

*Article*

## Comparison of Kinetic Models for CO<sub>2</sub> Gasification of Coconut-Shell Chars: Carbonization Temperature Effects on Char Reactivity and Porous Properties of Produced Activated Carbons

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**Abstract.** Solid chars were prepared from coconut shell at different carbonization temperatures in the range from 250-750°C and gasified in a thermogravimetric analyzer under the atmosphere of carbon dioxide at 850°C. The kinetic analysis showed an accelerating increasing of char conversion with reaction time, indicating an increase in the instantaneous gasification rate as the reaction proceeded. Four kinetic models for gas-solid reactions including, the volume- reaction model (VRM), the shrinking-core model (SCM), the random-pore model (RPM) and the modified volume-reaction model (MVRM) were tested against the measured kinetic data and the MVRM was found to predict the gasification kinetics most accurately. The char reactivity index was computed from the apparent rate constant of the MVRM and used to assess the reactivity of char towards carbon dioxide gasification. It was found that the char reactivity index decreased with increasing carbonization temperature, with the char produced at the lowest temperature of 250°C giving the highest reactivity. Surface area of activated carbon, produced from the gasification of various chars at 850°C for 60 and 120 min, correlated well with the char reactivity index, showing a proportional increasing of surface area with increasing reactivity index and passing through a maximum near the reactivity index of 0.02 min<sup>-1</sup>.

**Keywords:** Activated carbon, carbonization temperature, char reactivity, coconut shell char, gasification kinetic models.

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## 1. Introduction

Activated carbon is widely used in the separation and purification processes for both liquid and gas systems. It is commonly prepared by a two-step process, consisting of converting a carbonaceous precursor into solid char in an inert atmosphere, followed by activating (gasifying) the resulting char with an oxidizing agent such as carbon dioxide and steam. Char properties as affected by the time and temperature of carbonization as well as the conditions of activation used has a direct influence on the quality and porous structure of activated carbon being produced. There have been numerous investigations reporting on the effect of time and temperature of activation step on the porous and adsorptive properties of activated carbons prepared from a variety of raw materials [1-7]. On the other hand, the effect of carbonization condition on textural properties of activated carbons has received lesser attention [8-10]. Furthermore, there have been almost no studies on the effect of carbonization temperature on the gasification kinetics of biomass chars during activated carbon production. This kinetic information is of particular importance to the proper selection of carbonization condition as well as the logical design of a reactor for the subsequent char activation process.

Some previous works on the effect of carbonization condition on the gasification kinetics and porous texture of activated carbons are briefly presented as follows. Tancredi *et al.* [11] studied the CO<sub>2</sub> gasification of eucalyptus wood chars carbonized at 400-800°C in isothermal and non-isothermal TG experiments. Char reactivity was found to decrease with increasing carbonization temperature. In addition, the char reactivity appeared to increase linearly with char conversion up to the value of about 0.7, which was attributed to the corresponding increasing in the development of surface area. At higher conversion values, a sharp increase in the reactivity was observed which was hypothesized to result from the increasing catalytic effect of the metallic components (mainly Na and K) present in the chars. No attempt was made, however, to try to analyze the kinetic data using the available gasification kinetic models. Kumar and Gupta [12] found in their study that both the reactivity and activation energy for CO<sub>2</sub> gasification of acacia and eucalyptus wood chars were strongly influenced by the carbonization conditions, including temperature (800 and 1000°C), heating rate and soaking time. The reactivities of both chars decreased with increasing preparation temperature and slow carbonization, while the activation energy for their gasification increased. Wan Duad *et al.* [8] investigated the effect of carbonization temperature on pore development in activated carbon of palm shell by activating chars prepared at 500, 800 and 900°C in steam-N<sub>2</sub> mixture. It was discovered that char prepared at a high temperature gave higher micropore volume. For all chars, the micropore volume increased with increasing char burn-off and passed through a maximum at 40% burn-off. The drop in micropore volume at higher burn-off corresponded to the proportional increase in the mesopore volume. Similar results were obtained from the work of Li *et al.* [10] who reported that over the carbonization temperature from 400-1000°C, steam-activated carbon prepared from high temperature carbonized coconut shell char had higher BET surface area, total pore volume, micropore volume and yield as compared to those of low temperature carbonized char.

