SUPERCRITICAL WATER GASIFICATION OF BIOMASS – MAPPING OF KNOWLEDGE ON THERMODYNAMIC STUDIES

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ABSTRACT

Supercritical water gasification (SCWG) of biomass has been continuously studied during past two decades, due to its unique environmental and economic benefits. This process utilizes biomass wastes as feedstock and produces hydrogen; hence waste management and renewable energy production are satisfied simultaneously. To date, most of the efforts have been dedicated to experimentally assess SCWG process, but less attention has been made to theoretical studies. Although exergy and energy analysis, economic and political issues and life cycle assessment of SCWG are discussed in some precious researches, there is vast potential to study SCWG from thermodynamic point of view. In this article, a map of knowledge on theoretical and thermodynamic studies on SCWG of biomass is presented to give insight into different analysis methods and discuss about advantages, challenges and limitations of thermodynamic analysis methods (stoichiometric and non-stoichiometric). Various feedstock types including real biomass and model compounds, appropriate equations of states (EOS) for supercritical zone and target functions are also discussed to highlight the existing paths to determine equilibrium combination, hydrogen yield, gasification efficiency, energy demand and phase behavior of reacting mixture.

Keywords: Thermodynamic analysis, Hydrogen, Supercritical water gasification.

INTRODUCTION

Supercritical water gasification (SCWG) of biomass produces hydrogen and methane-rich gas from residual and waste materials and seems be to be one of the most promising sustainable solutions to meet energy demand of near future, due to its both economic and environmental benefits. Syngas, methane-rich gas and on-site pure hydrogen production for industry, vehicles and fuel cells are some of the prospected applications of this process.

Supercritical water (i.e. water above 374 °C and 22.1 MPa) possesses unique transport and solubilization properties as both solvent and reaction media. Near critical point, water undergoes significant variations of its physical properties, like a decreasing of the dielectric constant, thermal conductivity, ion product and viscosity while the density decreases slowly. Thus, supercritical water acts as a homogeneous non-polar solvent of high diffusivity and high transport properties, able to dissolve any organic compounds and gases [1]. In SCWG, with temperature higher than 600 °C, water becomes a strong oxidant, and oxygen in water

can be transferred to the carbon atoms of the biomass. As a result of the high density, carbon is preferentially oxidized into CO_2 but also low concentrations of CO are formed. The hydrogen atoms of water and of the biomass are set free and form H_2 [2]. Moreover, extremely fast kinetics can be achieved in supercritical water medium, thus inhibited formation of tar and char significantly improves the product gas quality [3].

This process has been experimentally studied in many precious efforts during past two decades, but less attention has been paid to theoretical activities. Various biomass feedstock, operating conditions, reactor design and catalyst development have been the scope of many experimental works. In contrast, prediction of gas product composition, gasification and energy efficiencies, exergy analysis and thermodynamic modeling of SCWG of biomass are scarce. This context tries to give a reviewing map of knowledge on thermodynamic and physic-mathematical modeling of SCWG of biomass process to give insight into different aspects of it.

THERMODYNAMIC APPROACHES

Thermodynamic approaches to model SCWG process are usually based on the chemical equilibrium and phase equilibrium assumption. Equilibrium modeling gives the thermodynamic constraints and product specifications, hence process optimization and design development could be easily achieved without extensive experimentation. There are two general equilibrium methods: stoichiometric and non-stoichiometric.

A non-stoichiometric method in based on “equilibrium composition” and only requires temperature, pressure and elemental analysis of feed to minimize total Gibbs free energy of the reacting mixture. This approach is very flexible and prevents main reactions to be ignored [3,4]. Moreover, it is an acceptable and easily applicable method when reactions and mechanism of the process are not completely known as in SCWG [5].

Stoichiometric approach is based on “reaction equilibrium” and has the advantage of making the contribution of each reaction easily identifiable, but its drawback is that all chemical species and potential reactions have to be known in advance [3]. A comprehensive review on previous studies on both approaches is presented in the following.

