A Kinetic Study on the Catalytic Carbon Dioxide Gasification of Pine Cone and Lignite Char Blends using Potassium Carbonate and Calcium Carbonate

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Abstract: In the design of energy conversion technologies such as gasifiers and reactors, kinetic data from the process and parameters of the raw feed are essential. One common feed to gasifiers is coal which when used alone as the primary source of energy conversion can cause environmental issues and economical concerns due of its high import cost to the country. Blending coal with biomass, which is an agricultural waste, was found to efficiently burn the coal and reduces harmful emissions into the environment. In this study Indonesian lignite coal (L) and Philippine pine cone (P) blends are studied using a thermogravimetric analyzer to obtain their kinetic data. The gasification of these blends was carried out at temperatures ranging from of 700°C to 900°C at 100°C interval using potassium carbonate (K_2CO_3) and calcium carbonate ($CaCO_3$) as catalysts at 1% loading. The conversion-time data obtained from the thermogravimetric analyzer were fitted using five different gas-solid reaction models namely, volumetric, or homogeneous model (VM), shrinking core model (SCM), random pore model (RPM), modified volumetric model (MVM), and extended modified volumetric model (EMVM). The effectiveness of the models in simulating the gasification reactions were ranked according to the following order – EMVM > MVM > RPM > VM > SCM. The catalyst that performed better at 700°C and 800°C with more coal content was K_2CO_3, while $CaCO_3$ performed better at 900°C with more pine cone content. Among the different blends, the blend 80% P + 20% L proved to have faster reaction rate than 50% P + 50% L.

Key Words: CO_2 gasification; pine cone; alkali carbonate, kinetics

1. INTRODUCTION

In the Philippines, energy consumption plays an important role in economic growth. According to the Department of Energy (2018), the country's energy consumption during 2017 increased to 94,370 GWh from the previous energy consumption during 2016 which was at 90,798 GWh. It was also recorded that during 2017, coal-based energy generation was used to supply 46,847 GWh of energy to the country, while 3,787 GWh of energy was supplied by oil-based energy generation, 20,547 GWh of energy was supplied by natural gas, and 23,189 GWh of energy was supplied by renewable energy sources. It is apparent that the country is still heavily dependent on coal-based energy generation based on coal-based energy generation being the major supplier of energy in the country. Due to the negative effects of coal-based power generation to the environment as well as its high cost, better alternatives are being tested such as biomass; an example of which is pine cone. Blending pine cone and coal could significantly reduce the amount of coal used in coal-based energy generation. The key process of converting these feedstocks to energy is gasification which is thought to be one of the better ways to efficiently complete the conversion of carbon dioxide, thus contributing to the reduction of greenhouse gas emissions in the atmosphere.

The gasification of coal char is an effective method to produce gases which are used in the generation of power. However, the gasification process could be greatly affected by factors such as the nature of the fuel, the catalysts used, and the

gasification temperature. A study by Takarada et al (1985) investigated 34 coals which verified that the reactivities of chars from low-ranked coals have no correlation with the carbon content of the parent coals. Biomass on the other hand, affects the gasification rate based on its size, shape, and structure. Kirubakaran et al (2009) used biomass in its pelletized form instead of powdered form to minimize the size of gasifier used in their study. However, pine cones on their own have a relatively small heating value than coal which produces less power. Additionally, the use of pine cone as the sole feedstock can lead to combustion and ignition problems because of its high moisture and ash contents and flame stability problems. Furthermore, Pan et al. (2000) proved that varying the ratio of pine chips and low-rank coal significantly affected the gasification process. In the gasification process, it is desired to have a catalyst to speed up the reaction rate of the process. Several studies were carried out to test different kinds of catalysts to optimize the process. It has also been reported that the inherent alkali and alkali earth metals (AEEM species) found in raw biomass possess catalytic effects can be beneficial to the gasification process as it accelerates the conversion of biochar and leads to higher product yield (Chan et al, 2016).

In our previous study (Ang, et al, 2019), the pyrolysis and CO_2-gasification of various pine cones and lignite blends were studied in the absence of a catalyst. In this study, the focus was to determine the optimal blend ratio of pine cone and lignite coal char, along with the better catalyst and the gasification temperature that will significantly increase the gasification rate, lower the gasification temperature, and decrease the activation energy of the reaction. Not only will the blend increase the resulting heating value which increases the power output and its efficiency to burn but also optimizes the consumption of coal while utilizing effective waste management of agro-forest wastes.

2. METHODOLOGY

2.1 Method Overview

The experiment involved sample preparation, CO_2 gasification of the samples and evaluation of the kinetic parameters. The blend ratio of pine cone to lignite coal, the catalyst, and gasification temperature are the factors considered in this study. Four blend ratios, two catalysts, and three gasification temperatures were observed. The gasification process was carried out twice for each blend ratio and temperature. Five gas-solid reaction models were used to simulate the gasification process.

