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Simulation and kinetic modeling of supercritical water gasification of biomass

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ABSTRACT

In this article, kinetic study is performed to construe the kinetics of gasification of model biomass compounds in supercritical water (SCW) in the presence of catalyst for hydrogen production using the mechanistic models developed applying Langmuir–Helshinwood–Hougen–Watson (LHHW) and Eley–Rideal (ER) procedure. Besides, two types of model biomass are used to perform simulation of SCWG for producing H₂ using the Aspen Plus®. Glucose is used for both kinetic study and simulation. As well, further simulation is performed using hydroxymethyle furfural and phenol mixture. A better justification is obtain between the simulation results and data from literature. Higher temperature shows better hydrogen yield whereas higher concentration of biomass shows decreased hydrogen production. None of the gasification efficiency, product yield and carbon conversion efficiency is significantly affected by pressure variation. It is found that gasification efficiency is higher than 100%, which means SCW actively takes part in the reaction as an important reactant. Higher temperature favor carbon conversion efficiency (CCE). With the increase in concentration, CCE increases for glucose. However, the mixture of phenol and hydroxymethyl furfural (HMF) showed a declining trend with an increase in biomass concentration. Among the proposed mechanistic models, three models converged. However, an ER based model described as the dissociation of adsorbed glucose through Retro-Aldol reaction is found to be the rate determining step with an average absolute deviation 10.6%.

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Introduction

“Hydrogen energy economy” has significant merit to address global CO₂ emissions, however, production of sufficient H₂ economically, and environmentally friendly is a major challenge. At present, fossil fuels contributes to 96% of the total H₂ production [1]. Thus, renewable resources are necessary if H₂ is to become a fundamental energy resource for the future.

Low quality wet and under-valued biomass represents an immense and renewable source using supercritical water gasification (SCWG) technique for the production of H₂. Compared to the traditional gasification process that requires dried biomass, SCWG utilizes the water and moisture content of the biomass to produce usable gaseous products. Hence low quality biomass (such as manure, algae, water hyacinth) with over 70% moisture content are favorable for SCWG. This is because, the behavior of water becomes very unique beyond

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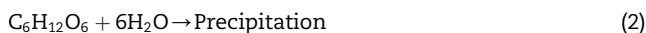
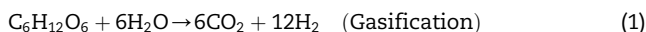
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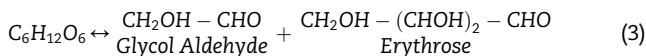
the critical point ($T_c = 373.95\text{ °C}$ and $P_c = 22.06\text{ MPa}$), a process condition above which SCWG process works. Nonpolar, organic compounds can be dissolved in SCW while they cannot be normally dissolved in water or steam. The absence of phase boundaries and high diffusivity in SCW leads to rapid and complete reactions [7,18,41]. In this condition, many organic substances, together with the precursors of tar and char (mainly polycyclic aromatic hydrocarbons) become soluble in SCW. As such, contrary to the conventional gasification process, higher transmutation to gas and less solid remnants (almost zero tars or char formed) of the solid feed material can be achieved by the SCWG [14,17,30,66].

Many quality studies have been done so far and some quality reviews are also available on both catalytic and non-catalytic SCWG [8,20,27,29,39,46,53,61]. These articles investigated different biomasses, ranging from simple model compounds to lignocellulosic biomasses, mostly by experimentation. A few studies have also been accomplished in the field of kinetic modeling and simulation of the SCWG using biomass [12,26,34,36,47,54,55]. Hashaikeh et al. [31] proposed that the catalytic glucose decomposition scheme proceeds with two competing reaction pathways: (i) the desired surface reaction producing hydrogen (Reaction 1) and (ii) the deposition of unwanted products in the catalyst active sites (Reaction 2):

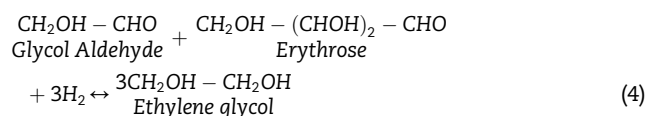


Hashaikeh et al. [31] also mentioned that the first and most important step of glucose decomposition during the gasification process is the adsorption of glucose on catalyst active sites. After the adsorption, glucose is decomposed to intermediates (e.g., Glycol aldehyde, erythrose) through the Retro-Aldol cleavage reaction, which is considered to be the preeminent step of catalytic decomposition. This leads to successive direct hydrogenation of the intermediates producing ethylene glycol [51]. The produced ethylene glycol then proceeds through steam reforming to produce carbon dioxide and hydrogen [15,22].

