainted by catalytic activities of the walls of the reactors used. Most of the results were obtained in reactors few mm in diameter, where reactor surfaces were very large compared to the reactant volume used. Owing to the high temperature and pressure of SCW gasifiers it was necessary for experimenters to use alloy steel like 625, Hest alloy, Inconel. All of these materials are found to have significant catalytic effect on the reaction. In one case (Diem et al., 2003), an alumina liner was used in the alloy steel reactor to avoid the catalytic effect of the reactor wall, and this resulted in a major drop in the conversion. To compare the catalytic effect of alloy 625, Boukis et al. (2006) conducted some of their experiments on conversion of methanol in SCW in a reactor made of 316 steel instead of the alloy 625. The conversion dropped from nearly 100% to only 53% owing to the reduced catalytic property of 316 steel.

Principal types of catalysts that have been used so far for SCW gasification are:

1. Metal Catalysts
2. Carbon based catalysts
3. Alkali catalysts

These catalysts are especially conducive for hydrogen production. A successful catalytic process depends on components, manufacturing process and morphology of catalyst. For the gasification of biomass in SCW, reactants, reaction environment, process parameters and reactor configuration are also important as much as surface area and pore diameter profile of the catalysts (Hao et al., 2005). Catalysts with larger surfaces have better catalytic effect. Adding catalyst with wider pore diameter profile could improve hydrogen yield.

Metal catalysts

Heterogeneous metal catalysts have one advantage over homogeneous base or alkali catalyst in the sense that it is relatively easy to recover. This helps reduce the cost of catalysts. Furthermore, granular metal catalysts could also serve as a heat carrier in a transport type flow reactor.

Hao et al. (2005) compared the performance of five types of metal catalysts: 5 wt% Ru on activated carbon, 5 wt% Pd on activated carbon, CeO₂ particles, nano-CeO₂ and nano-(CeZr)_xO₂ during the gasification of cellulose at 500°C at 27 MPa. Ruthenium based catalyst gave the best performance with highest yield of hydrogen and methane at that temperature. Others had similar level of performance.

Nickel is a commonly used catalyst for SCW gasification. Furusawa et al. (2007) found that carbon and hydrogen yields increased from 8.3% and 14.1% to 22.7% and 46.2% respectively when 0.05 g of 20 wt% Ni/MgO catalyst is added at 400°C.

The amount of catalysts also affects the reaction. Yoshida et al. (2004) found that increasing the amount of Ni catalyst improved the gasification efficiency of cellulose, lignin and cellulose-lignin mixture at 400°C, 25 MPa and for a 20 min reaction time. Experiment of Furusawa et al. (2007) on gasification of lignin with supported this observation that a higher amount of catalyst provides more gas yields. Additionally they noted that the amount of gas produced declined when re-used catalyst is used.

Alkali catalysts

Alkali catalysts are easily miscible with the water and it is more effective for biomass gasification. However, its recovery and re-use could be an issue.

Alkali such as NaOH, KOH, Na₂CO₃ and K₂CO₃ are also used as catalysts. Lu et al. (2006) found that the H₂ yield with K₂CO₃ is two times higher than that without catalyst at the same condition. Sinag et al. (2004) compared Raney nickel and K₂CO₃ to improve gas yields. At 1°C/min and 3°C/min heating rates, K₂CO₃ increased hydrogen yield at a greater degree than that by Raney nickel. The effect of K₂CO₃ on H₂ production can be explained by the catalyzed water-gas shift reaction via the formation of HCOO⁻K⁺:



Hydrogen is obtained by reaction of formate (HCOO⁻K⁺) with water.



The catalytic cycle is completed by the formation of CO₂ and K₂CO₃



Figure 10 shows the reaction pathway of glucose conversion in supercritical water. Sinag et al. (2004) detected formic acid (HCOOH) and furfurals while studying the effects of Raney nickel and K_2CO_3 on the glucose conversion reaction. Formic acid (HCOOH) is assumed to be an intermediate product in the water-gas shift reaction. Therefore, the high yield of formic acids suggests a high level of water-gas shift reaction leading to high gas yields. Furfurals may polymerize or may be left as tar after reaction. These two can be regarded as unwanted products.

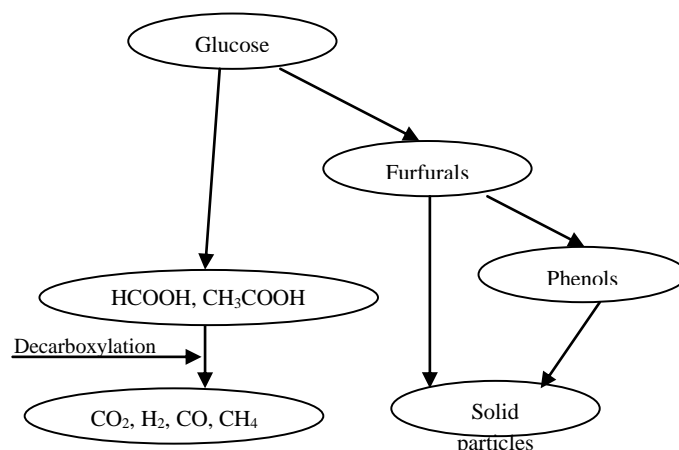


Figure 10. Reaction pathways of glucose conversion in supercritical water (after Sinag et al., 2004).

