



Research article

Testing the constrained equilibrium method for the modeling of supercritical water gasification of biomass



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ABSTRACT

Most of the modeling approaches for supercritical water gasification (SCWG) of biomass involve the global thermodynamic equilibrium approach which shows the thermodynamic limits of the gasification process. However, the constrained equilibrium method can be a useful tool for the modeling of SCWG of biomass processes for local equilibrium conditions. This study aims to determine the additional constraints for the Gibbs free energy minimization method and test the constrained equilibrium method for the modeling of supercritical water gasification of biomass. Using two different approaches: i) treating the fluid phase as it is composed of one “pseudo” gas phase and one “pseudo” aqueous solution phase (approach I) and ii) treating the fluid phase as one single phase (approach II). Additional constraints including carbon gasification efficiency (CGE), hydrogen gasification efficiency and constrained amounts for specific compounds have been introduced as process dependent values to predict the local equilibrium state compounds. CGE appears to be the most important additional constraint. Setting a constant amount for a specific compound as another constraint improves the accuracy of the model on predicting the composition of the gas products. The model not only predicts the gas formation behavior, but also gives insight into limiting reaction pathways taking place.

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1. Introduction

Biomass, which is a practically carbon neutral feedstock, has the potential to decrease the fossil fuel consumption as it can serve all types of energy markets by generating gaseous, liquid or solid biofuels via thermochemical or biochemical conversion routes [1]. Since the pioneering work of Amin et al. [2] in the 1970s, supercritical water has been the subject of many research works for the efficient conversion of wet biomass resources into useful gases that can be converted into chemicals or fuels to combust. The favorable physical properties of water and the way they change in the near critical and supercritical region [3] make water an excellent medium for salt separation and tar-free gasification of biomass. The low dielectric constant, gas-like viscosity and liquid-like density of water in its supercritical phase result in a higher solubility for organics and a lower solubility for inorganics, as well as an enhanced mass transfer and solvation properties during the gasification process [1,4].

Numerous research works [5–12] have been published on the kinetic or thermodynamic equilibrium modeling of supercritical water gasification of biomass systems. Most of these works have been carried out with simple or model biomass compounds. Kinetic studies have started with simple sugar compounds and have been extended to real biomass

feedstocks. Some of the key studies are shortly discussed below. Matsumura's group [5,6,12] has studied the glucose decomposition kinetics in water as well as the behavior of char and 5-HMF decomposition in sub- and supercritical water. Aida et al. have investigated the reactions of D-xylose, D-fructose and D-glucose in sub- and supercritical water [13–15]. Kabyemela et al. [9] have proposed detailed reaction pathways as well as a kinetic model for the decomposition of glucose and fructose in sub- and supercritical water. Goodwin and Rorrer [16] have investigated the xylose gasification kinetics in a microchannel reactor. To study lignin derived material, Wahyudiono et al. [17] have studied the thermal decomposition kinetics of guaiacol. Sasaki et al. have further studied the kinetics of cellulose and cellobiose conversion in sub- and supercritical water [18,19]. Regarding modeling, Resende and Savage [7] have developed a kinetic model for noncatalytic supercritical water gasification of cellulose and lignin at high temperatures. Castello and Fiori [20] have used detailed kinetic models for the supercritical water oxidation of methanol to model the gasification of methanol in supercritical water, and recently Guan et al. [8] proposed a reaction mechanism for the supercritical water gasification of a real biomass feedstock; microalgae.

In addition to the kinetic model development, supercritical water gasification of biomass compounds has also been modeled following a thermodynamic equilibrium modeling approach. Tang and Kitagawa [21] have performed a thermodynamic analysis and predicted the equilibrium amounts of gases for various model and real biomass

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compounds, Yan et al. [22] have performed a thermodynamic analysis of glucose gasification in supercritical water. Freitas and Guirardello [23] and Voll et al. [24] have investigated the thermodynamic analysis of gasification of various compounds in supercritical water. Castello and Fiori [10] have developed a thermodynamic model for the prediction of equilibrium amount of gases and solid carbon during supercritical water gasification of biomass compounds. Letellier et al. [25] and Marias et al. [26] have developed a thermodynamic equilibrium model for the prediction of compounds based on the reaction equilibrium constant method. Yakaboylu et al. [27] and Yanagida et al. [28] have used commercial software packages to predict not only the gas phase compounds but also the aqueous and solid phase compounds, and recently Yakaboylu et al. [11] have developed a multi-phase thermodynamic model for the prediction of equilibrium state compounds for real biomass systems.

On the one hand, in contrast to the conventional gasification processes, there is still not any generalized kinetic mechanism available in the literature to predict the formation of compounds during the supercritical water gasification of any type of real biomass. Besides, the aforementioned kinetic models may not be useful for different kinds of biomass feedstocks and process conditions (such as pressure, biomass concentration and reactor material) as the reaction pathway for the decomposition and gasification of biomass may change under new process conditions. Moreover, it is known that even a change in the reactor wall material may cause a significant change in the gas amounts (see ref. [29]) as it can act as a heterogeneous catalyst throughout the reactions.

