

KINETIC STUDY OF STEAM GASIFICATION SUB-BITUMINOUS CHARCOAL WITH CaO CATALYST

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Abstract- Gasification is an effective thermal process for converting carbon-containing feedstock into synthesis gas. In the design and operation of the gasification process, it is necessary to understand the effect of operating conditions (pressure or temperature), the ratio of feedstock to gasification agent and the catalyst on the composition of the gas produced. The impact of operating conditions can be known by studying the reaction mechanism that occurs. Mathematical models can be used to understand the mechanisms that occur. Although mathematical models cannot give exact results, they can quantitatively show the effect of feedstock and other process constants. This research aims to obtain the reaction rate constant using random pore and volumetric models. The calculation results show that the random pore model is consistent with the experimental results. On the other hand, the volumetric model is only suitable at the beginning of the reaction period.

Keywords: Gasification, Random Pore Model, Reaction Rate, Steam Gasification, Thermal Process, Volumetric Model.

1. INTRODUCTION

Clean energy and alternative energy is one of the main themes of several studies on sustainable energy development. As petroleum reserves are decreasing, the advancement of alternative energy is essential to prevent a fuel crisis [1–3]. Indonesia has plenty of coal reserves, but its quality is low. Therefore, its use needs to be improved. One method that can be used to improve the quality of coal as a fuel is gasification. Gasification is an effective and accurate technique for changing solid carbon materials into electricity-generating gas or synthesis gas. These gases can be used for electricity generation, thermal energy production, or synthetic precursors [4, 6].

Understanding the influence of feedstock, operational parameters, and interacting physical and chemical mechanisms during the gasification process is the basis for optimal gasifier design [5-7]. The reaction rate are essential parameters to obtain information about the mechanism of reaction in the gasification process [8]. Several researchers have investigated the influence of kinetic variables of gasification systems.

Babu and Sheth [11] predicted steady state temperature and composition profiles for the reducing region in biomass gasification. They concluded that the char reactivity coefficient can directly explain the char reactivity in the reduction region. Goebel, et al. [10] develop mathematical models from mass and energy balance, chemical equilibrium, and Langmuir-Hinshelwood to explain coal kinetic response. D.P. Ye and J.B. Agnew [11] studied the effect of active cations (Na, K, Ni, Ca) on the reactivity of low-quality coal from South Australia. These experiments showed that acid washing of coal causes the loss of carboxyl functional groups, and removing or adding active cations will change the reactivity of the coal. Furthermore, catalytic activity increases in the order of Na > K > Ca > Ni for the same anion.

Several scientists have developed reaction kinetic equations to analyze the reaction kinetics of gasification, for example Random Pore Model (RPM), Volume Model (VM), and Shrink Core Model (SCM). However, when the reaction rate constant of the coal gasification process is evaluated using the RPM equation, better results are obtained than the homogeneous model [12]. In this study, VM and RPM were implemented to evaluate the reaction rate constants of steam gasification. Gasification is carried out in an updraft reactor with different temperatures and atmospheric pressure, namely 600, 700, and 800 °C. The mass of charcoal used was 10 grams and the mass of CaO catalyst was varied as 0, 5, 10, and 15 grams. The random pore model results were compared with the volumetric model.

2. KINETIC MODEL

2.1. Volumetric Model (VM)

This model assumes that the coal surface has a homogeneous active surface, and that the particle size is kept as constant as possible during gasification [13], [11]. Based on this assumption, the rate of reaction can be represented as:

$$\frac{dX_A}{dt} = k_{VM} (1 - X_A) \quad (1)$$

Equation (1) could be integrated to give Equation (2).

$$\int_0^X \frac{dX_A}{(1-X_A)} = \int_0^t k_{VM} dt, X_A = 1 - \exp(-k_{VM}t) \quad (2)$$

where, k_{VM} is expressed in the Arrhenius Equation (3):

$$k_{VM} = k_o \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Furthermore, Equation (3) could be expressed in linear Equation (4):

$$\ln k_{VM} = \ln k_o - \left(\frac{E_a}{R}\right) \frac{1}{T} \quad (4)$$

The activated energy (E_a) and collision factor (k_o) can be acquired by plotting $\ln k_{VM}$ versus $1/T$.

