STEAM GASIFICATION OF A CELLULOSE SURROGATE USING A NEW Ni/La₂O₃-γ-Al₂O₃ CATALYST: KINETIC MODELING

Jahirul Mazumder and Hugo de Lasa*  
Chemical Reactor Engineering Centre (CREC), Dept of Chemical & Biochemical Engineering, The University of Western Ontario, London, ON, Canada N6A 5B9

Abstract

A Langmuir-Hinshelwood (LH) based mechanistic kinetic model is proposed for steam gasification of biomass surrogates. Catalytic gasification of glucose (a cellulosic biomass surrogate) is developed in a mini-fluidized CREC Riser Simulator allowing for intense mixing. Using a highly performing Ni/La₂O₃-γ-Al₂O₃ catalyst, H₂, CO, CO₂, CH₄ and H₂O are detected as the major gasification products with negligible coke and tar formation. The net rate of formation/disappearance of these chemical species is considered as the algebraic addition of the dominant reactions: water gas-shift reaction, steam reforming of methane and the reverse dry reforming of methane. Kinetic parameters are estimated using experimental data for different temperatures and reaction times. The estimated activation energies are statistically significant as well as in agreement with the reported values in the literature. The proposed model is also validated by comparing experimental data with the model predictions for different steam/biomass (S/B) ratios. Thus, the proposed model includes phenomenologically based parameters that can successfully account for various product species.

Keywords


Introduction

The overall biomass steam gasification process can be described by:

\[ C + H_2O \leftrightarrow CO + H_2 + CO_2 \]  
\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \]  
\[ CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \]  
\[ C + H_2O \leftrightarrow H_2 + CO \]  
\[ C + CO_2 \leftrightarrow 2CO \]  
\[ C + 2H_2 \leftrightarrow CH_4 \]

Coke and tar formation depend on the gasifier operating conditions and additives used. Use of an active and stable catalyst promotes coke and tar reforming operating close to thermodynamic equilibrium. In this regard, a highly active and stable fluidizable Ni/La₂O₃-γ-Al₂O₃ catalyst was developed in our previous study (Mazumder and de Lasa 2015). This catalyst yields over 98% carbon conversion of glucose to permanent gases with no tar formation and negligible coke deposition at 700 °C. The development of an efficient process also requires insights into biomass gasification mechanisms. This study focuses on the development of LH based mechanistic kinetics for biomass steam gasification.

Materials and Methods

A Ni/La₂O₃-γ-Al₂O₃ catalyst was prepared using a specially designed successive incipient impregnation technique. Catalytic gasification of biomass surrogates was performed in a mini-fluidized CREC Riser Simulator.

* To whom all correspondence should be addressed
Model Formulation

Glucose gasification results showed that H₂, CO, CO₂, CH₄, and H₂O are mainly present in the product gas with negligible C₂⁺ species and coke (less than 1 wt%). Coke yields are controlled by char gasification (CG), the Boudouard reaction (BR) and hydrogenation gasification (HG) reactions (Eqs. (5)-(7)). The thermodynamic analysis of these reactions shows that the forward CG reaction is always favored. At shorter reaction times, coke may form due to the reverse BR and HG reactions. However, with the increase of reaction times, BR and HG reactions are also shifted towards the forward direction. As a result, the net formation of carbon is negligible. This hypothesis is also consistent with the very small amount of coke found during the experiments. Therefore, the contribution of reactions involving coke can be considered insignificant. Moreover, reverse dry reforming of methane is favoured at the experimental conditions. On this basis, the water-gas-shift reaction (WGS), the steam reforming of methane (SRM) and the reverse dry reforming of methane (RDRM) are the dominant reactions. Rates of these reactions can be modeled using LH type rate equations. CO₂ adsorption parameters were determined experimentally. H₂, CO and CH₄ inhibition are neglected considering the range of operating temperatures (Maestri et al. 2008). After simplifications and linearization it results:

\[
\begin{align*}
   r_{WGS} &= \frac{k_{WGS} P_{CO} P_{H₂O}}{1+2 K_{CO}^W P_{CO}} \left(1 - \frac{P_{H₂} P_{CO₂}}{K_{WGS} P_{CO} P_{H₂O}} \right) \\
   r_{SRM} &= \frac{k_{SR} P_{CH₄} P_{H₂O}}{1+4 K_{CO}^SR P_{CO}} \left(1 - \frac{P_{CO} P_{H₂}}{K_{SR} P_{CH₄} P_{H₂O}} \right) \\
   r_{RDRM} &= \frac{k_{RDRM} P_{CO}^{2} P_{H₂}}{1+4 K_{CO}^{RDRM} P_{CO}^{2}} \left(1 - \frac{P_{CO₂} P_{CH₄}}{K_{RDRM} P_{CO}^{2} P_{H₂}} \right)
\end{align*}
\]

The overall rate of formation/disappearance of each species (H₂, CO, CO₂, CH₄ and H₂O) can be written as:

\[
r_i = v_{WGS}, v_{SRM} + v_{SRM}, v_{RDRM} + v_{RDRM}, \quad \frac{dp_i}{dt} = \frac{WRT}{V} r_i
\]

Thus, a set of differential equations representing the catalytic steam gasification can be obtained by substituting eqs. (8)-(11) into eq. (12).

Parameter Estimation and Model Validation

Intrinsic kinetic parameters were estimated via non-linear regression of experimental data at three thermal levels as reported in Figure 1. Estimated parameters are significant at the 95% confidence interval with moderate cross-correlation. The proposed model and the estimated parameters were also validated using the experimental data at different steam/biomass ratios, as shown in Figure 2. It shows that the model can well predict the gasification results with S/B variation with a regression coefficient of 0.9887. Moreover, the estimated activation energies are well in line with the literature (Maestri et al. 2008; Nikolla et al. 2009; Salaices et al. 2012).

Conclusions

a. A LH mechanistic kinetic model with statistically significant parameters is developed for biomass steam gasification. The estimated activation energies are also in agreement with the technical literature.

b. It is shown that an additive rate model is adequate to represent the steam gasification process.

c. It is demonstrated that the proposed model is applicable over a wide range of operating conditions.

References


