Modelling super-equilibrium in biomass gasification with the constrained Gibbs energy method

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HIGHLIGHTS

- New method for modelling super-equilibrium in biomass gasification.
- Thermodynamic equilibrium is extended with immaterial constraints.
- The formation of char, tar, ammonia and light hydrocarbons is taken into account.
- The kinetically controlled phenomena are implemented into the model.
- Chemical reactions and the enthalpic effect are resolved simultaneously.

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ABSTRACT

The biomass gasification process is modelled by utilising constrained thermodynamic equilibrium. The formation of char, tar, ammonia and light hydrocarbons and related syngas composition were described by extending the conventional chemical system with additional immaterial constraints and by defining process-dependent values for these constraints.

Six different model structures were evaluated from global thermodynamic equilibrium to fully constrained local equilibrium. When models were validated against gasification setups, it was not necessary to fully constrain the system, as sufficient results were obtained by implementing constraints for char, tar, ammonia, CH_4 formation as well as for the amount of carbon in light hydrocarbons. The method was shown to be versatile when it was validated against other gasification setups: by altering the models defining the constraints a new gasification conditions could be simulated.

A clear benefit of the proposed method is that the gasification process can be resolved as a restricted partial equilibrium with a single calculation step. Another benefit is that chemical reactions, gasification enthalpy and the states of the system are estimated concurrently.

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1. Introduction

Biomass gasification is seen as a viable option for high-efficiency electricity generation from bio-based raw materials or as an option for the production of liquid biofuels and chemicals. Gasification is a thermochemical conversion process that takes place at elevated temperatures in reductive conditions. For such circumstances, thermodynamic equilibrium is often assumed to be a guideline (e.g. lately by Kuo et al. [1], Hejazi et al. [2] and Materazzi [3]), but is not reached in practice: during biomass gasification, light hydrocarbons (e.g. CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_6H_6), ammonia, tars and char are also formed. The phenomena leading to their formation cannot usually be modelled with equilibrium assumptions. Instead, the modelling is often based on 'grey-box' approaches or on detailed mass transfer approaches with mechanistic reaction kinetics included. A review of biomass gasification models is conducted by Gómez-Barea and Leckner [4] and by Puig-Arnavat et al. [5].

Meticulous mass transfer models may include computational fluid dynamic (CFD) and fluidization calculations, and often give a comprehensive design basis for gasification processes occurring, for example, in fluidized bed reactors. However, the CFD models often appear too complex to be combined with for instance engineering flow sheet models, aiming at steady state simulation of energy and mass balances, including a dependable prediction of chemical conversions in the gasification reactor and related influence to mill-scale processes. For such purposes and in order to increase the accuracy of gasification models, both empirical and mechanistic models are often applied alone or combined with thermodynamic equilibrium calculations. This leads to modified equilibrium models – a 'dual' approach in which different parts of the process and their chemical reactions are modelled independently and results are merged in post-processing. As an example, Hannula and Kurkela [6,7] have extended the thermodynamic equilibrium model by introducing this dual-approach: part of the gasified material is converted to light hydrocarbons, tar, char and ammonia before the equilibrium reactor and by-passing the reactor. The remaining material is modelled using thermodynamic equilibrium. This approach gives satisfying results when the composition of syngas is considered, but includes tedious pre- and post-processing steps before and after the reactor itself. From the actual physical point of view, such an approach is also less justified, as the reactor operates as a single unit. A somewhat similar approach has been utilised by Li et al. [8]. They proposed a non-stoichiometric equilibrium model, where the amount of reactive carbon (namely carbon fed to equilibrium reactor) was limited, based on the kinetic equations. Barba et al. [9] have introduced an extended Gibbs free energy method, which includes additional parameters for the progress of steam formation and water gas shift reactions. Konttinen et al. [10] have reported a thermodynamic model with a constraint applied for the oxidation of char and utilised thermodynamic equilibrium in gaseous phase. Another option for gasification modelling is to apply the quasi-temperature model (QET) where the temperature of the reaction is lowered in order to estimate the formation of char, tars or light hydrocarbons. Temperatures can be substantially lower than the actual temperature: from 250 °C [8] to up to 500 °C [11] and need to be experimentally defined.

