Chemical Engineering Thermodynamics

Energetic analysis of gasification of biomass by partial oxidation in supercritical water ☆

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ABSTRACT

Partial oxidation gasification in supercritical water could produce fuel gases (such as H_2, CO and CH_4) and significantly reduce the energy consumption. In this work, an energetic model was developed to analyze the partial oxidative gasification of biomass (glucose and lignin) in supercritical water and the related key factors on which gasification under autothermal condition depended upon. The results indicated that the oxidant equivalent ratio (ER) should be over 0.3 as the concern about energy balance but less than 0.6 as the concern about fuel gas production. Feedstocks such as glucose and lignin also had different energy recovery efficiency. For materials which can be efficiently gasified, the partial oxidation might be a way for energy based on the combustion of fuel gases. Aromatic materials such as lignin and coal are more potential since partial oxidation could produce similar amount of fuel gases as direct gasification and offer additional energy. Energy recovered pays a key role to achieve an autothermal process. Keeping heat exchanger efficiency above 80% and heat transfer coefficient below 15 kJ·s^{-1} is necessary to maintain the autothermal status. The results also indicated that the biomass loading should be above 15% but under 20% for an autothermal gasification, since the increase of biomass loading could improve the energy supplied but decrease the efficiency of gasification and gaseous yields. In general, some specific conditions exist among different materials.

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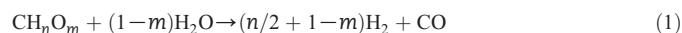
1. Introduction

Supercritical water (SCW) is water at temperatures and pressures that exceed its thermodynamic critical point ($T_C = 647$ K, $P_C = 22.1$ MPa). SCW exhibits properties that are very different from ambient liquid water, having a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than liquid water [1]. When temperatures and pressures are over the critical point, small organic compounds, even gases become completely miscible in SCW [2]. Therefore, a single homogeneous phase can exist at SCW conditions, leading to dramatically increase the reaction rates.

Since SCW offers unique advantages, there are increasing interests in using SCW for fuels production [3], biomass processing [4] and waste treatment [5,6]. Supercritical water oxidation (SCWO) is the process of

oxidation treatment of wastewater or waste in supercritical water. As SCWO can rapidly destruct organic wastes, commercial SCWO facility for treating industrial wastewater became operational early in 1994 [7].

With the current shortage of fossil fuel, it has become of increased strategic importance to use biomass for energy [8–10]. Supercritical water gasification (SCWG) is the process that makes gaseous fuels in supercritical water. Some researches indicate that SCWG can be described as a steam reforming Reaction (1), water–gas shift Reaction (2) and methanation Reaction (3) [11].

$$CH_nO_m + (1-m)H_2O \rightarrow (n/2 + 1 - m)H_2 + CO \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

Since SCW serves as both reactant and reaction medium, supercritical water gasification (SCWG) can lead to low tar and char formation and high hydrogen yields. Gasification of biomass in supercritical

water provides a potential way to convert biomass to fuel-rich gas containing H_2 and/or CH_4 [12,13]. Commercial SCWG facility can be found for treatment of surplus active sludge for gaseous fuels in Japan, but Matsumura's evaluation indicates that SCWG requires a significant amount of energy to pre-heat and maintain a desired high temperature for the reactions [14]. To reduce the energy-cost is still the key issue for its industrialized application.

Partial oxidation in SCW is the process that gasification of biomass with less amount of oxygen than the required amount for complete oxidation by stoichiometry. As the amount of oxygen is less than that required by stoichiometry, the reactions lead to significant amount of CO and intermediates to further produce gaseous fuels such as H_2 and CH_4 by water gas shift reaction and SCWG [15,16]. Therefore, partial oxidation in SCW is a combined process between SCWO and SCWG. It was found that the partial oxidation gasification could significantly reduce the energy consumption [17,18] since heat released from the exothermic reactions by oxidation can provide a supplemental energy source. Recently, some results even showed that when gasification of vinasse in supercritical water (SCW) in the presence of air, it might occur to keep the process in an auto-thermal status according to energetic analysis [19,20]. Some researches have already shown that the reforming of ethanol to produce hydrogen from a mixture of ethanol with oxygen and water [21–23] can be conducted under autothermal conditions, suggesting a commercial way to reform ethanol.

