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Effects of Temperature on Kinetics and Mechanism of CO_2 Gasification of Char from Indonesian Lignite

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Abstract: *The conversion rate of char highly depends on gasification temperature (T_g). However, knowledge about how the temperature affects the kinetics of CO_2 gasification is still unclear. We are therefore motivated to investigate relationships between Tg and behavior of catalysts activity as well the deactivation rate. Herein, we conducted the gasification of an Indonesian lignite (raw and demineralized) at 800, 850 and 900 °C until char conversion, X >99.9%. The gasification of demineralized coal can be predicted by applying random pore model (RPM). Meanwhile, the kinetics model in which consider the activity of three types of catalysts together with a type of precursor successfully predict conversion level, 1-X as result of the change in catalysts activity during gasification for X = 0-0.999 under different T_g. This paper address the higher gasification temperature increases the activity of catalyst but also the deactivation rate, but not linearly which affects conversion rate during gasification.*

Keywords: CO_2 Gasification; Lignite; Temperature; Kinetic; Catalyst

1. INTRODUCTION

The main challenge of applying low-temperature gasification is an incomplete conversion of char into syngas within allowed residence time in a practical size of the reactor.[1] The presence of alkali and alkali earth (AAEM) species as catalysts has been found effective to overcome slow reaction of carbon with CO_2.[2,3] Kudo et al.[4] examined the activity of Ca in steam gasification of char from Indonesian low rank coal. They found that even small amount of Ca addition can improve the reactivity of char. However, there is a maximum limit of Ca loading at which Ca particles start to deactivate by agglomerating during gasification. The reducing of catalyst activity as result of catalyst deactivation (by sintering/ agglomerating, the formation of aluminosilicate compounds, or through vaporization) is more obvious in higher temperature.[6,7] Thus, it is important in the kinetic and mechanistic investigation of CO_2 gasification of Indonesian lignite to consider the influences of temperature on the nature of activity of catalysts.

Hence, we are motivated to develop a kinetic model in which considers the activity of catalysts under different gasification temperature (T_g) that can describe the kinetics of CO_2 gasification of chars from Indonesian lignite on over wide ranges of char conversion (X) on the low-temperature region. In this study, an Indonesian lignite was gasified in the range of 800-900 °C. We performed kinetics analysis of char conversion by considering parallel reactions of catalytic and non-catalytic gasification over the entire range of conversion to quantitatively describe the change in initial catalyst activity as well catalyst deactivation. This paper shows the activity of catalysts is highly influenced by T_g. The behavior of catalytic gasification can be explained by considering the presence of three types of catalysts with different initial activities and deactivation kinetics for each T_g, together with that of the catalyst precursor. With those features, this model can predict char conversion level for X = 0-0.999. The kinetic analysis shows the increase of deactivation rate becomes higher than the increase of initial catalyst activity in higher temperature which describes the maxima in dX/dt.

2. MATERIAL AND METHODS

A lignite, Berau (is referred to as the raw coal, BR) from Indonesia, was dried, crushed, and sieved to a size smaller than 106 μm. Table 1 lists the elemental composition and ash content of the sample prepared.

Table 1. Elemental composition, ash content, and distribution of major metallic species in the ash from raw coal

coal	C	H	N	O+S	Ash	Na	K	Mg	Ca
	(wt%, daf)				(wt%, db)	(mol/kg-dry coal)			
BR	67.50	4.49	1.11	26.90	4.46	0.007	0.003	0.081	0.196

To remove the mineral matter, the coal was treated by sequential of acid-washing with the concentration of 12 N HCl – 12 N HF at 60 °C for 24 h.[7] The mineral-matter free samples then were called demineralized samples (DM). The chars were prepared by pyrolysis of the raw and demineralized coals in a horizontally fixed bed reactor in a flow of atmospheric and high purity N_2 (300 mL STP min^{-1}). The pyrolysis heating rate, peak temperature and holding time for the pyrolysis were 30 °C.min^{-1}, 600 °C, and 15 min, respectively. Then, raw and DM lignite is gasified with 50 vol% CO_2 in thermogravimetric analysis (TGA) at 800; 850; and 900 °C until all char completely convert to syngas. The conversion (X_t) of char mass was defined as the ratio of the gasified char at any time t to the initial char minus ash weight.

$$X = \frac{W_0 - W_t}{W_0 - W_{ash}} \tag{1}$$

Where W_0 is the initial mass of char; W_t is the instantaneous char mass at specific reaction time t; W_{ash} is the mass of ash at the end of reaction. It also important to measure the specific rate of gasification in certain range of conversion, R_{sp} as results of change in catalyst activity along conversion.