Since most of previous investigations have concentrated on the effect of high temperature range of carbonization, it is thus the purpose of this work to investigate CO<sub>2</sub> gasification kinetics of coconut shell chars having differing reactivities obtained by producing chars over a rather low carbonization temperature range from 250 to 750°C. The kinetic data of these gasified chars were collected by following the char residual weight in a thermogravimetric analyzer (TGA) as a function of heating time and various kinetic models tested. In addition, attempt was also made to correlate the char reactivity with porous properties of activated carbons produced from a laboratory tube furnace.

## 2. Experimental

### 2.1. Raw Material Characterization

Coconut shell in large pieces was crushed and sieved to obtain an average particle size of 1 mm (16 x 20 mesh screen fraction). The sieved sample was further dried at 120°C for 24 hours in an oven to remove excess moisture and kept for subsequent analysis. The pre-dried sample was characterized for true density using a helium pycnometer (AccuPyc 1330 Micromeritics), heating value using a bomb calorimeter, elemental analysis with CHNO analyzer (Perkin Elmer PE2400 series II) and proximate analysis using a thermogravimetric analyzer (SDT 2960 simultaneous DSC-TGA model, TA Instruments) and the

measurement scheme proposed in the literature [13]. Thermal decomposition behavior of the raw coconut shell was also determined by the thermogravimetric analyzer for a non-isothermal heating mode at 5°C/min to the final temperature of 750°C using nitrogen flow rate of 100 cm<sup>3</sup>/min.

## 2.2. Preparation of Char and Activated Carbon

For each run, 20 grams of coconut shell sample (average size of 1 mm) was loaded into a ceramic boat and heated from room temperature to the final carbonization temperature (250-750°C) at 5°C/min in a tube furnace (Carbolite, UK) under a constant flow of nitrogen (100 cm<sup>3</sup>/min) and kept at the desired temperature for 2 hours. The char obtained was cooled down inside the furnace to the ambient temperature under the flow of nitrogen. Next, 5 grams of each char produced from the carbonization step was thinly dispersed on a wire-mesh boat and activated in the same furnace by first heating the sample to the final activation temperature of 850°C at the rate of 5°C/min under nitrogen flow of 100 cm<sup>3</sup>/min. Then, the gas was switched to CO<sub>2</sub> flowing at a rate of 100 cm<sup>3</sup>/min and the system was held at this temperature for 60 and 120 min. Surface area and pore volume of activated carbon produced were determined from the isotherm data of nitrogen adsorption at -196°C as measured by an automated adsorption equipment (ASAP 2010, Micromeritics). Details of calculating porous properties of the prepared activated carbons are reported elsewhere [2, 14]. It should be noted that the char particle size was assumed to be that of the raw coconut shell, that is, 1 mm in average size. This is to assume that there was no shrinkage of char particles during the heat treatment both during the carbonization step and in the TGA.

## 2.3. Gasification Kinetic Study

The gasification kinetics of coconut shell char with carbon dioxide was investigated in a thermogravimetric analyzer (TGA). About 30 mg of char sample prepared at a specified carbonization temperature in a tube furnace was loaded into an alumina pan of the analyzer. The heating program of the char sample was chosen to simulate that of activation step used for activated carbon production in the tube furnace previously explained. That is, the char sample was first heated at a fixed heating rate of 5°C/min from room temperature to 850°C under a constant flow of nitrogen (100 cm<sup>3</sup>/min). Then, the purge gas was automatically switched from nitrogen to carbon dioxide flowing at 100 cm<sup>3</sup>/min and the temperature was maintained at 850°C for 120 min. The weight remaining of char during the flow of nitrogen and carbon dioxide was monitored continuously as a function of heating time. The repeatability of TGA data was found to be acceptable with the maximum deviation being less than 3% when one set of the analysis was performed on triplicate samples of the same char.