2.2 Materials and Reagents

In this study, one type of pine cone and one type of lignite coal was used. The pine cone used was *Pinus elliottii* from Tarlac, Central Luzon and the coal used was lignite from Indonesia. The catalysts used were K_2CO_3 of 99.5% purity, and $CaCO_3$ of 99% purity. The gases used were CO_2, compressed air, and Argon, all with 99.999% purity.

2.3 Sample Preparation

The pine cone was first pulverized using a Wiley Mill using a mesh of about 1mm. After which, the samples were then sieved using the Ro-Tap shaker to obtain particles of around 250μm in diameter. The two raw materials were blended by proportioning mass to obtain 3-gram samples as shown on Table 1. These samples were impregnated with the catalyst at 1% wt. loading and air-dried.

Table 1. Prepared sample blend ratio

Uncatalyzed samples				
Sample No.	1	2	3	4
Pine cone (wt.%)	100	80	50	0
Lignite coal (wt.%)	0	20	50	100
K_2CO_3 catalyzed samples (1 wt.% loading)				
Sample No.	5	6	7	8
Pine cone(wt.%)	100	80	50	0
Lignite coal (wt.%)	0	20	50	100
$CaCO_3$ catalyzed samples (1 wt.% loading)				
Sample No.	9	10	11	12
Pine cone (wt.%)	100	80	50	0
Lignite coal (wt.%)	0	20	50	100

2.4 Gasification Process

Around 10 mg of the prepared sample was first weighed on a 100μL platinum pan. The sample was preheated under argon environment at a temperature of 110ºC for 10 minutes to remove the moisture content of the pine cone and lignite coal. The change in mass between the initial mass reading and the constant mass reading during the isothermal preheating is observed as the moisture content of the sample. After removing the moisture content, the char is then subjected to heat under carbon dioxide environment at the gasification temperatures of 700ºC, 800ºC, and 900ºC to start the actual gasification of the char. The samples were then heated for 240 minutes under air environment to ensure that all carbon has been gasified.

2.5 Analysis and Evaluation of Data

The mass-time data in the gasification section was converted into a char conversion-time data. This data was processed using a curve fitting tool to evaluate the rate constants, and the goodness of fit to the five gas-solid reaction kinetic models. The gas-solid reaction models used are the volumetric model (VM), shrinking core model (SCM), random pore model (RPM), modified volumetric model (MVM) and the extended modified volumetric model (EMVM). The squared value of the correlation index, error sum of the squares, and activation energy were calculated.

3. RESULTS AND DISCUSSION

3.1 Char conversion

The fractional conversion of char was calculated using Eq. 1 and plotted versus a dimensionless gasification time. Since gasification may end at a shorter or longer time depending on the gasification temperature, all plots were made uniform by analyzing the gasification within the first 30 mins. The gasification was terminated by burning the sample with air to determine the total char present in the blends.

$$X = \frac{Wo - W}{Wo - W_{ash}} \qquad \text{(Eq. 1)}$$

where:

X = fractional conversion of char
W_o = initial mass of the pre-gasified char
W = mass of the char at any time t
W_{ash} = mass of ash in the primary sample

3.1.1 CO_2 Gasification with Varying Blends

The char conversion-time data for the uncatalyzed gasification of the two pure samples and two blended samples were determined at different gasification temperatures to serve as reference and in comparison, with the catalyzed samples. Figure 1 shows that both blends have similar gasification behavior which should be expected due to the inherent catalytic properties of the ash content of pine cones specifically alkali oxides that help hasten the reaction for the blend containing 50% P + 50% L. This is more evident at temperatures lower than 900°C.

Even though lignite coals also contain these alkali oxides in their ash content, pine cones typically contain more which give it a higher reactivity and conversion rate compared to lignite coals (Vamvuka & Kakaras, 2011; Vassilev et al., 2014; Rizkiana et al., 2014).

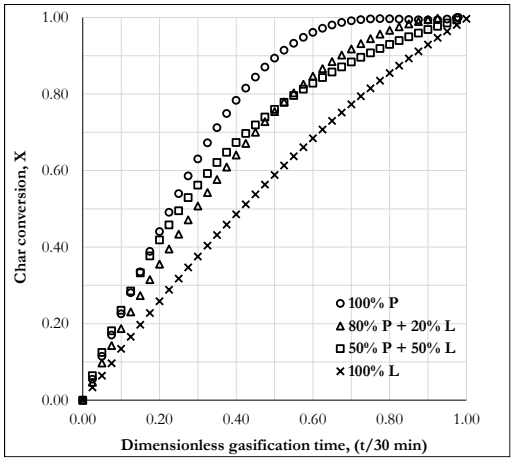

Fig. 1. Char conversion of uncatalyzed gasification of different blends at 900°C

However, in catalyzed gasification, especially at high temperatures, it is more evident that the blend 80% P + 20% L performed better in terms of its char conversion as seen in Figure 2. The addition of a catalyst significantly favors the blend with more pine cone content.