$$R_{sp} = \frac{(dX/dt)}{(1-X)} \tag{2}$$

3. KINETIC MODEL DEVELOPMENT

The non-catalytic and catalytic gasification occur simultaneously in gasification of lignite.[9,10] The conversion rate can be illustrated by general kinetics equation:

$$\frac{dX}{dt} = \frac{dX_{nc}}{dt} + \frac{dX_{cn}}{dt} \tag{3}$$

In non-catalytic reaction, the RPM can define the behavior of a system that shows a maximum rate at certain conversion levels ($X < 0.393$) as well as one that does not.[10] It means that reaction between the char and CO_2 with a small impact of catalyst can be well explained by pore growth and coalescence during gasification. The equations of this model are shown as follow.

$$\frac{dX_{nc}}{dt} = k_{nc}(1-X)\sqrt{1-\psi\ln(1-X)} \tag{4}$$

$$k_{nc} = A_0\exp(-Ea/RT) \tag{5}$$

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{{S_0}^2} \tag{6}$$

Where k_{nc} is the rate constant for non-catalytic reaction. ψ is a dimensionless initial pore structural parameter and is calculated as follows using pore length (L_0), porosity per unit volume of solid (ε_0) and initial surface (S_0) but was approached as a fitting parameter in this paper.[11] Meanwhile, for catalytic gasification, we consider the use of three types of catalysts and a catalyst precursor with different initial activities and its deactivation rate.[8] The rate of catalytic reaction is a function of the initial effective amount of three types catalysts/precursor ($m_{cn,0/cnprec,0}$), a concentration of catalyst in char (C_{cn}), deactivation rate ($k_{cn,loss}$) and transformation rate of catalyst 1 precursor ($k_{c1,prec,trans}$). While n is the number of catalyst, 1-3. This model can be written in three equations as follow.

$$\frac{dX_{cn}}{dt} = k_{cn} = k'_{cn}m_{cn} \tag{7}$$

$$\frac{dm_{cn/cnprec}}{dt} = m_{cn,0/cnprec,0} - k_{cn,loss}C_{cn} + (k_{c1,prec,trans}C_{c1,prec}) \tag{8}$$

$$C_{cn/c1,prec} = \frac{m_{cn/c1,prec}}{1-X} \tag{9}$$

4. RESULTS AND DISCUSSION

4.1 Non-catalytic gasification

Table 1 shows the rate constant of non-catalytic gasification (k_{nc}) and the change of structural parameter (ψ) under different T_g. While the comparison between measured and calculated value of 1-X versus time profile for gasification of demineralized coal is shown in Fig. 1. We did not measure the conversion until finish as result of a slow gasification. However, the available trends of 1-X are sufficient to determine the kinetic model.

Table 1. Rate Constant for CO_2 gasification of char from demineralized lignite

T (°C)	k_{nc} (min^{-1})	ψ	range of X	r^2
800	0.00375	1.21	0.00 – 0.878	0.994
850	0.00837	1.40	0.00 – 0.914	0.993
900	0.01460	2.10	0.00 – 0.998	0.998

The kinetic analysis confirmed that chars underwent gasification obeying random pore model (RPM), indicated by high correlation between measured and calculated value of 1-X. The application of RPM to predict kinetics of gasification with steam and CO_2 has been confirmed for chars from bituminous that had no or very little amount of catalytic species.[6] The value of ψ increase in the range of 800 to 900 °C due to change in structural ordering and micro pores coalescence resulting decreasing the surface area.[13,14]

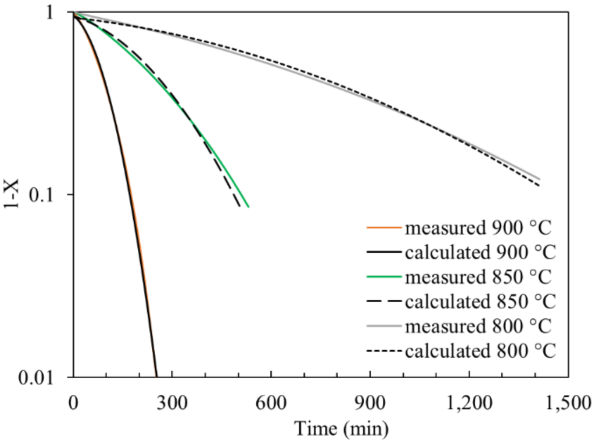

Fig. 1. Measured and calculated changes with time of (1–X) for gasification of chars from DM coal at different T_g on a logarithmic scale

4.2 Catalytic gasification

Fig. 2 shows the time-dependent changes in $1 - X$ for a char from the raw lignite with on decimal and logarithmic scales, respectively. The uses of three types of catalysts and a catalyst precursor give a good result in predicting conversion level. The required time to achieve 99.9% char conversion is varying between 8-60 minutes for T_g in the range of 800-900 °C.

