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Implementation of chemical reaction equilibrium by Gibbs and Helmholtz energies in tubular reactor models: Application to the steam–methane reforming process

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A B S T R A C T

In the tubular reactor models the mass and heat source terms due to chemical reactions in the species mass balances and temperature equation are conventionally determined from kinetic rate expressions. In many cases a kinetic rate model is not available but the chemical equilibrium conversion can be determined from reaction equilibrium calculations minimizing the Gibbs or Helmholtz free energies. Although a process is believed to behave physically like a tubular reactor, previous feasibility and design studies have typically disregarded fluid flow and mass- and heat transfer limitations and performed a classical chemical equilibrium calculation. For non-adiabatic cases, valuable information on the heat transfer flux limitations of the chemical process at the wall (often provided by a specified axial heating/cooling media temperature profile) is lost when simplifying a model representing the physical tubular reactor process behavior by considering a classical thermodynamic system having uniform state properties. For this reason, in the present study, a new type of tubular reactor model, which we name the differential Gibbs (or Helmholtz) reactor model, is presented to improve on the conventional feasibility and design model. In the differential Gibbs (or Helmholtz) reactor model, the chemical conversion and the reaction heat are determined assuming chemical reaction equilibrium conditions along the axial flow direction by minimizing the Gibbs (or Helmholtz) free energy. The new model is verified through comparison with the conventional differential tubular model using the fast reaction kinetics of the steam–methane reforming process and neglected mass diffusion limitation of the catalyst.

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1. Introduction

1.1. General

The Gibbs and Helmholtz free energies reflect the effect of entropic driving forces. That is, in a spontaneous process the entropy increases which corresponds to a decrease in the Gibbs and Helmholtz free energies. In a non-spontaneous process, the changes of the thermodynamic functions are reversed. At equilibrium state there is no change in the entropy, thus no change in the Gibbs and Helmholtz free energies. Working with the Gibbs or Helmholtz free energies rather than entropy is often more convenient because of the canonical variables associated with these energies. The chemical equilibrium composition can be determined minimizing the Gibbs free energy or Helmholtz free energy. The Gibbs free energy function has a global

minimum value at given T, p, and **n**. Likewise, the Helmholtz free energy function has a global minimum value at given T, V, and **n**. Two formulations are at our disposal minimizing the Gibbs or Helmholtz free energies: (i) the stoichiometric formulation or (ii) the non-stoichiometric formulation. The stoichiometric approach requires a clearly defined reaction mechanism which includes all the independent chemical reactions involved in the chemical reaction process. The non-stoichiometric method does not require any reaction mechanism, but the elements (atoms) and species (molecules) in the feedstock must be specified. Therefore, the non-stoichiometric method is particularly suitable for chemical reaction processes where the reaction mechanism is not clear. Thus, the stoichiometric and non-stoichiometric formulations differ in how the element balances are imposed. In the stoichiometric formulation the element balances are imposed by the stoichiometric reaction equations as constraints to the minimization of the Gibbs (or Helmholtz) free energy. In the non-stoichiometric method the element balances are imposed as constraints in the optimization problem minimizing the Gibbs (or Helmholtz) free energy. The minimum Gibbs or Helmholtz free

energies provide the maximum chemical conversion of equilibrium reactions, thus the chemical equilibrium conversion is often used in feasibility studies of industrial chemical processes.

1.2. Reactor models applied in design and feasibility studies

In chemical process design and feasibility studies, simpler reactor models such as the continuous stirred tank reactor (CSTR) and the plug flow reactor (PFR) models (e.g. Fogler, 2006) are frequently used. In the PFR model, the reactants flow along the length of the reactor and are continually consumed. There are axial variations in the temperature and velocity–pressure fields. In particular, in the PFR model, the fluid is modeled as flowing through the reactor as a series of infinitely thin coherent "plugs". Each such infinitesimal volume has a uniform composition, and is traveling in the axial direction of the reactor, with each infinitesimal volume having a different composition from the ones before and after it. The key assumption is that the fluid is perfectly mixed in the radial direction but not in the axial direction. The differential volume is considered an infinitely small CSTR, limited to zero volume. Thus, in some computer simulations the PFR is approximated with several CSTRs in series.

The conventional CSTR and PFR models apply a kinetic rate expression to determine the chemical conversion. On the other hand, the reaction kinetics of a novel chemical process is not always known or well developed. In computer simulations of a chemical process with unknown reaction kinetics, the chemical composition is often determined assuming Gibbs chemical equilibrium condition. In computer simulation studies of for example hydrogen production, the Gibbs free energy minimization approach is recently adopted by, e.g.: Khaodee et al. (2011), Xie et al. (2010), Amin and Yaw (2007), Ye et al. (2009), Wang et al. (2010), and Freitas and Guirardello (2012). The existing conventional chemical equilibrium "reactor" models, which assumes that the chemical composition is determined from the minimizing of Gibbs free energy, have severe limitations with respect to the "reactor" model complexity. The chemical equilibrium "reactor" models are in principle only an equilibrium calculation. However, an enthalpy balance of the system can be combined with the chemical equilibrium calculation. An important drawback associated with the conventional chemical equilibrium "reactor" models is that the effect of fluid flow is not considered. Thus, in the existing modeling framework of chemical reactors there is a missing link between fluid flow computations and minimization of Gibbs free energy of chemical reactions.