Since the primary purpose of this work was to investigate the effect of char reactivity on CO<sub>2</sub> gasification kinetics by varying the carbonization temperature, only one gasification temperature of 850°C was studied at this stage. An intermediate gasification temperature of 850°C was employed because the fractional char conversion close to unity could be achieved for all the gasified chars over a reasonable time period of 120 min. Pure carbon dioxide was chosen as a gasifying agent to exclude the effect of gas partial pressure on the rate of reaction.

## 3. Results and Discussion

Table 1 shows the basic physical properties and compositions of coconut shell studied. Proximate and ultimate analysis indicates that the main composition of coconut shell is volatile content with relatively low fixed carbon and ash, and carbon and oxygen are the major chemical elements. Figure 1 shows plots of TG data and its first derivative (DTG) of the raw coconut shell. The weight loss due to pyrolysis in N<sub>2</sub> takes place rapidly over the temperature from 200-400°C caused by the release of most volatile substances and then followed by a slow decrease of weight remaining, giving the final solid yield of about 26% at 750°C. It is also noted that there are two distinct peaks of the DTG curve with the two maximum of decomposition rates occurring at 280°C and 350°C, respectively. It is known that the major components of biomass are lignin, hemicellulose and cellulose [15]. Lignin decomposes first at a lower rate over the broad temperature range from 200-800°C. Hemicellulose decomposes at the low temperature region between 200-360°C, while cellulose decomposes at the higher temperature range of 240-400°C [16]. The two peaks characteristic of DTG curve for coconut shell has been explained to result from the decomposition and interaction

behaviors of its lignocellulosic components, consisting of 46% lignin, 32% hemicellulose and 14% cellulose [17].

Table 1. Physical and chemical analysis of coconut shell used in the present study.

<b>Proximate Analysis (Dry Basis) (wt%)</b>	
Volatile matter	82.38
Fixed carbon	16.33
Ash	1.29
Ultimate Analysis (wt%)	
Carbon	49.75
Hydrogen	5.60
Oxygen	44.30
Nitrogen	0.35
Calorific value (MJ/kg)	21.28
True density (g/cm <sup>3</sup> )	1.421
Average particle size (mm)	1.00

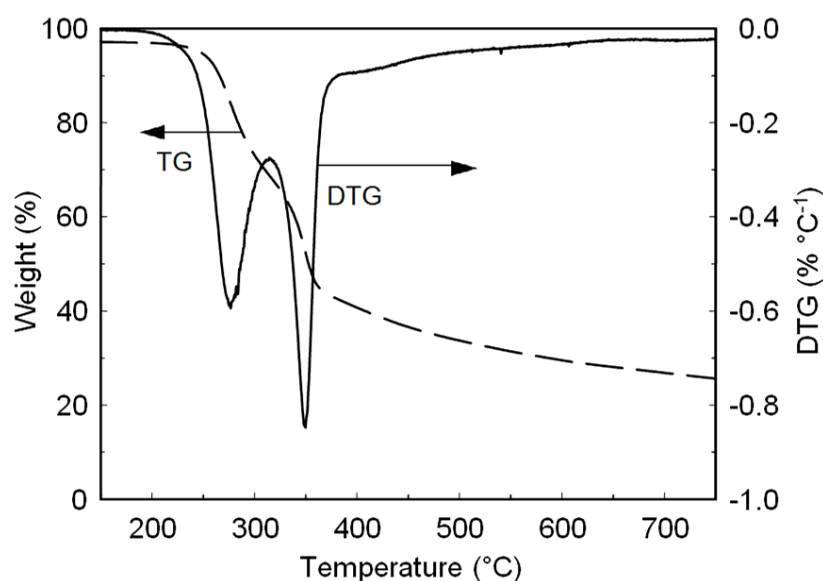


Fig. 1. TGA and DTG data of raw coconut shell.