2.2. Random Pore Model (RPM)

This model supposes that reaction starts in the pore surface and then a gaseous product layer forms near the coal surface. The reactants diffuse to the reaction surface where the reaction occurs through the gas-producing layer. This model takes into account the changes in physical structure during gasification [16]. The reaction rate was expressed in the following format:

$$\frac{dX_A}{dt} = k_{RPM} (1-X_A) \sqrt{1-\psi(1-X_A)} \quad (5)$$

where, k_{RPM} is expressed as follows:

$$k_{RPM} = k_o \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

3. RESULT AND DISCUSSION

3.1. Evaluation of the Kinetic Parameters

3.1.1. Volumetric Model

Figures 1-3 show correlations of char conversion (experimental and calculation) and time of reaction for gasification using charcoal and steam at temperatures of 600, 700, and 800 °C for 60 minutes and mass of CaO 0, 5, 10, and 15 grams. Dashed lines represent calculated results, and dotted symbols represent experimental results.

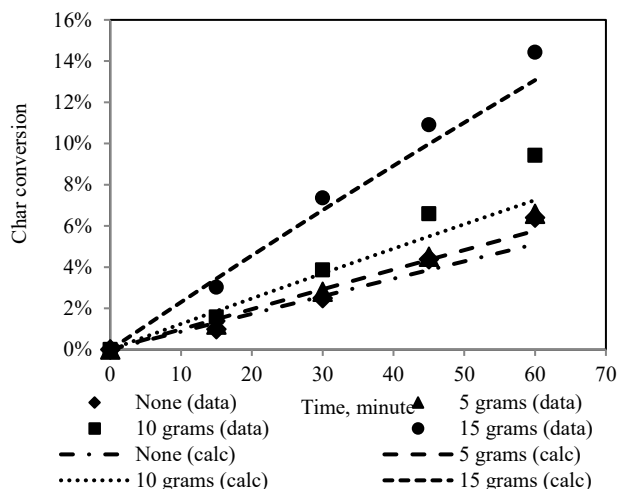


Figure 1. Comparison of conversion chart of observation results with calculation results for catalyst mass variation of 0, 5, 10, and 15 grams and temperature of 600 °C

From Figures 1 and 2, the average error is quite large. At a temperature of 600 °C with a catalyst mass of 0, 5, 10, and 15 g, the average error is 13.5%, 8.4%, 12.4%, and 7.94%, respectively. Meanwhile, for a temperature of 700 °C, the average error is 12.27%, 32.61%, 11.47%, and 15.72%, respectively. In Figure 3, it can be seen that the average error is quite small, namely 12.75%, 11.38%, 9.46%, and 8.76% for each catalyst mass of 0, 5, 10, and 15 g, respectively. However, the overall volumetric model can only represent data in the initial period of the reaction, which is 0 to 30 minutes. This indicates that there is a change in pore structure during gasification. This result corresponds to the work of previous research [12], [16], [17].

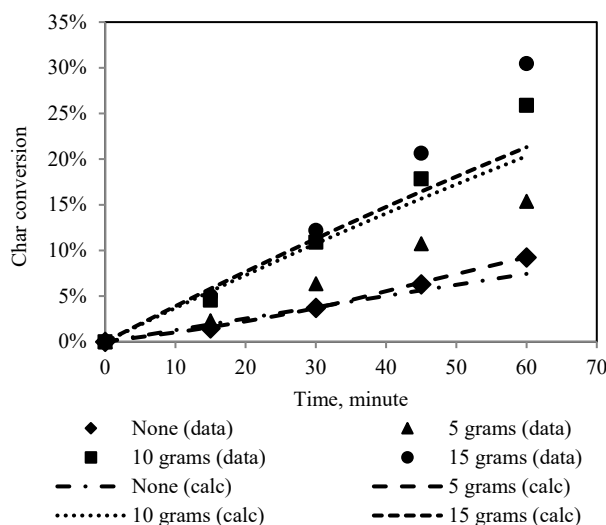


Figure 2. Comparison of conversion chart of observation results with calculation results for catalyst mass variation of 0, 5, 10, and 15 grams and temperature of 700 °C