Addition of Raney nickel or K_2CO_3 leads to a reduced yield of unwanted furfurals and increased yield of formic acid. Adding K_2CO_3 results in more formic acid than adding Raney nickel. This was in agreement with their results of gas yield. The catalyst, K_2CO_3 , however, has one disadvantage. It increases the phenol content of the product.

However, this disadvantage seems to be acceptable because phenols can be gasified at 600°C. Raney nickel decreases the phenols' yield but this catalyst is more difficult to handle than K_2CO_3 in view of a technical problem (Kruse et al., 2000)

Watanabe et al. (2003) studied the effect of both base (NaOH) and metal (ZrO_2) catalysts on the gasification of lignin in SCW. They also studied the effect of oxygen addition (partial oxidation) on the gasification. Lignin was specifically chosen as it is a major component of woody biomass and it is most difficult to gasify even in SCW. They also studied the gasification of *n*-Hexadecane. Table 7 compares the hydrogen yield under different conditions. This clearly shows that base catalysts give higher yield than heterogeneous metal catalysts

The hydrogen yield (Table 7) is admittedly low in absence of catalyst, but it was possible to increase the yield several times by using partial oxidation as well as catalysts. Irrespective of whether there was any partial oxidation or not, use of catalyst could help increase the hydrogen yield. The catalyst, NaOH proved more effective than ZrO_2 . In this particular case the base catalyst was 2-5 times more effective in hydrogen production.

If H_2 is formed only from water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), the ratio of H_2 yield to CO_2 yield (H_2/CO_2 ratio) must be unity as per the shift reaction. Watanabe et al. (2003) during gasification of $n\text{-}C_{16}$ obtained H_2/CO_2 ratio = 0.3 and 0.75 for no catalyst and ZrO_2 catalyst. This suggests a direct oxidation of biomass carbon into CO_2 beside that formed through water–gas shift reaction. But when the base catalyst NaOH was used H_2/CO_2 increased above to 1.76 and NaOH catalysts respectively (for $O/C=0.3$). This suggests that the water gas shift reaction must be favored by the base catalysts that suppressed the direct oxidation of the biomass into CO_2 . The value above unity with NaOH catalyst suggested that beside water gas shift reaction there must be another pathway for formation of hydrogen. This could be thermal decomposition of the hydrocarbon (Watanabe et al., 2003).

Table 7. A comparison of effect of catalysts and partial oxidation on the hydrogen yield (mole %) from gasification of lignin and n -Hexadecane in SCW at 400°C , 30 MPa and 15 min residence time (From Watanabe et al. 2003)

| | Hydrogen yield (mole %) | | |
|------------------------------|-------------------------|----------------------------|----------------------|
| | No catalyst | Metal catalyst (ZrO_2) | Base catalyst (NaOH) |
| Lignin | | | |
| Without oxygen | 0.5% | 1.0% | 5.0% |
| With oxygen ($O/C=1.0$) | 2.0% | 3.5% | 9.5% |
| n -Hexadecane | | | |
| With oxygen ($O/C=0.3$) | 2.0% | 3.0% | 8.5% |

For thermal decomposition of lignin the H_2/CO_2 ratio for no catalyst, ZrO_2 and NaOH catalysts respectively decreased from (0.17, 0.3, 0.68) to (0.06, 0.12 and 0.18) when the O/C ratio was increased from zero to 1.0. However, partial oxidation $O/C = 1.0$ resulted in a large increase in the molar yield of hydrogen, CO and CO_2 compared to an absence of oxygen ($O/C = 0$). This illustrates some beneficial effect of partial oxidation in SCW gasification.

Carbon catalysts

Xu et al. (1996) and Matsumura et al. (1997) studied the effect of carbon catalysts in the gasification of model biomass, glucose in supercritical water at 600°C and 34.5 MPa. Carbon catalysts used were spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut shell activated carbon.

Most carbon catalyst increased the carbon gasification efficiency while reducing the CO content of the gaseous products. This was apparently due to the enhanced rates of both the water-gas shift reaction and the methanation reaction. The carbon in fuel appeared through CO₂ and CH₄ instead of being in CO. This enhancement of methane yield was highest in case of activated carbon from macadamia shell charcoal. For coal activated carbon, the yield of CO is higher than that in other catalysts and the yields of H₂ was lower than those obtained with the other carbons. This suggests that the activated carbon from coal does not catalyze the water-gas shift reaction.