On the gasification kinetic study, Fig. 2 shows the TGA data of time-residual weight of chars prepared at various carbonization temperatures in the tube furnace. The TGA heating program consisted of heating char in N<sub>2</sub> (pyrolysis) from room temperature to the final activation (gasification) temperature of 850°C at 5°C/min and held at this temperature for another 120 min. in a stream of CO<sub>2</sub>. It is seen that the pyrolysis step continued for about 160 min. and followed by a sharp drop of weight remaining during the gasification by CO<sub>2</sub>. No temperature fluctuation was observed at the transition from the pyrolysis mode to the char gasification mode. Also noted from Fig. 2, due to the reheating of the initial chars during the pyrolysis step, the weight loss upon gasification of char prepared at a lower carbonization temperature was higher than that of char produced at a higher carbonization temperature.

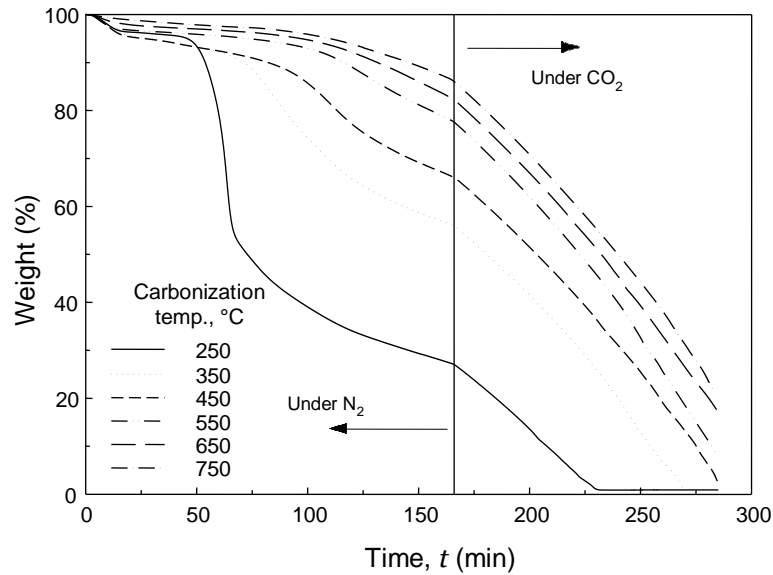


Fig. 2. TGA data of coconut shell chars produced at various carbonization temperatures, heating in  $N_2$  from room temperature to the final gasification temperature of  $850^\circ C$  in  $CO_2$ .

Based on the derived TGA data, the fractional char conversion ( $X$ ) for gasification with  $CO_2$  in a thermogravimetric analyzer was calculated based on the following defining equation,

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

where  $W_0$ ,  $W$  and  $W_{ash}$  are the initial weight of char prior to gasification, weight of char at time  $t$ , and the weight of ash in the char sample, respectively. Figure 3 shows the variation of char conversion with time for chars prepared from carbonizing coconut shell at different temperatures from  $250$ - $750^\circ C$  for 2 hours. It is seen that the conversion-time relation was not linear but showed a characteristic of increasing slope of the curve with time, with the degree of curvature tending to decrease with increasing carbonization temperature.

If the mass transfer resistances through an external fluid film and within the porous particle can be neglected, the overall rate of a gas-solid reaction is totally controlled by the chemical reactivity of the solid surface. A general expression for the char- $CO_2$  gasification rate can be represented by

$$\frac{dX}{dt} = kf(X) \quad (2)$$

where  $k$  is the apparent reaction rate constant ( $time^{-1}$ ) which is dependent on reaction temperature and partial pressure of  $CO_2$ , and  $f(X)$  is a function representing the structural change of char during the course of gasification reaction.

