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Review

Supercritical water gasification of biomass for hydrogen production

Sivamohan N. Reddy [a], **Sonil Nanda** [a], **Ajay K. Dalai** [b], **Janusz A. Kozinski** [a,*]

[a] Lassonde School of Engineering, York University, Toronto, ON, Canada
[b] Department of Chemical and Biological Engineering, University of Saskatchewan, SK, Canada

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ABSTRACT

Hydrogen from waste biomass is considered to be a clean gaseous fuel and efficient for heat and power generation due to its high energy content. Supercritical water gasification is found promising in hydrogen production by avoiding biomass drying and allowing maximum conversion. Waste biomass contains cellulose, hemicellulose and lignin; hence it is essential to understand their degradation mechanisms to engineer hydrogen production in high-pressure systems. Process conditions higher than 374 °C and 22.1 MPa are required for biomass conversion to gases. Reaction temperature, pressure, feed concentration, residence time and catalyst have prominent roles in gasification. This review focuses on the degradation routes of biomass model compounds such as cellulose and lignin at near and supercritical conditions. Some homogenous and heterogeneous catalysts leading to water–gas shift, methanation and other sub-reactions during supercritical water gasification are highlighted. The parametric impacts along with some reactor configurations for maximum hydrogen production and technical challenges encountered during hydrothermal gasification processes are also discussed.

1. Introduction

Consumption of fossil fuels is responsible to increase greenhouse gas emissions which have a great impact on the environment leading to global warming. Moreover, the limited reserves of fossil fuels drive the thinking towards alternate sources. The growing interest in the renewable energy to replace the conventional fossil fuels shows a path to produce clean fuel for transportation and other energy utilities [1]. Fuels from renewable waste biomass are suitable alternatives to the conventional fossil fuels. Waste or lignocellulosic biomass is a potential renewable energy source to meet the increasing energy demands [2]. In addition, fuels derived from waste biomass are considered carbon-neutral as the net CO_2 released from their combustion is utilized by the plants during

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Abbreviations: AC, activated carbon; CSTR, continuous stirred reactor; DAC, diamond anvil cell; GTL, gas-to-liquid; LHSV, liquid hourly space velocity; SMR, steam methane reforming; SCW, supercritical water; SCWG, supercritical water gasification; WGS, water–gas shift; WHSV, weight hourly space velocity.

* *Corresponding author*. Tel.: +1 416 736 5484; fax: +1 416 736 5360.
E-mail address: janusz.kozinski@lassonde.yorku.ca (J.A. Kozinski).

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photosynthesis [3]. Hydrogen is a clean fuel as its combustion results in water which makes it attractive compared to other gaseous fuels. Hydrogen is not readily available in nature and is generated by the reforming of natural gas. Exploiting lignocellulosic biomass could be a suitable option to produce H_2 through gasification technologies [4]. Compared to thermochemical gasification that consumes large amounts of energy for biomass conversion, supercritical water (or hydrothermal) gasification is relatively energy-efficient with no additional requirement of biomass drying. Lignocellulose biomass components can break down into simple molecules during supercritical water gasification (SCWG) to produce synthesis gas or syngas [5]. Syngas ($H_2 + CO$) is the main product of SCWG of biomass and can be used as a clean fuel or in the production of diesel fuel via gas-to-liquid (GTL) technologies such as Fisher–Tropsch catalysis or syngas fermentation [2].

A fluid cannot be liquefied beyond its critical temperature irrespective of the pressure applied. Every fluid is characterized by a unique critical point. With the operating temperature and pressure greater than its critical point, a fluid is termed as a supercritical fluid. The low-cost availability of water, its non-toxic nature and critical point (374 °C and 22.1 MPa) near to many chemical processes makes it an ideal solvent for many chemical reactions [6]. Supercritical water (SCW) has high kinetic energy like gases and densities similar to that of liquids. A combination of gas and liquid like properties makes SCW superior to various conventional solvents. The increase in temperature over the critical temperature of water weakens the hydrogen bonding between the molecules and also contributes to H_2 production [7]. The dielectric constant of SCW is much lower than that of normal water which makes SCW a non-polar solvent. The tuning of thermophysical properties of water with temperature and pressure makes it miscible with organics and gases forming a single homogenous phase appropriate for SCWG [8,9].

