Kinetic analysis of *Theobroma cacao* (UIT Variety) pod husks through gasification as an alternative to sub-bituminous coal

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Abstract

Co-gasification of biomass and coal is emerging as a potential clean fuel technology as it reduces greenhouse gas emissions, lowers gross power output, and increases thermal efficiency. The present study aimed to determine the potential of *Theobroma cacao* (UIT Variety) pod husks as an alternative to coal by investigating the gasification kinetics The proximate composition of five sample blends of cacao pod husks and sub-bituminous coal (CPH-SBC): 0%-100% wt/wt, 25%-75% wt/wt, 50%-50% wt/wt, 75%-25% wt/wt, 100%-0% wt/wt, were determined using the STA 8000 in a nitrogen-enriched atmosphere at 900°C. The conversion-time data obtained were fitted using the three different kinetic models namely: Volumetric Model (VM), Shrinking Core Model (SCM), and Random Pore Model (RPM). Results showed that the blend 75%-25% CPH-SBC is the most effective in terms of the overall proximate composition. Among the three kinetic models, the RPM had the best fit, having R^2=0.964, with the data, suggesting that the growth of the pores and coalescence of the pores causes a reduction of area through a combination of overlapping of pore surfaces. The activation energy of the blends, according to the best fit model, ranged from 93.919 kJ/mol to 105.73 kJ/mol. Based on the results, it can be concluded that *Theobroma cacao* (UIT Variety) pod husks can indeed act as a substitute to sub-bituminous coal.

Keywords: *co-gasification, biomass, coal, proximate composition, kinetic modeling*

Introduction. A large percentage of the Philippines' energy demand is obtained from the use of fossil fuel - despite efforts to transition to a cleaner alternative [1,2]. To fully support the transition, an equally or even more efficient energy resource is therefore necessary. Thus, it is imperative to find alternative energy resources in order to cut the use of fossil fuel in meeting the country's energy requirements. Biomass is the cheapest and most abundant renewable energy resource in the Philippines as the country produces tons of agricultural and forestry wastes [3]. This includes in great proportion the common agricultural wastes such as rice straws, husks, and sugar bagasse [4].

Co-gasification of coal has recently gained interest as a potentially clean and efficient technology for production of energy and biofuels [5]. Gasification is the most versatile thermal conversion process in energy production [6]. In the effort to sustainably reduce the use of coal in meeting the increasing energy demands, various studies have extensively investigated the gasification of other feedstocks, especially biomass waste materials [5]. The results of these studies show that co-gasification of coal and biomass has higher overall efficiency than the separate gasification of these materials [7]. The cellulose, hemicellulose and lignin content of biomass increases the rate of gasification [8]. Moreover, gasification of biomass in ash coal can reduce the slagging and fouling problems caused by high alkali contents [9]. Coal and biomass seem to have synergistic reaction rates with lower gross power output, but higher thermal efficiency [10]. Co-gasification also has reduced greenhouse gas emissions as compared to conventional methods. It also addresses the problems associated with sulfur and ash contained in coal as biomass comparatively contains less of the two [11].

Cacao pod husk has been extensively studied as a promising biomass for gasification due to its high cellulosic and hemicellulosic content [8]. However, it lacks sufficient kinetic characterization necessary for industrial translation. Given that there is limited research on the gasification of cacao pod husk, this study aims to fill in the gap by determining the kinetic parameters: activation energy, and rate constants (k_{VM}, k_{SCM}, k_{RPM}), and the proximate analysis properties such as the moisture content, volatile matter, fixed carbon, and ash content provided by the different reaction models used [10].

Gasification is an incomplete combustion process that partially burns and converts the feed. It is often shown by using models based on the behavior of the reaction and carbon conversion. [12] These models help suggest the most probable mechanism involved in the reaction. The kinetic models that would be used in this study are the Volumetric Model (VM), Shrinking Core Model (SCM), and Random Pore Model (RPM). VM assumes the reaction to be uniform throughout the volume of the particle [13]. While the SCM assumes

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that the reaction takes place on the surface of the particle only and not throughout the particle, reducing the core radius; hence the 'shrinking' [14]. On the other hand, RPM assumes two opposing structural changes: growth and coalescence of the pores resulting in the reduction of area due to pore overlaps [15].