There are four models that are commonly employed in describing the kinetics of a gas-solid reaction namely, the volume-reaction model (VRM) [18], the shrinking-core model (SCM) [19], the random-pore model (RPM) [20] and the modified volume-reaction model (MVRM) [21]. Table 2 gives a brief description of these four kinetic models. The linear forms of these kinetic models, which can be used to obtain the kinetic parameters from experimental data, are as follows:

For VRM: 
$$-\ln(1 - X) = k_V t \quad (3)$$

For SCM: 
$$3[1 - (1 - X)^{1/3}] = k_S t \quad (4)$$

For RPM: 
$$(2/\psi) \left[ \sqrt{(1 - \psi \ln(1 - X))} - 1 \right] = k_R t \quad (5)$$

For MVRM: 
$$-\ln(1 - X) = k(X)t \quad (6)$$

In this work, these models were tested against the kinetic data ( $X$  vs.  $t$ ) for all the chars studied. It should be noted, however, that the modified volume-reaction model (MVRM) cannot be directly applied to fit the gasification kinetic data in the present work. This model, based purely on empirical observation, accounts for the variation of the apparent rate constant with conversion by introducing an empirical equation relating the conversion with time in the form,

$$X = 1 - \exp(-at^b) \quad (7)$$

However, this previously proposed equation cannot describe our conversion data correctly for it predicts the conversion-time curve with decreasing slope at a high conversion range. It was found, as Fig. 3 shows, that the measured kinetic data in this work can be well described by a simple power-law equation,

$$X = at^b \quad (8)$$

Therefore, Eq. (8) was adopted here and used for the analysis of gasification kinetic data with the MVRM.

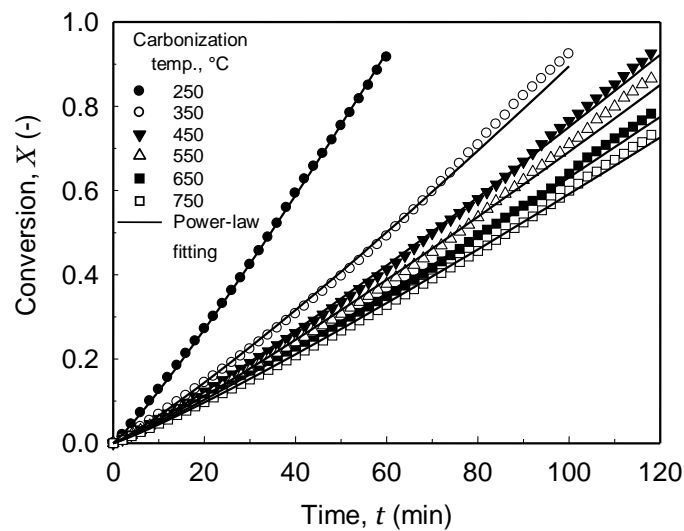


Fig. 3. Effect of reaction time on the conversion of coconut shell chars gasified in  $\text{CO}_2$  at  $850^\circ\text{C}$ .

Table 2. Summary of gas-solid reaction kinetic models for reaction-controlled regime.

Model	Assumption	Rate Equation	Conversion Equation
Volume Reaction (VRM)	Homogeneous reaction of a reactant solid	$\frac{dX}{dt} = k_V(1-X)$	$X = 1 - \exp(-k_V t)$
Shrinking Core (SCM)	Shrinking core of nonporous grains as reaction proceeds	$\frac{dX}{dt} = k_S(1-X)^{2/3}$	$X = 1 - (1 - k_S t/3)$
Random Pore (RPM)	Creating and overlapping of pore surfaces as reaction progresses	$\frac{dX}{dt} = k_R(1-X)[1 - \psi \ln(1-X)]^{1/2}$	$X = 1 - \exp\{[1 - (1 + k_R \psi t/2)^2]/\psi\}$
Modified Volume-Reaction (MVRM)	Apparent rate constant changes with solid conversion	$\frac{dX}{dt} = k(X)(1-X)$	$X = 1 - \exp(-k(X)t)$

Next, the rate equation of the MVRM can be written as

$$\frac{dX}{dt} = k(X)(1-X) \quad (9)$$

where  $k(X)$  is the apparent rate constant that changes with reaction conversion. Now, differentiating Eq. (8) with respect to time, we obtain the instantaneous reaction rate as

$$\frac{dX}{dt} = abt^{b-1} \quad (10)$$

Combining Eqs. (8)-(10) gives the apparent rate constant to be a function of conversion, thus

$$k(X) = \frac{a^{1/b} b X^{(b-1)/b}}{(1-X)}, \quad X \neq 1 \quad (11)$$

Since for the MVRM the apparent rate constant varies with conversion as the gasification progresses, an average value of  $k(X)$  is therefore defined as in Eq. (12) to represent the reactivity of reacting char towards gasification reaction and is termed *the char reactivity index* ( $k_m$ ). Therefore

$$k_m = \int_0^X k(X) dX = \int_0^X \frac{a^{1/b} b X^{(b-1)/b}}{(1-X)} dX, \quad X \neq 1 \quad (12)$$