Withag et al. [5] thermodynamically analyzed gasification of model compounds in supercritical water and discussed two general methods to calculate the thermodynamic and transport properties: (1) using activity coefficient for fluid phase and (2) using equation of state for all phases. The advantage of the activity coefficient method is its capability to predict the behavior of strong polar components such as water-alcohol mixtures. A weakness for the activity coefficient models is that they can be used up to a maximum pressure of approximately 10 bar, that limits the possible application of these methods for the study of SCWG. The advantage of using equation of state method is the wide range of temperature and pressure for which it is applicable.

Fugasity also can be calculated from either activity coefficient or EOS. To this regard, there are several problems while dealing with supercritical fluid mixtures. First, supercritical fluid mixture is very complex and hence use of conventional EOSs makes considerable error in calculation. Second, water is a strong polar substance and hydrogen bonds remain even in

supercritical region, therefore the mixture properties could be hardly achieved. Finally, due to complexity of supercritical fluids, finding the fugasity of every species as a function of temperature, pressure and mole fraction is very intolerable. For this reason, direct minimization of Gibbs free energy method is highly effective for complex chemical equilibrium problems [4,6].

NON- STOICHIOMETRIC METHODS

Most of the theoretical studies on SCWG of biomass have been conducted using a non-stoichiometric method, which apply Gibbs free energy minimization. In this section, a brief description of each research is presented, with a glimpse on bold points of the whole procedure and their novel measures. In this approach, usually three main reactions are considered, including biomass (with the general formula of CH_xO_y) reforming, water-gas shift and methanation, which are represented in Eq. (1) to (3), respectively:

$$CH_xO_y + (1-y)\ H_2O \leftrightarrows CO + (x/2+1-y)\ H_2 \quad (1)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (2)$$

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \quad (3)$$

Feng et al. [2] investigated phase equilibria for cellulose conversion in sub- and supercritical water using four different equations of state, including PR, SRK, predictive SRK and SAFT. They used water and 1-hexanole as solvents to identify the effectiveness of each in CO_2 separation. The process was at 600 ^{0}C and 350 bar, under the assumption of complete conversion of cellulose to gas products. The knowledge of phase equilibrium helped process design and separator operation. They reported mole fractions of H_2, CH_4, CO_2, CO and H_2O in vapor phase obtained from aforementioned equations of state, but due to the fact that experimental results were not available, they didn't determine the most suitable thermodynamic model for this process.

The same research team thermodynamically analyzed the phase equilibrium and phase behavior in both reactor and separator and optimized operating conditions of SCWG of cellulose [7]. They also obtained driving force of conversion reaction paths (decrease in Gibbs free energy on going from the reactants to the products) and used SAFT EOS to calculate mass distribution in phases.

Tang and Kitagawa [6] performed a precious modeling work on SCWG of biomass with Gibbs free energy minimization, utilizing Peng-Robinson EOS and Van der Waals mixing rule. Significant improvements of fitness between model predictions and experiment data from literature have been obtained by accounting reaction networks and rate controlling steps of these processes into calculations.

Calzavara et al. [1] evaluated energy efficiency of the process from Gibbs free energy minimization and evaluated the model with experimental findings. Assuming energy balance depends only on the initial and final states; their calculation of the energy balance of the overall transformation was based on the mass balance.

Yan et al. [4] also developed a non-stoichiometric model to predict the SCWG of glucose, based on Gibbs free energy minimization and used Duan equation of state for the first time for

this process. The Duan EOS is based on a corresponding states assumption with only two parameters for each pure component and two additional parameters for each binary mixture. For details of this method refer to Ref. [4]. They validated their model using two methods: (1) comparing SCW properties with literature data and (2) comparing the gasification results with AspenPlus^{TM} simulation findings of Kruse et al. [8].