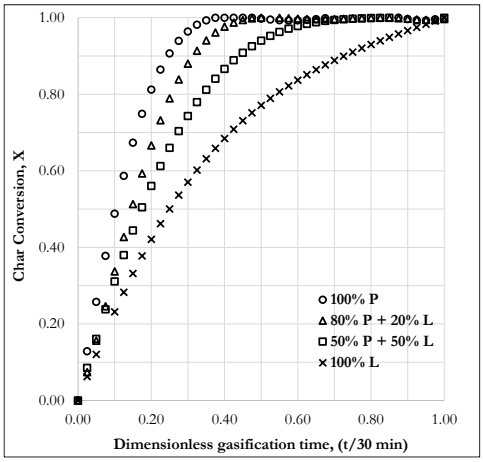

Fig. 2. Char conversion of $CaCO_3$-catalyzed gasification of different blends at 900°C

Based on these results, it can be deduced that pine contributes to the increase in the rate of gasification due to its inherent ash content and enhanced further with the addition of the alkali carbonate.

3.1.2 CO_2 Gasification with Varying Catalysts

With the addition of catalysts like K_2CO_3 and $CaCO_3$ to the pure samples, the reaction time typically decreases and lowers the activation energy, especially at higher temperatures. It was observed that for the four samples, the K_2CO_3 – catalyzed samples showed better results at 700°C, while the $CaCO_3$ – catalyzed samples showed better results at 800°C and 900°C. However, the difference in effectiveness for both catalysts is minimal, which may be attributed to the small catalyst loading of 1%. Previous studies have shown that a minimum catalyst loading of 5% is required to produce a significant effect in the gasification rates. For the 80% P + 20% L blended sample, the catalyzed samples only showed significant better results at 900°C as seen in Figure 3. Additionally, $CaCO_3$ synergized better with higher pine cone concentration which can be due to the inherent catalytic compounds in the pine cone ash.

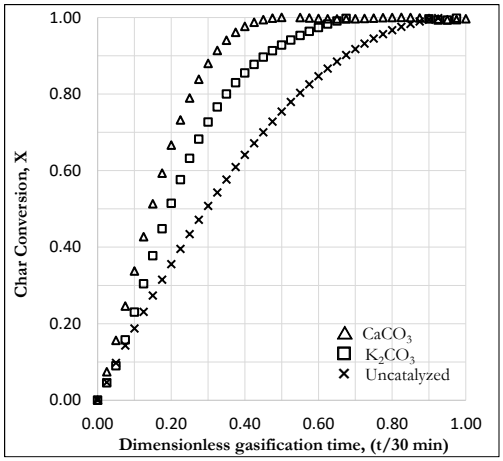

Fig. 3. Char conversions of 80% P + 20% L with different catalysts at 900°C

For the K_2CO_3-catalyzed gasification runs, the catalyst proved better at temperatures lower than 900°C since K_2CO_3 melts at 891°C, and the solid-liquid interface of potassium with the carbon of the sample improves its dispersion to the sample (Akyurtlu & Akyurtlu, 1995). Furthermore, at 900°C, it is highly possible that the decomposition of K_2CO_3 occurs. This aids to the redox cycle wherein the catalyst is reduced and reacts with the carbon from the lignite coal to produce CO which acts as the free active site for gasification. Thus, K_2CO_3 performs better with higher lignite char content at lower temperatures.

3.2 Fitting of Data to Kinetic Models

Using the five gas-solid reaction models, the char conversion-time data were fitted to determine its goodness of fit, along with the kinetic parameters. These kinetic parameters (k_{VM}, k_{SCM}, k_{RPM}, k_{MVM}, k_{EMVM}, α, β, f, R^2, and SSE) are obtained using the MATLAB software. All the theoretical and the non-theoretical models used a MATLAB program.

The average R^2 values from the different models are 0.9521 (VM), 0.9513 (SCM), 0.9726 (RPM), 0.9900 (MVM), and 0.9984 (EMVM). From the theoretical models, it was observed that the RPM was the most effective model in representing the reaction, while the SCM was the most ineffective model in representing the reaction.

For both the non-theoretical models, it was evident that the EMVM was better than the MVM. However, both models are effective in simulating the gasification reactions based on the low values of SSE and R^2 values very close to 1. In comparing the average R^2 values of all the different models, the experimental data best fits the model in the following order: EMVM > MVM > RPM > VM > SCM.