To obtain the numerical value of  $k_m$ , Eq. (12) is integrated from  $X = 0$  to a hypothetical value of  $X = 0.99$  so that Eq. (12) becomes

$$k_m = a^{1/b} b \int_0^{0.99} \frac{X^{(b-1)/b}}{(1-X)} dX, \quad X \neq 1 \quad (13)$$

As the gasification proceeds simultaneously with the creation of internal pores of activated carbon, it is difficult to assess the relative effect of mass transport on the rate of surface reaction. The reacting  $\text{CO}_2$  will transport rather readily in large pores, but will diffuse at a slower rate in smaller micropores which contribute most of the solid surface area. Reducing particle size may not eliminate entirely the resistance of pore diffusion unless the particle is extremely small and operating the gasification at a high temperature

would lower the intra-particle mass transfer resistance to a certain extent [22]. As a result of this complicating effect, the kinetic parameters derived from the application of various kinetic models should be considered as apparent values that are valid under the conditions studied, for example, the type of precursor, particle size, heating rate, gasification temperature, etc. However, there has been ample evidence that internal mass transfer resistance could be neglected for particle size smaller than 0.5-1.0 mm [21, 23]. Therefore, the gasification of char particles with 1 mm in size used in this study could be assumed to be in reaction-controlled regime.

Figure 4 illustrates the linear plots of the four gasification kinetic models in comparison with the experimental kinetic data, from which the model parameters were estimated. It should be noted that the linear relationship of the MVRM as shown in Fig. 4(d) was obtained from Eq. (8) by taking natural logarithm on both sides to give,  $\ln[X] = \ln[a] + b\ln[t]$ . Table 3 lists the fitted kinetic parameters of the four models obtained by a linear regression analysis for coconut shell chars prepared at different carbonization temperatures, along with the value of regression coefficients ( $R^2$ ). The accuracy of model prediction can be assessed by computing the standard error of estimate (SEE),  $\sigma_{est}$ , defined by the following equation [24],

$$\sigma_{est} = \sqrt{\frac{\sum_{i=1}^N [(X_{pred} - X_{exp}) / X_{pred}]^2}{N - 2}} \quad (14)$$

where  $X_{pred}$  and  $X_{exp}$  are the model predicted and experimental char conversion, respectively, and  $N$  is the number of data points of conversion( $X$ )-time( $t$ ) data. Table 4 compares the values of SEE for the four kinetic models tested.

Based on the values of regression coefficients ( $R^2$ ) in Table 3 and SEE in Table 4, it is noted that the experimental kinetic data for coconut-shell char gasification with  $\text{CO}_2$  at  $850^\circ\text{C}$  are best described by the MVRM and the order of increasing predictive capability of the models is,  $\text{VRM} < \text{SCM} < \text{RPM} < \text{MVRM}$ . The validity of these kinetic models is further observed by comparing the intrinsic gasification rates from experiments and model prediction for the typical char carbonized at  $250^\circ\text{C}$ , as depicted in Fig. 5. Both the VRM and SCM failed to give the correct trend of experimental reaction rate as a function of char conversion. As expected, these two models predict a continued decreasing of the rate as reaction proceeds due to the progressive reduction of solid surface area which is the basic assumption inherent with these two models. The RPM, which takes into account the effect of pore creation and coalescence of neighboring pores during the course of gasification, gave better improved prediction and showed a maximum of reaction rate at the conversion around 0.4. Again, the MVRM gave the best estimation of reaction rates that was consistent with the experimental results, showing a rapid initial increase of reaction rate followed by an almost linear increasing of the rate up to the conversion of around 0.9. The linear increasing of gasification rate with increasing char conversion should result from the proportionally increasing in surface area of the reacting char as reaction proceeds. This implies that the concentration of active sites (number per unit surface area) available for the reaction, resulting from plane defects, unpaired electrons or the presence of hetero-atoms on the carbon surface, should be relatively constant irrespective of increasing char conversion.