In another work [9], they conducted a comprehensive thermodynamic analysis, including chemical equilibrium in the reactor, gas–liquid equilibrium in the high-pressure separator, exergy and energy analysis of the whole system. A high-pressure gas–liquid equilibrium model was proposed based on modified universal functional activity coefficient (UNIFAC) model, Soave–Redlich–Kwong (SRK) equation of state and modified Huron–Vidal second-order (MHV2) mixing rule. They investigated the effects of temperature, pressure and water recycled ratio on gas–liquid equilibrium in high-pressure separator. Therein again, Duan EOS was used to calculate the fugasity of species.

In the work of Voll and his coworkers [10], Gibbs free energy minimization, using a non-linear programming formulation and an approximation in the gas fugacities, was used to calculate the equilibrium composition for supercritical water gasification of model compounds. They used GAMS 21.6 software with the CONOPT2 Solver to solve chemical equilibrium problems.

Gutierrez Ortiz et al. [11] studied the supercritical water reforming of glycerol using AspenPlus^{TM} and calculated equilibrium composition of produced syngas with Gibbs free energy minimization method. The predictive Soave-Redlich-Kwong equation of state was used as thermodynamic method in the simulation of the supercritical region, after evaluating it against other EOS methods (SRK and PR). Their model used model the HolderbaumeGemehling mixing rules. The effect of the temperature, concentration of glycerol feed, glycerol purity in the feed of crude glycerol and pressure had been investigated in the reforming process, by obtaining the mole fraction and molar flow-rate of components in syngas, as well as the hydrogen yield. In subsequent effort, Gutierrez Ortiz et al. [12] performed similar procedure to optimize autothermal conditions of SCWG of glycerol and assess the process based on energy integration and exergy analysis.

Withag et al. [5] generated a thermodynamic model in ASPEN 12.1 under the assumption of chemical equilibrium and using model compounds (methanol, cellulose and glucose) to represent the organics in the wet biomass. SRK EOS and the BM alpha function were considered for this study. The focus was on verifying the effects of operational parameters on thermal efficiency of the whole process and the heat exchanger effectiveness was one of the most important of those parameters. They finally compared the simulated results with the experimental findings of Boukis et al. [13].

Fiori et al. [14] proposed a conceptual design of a SCWG process plant involving several substrates (glycerol, microalgae, sewage sludge, grape marc and phenol), simulated by means of AspenPlus™. The influence of various parameters (biomass concentration and typology, reaction pressure and temperature) was analyzed. They considered H_2O, CO, CO_2, N_2, N_2O, NO, NO_2, SO_2, SO_3, H_2, CH_4 and solid carbon (graphite) for model development.

Tar and char formation significantly reduce gaseous product quality, contaminate catalysts and increase the plugging rate of the reactor. For the first time, Castelllo and Fiori [3] considered thermodynamic constraints of SCWG biomass, particularly, issues concerning the

formation of solid carbon and the process heat duty. They introduced a two-phase non-stoichiometric thermodynamic model, based on Gibbs free energy minimization, which was capable of simultaneously calculating the equilibrium composition of supercritical phase and assessing the solid phase formation (graphite, representing of char). Glycerol and *Spirulina* microalgae were selected as feedstock of these analyses. Peng-Robinson EOS with Van der Waals mixing rule was used in this model.

Yakaboylu et al. [15] examined SCWG of real biomass (pig-cow manure mixture) using an equilibrium modeling approach with Gibbs free energy minimization method. For the equilibrium calculations, the software programs FactSage 5.4.1 and SimuSage 1.12 had been used. FactSage is an integrated thermochemical databank system consisting of calculation modules and databases. Moreover, fugacity coefficients of the gases were calculated by the Virial EOS. They evaluated the effect of temperature, pressure and water content of feed and validated their model with some experimental data from literature.