There have been some previous studies of SCWG by partial oxidation, but relatively few that deal with thermodynamics. The results of earlier gasification of glycerol under autothermal mode were based on the use of Gibbs free energy minimization with equation of state of Peng–Robinson (PR) to predict both the product compounds and the mass enthalpy without considering the energy loss in the exchanger and the reactor and with high gasification efficiency [24]. Partial oxidative gasification of biomass indicates that gasification efficiency such as lignin is far less than 100% [25]. Gasification process is controlled by kinetics of reactions in experimental cases, and it is difficult to reach equilibrium as theory. Also, reforming of ethanol to produce hydrogen from a mixture of ethanol with oxygen and water [21–23] is different from partial oxidation in supercritical water since the amount of water is predominant in SCW system.

As the effect of lower gasification efficiency and energy loss, autothermal process in SCW was not reported by Jin et al. even with very high oxidant equivalent ratio (ER, 0.6) and 24% (by mass) biomass loading [26]. Understanding the energetic process can provide basic knowledge for optimal thermodynamic conditions to make the process self-sustaining. Therefore, it is necessary to conduct a thermodynamic analysis of the biomass gasification in SCW process by partial oxidation. The present paper focuses on the key factors such as oxidant equivalent ratio, energy recovery efficiency, biomass loading and temperature upon which autothermal gasification of biomass by partial oxidation might depend, which tries to provide detailed information to optimize the process to achieve an autothermal status for commercial operation to get fuel gases.

2. Model Development

Jin et al. have investigated gasification of glucose and lignin by partial oxidation under wide conditions in supercritical water [26]. In this work, we referred their results such as gaseous yields and gasification efficiency to analyze reactions. Base on those reactions and the typical gasification process, we develop the energy balance of reactions and the energetic model.

2.1. System under consideration

The typical system under study is shown in Fig. 1. This system is composed of two high pressure pumps (one for feedstock and
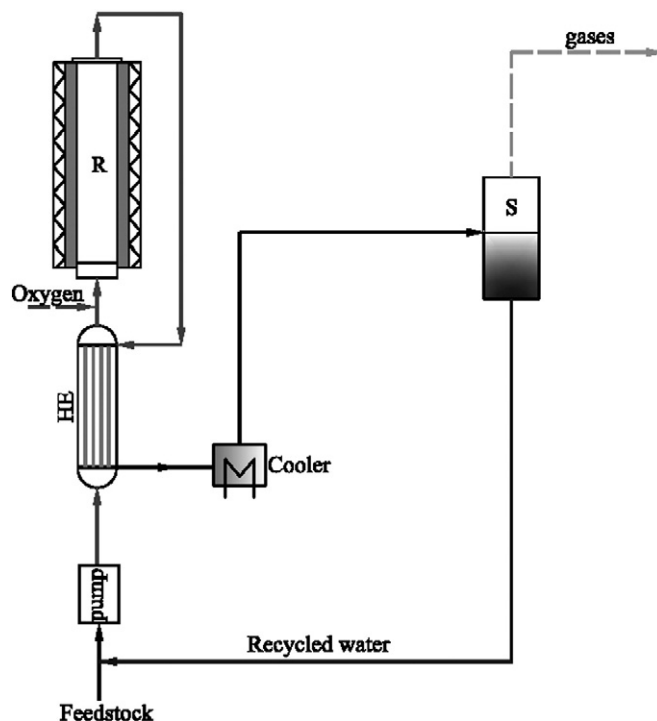

Fig. 1. System under study. S—separator; R—reactor.

one for oxygen), a heat exchanger (HE), a reactor, a cooler and three separators for high rich hydrogen gas. For a simplified evaluation of thermodynamic process and the energy exchange took place in the system, thermostatic and isobaric reactor model was considered. The biomass mixed with water at room temperature (298 K) was pressurized into HE and then entered the reactor. Meanwhile, the oxygen was pressurized into the reactor directly for partial oxidative gasification of biomass. The feedstock was heated up quickly at the reaction temperature at the inlet of reactor. After leaving the reactor, the effluent was cooled down to about 373 K in the HE for recycling energy and then cooled at room temperature in the cooler. In the separator, gaseous products were separated.

2.2. Development of the thermodynamic model

In an auto-thermal system, the energy and enthalpy output by partial oxidative reactions and recovered in HE should supply enough energy for system heating-up, energy loss and so on. As the reactor and HE were the key parts for this system, in which the largest enthalpy changes took place, the energy change of influent and effluent in HE and reactor was calculated. The flows of the mass and heat are shown schematically in Fig. 2.

In supercritical water state, water is like a dense gas and has salvation properties like non-polar fluids. Therefore, hydrocarbon, gases and supercritical water may be assumed to be single homogeneous fluid. PR equation of state is used to conduct analysis of supercritical water reactions. PR equation of state for pure fluids [27] is as

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{1}$$

with

$$b = \frac{0.0778RT_C}{P_C} \tag{2}$$