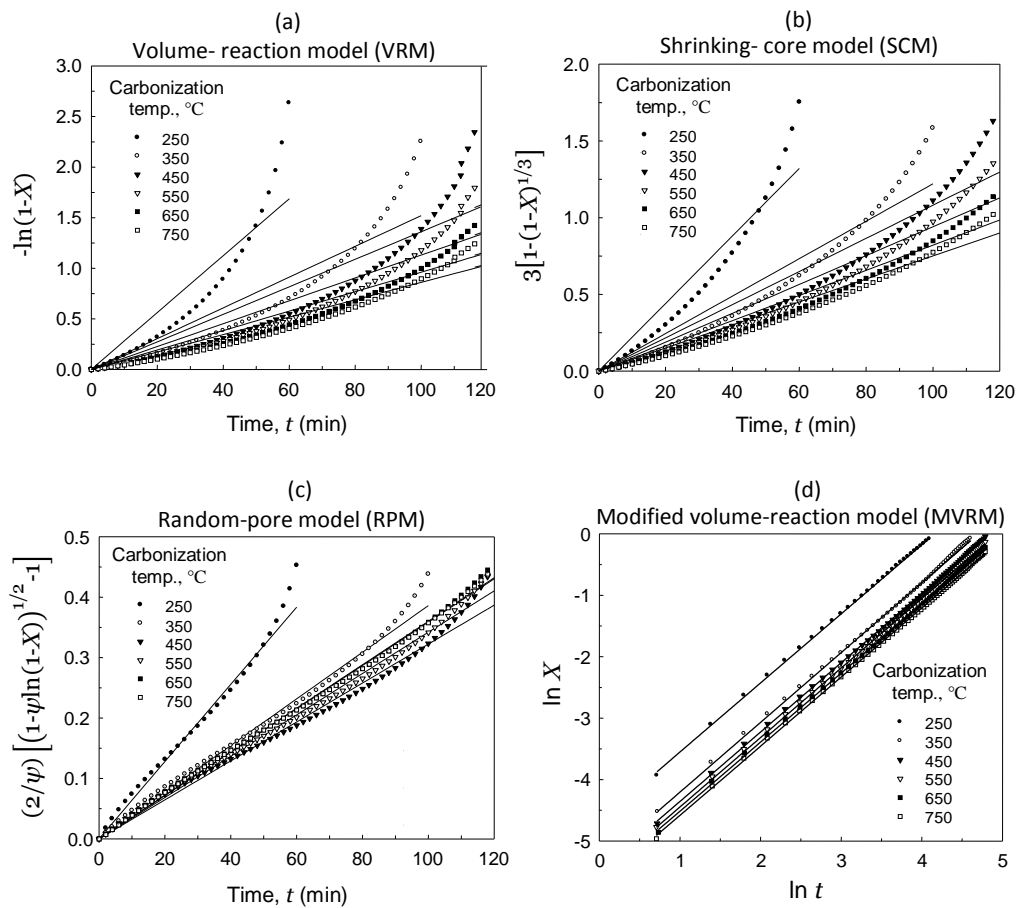


Fig. 4. Testing of gasification kinetic models with experimental kinetic data.

Table 3. Fitted parameters of gasification kinetic models for coconut shell chars produced at different carbonization temperatures.