Supercritical water gasification of biomass in various reactor configurations such as batch, tubular and continuous stirred tank reactors has been investigated in the past and current years. A new emerging reactor configuration to gasify the biomass in fluidized bed at supercritical conditions has been found to be attractive to overcome the current technical problems of the SCWG processes. This review is focused on discussing these various SCWG reactor configurations for H_2 production from biomass. In addition, different process parameters are also known to influence the yields of H_2 during SCWG of biomass. In a study by Lu et al. [10], the parameters that influenced the SCWG of corn cobs followed the order: temperature > pressure > feedstock concentration > residence time. Hence, this paper also presents an overview of the process parameters such as temperature, pressure, feed concentration, catalyst type and loading along with reactor configurations that influence the overall reaction mechanisms and H_2 yields.

2. Supercritical water gasification of biomass components

Lignocellulose biomass is the non-edible part of the plants that is composed of cellulose, hemicellulose and lignin [11]. Lignocellulosic biomass can be categorized into agricultural and forest residues, dedicated energy crops and municipal paper waste. Lignocellulose forms a complex network in the plant cell wall that is held together by covalent bonding, intermolecular bridges and van der Waals forces. A lignocellulosic biomass typically has 30–60% cellulose, 20–40% hemicellulose and 15–25% lignin [12].

Gasification can be defined as the conversion of biomass to H_2, CO, CO_2 and CH_4 through high temperature (>700 °C) reactions with controlled amounts of oxygen and/or steam. Supercritical water gasification is a type of biomass gasification where supercritical water (374 °C and 22.1 MPa) is used as the medium. Thus, the main difference between SCWG and other thermochemical gasification techniques is related to their gasification medium i.e., supercritical water or inert gas and/or steam. Supercritical water has a dual role as a reactant and medium in the gasification of biomass. The probability of generation of H^+ and OH^- ions at high density is greater at supercritical conditions creating an environment for hydrolysis and pyrolysis reactions [13]. Free radicals are also generated at high temperatures over the supercritical temperatures [14]. Production of H_2 through SCWG of biomass irrespective of the moisture content makes it superior to other conventional thermochemical routes.

The added advantage of SCWG of biomass is its high pressure H_2 production which cuts down the compression energy costs during its storage [1]. Around the supercritical point, water has ability to form ions which helps in degradation of biomass components [8]. Lignocellulosic biomass which consists of cellulose and hemicellulose gets dissolved at high temperature and pressure in SCW. These molecules further breakdown to simple sugars which are gasified by increasing the reaction temperature and pressure [5]. Lignin in biomass converts to phenolic compounds which are further reformed to simple gases such as H_2, CO, CO_2 and CH_4 [15].

Since diverse groups of compounds are produced from cellulose, hemicellulose and lignin, it is therefore necessary to study the behavior of the intermediates and their degradation or reformation routes to gases. Prior to understanding the mechanisms, behavior and the breakdown of the complex lignocellulosic biomass in supercritical conditions, it is essential to investigate the SCWG of their model compounds such as cellulose, glucose, glycerol, lignin and phenolics. Some of the vital reactions that occur during the gasification of biomass in SCW are as given below.

The overall reactions of biomass gasification are mentioned below:

$$CH_xO_y + (2-y)\ H_2O \rightarrow CO_2 + (2-y+x/2)H_2 \tag{1}$$

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (1-y+x/2)H_2 \tag{2}$$

Cellulose hydrolysis:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \tag{3}$$

Glucose reforming reaction:

$$C_6H_{12}O_6 \rightarrow 6CO + 6H_2 \tag{4}$$