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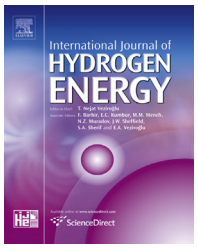

Kinetic parameters determination using optimization approach in integrated catalytic adsorption steam gasification for hydrogen production

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ABSTRACT

Integrated catalytic adsorption (ICA) gasification provides an efficient mean to produce hydrogen rich gas. This article presents the prospect of ICA steam gasification of palm kernel shell. The effect of temperature, steam to biomass ratio and adsorbent to biomass are investigated for H_2, CO, CO_2 and CH_4 composition to determine kinetic parameters by minimizing the error between experimental and modelling results. Based on the evaluated kinetic parameters, the model predicts the product gas composition for the effect of temperature, steam to biomass ratio and adsorbent to biomass ratio. A significant fitting of model predicted values to the experimental results is achieved. Furthermore, it is also found that the water gas shift reaction is non-spontaneous and far away from the equilibrium at a temperature range of 600 °C–675 °C which may be due to strong CO_2 adsorption reaction.

Introduction

Fossil fuel energy dependency causes numerous environmental problems such as greenhouse effect, ozone layer depletion and acid rain. Due to associated problems with fossil fuel, the search for alternative clean, sustainable and environmental friendly energy sources should be intensified. Hydrogen as an energy carrier comprises of numerous advantages over other conventional energy carriers. Hydrogen combustion provides more energy (lower heating value based on mass basis) than that of methane, gasoline and coal [1]. In addition, it is a clean fuel as the combustion of hydrogen produces only water as by-product.

Biomass is a promising source among the renewable sources to produce clean and renewable hydrogen due to its net zero carbon, and low NO_x and SO_x emissions in the product gas. Among thermal conversion processes, gasification is

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considered as most potential process for hydrogen production. Biomass steam gasification is recognized as an efficient process to produce hydrogen rich gas.

Use of catalyst in biomass steam gasification is attained prime interest due to enhancement of H_2 content up to more than 60 vol% in product gas [2]. Catalyst reduces tar content significantly in product gas and improves the gas quality [3]. Besides, in situ CO_2 adsorption in biomass gasification increases hydrogen content up to 75 vol% (dry basis) which has been reported 40 vol% (dry basis) in conventional biomass gasification [4]. CO_2 adsorption process is an exothermic reaction thus it provides heat for endothermic gasification reactions and reduces overall energy requirement for the process in the gasifier [5]. Addition of CO_2 adsorbent allows gasification process to take place at temperature less than 800 °C [5–7].

Biomass gasification is a mixture of complex reactions. Numerous models are reported to simulate biomass gasification reactions. These models are based on different aspects of the process such as kinetic, equilibrium and hydrodynamics of different types of reactors [8]. The modeling approaches for biomass gasification can be divided into kinetic modeling and equilibrium modeling [9]. A kinetic model predicts the product gas composition and gas yield based on the kinetics of main reactions involved in the process. At given operating conditions, kinetic model is capable to predict product gas profiles and overall gasification efficiency of the process. Limited studies have been conducted on the modeling and simulation of hydrogen production via biomass steam gasification with in-situ CO_2 capture. Florin and Harris [10] developed a thermodynamic equilibrium model to investigate the effect of fundamental process parameters such as temperature, steam to biomass ratio, adsorbent to biomass ratio and pressure on the hydrogen production from methyl cellulose using concept of gasification and combustion steps in separate reactors. The model prediction was also compared and validated with experimental work taken from the literature [11]. Pröll and Hofbauer [12] presented thermodynamic equilibrium model for hydrogen rich gas production by selective CO_2 transport in dual fluidized bed system. The $CaO/CaCO_3$ system was used as bed material for selective CO_2 transport from gasification to the combustion reactor by carbonation and calcination reactions. Mahishi et al. [5] developed an equilibrium model for biomass steam gasification using CaO as an adsorbent. Ethanol was taken as the model compound for the steam gasification using Gibbs free energy minimization approach. Very few kinetic models have been reported for biomass steam gasification with in-situ CO_2 adsorbent. Inayat et al. [13] developed a reaction kinetic model for oil palm empty fruit bunch (EFB) to produce hydrogen using sum of squared technique in MATLAB. The CO_2 adsorbent reaction along with water gas shift, steam methane reforming, char gasification, methanation and Boudouard reactions were considered to simulate the process. The reaction kinetics data was taken from the literature [14–19]. They predicted the increment of hydrogen composition with temperature and steam to biomass ratio. For similar reactions in the subject study [13], Yunus et al. [20] simulated kinetic model in iCON software and predicted the effect of temperature, steam to biomass ratio and adsorbent to biomass ratio. Sreejit et al. [21] carried out the process simulation of biomass air-steam gasification with CO_2 sorption through kinetic approach using kinetics data from the literature [13,14,22]. Biomass gasification processes include drying; pyrolysis, char gasification and homogeneous gas phase reactions were considered. They predicted the increase of hydrogen composition and heating values with CO_2 sorption in the process. In further kinetic study by Sreejit et al. [23], tar cracking and reforming reactions were also considered along with other reactions in the previous study [21]. For kinetic parameters determination, Inayat et al. [24] carried out optimization approach in MATLAB to produce hydrogen from oil palm wastes steam gasification with in-situ CO_2 sorption. They evaluated kinetic parameters by fitting experimental data to kinetic model, and minimized least squared error between the experimental data and model predictions. The experimental data was taken from the previous work [24].

To date, the kinetic studies of biomass steam gasification are carried out by using in-situ CO_2 sorption in the process. The present work extends the kinetic study to the effect of catalyst and CO_2 adsorbent together in a pilot scale fluidized bed reactor for biomass steam gasification. The present study investigates the kinetic parameter evaluation using optimization approach for hydrogen production in integrated catalytic adsorption (ICA) steam gasification of palm kernel shell. The kinetic parameters are evaluated by minimizing the residual error between model predictions and experimental values. The model prediction of product gas composition is then generated via evaluated kinetic parameters and compared with experimental data. In addition, thermodynamic parameters i.e. Gibbs free energy and equilibrium constant for water gas shift reactions are evaluated and compared with the previously reported literature.

Methodology

Reaction kinetics model

The kinetic modeling approach was carried out by considering six reactions occurring in the gasification process. The product gas from these reactions was mainly consisted of H_2, CO, CO_2 and CH_4. These reactions are presented in Table 1. Among these reactions, char gasification, methanation and boudouard reactions were modified by replacing C (carbon) in the chemical formula of palm kernel shell. This approach was adopted due to its applicability in biomass steam gasification with in-situ CO_2 adsorbent [25]. The chemical formula of palm kernel shell is $C_{4.15}H_{5.68}O_{2.71}$.

The following assumptions were made for the kinetic model:

- The fluidized bed was under isothermal conditions, temperature distribution was homogeneous throughout the bed and operation was at atmospheric pressure [14,26].
- The simple approach of first order kinetics with respect to reacting species was selected, as the reactions are assumed to take place under isothermal and constant reactor