SUPERCRITICAL WATER GASIFICATION OF WASTE BIOMASS FOR HYDROGEN SYNTHESIS

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ABSTRACT

The rapid global industrial development is stimulating the exploration of new routes to meet the increasing energy demands. Additionally, decline in fossil fuel reserves and climate change promotes the utilization of renewable resources. Biomass is one of the most promising renewable sources for valuable fuels such as biodiesel, bioethanol, biobutanol and syngas (H_2 + CO). The advancement in supercritical water technologies has benefits to synthesize fuels from biomass gasification. Variation of thermo-physical properties of water beyond the supercritical point helps in dissolving these organic compounds leading to the release of gases such as H_2 and CO. A large number of studies on gasification of biomass model compounds such as cellulose, glucose, lignin and glycerol in supercritical water are available in literature. Potential commercialization of the supercritical water gasification of biomass requires the understanding of various routes for the process evolution. This paper presents results concerning supercritical water gasification of waste biomass and provides insights on hydrogen production.

INTRODUCTION

The striking increase in energy demands is leading the current research to focus on renewable energies such as solar energy and waste biomass. The higher emissions of greenhouse gases due to the burning of fossil fuels have led to environmental impacts via global warming. Renewable energy, particularly biomass, is becoming increasingly important for sustainable development. Biomass is largely recognized in dealing with environmental issues regarding fossil fuels usage. Bioenergy i.e., energy derived from biomass is an immense source of sustainable energy which is renewable. The energy from biomass can be harvested in the form of liquid or gaseous fuels such as bio-oils, ethanol, butanol, synthesis gas (syngas - CO + H_2) or even pure hydrogen gas [1]. Recently, there is a growing interest in the production of hydrogen that has been found to be an alternative clean fuel with zero greenhouse gas emissions.

Lignocellulosic biomasses are cost-effective resources that are abundantly available for the production of biofuels and bio-chemicals. Lignocellulosic biomass can be categorized into agricultural and forest residues, energy crops and municipal paper waste. Lignocellulose is the major building block of plant cell wall and is primarily made of cellulose, hemicellulose and lignin [2]. A typical lignocellulosic biomass has 30-60% cellulose, 20-40% hemicellulose and 15-25% lignin [3]. Supercritical water gasification (SCWG) technology has been found to effective for the production of gaseous fuels (especially hydrogen) from biomass. During gasification, cellulose and hemicellulose initially breaks down into simple sugars such as

glucose, whereas lignin converts to phenolics. These intermediates further convert to gases in supercritical water (SCW). The behavioral knowledge of biomass constituents and their reaction mechanisms are essential for the effective fuel production.

The implication of supercritical fluids for various processes has been increasing in the past few years. The combination of liquid and gas properties makes supercritical fluids attractive to many chemical and biochemical processes [4-6]. Water being non-toxic, abundant and cheaply available serves a good choice as a supercritical fluid. Water near and above its critical temperature (374°C) and pressure (22.1 MPa) has the ability to dissolve the organic components forming a homogenous medium suitable for gasification process [7]. The flexibility in tuning the thermo-physical properties (i.e., thermal conductivity, viscosity, diffusivity and solvating properties) with temperature and pressure promotes SCW technology for the gasification of biomass [8].
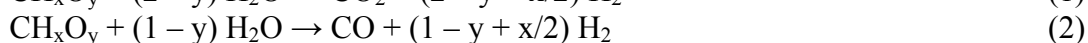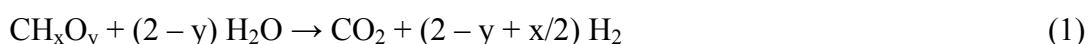
There are various parameters that can influence the gasification efficiency and the gas composition. This paper highlights significant researches focused on gasification of biomass in SCW. The effects of operating parameters such as temperature, pressure, residence time, feed concentration and catalysts on gasification efficiency and hydrogen yields of SCWG of biomass are discussed. For better understanding of the SCWG of biomass material, it is essential to study the performance of its model compounds such as cellulose, lignin, glycerol, phenolics etc. The insights of SCWG of these model compounds can be extended to biomass constituents to recognize the biomass reactions in H_2 production.

ROLE OF SUPERCRITICAL WATER IN GASIFICATION

SCW possesses gas-like viscosity and liquid-like density properties allowing it to have better mass transfer and salvation abilities [9]. The viscosities of gases and liquids differ by about two orders of magnitude under normal conditions. When the density is between 0.6 and 0.9 gcm^{-3}, the viscosity depends only weakly on temperature and density. In this range, the viscosity amounts only to about one tenth of its value under normal conditions [10]. This high fluidity is attractive in many chemical processes because mass transfer and diffusion-controlled chemical reactions are largely enhanced. With increasing temperature and pressure, the density of water decreases. At the critical point, the density of the liquid and gas phases are equal. Therefore, above the critical point, the density of SCW can be changed continuously with variation in temperature and pressure [11].