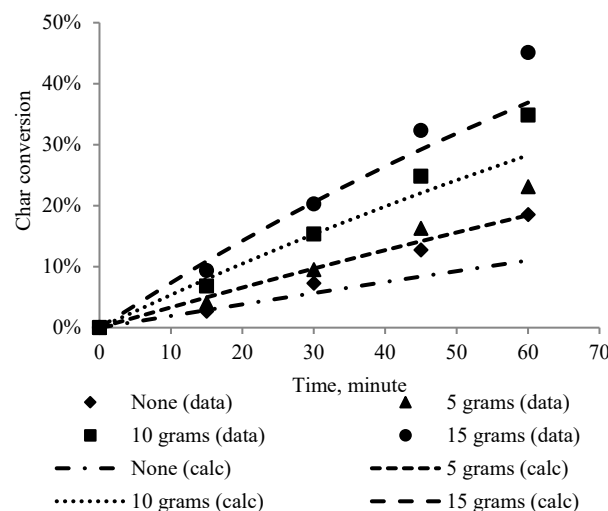


Figure 3. Comparison of conversion chart of observation results with calculation results for catalyst mass variation of 0, 5, 10, and 15 grams and temperature of 800 °C

The collision factor (k_o) and activation energy (E_a) will be determined by plotting $\ln k$ vs $1/T$, as shown in Figure 4. These plots were obtained by calculating the reaction rate constants from three different temperatures. Table 1

shows the rate parameters of steam gasification obtained from Figure 4. Table 1 shows that the activation energies for coal gasification of 0, 5, 10, and 15 grams CaO catalyst are 31.757 kJ/mol, 28.607 kJ/mol, 27.797 kJ/mol, and 27.7 kJ/mol, namely. It shows that it was 582 kJ/mol. When 5, 10, and 15 grams of CaO catalyst were added to 10 g of charcoal, the activated energy decreased by 3.15 kJ/mol, 3.96 kJ/mol, and 4.175 kJ/mol, respectively. Therefore, the presence of CaO catalyst can increase the rate of steam gasification reaction. Additionally, Table 2 also considers the activation energy at 10 grams of Ca catalyst, which is close to 15 grams of CaO catalyst.

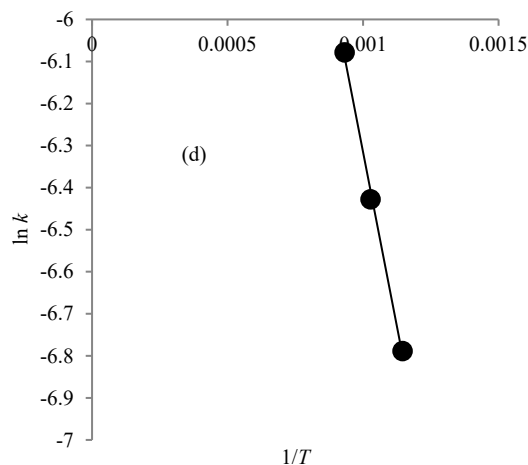
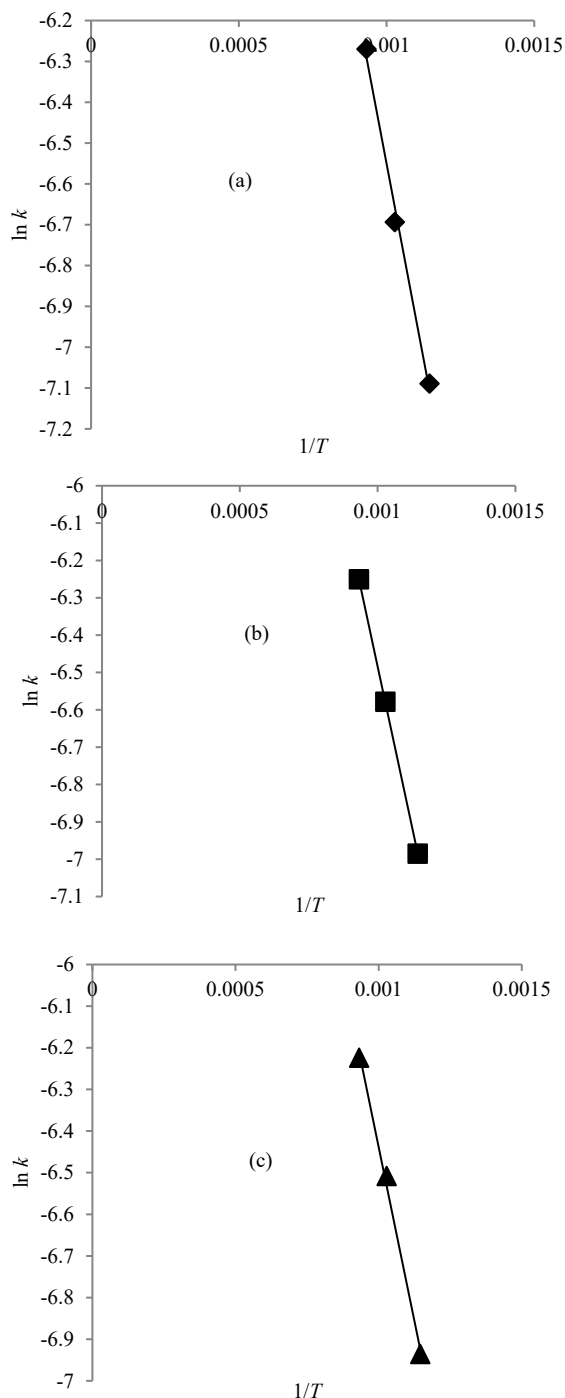