The kinetic study and other scientific data reported in this study can be used as a guide in designing more comprehensive and systematic studies that, in turn, would help in the design of an efficient gasifier or reactor system. Cacao pod husks are usually unutilized waste products of cacao bean production, which is a growing agricultural industry in the Philippines. The pod husk represents 70 to 75% of the whole weight of the cacao fruit [16], and thus can be promising feedstock in the co-gasification process.

The co-gasification of biomass and coal for power generation provides a real option to expand the energy supply in the Philippines and thus may reduce the country's utilization of coal and other fossil fuels, and thereby reducing the greenhouse gas and air pollutant emissions. The stated valorization of the cacao pod husk may also be economically significant as this could be a new source of income for the Filipino cacao farmers.

This study aimed to investigate the gasification kinetics of *Theobroma cacao* (UIT Variety) pod husks and coal blends as an alternative energy. It specifically aimed to:

(i) perform proximate analysis of the different ratio of cacao pod husk-sub-bituminous coal (CPH-SBC) blends: 0%-100%, 25%-75%, 50%-50%, 75%-25%, 100%-0%;

(ii) compare the different gas-solid models: Volumetric Model (VM), Shrinking Core Model (SCM), and Random Pore Model (RPM), through comparison of the coefficient of determination (R^2); and

(iii) calculate the reaction rate constant and the activation energy of the gasification reaction based on the kinetic parameters.

Methods. Five samples were analyzed in the study, this consists of CPH-SBC of 0%-100%, 25%-75%, 50%-50%, 75%-25%, 100%-0%. The blends then underwent gasification at a temperature of 900°C using a Simultaneous Thermal Analyzer 8000 (Perkin Elmer STA 8000), which undergoes the process of drying, devolatilization, gasification and combustion. The weight loss history and heat absorption of the individual blends were studied in a linearly heated environment. The char conversion obtained was then used to fit in the three kinetic models namely, Volumetric Model (2) Shrinking Core Model (3), and Random Pore Model (4).

Thermal analysis. The Thermogravimetric analyzer (PerkinElmer Simultaneous Thermal Analyzer 8000) was used in the gasification process. Thermogravimetry was used as an alternative method for obtaining the proximate analysis as it shows good correlation in results compared to the classical method [17]. For each blend, a sample weighing 20 mg was heated in a small furnace in the thermal analyzer to study its thermal degradation. The samples were heated from 20°C to 900°C at a linear heating rate of 50°C·min^{-1}. The samples were then gasified at 900°C to promote the different endothermic reactions that are occurring during gasification. Table 1 shows the summary of steps.

Table 1. Running program inputted in STA 8000.

Method	Description	Purpose
Isothermal	Heat for 2.0 min at 20°C	Mass stabilization
Temperature-Ramp	Heat for 20°C to 110°C at 50°C/min	Increase to the drying temperature
Isothermal	Hold for 4.0 min at 110°C	Moisture removal
Temperature-Ramp	Heat from 110°C to 900°C at 50°C/min	Increase to the devolatilization, gasification, and combustion temperature
Isothermal	Hold for 10.0 min at 900°C	Devolatilization, gasification, and combustion

Data Analysis. The fractional char conversion rate constant was calculated and plotted in a conversion-time graph. Then, kinetic model fitting was done by calculating for the first-order kinetic model constant with respect to the fractional char conversion.

The evaluation was carried out by determining the fractional conversion using Equation 1 (1). The fractional char conversion ratio X, at any given time t can be expressed as follows:

$$X = \frac{W_0 - W}{W_0 - W_{ash}} \quad (1)$$

where W_0 is the initial mass of the pre-gasified char, W_{ash} is the mass of ash in the primary char sample, and W is the mass of the char at any time t [18].

After which, it was fitted into the gas-solid reaction model, namely Volumetric Model, Shrinking Core Model, and Random Pore Model given by equation 2 (2), 3 (3), and 4 (4), respectively.

$$X = 1 - e^{-k_{vm}t} \quad (2)$$

where k_{VM} is the first-order reaction rate constant.

$$3\left[1 - (1 - X)^{\frac{1}{3}}\right] = k_{SCM}t \quad (3)$$

where k_{SCM} is the average rate reaction constant,

$$X = 1 - e^{\left[-k_{RPM}t\left(1 + \frac{\Psi k_{RPM}t}{4}\right)\right]} \quad (4)$$

where k_{RPM} is the reaction rate constant, Ψ is a structural parameter which describes the particle's internal structure given by

$$\Psi = \frac{2}{2ln(1 - X_{max}) + 1}$$

where X_{max} is the conversion at the maximum rate of gasification.