SCW plays a dual role as a reaction medium and catalyst during gasification. The moisture content of biomass, which is a major technical problem with conventional thermochemical routes (e.g., pyrolysis) is also controlled during SCWG. The energy requirements for drying of biomass can be ruled out with gasification of biomass in SCW. The high selectivity for H_2 production and greater reaction efficiency of SCW as a medium for gasification provides an alternative to produce H_2 rich syngas.

SCWG of biomass produces CO, H_2, CO_2, CH_4 and traces of other gaseous products. H_2 production in SCW is endothermic in nature [12]. The overall chemical reaction for SCWG (equation 1) along with three major reactions, namely steam reforming reaction (equation 2), water-gas shift reaction (equation 3) and methanation reaction (equation 4):

$$CH_xO_y + (2 - y) \, H_2O \rightarrow CO_2 + (2 - y + x/2) \, H_2 \tag{1}$$
$$CH_xO_y + (1 - y) \, H_2O \rightarrow CO + (1 - y + x/2) \, H_2 \tag{2}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{4}$$

High yields of H_2 are obtained at higher temperatures that favor water gas-shift reactions and restrict methanation reactions. In addition to water gas-shift reaction, steam reforming reaction also plays a significant role in incrementing H_2 yields at high temperatures [13, 14]. Water-gas shift reaction is weakly exothermic ($\Delta H = -41$ kJ/mol) and thermodynamically limited at the operational temperatures, but allows a significant CO abatement and further H_2 formation [15]. Lee et al. [16] studied the non-catalytic SCWG of glucose at 480-750°C and 28 MPa for 10-50 s. They observed that CO yield was high initially but with the increase in temperature beyond 650°C, CO concentration decreased and H_2 yield increased due to water-gas shift reaction.

Water molecules also participate in SCW reactions as catalysts. Under SCW conditions, H^+ and OH^- exist in high concentration, which creates favorable conditions for acid-base catalytic reactions. Temperature has a great influence on the ionization of water [11]. Acid-catalyzed reaction of organic compounds occurs in pure subcritical and supercritical water without any catalyst [9]. It has been reported that dehydration of cyclohexene occurs at subcritical conditions without addition of catalyst. With this result, it was supposed that the reaction was catalyzed by H_3O^+ generated from water at high temperature. Water can be an effective acid catalyst at subcritical condition. In addition, Ikushima et al. [17] reported that SCW functions as an acid catalyst in accelerating Beckmann and pinacol rearrangements.

Many chemical reactions take place in SCW; while under normal conditions, these reactions are only possible with the addition of base catalyzed materials. To confirm base catalytic effect of supercritical water, Ikushima et al. [17] conducted an investigation on benzaldehyde disproportionation without catalyst that demonstrated the participation of OH^- ion in the disproportionation using SCW. Usually, OH^- is responsible for the formation of alcohol in any chemical reaction. Ethanol and formic acid can be produced from Cannizzaro-type reactions of formaldehyde in subcritical water without catalyst, which is well-known to occur in the presence of a large amount of base catalyst under ambient conditions [9].

PARAMETRIC EFFECTS ON SCW GASIFICATION

Many investigations have been performed to understand the effect of operating parameters such as temperature, heating rate, pressure, residence time, feed concentration, biomass-water ratio, and catalyst type and loading on SCWG of biomass. In one of the studies, H_2 production by SCWG of corn cob was found to be influenced by parameters following the order: temperature > pressure > feed concentration > residence time [8].

The effect of parameters on gasification is quite intricate. High temperatures and pressures are required to achieve maximum gas yields. The gasification of biomass in SCW can be classified into two processes based on the temperature used, namely low temperature gasification (300-500°C) and high temperature gasification (500-800°C). At low temperatures, gas yields are low with significant amount of liquid and solid products. With the increase of temperature, the gasification efficiency increases with maximum gas yields [12].

Maximum H_2 production is favored at high temperatures. Concentrations of CO and CH_4 are high in low temperature gasification, whereas in high temperature gasification H_2 and CO_2 have maximum concentrations in the gaseous product [18]. A high heating rate generally favors SCWG of biomass with higher yields of H_2, CH_4 and CO_2 and lower yields of CO [19]. As the residence time in subcritical region is short, the formation of coke and/or char is

reduced. Matsumura et al. [20] observed that tar production decreases with temperature due to the formation of furfurals. Minimum residence time is required to gasify biomass after which the gasification efficiency does not improve significantly.

The properties of SCW are required to be considered while studying the effect of pressure on the process. Density, ionic products concentration and dielectric constant increase with pressure [21]. The increase in ionic products with pressure enhances the generation of H^+ and OH^-, thereby significantly improving the hydrolysis rate [22]. Ionic mechanisms are dominated with the increase in pressure during SCWG of biomass, while free radical mechanisms are restrained [9].