Figure 4. a) Plot of ln k vs 1/T for steam gasification at 0 grams' catalyst, b) Plot of ln k vs 1/T for steam gasification at 5 grams' catalyst, c) Plot of ln k vs 1/T for steam gasification at 10 grams' catalyst d) Plot of ln k vs 1/T for steam gasification at 15 grams' catalyst

Table 1. Kinetic parameters in steam gasification process at 600 °C to 800 °C for 60 minutes

Mass of Ca catalyst (g)	Activation energy (kJ.mol ⁻¹)	Frequency factor (min ⁻¹)	Equation of reaction kinetics constant
0	31.757	0.0652	$k = 0.0652 \exp\left(\frac{-31.757}{RT}\right)$
5	28.607	0.0453	$k = 0.0453 \exp\left(\frac{-28.607}{RT}\right)$
10	27.797	0.0477	$k = 0.0477 \exp\left(\frac{-27.797}{RT}\right)$
15	27.582	0.0499	$k = 0.0499 \exp\left(\frac{-27.582}{RT}\right)$

3.1.2. Random Pore Model

Figures 5-7 show comparison of conversion chart of observation results with calculation results using random pore model at temperatures of 600 °C to 800 °C at 60 minutes with CaO catalyst masses of 0, 5, 10, and 15 grams. As shown in Figures 5-7, the carbonization transformation from the calculation results using the random pore model is in close with the results obtained from the experimental data. The results showed that the changes in the pore structure during charcoal gasification can affect the reactivity of charcoal during the reaction. This experimental result is consistent with the study of Sangtong-Ngam and Narasingha [12].

Figure 8 shows the relationship between 1/T and lnk for steam gasification with four different CaO catalyst masses. A random pore model determined the reaction rate constants for three different temperatures. Table 3 presents activated energies and collision factor obtained from Figure 8.

Table 2 shows that without CaO catalyst, the activation energies of 5, 10, and 15 grams are 31.002 kJ/mol, 30.670 kJ/mol, 30.140 kJ/mol, and 29.879 kJ/mol, namely. This shows that the addition of 5, 10, and 15 grams of catalyst can reduce the activated energy by 0.216 kJ/mol, 0.862 kJ/mol, and 1.123 kJ/mol, namely. Thus, CaO addition can accelerate the reaction rate in charcoal gasification.

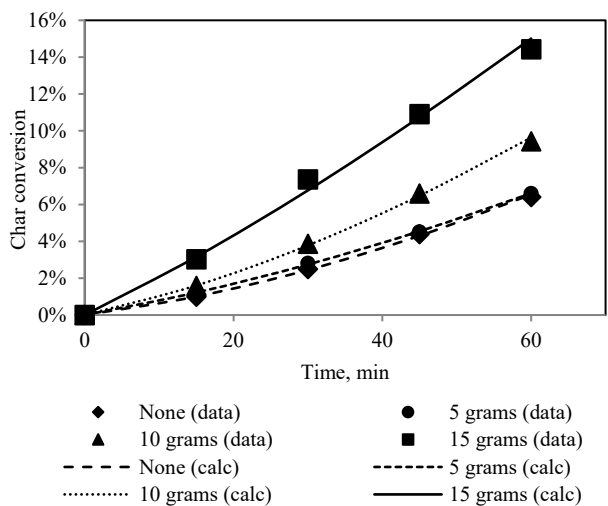


Figure 5. Comparison of conversion chart of observation results with calculation results using random pore model for catalyst mass variation of 0, 5, 10, and 15 grams and temperature of 600 °C