In conclusion, catalysts have a major effect on the gasification of biomass in SCW. Besides improving the gasification yield, it also allows to reduced the reactor temperature and thereby improves the thermodynamic efficiency of the system.

THERMODYNAMIC MODELING AND ANALYSIS

Supercritical water reactors are used for three main purposes:

- Gasification of biomass
- Oxidation for waste remediation
- Synthesis for chemical production

In oxidation and synthesis processes the yield of chemical products is of primary concern. Energy usage or generation is of secondary importance. Such a process may even be a net energy consumer. Primary purpose of supercritical gasification (SCWG), on the other hand, is conversion of energy in the biomass into another convenient form. Thus energy conversion efficiency is of paramount importance. A SCWG process; however good, may not be accepted unless it is a net energy producer with reasonable energy conversion efficiency. Unlike conventional thermal gasification SCWG requires a large amount of pumping power and often needs external energy for gasification. Thus the energy content of its product needs close scrutiny to ascertain if the process is viable. This makes a thermodynamic analysis of supercritical water gasification of biomass more important than the other two uses of supercritical reactors (Yoshida et al., 2003).

The main components of a SCWG system include the reactor, gas-liquid separator, pump and heat exchanger (Figure 4). The feed is pumped above the critical pressure, and then preheated to the reaction temperature by using a product-feed heat exchanger as well as by some external source of heat. Biomass is gasified in the reactor into several components of gas and liquid, which are subsequently separated in one or more separators mainly using their phase separation at different temperature and pressure.

Every design has its priority. For example some want to maximize the hydrogen yield, while some wants some liquid products. If the energy conversion is primary motive, the overall energy efficiency of the process is important.

Thermodynamic analysis is very helpful in providing theoretical base for design, its optimization and operation of a biomass gasification system where the energy efficiency is important (Lu et al., 2007). Thermodynamic analysis involves equilibrium calculations as well as exergy analysis. Equilibrium calculations predict the theoretical composition of the product of biomass gasification for a given feedstock subjected to a given temperature and pressure, the exergy analysis on the other hand can decide how the heat exchanger unit of the plant should be designed to optimize the efficiency of the plant.

Two thermodynamic analyses discussed here in the context of SCWG are:

- Equilibrium modeling and
- Exergy analysis.

The equilibrium models provide gas composition of the product leaving the reactor. Beside this, it also gives the phase equilibria of gases in water, which determine how much of a mixture will be in gas phase or in liquid phase at a given temperature and pressure. In a SCWG, product gases are separated from each other as well as from the solvent water by passing them through separators at designed temperature and pressure. Equilibria calculation provides information for the design of such gas-liquid separators.

The exergy analysis, on the other hand, analyzes the degree of thermodynamic perfection of an energy system (Lei et al., 2007). It needs equilibrium results of equilibrium calculation to compute the exergy of flow streams at different units of a SCWG plant.

Equilibrium model

A system is in equilibrium when it has no tendency to change. Therefore, an equilibrium system is in thermal, mechanical, chemical and phase equilibrium. These conditions are met when in the system there is no heat transfer from one location to another, no unbalance forces between parts of the system, no chemical reaction or any transfer of mass between phases.

Equilibrium models can predict the equilibrium composition and thermodynamic limits of gasification of the biomass in supercritical water, which could serve as a guide to its process design, evaluation and improvement. There are two approaches to equilibrium modeling:

1. Stoichiometric
2. Non-stoichiometric.

The stoichiometric approach requires knowledge of a clearly defined reaction mechanism including information on reaction rates of all the chemical reactions and species involved. In most gasification processes, within the given

residence time the chemical reactions are not sufficiently fast to reach equilibrium (Li et al., 2004). The stoichiometric, approach, however, gives the limiting conditions for a known gasification reaction rather than the true composition of the product gas. An example of such stoichiometric equilibrium calculation for biomass gasification is given in Basu (2006).

The non-stoichiometric method, on the other hand, requires information only on reaction temperature, pressure and an elemental composition of the feedstock. Some of these data are available directly from the ultimate analysis of the feed. The non-stoichiometric approach is suitable for reactions whose mechanism is less clear, such as hydrogen production from biomass gasification in SCW.

For the design of a supercritical water gasifier (SCWG), one needs to know the composition of the product leaving the reactor. The product gas remains dissolved the supercritical water. The gas is separated from the water depending upon its characteristic temperature and pressure. The separators are designed such that desired gases are separated individually in separate places and thereby obviate the need of expensive separation devices. The phase equilibrium calculation gives the necessary information needed for the design and operation of a particular separator.

Thus both chemical equilibrium and phase equilibrium problems have to be solved for the design of a SCWG. One of the most effective means of solving this problem is the use of minimization of Gibbs free energy subject to molar balance constraints. This is based on premise that at equilibrium state the total Gibbs free energy of a system is minimized.