High concentrations of biomass in SCWG are generally difficult to gasify. Increasing the feed concentration also decreases H_2 yields along with lower gasification efficiency [12]. Lu et al. [22] found that smaller feed particles improve H_2 yields, gasification efficiency and carbon efficiency during SCWG. Issues regarding biomass pumping into the reactor can also be encountered with higher particle size of biomass and feed concentration.

The implication of catalysts in SCWG greatly reduces the formation of tars and chars, making the process more effective. In order to increase the selectivity for H_2 and to reduce high temperature and pressure conditions, catalysts can be employed. Various catalysts that have been implemented for SCWG of biomass include alkali metals, transition metals and activated carbons [9, 23, 24]. The main characteristic feature of alkali metal catalysts in SCWG is to improve the water gas-shift reaction. Transition metal catalysts such as Ni and Ru exhibit high catalytic activity in SCWG of biomass [9, 23]. It was found that Ni can accelerate the conversion of biomass, but it can cause sintering and deactivation in the reaction process in both batch and continuous flow experiments [12]. Ru is a very active catalyst for low temperature catalytic gasification. In SCWG of glucose, the addition of Ru/Al_2O_3 catalyst has been found to improve the conversion rate and H_2 yield. Pt-based catalysts have also shown high activity and good selectivity for the production of H_2 in SCWG of sugars and alcohols at low temperature.

SCW GASIFICATION OF BIOMASS–INTERMEDIATE MIXTURES

It is essential to understand the behavior of biomass model compounds and their intermediates at supercritical conditions to improve the efficiency of H_2 production by suppressing undesired reactions as the reaction routes vary depending on the intermediates generated. The composition of syngas largely varies depending on the biomass and intermediate mixture [25]. Phenol and acetic acid are found to be persistent even at high operating temperatures (> 700°C) and pressures (> 25 MPa) [13].

SCWG of biomass components and its intermediate mixtures reveal that the interactions between the components have a significant role in product gas composition. Yashida and Matsumura [25] reported that intermediates from cellulose, xylan and lignin mixture showed decrement in the yields of H_2 at 400°C and 25 MPa. Phenol which is the stable intermediate of SCWG of lignin has been found to enhance the degradation of the [lignin + phenol] mixture [26]. The addition of phenol to lignin during SCWG hinders the re-polymerization reactions resulting in lower yields of char [27]. The investigations on the mixture of model compounds of lignin indicate that each of the biomass components have a separate effect which leads to the formation of diverse products [28].

In another study, research on the mixtures of cellulose and lignin model compounds i.e., [glucose plus phenol mixture] was conducted [29]. It was found that the theoretical sum of the volume of produced gases from their independent solutions was less than that from the

mixture solution of 1 wt.% each at 500°C and 25 MPa in presence of $KHCO_3$. This result reveals that phenol has a negative impact on glucose gasification. Moreover, it was observed that addition of phenol to glucose solution increased the total organic carbon and residual phenol in the liquid phases, confirming its adverse effect during SCWG. The presence of small amounts of phenol in SCWG of glucose reduces the total volume of gas production and also H_2 yields.

Acetic acid is the refractory intermediate component of SCWG of glucose and cellulose, while phenol is the recalcitrant compound of lignin. Experiments were done to investigate the SCWG of mixture of acetic acid (0.5 wt.%) and phenol (1 wt.%) with/without catalyst (NaOH) [30]. Their findings showed that 0.2 wt.% NaOH resulted in maximum yields of H_2. They attributed that the increase in H_2 production was due to the enhancement of water-gas shift and steam reforming reactions. In addition to that, they have also investigated SCWG of [methanol + acetic acid + phenol] mixture. The presence of methanol and acetic acid remarkably altered the reaction path of SCWG of phenol. In addition, total organic carbon removal, H_2 production and carbon gas efficiencies decreased with increasing concentrations of acetic acid and phenol, latter having the major impact. The minimal effect of acetic acid on the efficiencies is due to the decarboxylation reactions to produce simple carbon-containing gases (e.g., CH_4 and CO_2).

CONCLUSIONS

Supercritical water gasification is an efficient method for waste biomass conversion to H_2 gas fuel. However, the efficiency of biomass in supercritical water is governed by several parameters such as temperature, heating rate, pressure, residence time, feed concentration and catalyst type. High temperatures, higher densities of supercritical water, longer residence time and low feed concentrations of biomass usually result in high H_2 yields with maximum gasification efficiency. H_2-rich syngas can be produced in the presence of Ni or Ru-based catalysts at relatively low operating temperatures. Water gas-shift and steam reforming reactions also have major effects on H_2 yields in supercritical water gasification of biomass. This paper implies that an optimum and efficient way to produce H_2-rich syngas requires a better understanding of the influence of process parameters on supercritical water gasification of biomass.

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