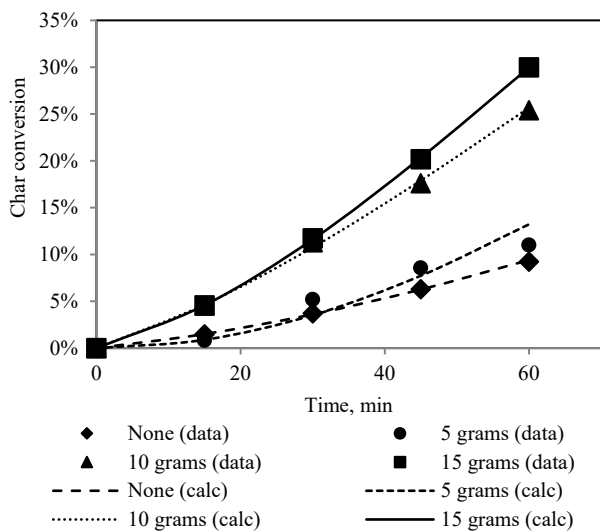


Figure 6. Comparison of conversion chart of observation results with calculation results using random pore model for catalyst mass variation of 0, 5, 10, and 15 grams and temperature of 700 °C

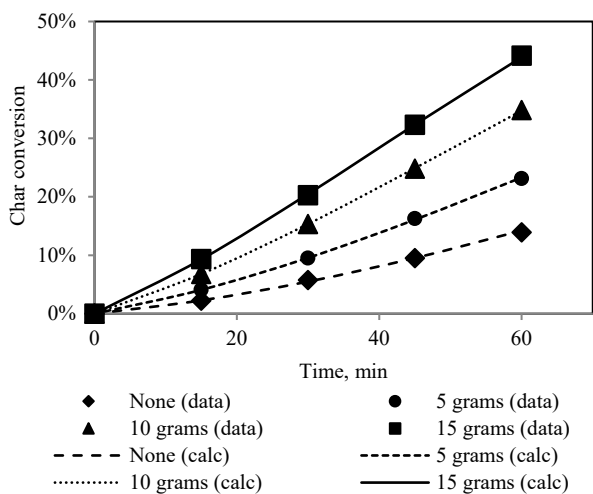


Figure 7. The relationship between reaction time and char conversion with the mass of Ca catalyst 0 grams, 5 grams, 10 grams, and 15 grams in steam gasification at 800 °C for 60 minutes

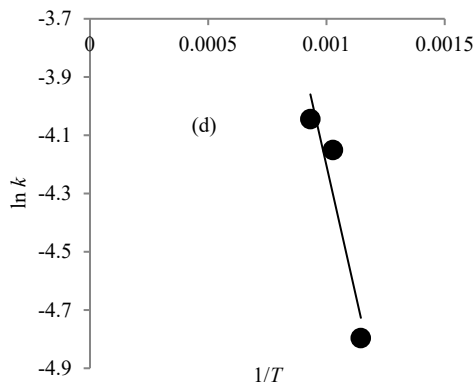
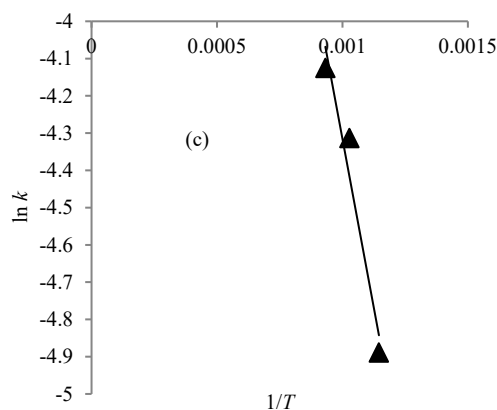
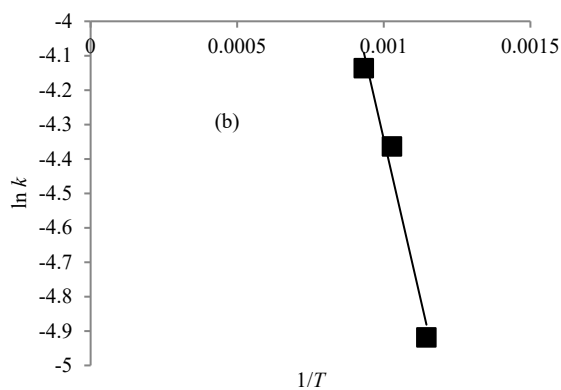
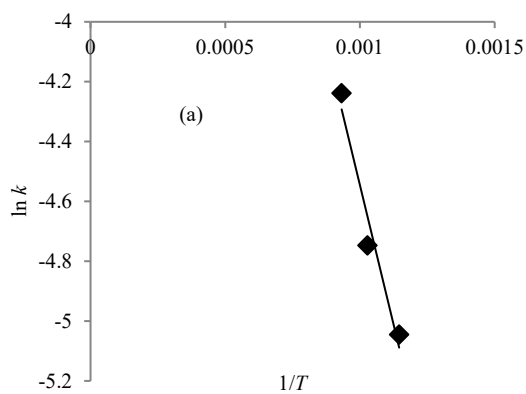