The aim of this study is to further develop the gasification reactor model and to present a unified solution for the simultaneous calculation of the super-equilibrium reactions of hydrocarbons, ammonia and 'tars' as well as their related reaction enthalpies in the gasification process. The proposed solution is based on the constrained free energy (CFE) method, where equilibrium computation is extended with additional immaterial constraints (or virtual constraints) for solving the local or partial constrained equilibrium, instead of the global thermodynamic equilibrium. As the conventional Gibbs energy minimisation method applies mass balance constraints for the thermodynamic system components as the necessary conditions in the Lagrange method, the analogous additional constraints have been designated 'immaterial', while a common feature for these conditions is that they are related to work factors or e.g. to extents of reaction (that is, to physical entities without material content) [12]. Differences between possible thermodynamic approaches used for the modelling of the gasification process are shown in Fig. 1: (i) equilibrium model, (ii) modified equilibrium model, (iii) quasi-temperature approach and (iv) constrained free energy-based model.

The proposed constrained free energy method has been adapted with success in several applications areas: Alberty applied the method to the conservation of 'aromaticity' in benzene combustion [13]. The chemical kinetics and related extent of the reaction were defined by Koukkari for high-temperature metallurgy processes [14], and by Keck for internal combustion problems [15]. Pajarre

et al. applied the methodology to the partitioning of electrolytes in aqueous membrane systems [16] and to surface energy in multicomponent systems [17]. Reaction pathways were analysed by Blomberg and Koukkari [18] by utilising CFE methodology. Also, super-equilibrium conditions in a black liquor recovery boiler have been modelled by Kangas [19]. The methodological development of CFE has been conducted by Koukkari and Pajarre, for example by introducing virtual constituents to system [20]. Concurrently, the constrained free energy method is seen as a versatile tool for various fields of application.

In the current study, the CFE methodology is utilised for describing the super-equilibrium occurring in biomass gasification. Light hydrocarbons, ammonia, tars and char tend to decompose if thermodynamic equilibrium calculation is performed for high temperatures, and thus constraints are needed for the modelling of their presence in the super-equilibrium conditions as a local equilibrium.

2. Methods

This study focuses on the computational methodology for modelling thermal treatment of carbohydrate-containing raw material (biomass). The supporting empirical is obtained from the literature [7,21,22]. Thermodynamic standard state data is from HSC [23]. ChemSheet [24] is used as the modelling tool, as it allows extending the thermodynamic system with immaterial constraints, and thus enables the calculations of constrained free energy models. Model validation is conducted against the literature data [7,21,22].

2.1. Constrained free energy method

Thermodynamic equilibrium can be calculated by minimising the Gibbs energy of a closed isothermal system. In practice, this is done by applying the Lagrange method of undetermined multipliers (Eq. (1)) [25,26]. The minimum of the system is obtained when its partial derivatives are zero (Eqs. (2) and (3)):

$$L = G - \pi \Psi = \sum_{k=1}^{K} n_k \mu_k - \sum_{l=1}^{L} \pi_l \left(\sum_{k=1}^{K} v_{kl} n_k - b_l \right) \quad (1)$$

$$\left(\frac{\partial L}{\partial n_k} \right)_{n_n \neq k} = \mu_k - \sum_{l=1}^{L} \pi_l v_{kl} = 0 \quad (2)$$

$$\left(\frac{\partial L}{\partial \pi_l} \right)_{\pi_{n \neq l}} = \sum_{k=1}^{K} v_{kl} n_k - b_l = 0 \quad (3)$$

where G is the Gibbs free energy of the system; π is the Lagrange multiplier vector; Ψ is the mass balance of the different components of each constituent written in terms of the amounts of matter (mol); n is the molar amount of constituent k; μ is the chemical potential of the constituents k; k refers to each constituent in the multi-phase system; L is the number of components in the system and K the number of constituents respectively. π_l is the Lagrange multiplier of component l, and b_l is the total amount of component l in the system. The chemical potential of each component is defined in Eq. (2) as a linear combination of the Lagrange multipliers. The mass balance of the chemical system is defined in terms of the amounts of components defined by Eq. (3). A detailed description of how to compute the equilibrium can be found in [25–27]. A Gibbs energy solver such as SolGasMix and ChemSheet [24,26] can be used for practical computational work.

When the constrained thermodynamic equilibrium is calculated based on the CFE method, the stoichiometric matrix is extended with additional virtual components and constituents.