Using the standard deviation formula given in (5), the overall goodness of fit would then be determined.

(5) $$SD = \sqrt{\frac{\sum(X_{exp}-X_{model})^2}{N-p}}$$

where X_{exp} and X_{model} are the conversion data from the experiment and each individual model and N is the number of data while p is the number of parameters fitted.

(6) $$R^2 = 1 - \frac{\sum_1^n(X_{exp}-X_{model})^2}{\sum_1^n(X_{exp}-\bar{X})^2}$$

where $\bar{X}$ is the average values of char conversion.

Finally, the activation energy was calculated using the Van't hoff equation given in (7):

(7) $$ln\frac{k_2}{k_1} = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k_1 is the kinetic model constant at temperature T_1 where the first change in sample mass is observed, k_2 is the kinetic model constant at temperature T_2 (900°C or 1173 K), E_a is the activation energy, and R is the gas constant 8.314 J/mol·K.

The reaction rate for the models was then graphed using a graphical and statistical analysis software to obtain the R^2 value and the graph of the predicted curve. The Root Mean Square Error (RMSE) was calculated to find the kinetic model with the lowest deviation from the predicted reaction curve.

Statistical Analysis. Analysis of Variance (ANOVA) of α=0.05 was done to determine if there is a significant difference in the R^2 and RMSE of the rate constants from the kinetic models for the five sample blends.

Safety Procedure. There was no special treatment for waste disposal of the samples, and ash content. The ash which remained in the pan after the thermal analysis was disposed of in a container as it does not contain any toxic residue.

Results and Discussion. The results and discussion were divided into four parts namely: proximate analysis, char conversion-time graph analysis, determination of kinetic parameters, and determination of Arrhenius parameters.

Proximate analysis. The desired sample blend ratio should have a low moisture content, higher amount of fixed carbon, and low ash content [8]. A lower amount of moisture would yield faster pyrolysis, while a higher amount of fixed carbon and lower ash content would help increase its rate of gas conversion. As seen in Table 2, among the five different sample blends, the ratio having 0%-100% cacao pod husks-sub-bituminous coal (CPH-SBC) contains the highest amount of moisture while 100%-0% CPH-SBC contains the lowest amount.

Table 2. Proximate composition of the samples.

Component (CPH-SBC)	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)
0%-100%	13.02	41.56	9.25	36.16
25%-75%	12.30	46.50	11.13	29.89
50%-50%	12.00	50.49	15.43	22.08
75%-25%	11.25	64.04	19.99	4.71
100%-0%	9.39	66.15	15.34	9.11

In order to determine the most viable type of blend, these properties must be accounted for which is why in order to summarize these parameters, the following characteristics is desired: low moisture content, 40% or higher amount of fixed carbon, and less than 10% amount of ash content [10]. The blend 0%-100% CPH-SBC has the highest ash content, it was therefore arbitrarily designated as the least efficient among the blends, especially upon determination of activation energy and coefficient of determination.

Char conversion-time graph analysis. Figure 1 shows the conversion-time graph which has a direct correlation to the proximate analysis. For the moisture removal, the 100%-0% CPH-SBC has the slowest conversion rate while the 0%-100% CPH-SBC has the fastest with respect to their moisture content being the lowest and the highest among the sample blends.

The volatile matter of the sample blend increases as biomass ratio increases. This makes biomass easier to ignite than coal resulting in a faster conversion rate for the 100%-0% CPH-SBC followed by the 75%-25% CPH-SBC in the earlier parts of volatile matter removal. After 18.26 minutes, both 25%-75% CPH-SBC and 0%-100% CPH-SBC have higher conversion rates than 100%-0% CPH-SBC. At 23.89 minutes, the conversion rates are in order of higher coal ratio in the sample blend.

The fixed carbon is the carbonaceous residue when volatile matter is removed. The 75%-25% CPH-SBC has the fastest conversion rate followed by the 50%-50% CPH-SBC and the 100%-0% CPH-SBC.