Figure 8. a) Plot of $\ln k$ vs $1/T$ for steam gasification at 0 grams' catalyst, b) Plot of $\ln k$ vs $1/T$ for steam gasification at 5 grams' catalyst, c) Plot of $\ln k$ vs $1/T$ for steam gasification at 10 grams' catalyst, d) Plot of $\ln k$ vs $1/T$ for steam gasification at 15 grams' catalyst

Table 2. Kinetic parameters in steam gasification process at 600 °C to 800 °C for 60 minutes

Mass of Ca catalyst (grams)	Activation energy (kJ.mol ⁻¹)	Frequency factor (min ⁻¹)	Equation of reaction kinetics constant
0	31.002	0.0662	$k = 0.0662 \exp\left(-\frac{31.002}{RT}\right)$
5	30.786	0.528	$k = 0.528 \exp\left(-\frac{30.786}{RT}\right)$
10	30.140	0.532	$k = 0.532 \exp\left(-\frac{30.140}{RT}\right)$
15	29.879	0.543	$k = 0.543 \exp\left(-\frac{27.879}{RT}\right)$

Table 3. Comparison standard error between volumetric model and random pore model

Mass of Ca Catalyst (g)	Error (%)					
	Volumetric Model			Random Pore Model		
	600	700	800	600	700	800
0	13.50	12.27	12.75	1.39	1.38	1.85
5	8.40	32.61	11.38	0.83	13.93	0.50
10	12.40	11.47	9.46	1.51	1.92	0.15
15	7.94	15.72	8.76	3.61	0.46	0.46

3.2. Comparison between the Random Pore Model and the Volumetric Model

From Figures 1-3 and 5-7, it can be shown that the volumetric and random pore models can represent the behavior of charcoal gasification in the early reaction period. However, the random pore model can represent the data until the late reaction period. This is because changes in the pore structure are more influential in the late reaction period. Table 3 shows that the standard error calculated based on the volumetric model is higher than the random pore model in each condition. Thus, the random pore model can provide better accuracy than the volumetric model because the RPM considers changes in the pore structure during the gasification process. Based on these results, it can be said that the random pore equation has better precision than the volumetric model.

4. CONCLUSIONS

The CaO catalyst can improve the conversion of steam gasification. The activation energy can be lowered by using CaO as a catalyst. The calculation results show that the random pore model matches the observation data. The volumetric model can only represent the data in the early period of the reaction, while the Random pore model can represent the data until the end of the reaction period. This indicates that during the reaction period, changes in the pore structure affect the reactivity of the reaction. The results also show that changes in the pore structure affect the reaction's reactivity.

Based on calculations using the random pore equation, the reaction rate constant is $k = 0.543 \exp\left(-\frac{29.879}{RT}\right)$ (kJ/mol) (catalyst mass 15 grams), and SSE of 0.46% was obtained. Meanwhile, by using a volumetric model, $k = 0.0499 \exp\left(-\frac{27.582}{RT}\right)$ (kJ/mol) (catalyst mass 15 grams) and SSE of 8.76% were obtained.

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