This approach has been used for successfully for conventional thermal gasification in air or oxygen (Li et al., 2001 and Jarungthammachote and Dutta, 2007). The situation with supercritical water gasification is more complex than that in conventional gasification because the equation of state of the mixture, the fugacity of each species is an extremely complicated function of pressure, temperature and mixture composition. Thus, it is beyond the scope of most commercial packages for equilibrium calculation (Tang and Kitagawa, 2005). The following section discusses the non-stoichiometric equilibrium based on Gibbs free energy minimization approaches used by researchers for supercritical gasification in water.

Lu et al. (2007) and Tang and Kitagawa (2005) performed chemical equilibrium analysis of hydrogen production by biomass gasification in SCW based on Gibbs free energy minimization. Yan et al. (2006) also used the non-stoichiometric approach based on Gibbs free energy minimization to predict the performance of hydrogen production in SCW.

Equilibrium model in reactor

Tang and Kitagawa (2005) used Peng-Robinson equation of state, while Lu et al. (2007) and Yan et al. (2006) used Duan's equation of state, put forward by Duan et al. (1996) for the reactor.

The equation of state is used to describe the thermodynamic behavior of each species in the SCWG system. The model of Tang and Kitagawa (2005) predicted the gas composition for SCWG of glucose, cellulose and biomass (starch and sawdust) very well above 650°C. Minimization of Gibbs free energy was carried out for estimation of the equilibrium composition. A local optima solver and a global optima solver were used to search the equilibrium point. The predicted trend of gasification from the model developed by Yan et al. (2006) is also in good agreement with their experimental data even though the predicted hydrogen yield and gasification efficiency from computation are higher than experimental data.

Feng et al. (2004a) used statistical association fluid theory (SAFT) equation of state as the thermodynamic model to describe the phase behavior, and phase equilibria by calculating the enthalpy and entropy values of mass streams in the reactor as well as in the separator. These values allowed calculations of Gibbs free energy and its minimization for estimation of equilibrium composition of the product in the reactor.

Equilibrium model in phase separator

The phase equilibrium calculation is useful in finding potential routes and operating conditions for separating desired products from the mixture leaving the reactor.

Lu et al. (2007) used Soave-Redlich-Kwong (SRK) equation of state for determination of the gas-liquid equilibrium for the high-pressure separator.

Feng et al. (2004b) used four equations of states, Statistical Association Fluid Theory (SAFT), to calculate the composition of the products in different phases (vapor, water and bio-crude) in the hydrothermal reactor as well as in different downstream separators. Additionally, they also used Peng-Robinson (PR), Soave-Redlich-Kwong (SRK) and Predictive Soave-Redlich-Kwong (PSRK), to calculate the phase equilibria for hydrothermal upgrading as well as supercritical water gasification processes for comparison.

Table 8, shows a comparison of predicted equilibrium fraction of different gas constituents of the products of a SCW gasifier using phase equilibria calculation techniques based on four different equations of state. Feng et al. (2004b) observed that the predicted results of H₂, CO₂ and CH₄ solubility in water from PR and SAFT agree better with experimental data compared to those from other two equations of state.

Table 8. Phase equilibria results at 25°C and 35MPa (Feng et al., 2004b)

| | Component | Mole fraction in vapor phase | | | |
|--------------|--|------------------------------|-------|-------|-------|
| | | PSRK | SAFT | SRK | PR |
| Vapor phase | CO ₂ | 0.087 | 0.089 | 0.086 | 0.083 |
| | CH ₄ | 0.093 | 0.098 | 0.094 | 0.093 |
| | CO | 0.043 | 0.052 | 0.070 | 0.069 |
| | H ₂ | 0.777 | 0.760 | 0.749 | 0.754 |
| Liquid phase | Percentage of total H ₂ dissolved in liquid phase | 20.68 | 26.73 | 28.75 | 26.77 |

Exergy analysis

The exergy of a system is the maximum theoretical useful work possible when a system is brought into complete thermal, mechanical, and chemical equilibrium with its thermodynamic environment and heat transfer takes place exclusively with this environment.

The cost and environmental impact of the plant operation depend on the process on which the plant is based. It is especially important for energy intensive processes like supercritical gasification. For such a process, exergy analysis can identify the origin, cause and the extent of real losses (Bejan et al., 1996). This analysis is particularly important at the development stage of a new process like supercritical water gasification (SCWG), as it could give directions of further research and suggest areas of process optimization.

The first law of thermodynamics asserts that the energy must be conserved irrespective of how it is converted, while the second law says that all energy cannot be utilized due to irreversibility. The energy is never destroyed, but a part of the exergy is always lost. The exergy analysis shows how this energy, which is leaked out to the environment unused can be minimized, and therefore enhance the thermodynamic efficiency of the process. The exergy analysis of SCWG plant involves an added complexity that a steam power plant or other thermal system did not have. Here the flow stream is a mixture of multiple chemicals and they could be partly in gas and partly in liquid phase. Furthermore, the composition of the flow stream and their phase is not known. It is necessary to carry out detailed chemical and phase equilibria calculation to know the constituents of the flow streams.