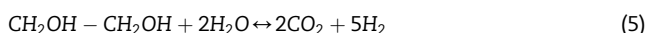
Retro-aldol reaction:



Hydrogenation:



Steam reforming reaction:



Contrary to this, the existence of acidic media and dehydrating temperatures in hydrothermal conditions, furfural and furfural derivatives (e.g., HMF) are formed due to acid-catalyzed reactions [31]. It is also well known that due to their likeliness to be influenced by electrophilic substitution of the furan rings, they produce resins and polymers [24]. Hashaikeh et al. [31] observed that the formation of cyclic and

linear oligomers by polymerization and condensation reactions with 5-HMF during the hydrothermal treatment of glucose, produces the precipitates on catalysts. Nevertheless, both Reaction 1 and Reaction 2 emanate at almost same temperature, however the main objective is to boost Reaction 1 while suppressing Reaction 2. As such, there is an essential need to study the elementary steps of the SCWG reaction system to increase the hydrogen yield.

In order to upscale SCWG process, it is important to minimize the tar and char production which causes the reactor plugging [43]. Use of catalysts during the SCWG draw the attention of the researchers as they help to improve the efficiency, increase hydrogen production while reducing the undesirable byproducts (tar and char) at a lower temperature. The product gas composition varies based on feedstock, reactor type, various operating condition and also type of catalyst. However, product gas is usually rich in methane at lower temperature (374–500 °C) and rich in hydrogen at higher temperature (>500 °C) in the presence of catalyst [12,20,39,52]. Guo et al. [27] mentioned some advantages of heterogeneous catalysts which have higher selectivity, are recyclable and environmentally benign as compared with the homogeneous catalysts. A report by Ref. [21] showed rhodium (Rh), ruthenium (Ru) and nickel (Ni) are the most effective and stable heterogeneous catalysts, especially for organics, for SCWG. Experiments have shown that 16wt%Ni/AC can gasify 0.6 M glucose solution almost completely at 575–725 °C [42].

An interesting finding is reported by Modell [48] using sawdust as feed. According to the study, gases and tar are formed as soon as the feed is submerged in SCW without any trace of char. First faster decomposition of cellulose is observed at around 190 °C beyond which lignin and part of hemicellulose undergo through solvolysis. As they have different chemical structures, during the SCWG process, different types of products are obtained through fragmentation, dehydration, degradation, condensation and isomerization. At this stage formation of gases and tars are observed. However, as the temperature and pressure increases, the unreacted biomass solids get hydrothermalized and gases and tars are formed from this remained compounds beyond 600 °C. As per this study, it is more evident to study the reaction characteristics of each ingredients of biomass step by step in SCW. Since biomass mainly consists of three components: hemicellulose, cellulose, and lignin; it is imperative to have individual studies for each component. As such, in this article, a step by step reaction mechanism of glucose in SCW is proposed and analyzed. Kinetic study of SCWG of lignocellulosic biomasses studied in the absence of catalysts using the variations of the major reaction parameters were studied extensively [2,25,37,56–59]; however, kinetic study of catalytic SCWG of biomass with elementary steps were not studied so far.

In the present paper, simulation of glucose and a mixture of phenol and HMF are performed using Aspen Plus® software. For the Aspen Plus® simulation, two types of feedstock are considered. Glucose is considered in the first case as biomass consists of cellulose and hemicellulose which are a β -1,4-homopolymer of glucose [49,51]. In the second case of simulation, a mixture of phenol and hydroxy methyl furfural is considered as feed. The main reason is, phenol is the major

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