After removing the fixed carbon, the 75%-25% CPH-SBC was calculated to reach 0.99 conversion after 31.02 minutes. Other sample blends were found to have reached the same conversion at 33.13, 33.11, 33.02, and 32.71 minutes for the 100%-0% CPH-SBC, 50%-50% CPH-SBC, 25%-75% CPH-SBC, and 0%-100% CPH-SBC respectively.

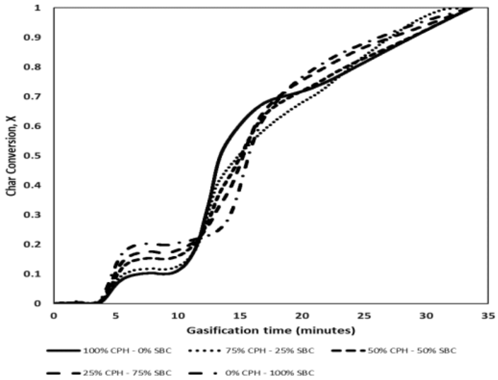

Figure 1. The graph shows char conversion (denoted by X) as a function of time (in minutes).

Determination of Kinetic parameters. Table 3 shows the different parameters of the blends obtained from the simulation of the conversion-time using the kinetic models namely: Volumetric Model (VM), Shrinking Core Model (SCM), and Random Pore Model (RPM). As well as the determination of the kinetic rate constant (k_{VM}, k_{SCM}, k_{RPM}), the coefficient of determination (R^2), and Root Mean Square (RMSE) and the standard deviation (SD).

Table 3. Kinetic parameters of the sample blends.

		0%-100%	25%-75%	50%-50%	75%-25%	100%-0%
VM	k_{VM}	0.321	0.309	0.299	0.338	0.301
	R^2	0.896	0.865	0.845	0.902	0.760
	SD	0.649	0.650	0.638	0.627	0.645
	RMSE	0.0128	0.0131	0.0125	0.0168	0.0148
SCM	k_{SCM}	0.087	0.086	0.086	0.089	0.086
	R^2	0.883	0.901	0.899	0.928	0.749
	SD	0.675	0.673	0.657	0.658	0.664
	RMSE	0.00620	0.00520	0.00483	0.00520	0.00811
RPM	ψ	2+8E-5	2+6E-5	2+6E-5	2+5E-5	2+E-5
	k_{RPM}	0.192	0.147	0.133	0.109	0.125
	R^2	0.964	0.964	0.964	0.964	0.964
	SD	0.652	0.667	0.654	0.667	0.666
	RMSE	0.0204	0.0155	0.0139	0.0116	0.0132

*All the kinetic rate constants (k_{VM}, k_{RPM}, k_{SCM}) are in the units of (1/s).

Determination of Arrhenius parameter. The activation energy (E_a) of the sample blend for the different models can be found in Table 4. The pre-exponential factors differ largely from one model to another with the lowest values from the Random Pore Model (RPM). This implies that different models result in different plots as both Arrhenius constants showed large difference of deviation from one another, thus, it is difficult to fully compare the ratios to one another.

Table 4. Activation Energy of the sample blends.

Component (cacao pod husk mass-coal mass)	Volumetric Model (E_a(kJ))	Shrinking Core Model (E_a(kJ))	Random Pore Model (E_a(kJ))
0%-100%	108.204810	104.034751	94.561378
25%-75%	109.752677	105.731682	94.096491
50%-50%	108.456908	104.5399463	93.932360
75%-25%	113.050501	108.741224	93.945847
100%-0%	106.424085	102.487189	93.919190

The RPM with R^2=0.964 was found to be the best fit model for the sample blends. The Shrinking Core Model with RMSE ranging from 0.00483-0.00811 has its experimental plot closest to the predicted model curve for all sample blends. After using ANOVA on the R^2 and RMSE of rate constants, a p-value of 0.01299 and 0.001 respectively suggests that there is no significant difference in the effect of blend ratios between cacao pod husk-sub-bituminous coal (CPH-SBC) on the gasification reaction of the sample blends.

To determine the most efficient sample blend ratio, the activation energy (E_a) and the proximate analysis must also be accounted for.