Many studies (Suresh et al., 2006, De and Nag, 2000) have been carried out on supercritical steam power plants firing fossil fuels, but only a limited number of work (Hao et al., 2003, Gasafi et al., 2007, Lu et al., 2007 and Lei et al., 2007) is reported on the exergy analysis of biomass gasification in

supercritical water. Smith et al. (1999) presented an exergy analysis of a process for a supercritical carbon dioxide extraction process.

A brief outline of this approach and a discussion of the results obtained by these researchers (Hao et al., 2003, Gasafi et al., 2007, Lu et al., 2007 and Lei et al., 2007) are presented below. Most of these analyses involved calculation of exergy flow rates into different components of the process and their balance for steady state operation.

Enthalpy and entropy computation

Thermodynamic properties of a real gas may differ from those of its ideal form. The properties like enthalpy or entropy of a real gas may, therefore, be written as the sum of the ideal gas property of that gas plus a residual component. The residual term is a function of the ideal gas property at reference state and temperature.

Exergy computation

To analyze a process, it is necessary to compute the exergy of its individual component, and carry out its balance. The following section shows this approach as used by Gasafi et al. (2007).

Exergy components

The total exergy of a substance \dot{E}^{TOT} is made up of four components:

$$\dot{E}^{TOT} = \dot{E}^{PH} + \dot{E}^{CH} + \dot{E}^{KN} + \dot{E}^{PT} \quad (35)$$

Physical exergy is the maximum theoretical useful work obtained from a system when it is brought into thermal and mechanical equilibrium with its environment. Physical exergy of a flow depends on the temperature and pressure difference of the flow compared to the thermodynamic environment. The physical exergy of a pure compound in a mixture can be calculated knowing the enthalpy and entropy for the compound at both given and reference states (Lu et al., 2007):

$$E^{PH} = (H - H_o) - T_o(S - S_o) \quad (36)$$

For a mixture, the physical exergy is derived from the conventional linear mixing rule (Lu et al., 2007):

$$E^{PH} = \sum_i y_i E_i^{PH} \quad (37)$$

Chemical exergy of a fuel is the maximum obtainable work when the system is brought into complete (chemical) equilibrium with the thermodynamic environment (Gasafi et al., 2007). The chemical exergy of gas mixture is calculated based on the values of its constituents at their reference states (Lu et al., 2007):

$$E^{CH} = \sum_i y_i \varepsilon_{0,i} + RT_0 \sum_i y_i \ln y_i \quad (38)$$

For calculation of the chemical exergy of feed (sewage sludge), Gasafi et al. (2007) took it as being equal to the higher heating value of glucose on ground that Baehr (1979) found that for solid and liquid fuels the chemical exergy is very close (within 1-2% error) to the higher heating value of the fuel. But Lu et al. (2007) presented more comprehensive expression as a factor of the lower heating value of the feed biomass.

$$\varepsilon_{0,\text{biomass}} = \beta \text{LHV}_{\text{biomass}} \quad (39)$$

β is calculated by

$$\beta = \frac{1.0412 + 0.2160(Z_H / Z_C) - 0.2499Z_O / Z_C [1 + 0.7884Z_H / Z_C] + 0.0450Z_N / Z_C}{1 - 0.3035Z_O / Z_C} \quad (40)$$

Exergy balance

For a steady-state flow process the total exergy balance can be formulated as follows:

$$0 = \dot{W} + \sum_{in} \dot{E}_{in} + \sum_{out} \dot{E}_{out} + \sum_j \dot{E}_{q,j} - \dot{E}_D \quad (41)$$

The exergy associated with the transport of heat beyond system boundaries $\dot{E}_{q,j}$ (kJ/s) is calculated as:

$$\dot{E}_{q,j} = \left(1 - \frac{T_0}{T_j}\right) \times \dot{Q}_j \quad (42)$$

Exergy destruction, \dot{E}_D , caused by irreversible process in a system or a plant component can be calculated as:

$$\dot{E}_D = T_0 \dot{S}_{gen} \quad (43)$$

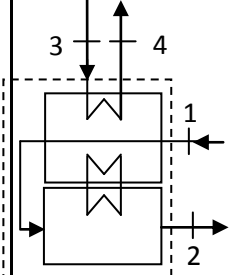
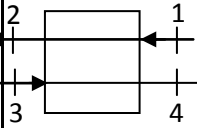
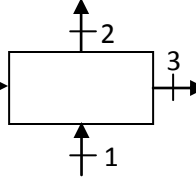
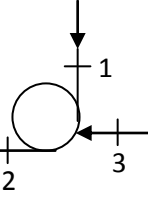
Possible causes of exergy destruction are chemical reactions, heat transfer, mixing processes, and friction.