1.3. Reactor models implemented in HYSYS

The *equilibrium reactor* implemented in the simulation program HYSYS computes the chemical composition by the stoichiometric equilibrium method for Gibbs free energy minimization. Another chemical equilibrium "reactor" model implemented in HYSYS is the *Gibbs reactor*. This reactor is based on the non-stoichiometric formulation minimizing the Gibbs free energy. In both cases, the "reactor" can be modeled as isothermal by specifying the operating temperature. Alternatively, a fixed value for the heat duty can be given. In the latter case, the "reactor" temperature is calculated from an energy balance. In both the *Gibbs reactor* and the *equilibrium reactor*, no volume needs to be specified.

The PFR implemented in HYSYS requires a kinetic rate expression to be specified and does not allow for the Gibbs free energy minimization method. In contrast to the Gibbs and equilibrium reactors in HYSYS, the PFR model allows the implementation of the heat source term $UA(T_a - T)$ in the energy balance. Thus, allowing a variable heat duty along the axial reactor tube length.

Chemical equilibrium by minimizing Gibbs free energy (stoichiometric or non-stoichiometric formulations) cannot be applied in the CSTR model implemented in HYSYS. The conversion in this reactor model is computed from kinetics rate expressions of the chemical reactions.

"Reactor" models such as the *equilibrium reactor* and the *Gibbs reactor* implemented in HYSYS are frequently applied in process design and feasibility studies. The choice of such simple reactor models is often employed because one wants to keep the level of physical details low for the reactor unit, and thus lower the computational cost simulating an industrial plant consisting of several process units. Another important reason for choosing these simple reactor models is that the reaction kinetics is not known for the particular chemical process studied, thus simulations have been limited to chemical equilibrium "reactor" models such as those implemented in HYSYS.

1.4. Limitations of the existing reactor models

In the conventional reactor model framework, chemical equilibrium calculations by minimum Gibbs free energy are not combined with fluid flow. The Gibbs and equilibrium "reactor" models in HYSYS are stoichiometric and non-stoichiometric formulations of the minimum Gibbs free energy of chemical reactions, eventually combined with an energy balance. On the other hand, the conventional CSTR and PFR models consider fluid flow, but are limited to kinetics expressions for determining the chemical conversion. When no volume is associated with the chemical equilibrium reactor models, it is difficult to consider more complicated heat transfer terms of the energy balance, i.e. $UA(T_a - T)$.

In the present study, the main objective is to extend the existing framework of chemical equilibrium reactor models from those considering only Gibbs free energy minimization (and a simple enthalpy balance), such as the *Gibbs reactor* and *equilibrium reactor* in HYSYS, to a reactor model that combines fluid flow and chemical equilibrium calculations. In particular, we consider the differential tubular reactor model. To the authors best knowledge, chemical equilibrium conditions by minimizing the Gibbs or Helmholtz free energy in a tubular reactor has not yet been proposed in the literature.

1.5. Reactor model proposed in this work

The minimum Gibbs free energy condition of a chemical reacting system is most frequently adopted. A discussion of the T, p, **n**-ensemble (Gibbs) and T, V, **n**-ensemble (Helmholtz) becomes relevant when chemical equilibrium calculations are combined with fluid flow because of issues related to the numerical solution technique. Thus, both the Gibbs and Helmholtz formulations of chemical reaction equilibrium are considered in the present work. In particular, in this work, plug flow conditions and the steam–methane reforming process are adopted for the study of a tubular reactor model with chemical composition determined from minimum Gibbs or Helmholtz free energies. The novelty of this reactor model is the combination of fluid flow and chemical equilibrium calculations. The proposed framework, or solution strategy, for combining fluid flow and chemical equilibrium calculations is not limited to tubular reactor models but can be adapted to other reactor model concepts such as, e.g., CSTR. The steam–methane reforming process is chosen in the present study because in a commercial steam–methane reforming reactor the partial pressures of the species are very close to the equilibrium values at the reactor exit (Froment and Bischoff, 1990). The new differential Gibbs (or Helmholtz) reactor model is validated with the conventional differential reactor model based on a reaction kinetic model. The kinetic model for steam–methane reforming by Xu and Froment (1989a,b) is widely applied in chemical reactor modeling studies, e.g. the recent studies: Wilde and Froment (2013), Baek et al. (2014), Mokheimer et al. (2015), Said et al. (2015), Solsvik et al. (2013), Hong et al. (2013), Lee et al. (2013), Ghouse and Adams (2013), Asleshirin et al. (2012), and is also applied in the present work.