Since there is no significant difference between the blends among all models, the deciding factor would be in the proximate analysis; hence, the blend 75%-25% CPH-SBC is the most efficient. It shows great variability in terms of ash content and amount of fixed carbon having the lowest value with 4.71% and the highest with 19.99%, respectively. This suggests that the conversion from biomass to biogas is most effective in the process. It is ideal to have low ash content to avoid problems with the gasifiers which include slagging, and fouling of the equipment [19], as well as high fixed carbon as this would enable the process to fully convert the feedstock. The conversion-time graph for 75%-25% CPH-SBC also shows that 0.99 conversion is reached after 31.02 minutes, earlier than other blends which are at around 33 minutes, this suggests that char conversion for this sample blend is more efficient than others. This is followed by the blend 100%-0% CPH-SBC with the second lowest value of ash content with 9.11% making it the second most efficient. The increase in ash content may be due to the increase in the coal content of the blend.

The ash content is significantly greater when the blend contains more coal than cacao based on the proximate analysis. This causes the sample blend to have a higher heat capacity and therefore should take more time to burn and/or gasify [8].

With all parameters considered, the most efficient ratio of blends would be 75%-25% CPH-SBC, followed by 100%-0% CPH-SBC. This conclusion was made due to the (1) proximate analysis (2) and lower activation energy.

The sample blend ratio is in line with the results of Kamble et al. [8] that biomass-coal ratio should contain around 70% biomass for gasification at lower temperatures because more biomass in blends result to higher amounts of hydrocarbons enhancing the calorific value of gaseous products. It also suggests that *Theobroma cacao* (UIT variety) can be used as a substitute to coal as it has better kinetic properties than sub-bituminous coal due to its higher coefficient of determination and lower activation energy. Moreover, since slagging did not occur during the gasification process despite having ash content higher than 5%, it does not make 100%-0% CPH-SBC disadvantageous when gasified at 900°C. However, it may be disadvantageous when undergoing gasification at lower temperatures.

Limitations. The study involved *Theobroma cacao* (UIT Variety), as a biomass for gasification. Each blend was tested only once due to limited resources. Only 90 minutes of the gasification time was considered in this study. Instead of using the ASTM (American Society for Testing and Materials) standards in determining the proximate analysis, the data from the thermal analysis was used to obtain the different parameters. The experiment was carried out on a laboratory scale, so it did not involve any economic analysis for the gasification. In addition, the experiment did not include neither quantitative nor qualitative analysis of the output gas. Only SCM, RPM, and VM were used to evaluate the kinetic parameters.

Conclusion. The kinetics of *Theobroma cacao* pod husks (CPH) was investigated. Proximate analysis and kinetic parameters suggest that the gasification of a CPH-sub-bituminous-coal (SBC) mixture is a viable alternative energy source to that of pure coal. The kinetic models that were used in this study are the Volumetric Model (VM), Shrinking Core Model (SCM), and Random Pore Model (RPM), which were chosen based on the type of feedstock used. Plots of the kinetic reaction models suggest that the RPM is the best fit model according to the coefficient of effectiveness (R^2), suggesting that the mechanism of reaction has two opposing structural changes: growth and coalescence of the pores resulting in the reduction of area due to pore overlaps. However, there was no significant difference found between the blends in RPM. Therefore, the only viable basis for efficiency is the proximate analysis which is reflective of the rate constants (k) and activation energy (E_a). Among the blends, 75%-25% CPH-SBC showed the highest efficiency in terms of its proximate analysis, specifically its amount of fixed carbon and ash content with implications of better biomass to biogas conversion of the sample blend, and its activation energy of 93.945 kJ. This can be used as a guide in the design of an efficient gasifier or reactor system.

Recommendations. Smaller interval of gasification temperature (50°C) is recommended in order to study the rate limiting behavior as it could affect the gaseous reaction of the gasification. Since great variability is shown in the ash content, it is also recommended to have the blends gasified at lower temperature, as it may yield better results. It is also recommended to run an ash analysis in order to determine the composition of the ash. As well as a gas analysis to determine the different products formed during the gasification. Determining the synergistic effect when combined with other grades of coal is also recommended because sub-bituminous coal is only a fourth-grade type of coal. There are higher grades of coal which have higher carbon and fewer moisture, volatile matter, and ash.

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