Exergy efficiency

The exergetic efficiency ε of individual components or the overall system was defined by Gasafi et al. (2007) as:

$$\varepsilon = \frac{\dot{E}_P}{\dot{E}_F} = 1 - \frac{\dot{E}_D + \dot{E}_L}{\dot{E}_F} \quad (44)$$

Table 9. Exergy balance of individual components of a SCWG plant in Figure 4 (from Gasafi et al., 2007)

| | Reactor | Heat exchanger | PSA | Pump |
|--------------------------|--|---|--|---|
| Schematic representation |  |  |  |  |
| Flows | 1 Biomass 2 Product gas 3 Heating gas, in 4 Heating gas, out | 1 Cold flow, in 2 Cold flow, out 3 Hot flow, in 4 Hot flow, out | 1 Hydrogen-rich gas 2 Hydrogen 3 Methane 4 Electricity | 1 Input 2 Output 3 Electricity |
| Exergetic fuel, E_F | $E_1 + (E_3 - E_4)$ | $E_3 - E_4$ | $E_1^{PH} + E_2^{PH} - E_3^{PH} + E_4$ | $E_1 + E_3$ |
| Exergetic product, E_P | E_2 | $E_2 - E_1$ | $E_2^{CH} + E_3^{CH} - E_1^{CH}$ | E_2 |

The term ‘fuel’, here, represents the energy-delivering stream. For example, for the SCW gasifier it includes the fuel, ash and the heating medium if any, while in case of the heat exchanger it refers to the hotter fluid stream. Similarly, the ‘product’ represents the stream that carries the result of the unit. For

example, in the gasifier unit it is the product gas generated, in case of heat exchanger it is the cooler stream that is heated, in case of pump it is the pumped fluid. Thus (\dot{E}_F) is algebraic sum of exergy input in the system. Table 9 explains the terminology used.

To evaluate the relative exergy destruction for a component of the plant, a parameter, the exergy destruction ratio (y_D^*) is defined. It describes how much an individual component contributes to the total exergy destruction of the overall system (Gasafi et al., 2007):

$$y_D^* = \frac{\dot{E}_D}{\dot{E}_{D,tot}} \quad (45)$$

The overall exergy efficiency of a system, producing hydrogen is calculated as follows:

$$\varepsilon_{tot} = \frac{\dot{E}_{H_2}}{\dot{E}_F + \dot{E}_Q + \dot{W}} \quad (46)$$

Energy efficiency of the overall system is calculated by taking the ration of heat in the hydrogen produced and that input the system.

$$\eta = \frac{\dot{m}_{H_2} \times \text{LHV}_{H_2}}{\dot{m}_F \times \text{LHV}_F + \dot{m}_Q \times \text{LHV}_Q + \dot{W}} \quad (47)$$

Table 10. Energy and Exergy efficiency of SCWG

| Fuel | Energy efficiency (%) | Exergy efficiency (%) | reference |
|---------------|-----------------------|-----------------------|-------------------------|
| Sewage sludge | 56 | 52 | Gasafi et al. (2007) |
| Hyacinth | 64.8 | - | Matsumura et al. (2002) |
| Sawdust | 50 | - | Calzavara et al. (2005) |
| Sawdust | 44.21 | 42.46 | Lu et al. (2007) |
| Cellulose | - | 40.6 | Feng et al. (2004a) |

Table 10 presented energy and exergy efficiency of an integrated plant for SCW gasification by combining values of individual units of this plant. The

predicted efficiencies of the plant varied resulted from the different means of preheating the feed and efficiencies of the heat exchangers used.

Heat transfer effect

The exergy loss in the reactor occurs due to irreversibility and heat transfer. Lu et al. (2007) computed it to be 36.8% while it was only 12% in case Gasafi et al. (2007). This depends to a great extent on the process adopted. The highest amount of exergy destruction in Gasafi et al. (2007)'s system occurred in the combustion chamber where natural gas was burnt to preheat the feed. This loss constituted 34% of the total exergy destruction in the system. For Lu et al. (2007) the heat exchangers accounted for 32% exergy loss.

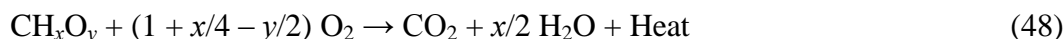
The exergy destruction in preheater is caused primarily by heat transfer. Higher the temperature higher is the loss. Thus, by increasing the heat transfer areas or by reducing the fluid-flow rate one can reduce the exergy destruction through heat transfer. Increasing the heat transfer surface area will add to the capital cost of the plant while higher exergy loss might impact the operating cost. Thus finding the best compromise or tradeoff between these two is important.

The heat exchanger efficiency has an important bearing on the design of SCWG. An increase in heat transfer efficiency of heat exchanger, reactor and preheater results in the increase in total energy and exergy efficiencies as illustrated in Figure 11.