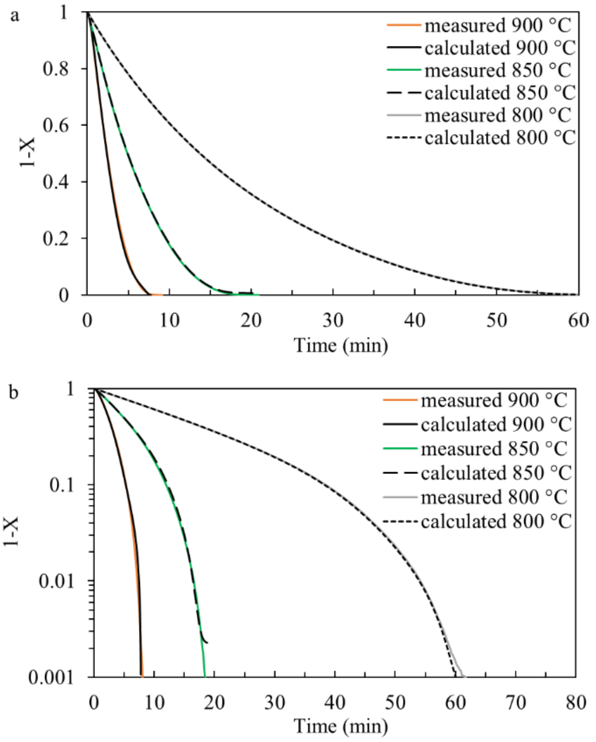

Fig. 2. Measured and calculated changes with time of (1–X) for gasification of char from raw coal at different T_g on a (a) decimal scale, (b) logarithmic scale

The 8 fold times disparity on gasification time is mainly caused by varying temperature 100 °C. The explanation of this result can be seen on the conversion rate (d*X*/dt) of chars from raw lignite vs *X* as presented in Fig. 3. The change in profiles of d*X*/dt under different T_g shows the significant influence of temperature on catalytic activity. There are changes in the catalytic activity with T_g along *X*, in other words, that of kinetics of catalyst generation and deactivation during gasification depend on T_g. The d*X*/dt values for three different gasification temperatures appear to reach maxima in early stages were resultant of a maximum concentration of catalyst-1. In this work, catalyst-1 has the greatest concentration compare to the two others catalysts make its contribution dominant.

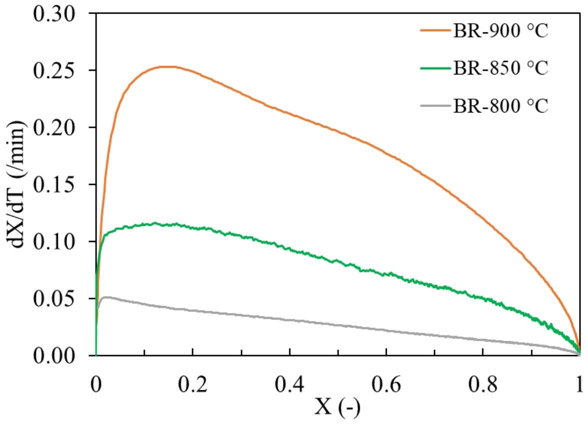

Fig. 3. Profile of d*X*/dt vs *X* for gasification of char from raw coal at different T_g

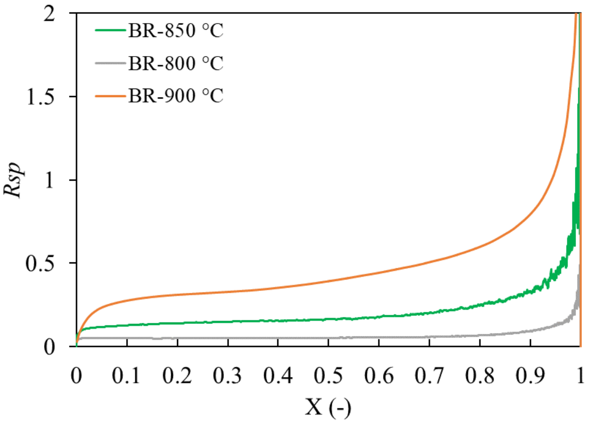

Fig. 4. Profile of measure and calculated of R_{sp} vs *X* for gasification of char from raw coal at different T_g