3.3 Effect of Blend Composition and Catalyst on the Rate Constant

Using the gasification rate constant is a good method to better visualize the effect of the blend composition and type of catalyst on the gasification process. Figure 4 presents the rate constants of pure and blended samples using different catalysts at 900°C.

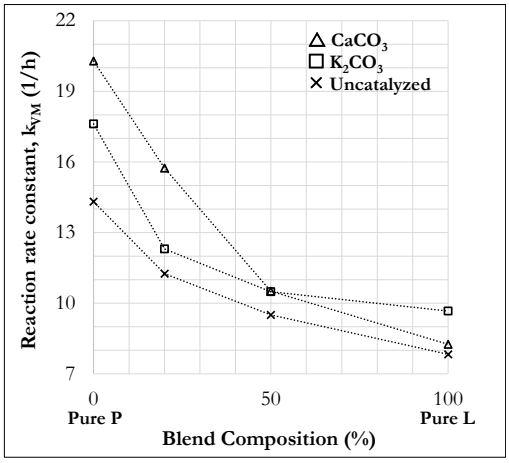

Fig. 4. Reaction rate constants of pure and blended samples using different catalysts at 900°C

From this figure, it was revealed that the blend 80% P + 20% L together with $CaCO_3$ as the catalyst have the highest reaction rate constant. $CaCO_3$ synergized better on samples with a higher pine cone content which may be due to its compatibility with the inherent catalytic compounds in the pine cone ash.

3.4 Effect of Temperature on Rate Constant and Activation Energy

With the increase in gasification temperature, it is expected that the reaction rate constant will also increase exponentially because heating the reaction will result in an increase in the number of high energy collisions which leads to a faster reaction because the particles only react when in collision with other particles. Figure 5 shows the negative relationship between the natural logarithm of the reaction rate constant and the reciprocal of the temperature.

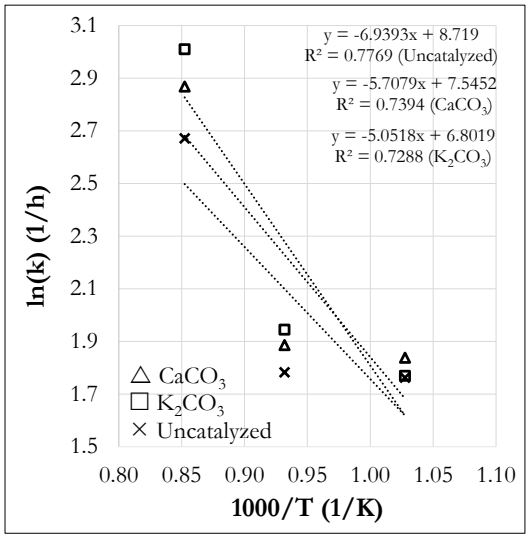

Fig. 5. Arrhenius plot for 80% P + 20% L sample

With the generated Arrhenius equations, Table 2 summarizes the calculated activation energies of the uncatalyzed and catalyzed gasification.

Table 2. Summary of activation energies

Sample Composition	E_a, kJ/mol		
	Uncatalyzed	$CaCO_3$	K_2CO_3
100% P	22.3125	13.9709	20.4366
80% P + 20% L	24.4182	20.9496	23.2310
50% P + 50% L	44.5107	31.1010	29.9113
100% L	57.6933	47.4588	42.0007

From the activation energies obtained, it was observed that gasification of samples with pine cone have lower activation energies when catalyzed with $CaCO_3$. On the other hand, only pure lignite samples have a lower activation energy when catalyzed with K_2CO_3. Since K_2CO_3 was added to the samples with volatile combustible matter, the catalyst may have formed compounds with the components of the volatile combustible matter which may have rendered some catalytic effects on the gasification to be ineffective. However, since lignite has lower volatile combustible matter than pine cone, the effect of the catalyst is more efficient. Furthermore, in comparing the activation energies for the blended samples, it was observed that the 80% P + 20% L blend has a lower activation energy than that of the 50% P + 50% L blend.

4. CONCLUSIONS

The sample blends of pine cone to lignite coal char has a significant effect on the carbon dioxide gasification process. Moreover, the use of catalysts has been proven to enhance the gasification process as represented by faster gasification rates, higher reaction rate constants, and lower activation energies. The blend 80% P + 20% L has produced better reaction rate constants and activation energies than that of the blend 50% P + 50% L. $CaCO_3$ reduced the activation energy better than K_2CO_3 for samples containing more pine cone content, while K_2CO_3 reduced the activation energy better for pure lignite samples. The extended modified volumetric model (EMVM) is the best fit for the simulation of the gasification reaction (R^2 =0.9984). The overall ranking of the effectiveness of the gas-solid reaction models is as follows: EMVM > MVM > RPM > VM > SCM. Lastly, increasing the gasification temperature resulted to an increase in reaction rate constant.

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