Heat transfer efficiency is the amount of heat that can be absorbed by fluid inside a heat exchanger divided by the amount of heat provided by the heat source. It can be seen that the heat transfer efficiency has a major influence on the energy and exergy efficiencies. Generally, heat is supplied to the reactor by external heat resource, but this method provides low heat transfer efficiency and heating rate. Consequently, changing the external heating into the internal heating can greatly improve the exergy efficiency.

Hao et al. (2003) made similar observations. Additionally, they noted that an increase in the temperature of the heat source would reduce the exergy efficiency of the system. The analysis of Hao et al. (2003) also showed that higher biomass concentration in the feed would reduce the exergy efficiency.

As biomass gasification in SCW is an endothermic reaction, the process requires the addition of heat to drive the chemistry. Partial combustion of biomass, which is an exothermic reaction could provide this heat and hence can enhance exergy efficiency of the system. The in-situ exothermic oxidation reaction of biomass is as follow:



Biomass thus may be gasified with addition of less than stoichiometric quantities of oxygen such that only partial oxidation takes place. The effect of partial oxidation on SCWG is summarized in Guo et al. (2007), Lu et al. (2007) and Watanabe et al. (2003).

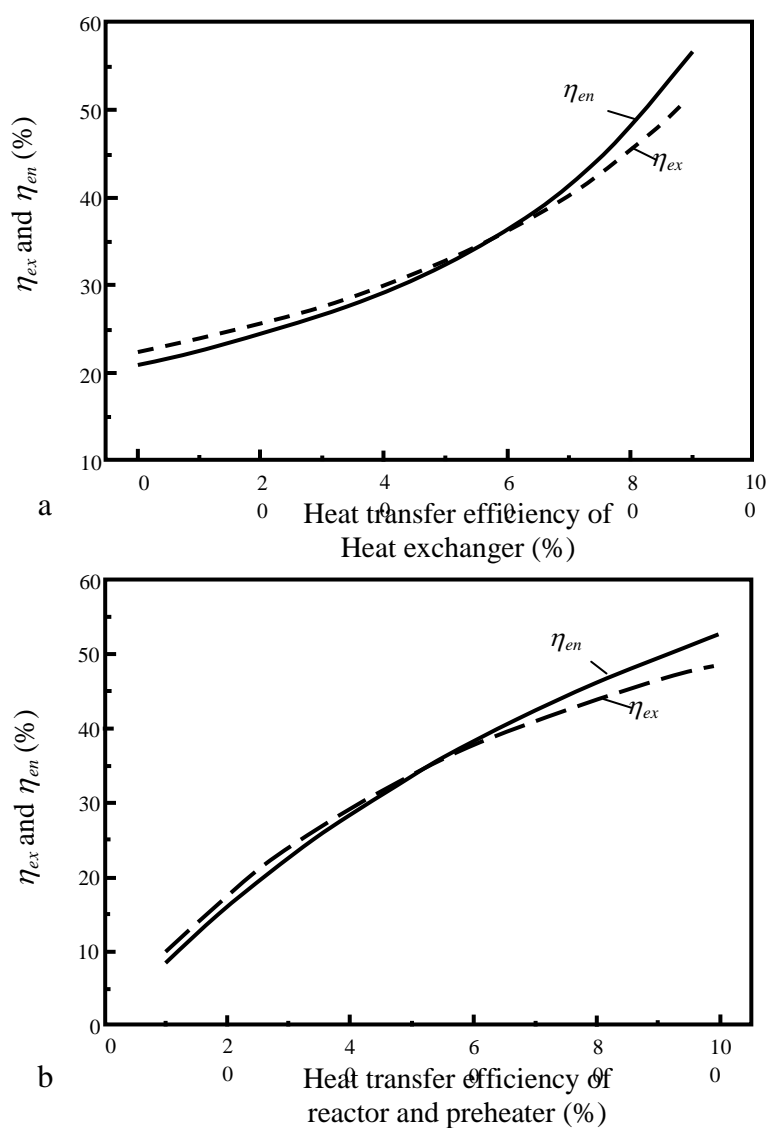


Figure 11. Effects of heat transfer efficiency of heat exchanger (a), reactor and preheater (b) on the exergy conversion efficiency of gasification system (Lu et al., 2007).

CONCLUSION

Gasification in supercritical water is a promising option for biomass conversion. Experiments carried out till date, are confined to small laboratory units. Large or pilot scale units are awaited.

An increase in the gasification temperature and the heating rate would improve the gasification efficiency, while an increase in the biomass concentration and biomass particle size will reduce it. Effects of pressure, type of reactor and diameter of reactor tube are still not clear. Above a minimum value, the residence time in the reactor does not have a major influence on the gasification yield, but this minimum is required for complete gasification. Some constituents of the biomass, like lignin and cellulose influence the gas yields. Three main types of catalysts (metals, alkaline and carbon), when added to the supercritical water gasification process improve the gasification efficiency and reduces the required temperature for gasification. Reactor materials, especially those containing nickel have a catalytic effect on the gasification reaction. The carbon build up on reactor walls could reduce the conversion in SCW.