STOICHIOMETRIC METHODS

Among the published articles on thermodynamic approaches to assess SCWG of biomass during last two decades, only one research group was found who developed their physic-mathematical model based on a stoichiometric method. Letellier and Marias and their coworkers [16,17] were the first to build a stoichiometric mathematical model based on thermodynamic equilibrium, using Peng-Robinson EOS. As it was mentioned before, all possible independent reactions have to be known and activities of all species have to be calculated, while applying this method. In first attempt, they modeled methanol and glucose gasification in SWC and considered CH_4, H_2, H_2O, CO, CO_2, O_2, H_2S, NH_3, C_6H_5OH, CH_3COOH, CH_3CHO, C(s) and minerals as participating compounds [16]. It was assumed that this inorganic material does not undergo any chemical reaction, even though there is evidence that these materials can modify the reactivity of the mixture. The chemical equilibriums that were considered are as follow:

$$C_s + CO_2 \leftrightarrows 2CO \quad (4)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (5)$$

$$C_s + 2H_2 \leftrightarrows CH_4 \quad (6)$$

$$C_s + O_2 \leftrightarrows CO_2 \quad (7)$$

$$C_6H_5OH + 5H_2O \leftrightarrows 6CO + 8H_2 \quad (8)$$

$$CH_3COOH + 5H_2O \leftrightarrows 2CO + 2H_2 \quad (9)$$

$$CH_3CHO + H_2O \leftrightarrows 2CO + 3H_2 \quad (10)$$

Their model is capable to calculate three phases of gas, liquid and solid in reactor and separator. The results were finally quite novel compared to other data available in the literature. This research group used the same model for energetic analysis of SCWG of distillery wastewater (vinasse), hence evaluation of mass enthalpy of three phases was of great importance [17]. The mass enthalpies of solid phase (inorganic materials) and liquid phase (water) were calculated according to the calorific value at constant pressure, while enthalpy of gaseous (supercritical) phase was obtained through molar enthalpy of species by PR EOS. Finally, autothermal condition of process was successfully checked using the proposed model.

CLASSIFICATIONS

In this section, a map of procedures, tools and other classified information is proposed that could be useful to study SCWG of biomass through thermodynamic and theoretical methods. Different feedstock, equations of state, mixing rules and software tools that have been used in reviewed studies are presented.

Table 1 summarizes equations of state and mixing rules that have been used for SCWG of biomass modeling. As it can be seen, Peng-Robinson EOS and Van der Waals mixing rule is widely used in modeling of SCWG, while other property methods are available and frequently used.

Table 1: Equations of state and mixing rules used for SCWG

Equation of state	Mixing rule	Reference
PR	Van der Waals	2, 3, 6, 16, 17
SRK	MHV2 and Wong–Sandler (WS)	2, 5, 9
PSRK	Holderbaum-Gemehling	2, 11, 12
SAFT	u/k	2, 7
Duan	k_{ij}	4

Many types of biomass have been studied in experimental activities, including wet solid wastes, industrial wastewater, aquatic plants, agricultural residues, etc; but most of the theoretical investigations have used model compounds, like cellulose [2,5,7], glucose [4,5], glycerol [10, 11], glycol [12,14] and methanol [4,10]. Some other researchers have theoretically assessed real biomass, using the elemental analysis of those kinds of feedstock that is commonly introduced as CHONS with their contributing mole fractions. Vinasse [17], sewage sludge [16], saw dust [6] and pig-cow manure [15] have been found in literature.

Chemical equilibrium problems involve mathematical models with relatively large equations and various parameters, and fortunately there are several software programs to help calculations converge easier, among which AspenPlus^{TM}, MatLab, SimuSage 1.12 and GAMS 21.6 are the most applicable ones.

CONCLUSION

Supercritical water gasification (SCWG) of biomass seems to be one the dominant methods of hydrogen production in near future. This process has been extensively experimentally studied but there is great need and potential to assess it from the thermodynamic point of view. This context has focused on theoretical activities on SCWG of biomass with the aim of preparing a map of knowledge and give insight into different aspects of it. Both stoichiometric and non-stoichiometric methods of analysis were discussed and the literature was fully reviewed. Various equations of state and mixing rules that are appropriate for supercritical zone of water, different types of feedstock and modeling tools have been also introduced. Equilibrium composition, phase behavior, gasification efficiency, gas yield, energy efficiency and

optimized operating conditions of this process could be evaluated using thermodynamic and physic-mathematical modeling approaches, without experimentation requirements.

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