We also notice there is a tendency of catalyst-1 to deactivate quickly after reaching the maxima and become zero at the end of conversion. With this behavior, it is possible to refer catalyst-1 as calcium. Similar results also found by Zhang et al. [10,14] for gasification of Ca-char. As seen in Fig. 4, the specific reactivity, R_{sp} increase along conversion with different gradient. At 800 °C, R_{sp} is relatively flat until $X = 0.8$, and suddenly start to increase quickly at $X = 0.95$. Similar trend is found for $T_g = 850$ °C. Meanwhile for $T_g = 900$ °C, R_{sp} increase until $X = 0.05$, relatively flat, then increase slowly for $X = 0.4$–0.9 and later increase significantly at $X > 0.9$.

R_{sp} represent the pattern of kinetic respect with *X*. So, it is interesting to know the standard pattern for all temperatures by normalizing the value of R_{sp} by dividing it with R_{sp} at $X = 0.5$ for each temperature. The results of normalization can be seen in Fig. 5. Generally, the normalized R_{sp} profiles for three different T_g is relatively comparable. In the initial stage, the acceleration of conversion rate by high transformation rate of catalytic precursor to catalytic-1 causes an inclination in R_{sp} until reaching the maxima. Then, the gasification occurs stably relative to remain char. After there is collapse in char structure, the gasification rate increase significantly relative to (1-*X*) at $X > 0.5$.

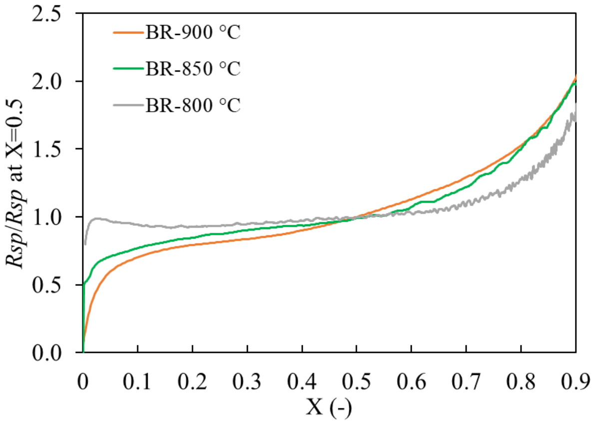

Fig. 5. Normalized R_{sp} profiles for different T_g

4.3 Kinetic analysis

This subsection discussed the change in the initial catalytic activity and deactivation rate by varying the gasification temperature. Table 2 summarizes the optimized kinetic parameters for the catalytic gasification, which were applied to draw the lines in Fig. 2. It was unavoidable to assume the presence of the catalyst precursor to transform into catalyst-1 during gasification for describing the profiles of 1-*X*. It is interesting how the temperature affects the value of the total of rate constant for catalytic reaction, $\sum k_{cn,0}$ and the total of deactivation rate, $\sum k_{loss,0}$.

The increasing of $\sum k_{cn,0}$ (2.1 times) is accompanied by higher increment of $\sum k_{loss,0}$ (9.8). This is a reason why the declining rate of dX/dt as shown in Fig. 3 is higher for 900 °C. With all those attribute, the model describes successfully the kinetics of CO_2 gasification of all of the temperatures over the range of 1-*X* from 1 to 0.001.

Table 2. Kinetic parameters for catalytic gasification under different *T*g

	(min^{-1})				
T (°C)	$\Sigma k_{cn,0}$	$k_{c1,prec}$	$k_{c1,0}$	$k_{c2,0}$	$k_{c3,0}$
800	0.125	0.076	0.031	0.004	0.014
850	0.130	0.040	0.008	0.052	0.030
900	0.272	0.239	0.001	0.011	0.021

T (°C)	$\Sigma k_{loss,0}$	$k_{loss\text{-}1,prec}$	$k_{loss\text{-}1,0}$	$k_{loss\text{-}2,0}$	$k_{loss\text{-}3,0}$
800	0.249	0.047	0.195	0.001	0.007
850	1.616	1.332	0.234	0.043	0.007
900	2.440	2.317	0.122	0.001	0.001

T (°C)	$\Sigma m_{cn,0}$	$m_{c1,prec}$	$m_{c1,0}$	$m_{c2,0}$	$m_{c3,0}$
800	1.000	0.608	0.250	0.028	0.113
850	1.000	0.308	0.065	0.400	0.227
900	1.000	0.880	0.002	0.041	0.077

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