On the other hand, for the prediction of product compounds, a global thermodynamic equilibrium approach using the Gibbs free energy minimization method has been successfully applied by many authors [10,11,27,28] for different kinds of biomass feedstocks under different process conditions. However, the predicted compounds are the “unconstrained” equilibrium state compounds. Most of the real conversion systems do not reach that state due to the natural constraints that could keep the system away from it [30]. Nevertheless, adding more constraints into the Gibbs free energy minimization method has the potential to predict the local equilibrium state compounds more accurately. Keck and Gillespie [31] successfully applied a similar method for combustion systems as an alternative to detailed kinetic modeling. They introduced the rate-controlled constrained–equilibrium (RCCE) method; the basis of this model was to combine Gibbs free energy minimization with the reaction rates of slow reactions as well as introducing extra constraints throughout the minimization routine which significantly decreased the number of kinetic equations needed to predict the gas composition for reacting gas mixtures. Keck [32] further improved and tested this model for different systems. Validity of constrained equilibrium method in combustion systems has been tested by many other researchers [33–36] as well. Unfortunately, this method is not viable for the systems of which the detailed kinetic mechanisms and reaction pathways are not known. However, the relationship between reaction kinetics and thermodynamic equilibrium as well as the use of both of them in calculating the multicomponent chemical reaction mixtures were investigated by Alberty [37] and Koukkari [38]. Koukkari and his co-workers [39–44] later improved their approach and extended the applicability of the constrained equilibrium method for different systems. Recently, Kangas et al. [45,46] have successfully applied the constrained equilibrium method for the conventional biomass gasification and conversion systems. Here, Kangas et al. [45] have introduced process dependent values (such as the amounts of carbon conversion, tar, ammonia, hydrogen, methane and other hydrocarbons) as additional constraints in modeling the conventional biomass gasification. The physical values of the additional constraints were acquired from experimental data that exist in literature. The authors concluded that the accuracy of the model increases with the formulation of additional constraints, however, the use of the additional constraints requires at least partly process specific

experimental information which might need to be adapted in order to use in different gasification setups and conditions. Nevertheless, the model was found to be promising as the chemical reactions, product streams' enthalpy and the states of the system can be estimated concurrently.

The use of such a constrained equilibrium method in SCWG of biomass systems has not been investigated so far. Unfortunately, the method of Keck and Gillespie [31] is not viable for SCWG of biomass systems as the detailed reaction expressions and the pathway for complex real biomass are not known yet. Besides, there is not any thermodynamic data available in literature for complex biomass constituent compounds at high temperatures and pressures or in a hydrothermal medium. However, like the work of Kangas et al. [45] that involves conventional biomass gasification systems, with the introduction of additional physical constraints in the minimization routine, supercritical water gasification of biomass products can also be better predicted. Yan et al. [22] have introduced carbon conversion efficiency as a constraint into their model which resulted in a better prediction of the gas products. This study aims to determine the additional constraints for the Gibbs free energy minimization method and to test the constrained equilibrium method for the modeling of SCWG of biomass.

2. Model

The model proposed within the paper is composed of two parts: i) the “unconstrained” equilibrium which directly uses the Gibbs free energy minimization method and ii) the additional “constraints” added into the minimization algorithm to obtain a better prediction of the real system.

2.1. The thermodynamic background for the unconstrained equilibrium

One can predict the unconstrained equilibrium (or global thermodynamic equilibrium) state of a system via the Gibbs free energy minimization method. The basis of the methodology used within this paper is the same as the model defined in a recently published paper [11]. Here it is briefly summarized.

The equilibrium state of a closed system can be defined as the state in which the total Gibbs free energy is at a minimum with respect to all possible changes at constant temperature and pressure [47].

The definition is given in Eq. (1) as

$$(dG^t)_{T,P} = 0. \quad (1)$$

For a given temperature, pressure and composition, the total Gibbs free energy of the system which has to be minimized to reach the equilibrium state can be defined as

$$G = \sum_{\varphi} N^{\varphi} G_m^{\varphi} \quad (2)$$

where φ is a phase index and where N^{φ} is the amount and G_m^{φ} is the integral mole based Gibbs energy of phase φ [48]. For a given multiphase system, the total Gibbs free energy is defined as

$$G = \sum_{\substack{\text{ideal} \\ \text{gas}}} n_i (g_i^{\circ} + RT \ln P_i) + \sum_{\substack{\text{pure} \\ \text{condensed} \\ \text{phases}}} n_i g_i^{\circ} + \sum_{\text{solution}-1} n_j (g_j^{\circ} + RT \ln x_j + RT \ln \gamma_j) + \sum_{\text{solution}-2} n_i (g_i^{\circ} + RT \ln x_i + RT \ln \gamma_i) + \dots + \dots \quad (3)$$

where n_i is the mole amount of compound i , P_i is its gas partial pressure divided by the standard pressure (0.1 MPa for this work), x_i is

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