Equilibrium models can effectively predict the performance of the SCWG reactor and the gas-liquid separator in terms of product gas composition and solubility of gases in water.

Thermodynamic analyses carried till date, put the energy efficiency of biomass gasification in the range 44-64% while the exergy efficiency is in the range of 40-52%. The heat exchanger used for preheating the feed had an important effect on the exergy efficiency. Improved heat transfer efficiency of the heat recovery heat exchanger is a key to increasing the total exergy efficiency of the SCWG process.

A great deal of engineering research is required to allow this option to enter the mainstream gasification market. Heat transfer (SCW to solids) and mass transfer are amongst some of the important areas that are to be explored for the development of a good engineering design.

NOMENCLATURE

| | |
|----------|--|
| A | pre-exponential factor, s^{-1} |
| C_c | concentration of feed |
| CC | cellulose content, wt% |
| C_{c0} | initial concentration of carbon in the feed, mol/L |
| CE | carbon efficiency |
| d | reactor diameter, m |
| D | axial dispersion coefficient, m^2/s |
| E | activation energy, kJ/mol |

| | |
|---------------------------------------|--|
| $\dot{E}_{D,tot}$ | total exergy destruction of the overall system, kJ/s |
| \dot{E}_F | exergetic fuel rate, kJ/s |
| \dot{E}_F | exergy rate of feedstock, kJ/s |
| \dot{E}_{H_2} | exergy rate of flow of product hydrogen, kJ/s |
| E_i^{PH} | physical exergy of component i in the mixture, J/mol |
| \dot{E}_Q | exergy of flow for heat supply to the system, kJ/s |
| $\dot{E}_{q,j}$ | exergy rate associated with the transport of heat beyond system boundaries, kJ/s |
| \dot{E}^{TOT} | total exergy rate of a material flow, kJ/s |
| $\dot{E}_{in}, \dot{E}_{out}$ | exergy rate associated with the material flowing in and out, kJ/s |
| $\dot{E}^{KN}, \dot{E}^{PT}$ | kinetic exergy rate, potential exergy rate of a material flow, kJ/s |
| $\dot{E}^{CH}, \dot{E}^{PH}$ | chemical exergy rate, physical exergy rate of a material flow, kJ/s |
| $\dot{E}_D, \dot{E}_L, \dot{E}_P$ | exergetic destruction rate, exergetic loss rate, exergetic product rate, kJ/s |
| F | factor in equation 1 |
| GE | gas efficiency |
| H, H_0 | enthalpy, enthalpy at environmental temperature and pressure |
| K | reaction rate constant in equation 23, s^{-1} , min^{-1} |
| LHV_F, LHV_{H_2} | lower heating value of feedstock, lower heating value of hydrogen, kJ/kg |
| LH_Q | lower heating value of flows for heat supply to the system, kJ/kg |
| $\dot{m}_F, \dot{m}_{H_2}, \dot{m}_Q$ | mass flow rate of feedstock, mass flow rate of product hydrogen, mass flow rate of flow for heat supply to the system kg/s |
| N_{wa} | weighted average |
| N_c, N_l, N_x | values for the single-component gasifications of cellulose, lignin, xylan |
| P | pressure, Pa |
| P_c | critical pressure, Pa |
| Pe | Peclet number |
| \dot{Q}_j | heat transfer rate through system boundary, K |
| r | related correlation coefficient |
| R | universal constant of gases |
| r_C | reaction rate of carbon, mol/L.s |
| \dot{S}_{gen} | entropy generation rate |

| | |
|----------------------|--|
| S, S_0 | entropy, entropy of a system at environmental temperature and pressure |
| T | temperature, K |
| T_0 | environmental temperature, K |
| T_c | critical temperature, K |
| T_j | temperature of flow j , K |
| T_{sc} | pseudo-critical temperature, K |
| u | axial velocity, m/s |
| \dot{W} | work rate as electric power supplied to or removed from the system, kJ/s |
| X_C | carbon conversion of biomass (mol C in gas/mol C in feedstock) |
| X_C, X_l, X_x | weight fraction in the mixture of cellulose, lignin, xylan |
| Y_C | carbon gasification, kg C in gas/ kg C in feedstock |
| YH | yield of hydrogen, wt% of dry basis |
| y_i | molar fraction of component i |
| y_D^* | exergy destruction ratio |
| Z_C, Z_H, Z_N, Z_O | weight fractions of carbon, hydrogen, nitrogen, oxygen, |

Greek Letters

| | |
|---------------------|--|
| β | factor in equation 39 and 40 |
| ε | exergetic efficiency |
| $\varepsilon_{0,i}$ | standard chemical exergy of pure chemical compound i , J/mol |
| η | energy efficiency |
| τ | residence time, s or min in equation 24 |

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