Carbonization Temperature (°C)	VRM		SCM		RPM			MVRM			
	$k_V$ (min <sup>-1</sup> )	$R^2$	$k_S$ (min <sup>-1</sup> )	$R^2$	$k_R$ (min <sup>-1</sup> )	$\psi$	$R^2$	$a$	$b$	$k_m$ (min <sup>-1</sup> )	$R^2$
250	0.0281	0.8224	0.0220	0.9091	0.0066	42.6	0.9827	0.00930	1.124	0.0847	0.9991
350	0.0152	0.8526	0.0122	0.9211	0.0039	37.8	0.9895	0.00478	1.136	0.0474	0.9992
450	0.0136	0.8327	0.0108	0.9129	0.0033	40.8	0.9853	0.00415	1.129	0.0405	0.9995
550	0.0113	0.8810	0.0094	0.9348	0.0035	28.7	0.9939	0.00377	1.132	0.0371	0.9991
650	0.0096	0.9129	0.0082	0.9509	0.0036	19.9	0.9974	0.00355	1.125	0.0339	0.9996
750	0.0086	0.9267	0.0075	0.9577	0.0036	16.9	0.9984	0.00331	1.126	0.0323	0.9997

Table 4. Standard error of estimate (SEE) for testing the accuracy of kinetic model prediction.

Char Sample (Carbonization Temp., °C)	Number of Data Points ( <i>N</i> )	Standard Error of Estimate ( $\sigma_{est}$ )			
		VRM	SCM	RPM	MVRM
250	41	0.326	0.259	0.129	0.017
350	51	0.326	0.266	0.132	0.031
450	61	0.331	0.269	0.137	0.022
550	61	0.308	0.256	0.099	0.037
650	61	0.277	0.229	0.071	0.021
750	61	0.264	0.221	0.055	0.022

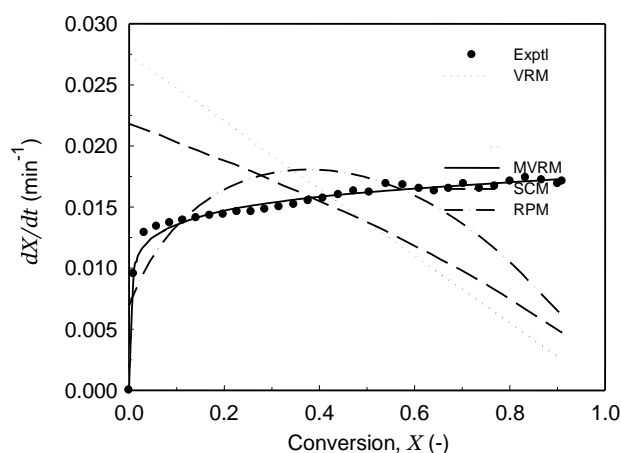


Fig. 5. Typical comparison between measured gasification rates of coconut shell char and those predicted by various kinetic models, for char produced at carbonization temperature of 250°C for 2 hours.

Figure 6 shows the variation of  $k(X)$  of the MVRM, calculated by Eq. (11), with char conversion ( $X$ ) for all the char samples studied. In general, the results show that the apparent or instantaneous rate constant increased with conversion and the rate of increase (slope of the curve) appeared to be more pronounced over a high conversion region, say for  $X > 0.4$ . In addition, the char produced at a lower temperature gave a higher rate constant for a given char conversion. The effect of carbonization temperature on the char reactivity index,  $k_m$ , is shown plotted in Fig. 7. As seen, increasing carbonization temperature from 250 to 750°C produced char with decreased chemical reactivity towards  $\text{CO}_2$  gasification, with the char prepared at the lowest temperature of 250°C giving the highest reactivity. To examine further, three char samples prepared at 250, 450 and 750°C were heated from room temperature to the gasification temperature of 850°C in a tube furnace at 5°C/min in an inert atmosphere of nitrogen. Then, the furnace was turned off and cooled down to ambient temperature under the nitrogen flow. The sample products obtained were further subjected to air oxidation at 300°C for the period of 24 hours. The amounts of total functional groups formed on the char surface, consisting of acidic and basic groups, were determined quantitatively using Boehm's titration method [25], and used to indirectly assess the reactivity of char prior to  $\text{CO}_2$  gasification. That is, the higher the amount of surface functional groups, the higher the char reactivity. As shown in Fig. 7, the change in surface group concentration with respect to carbonization temperature followed the same pattern as that of char reactivity index, thus confirming the significance of carbonization temperature level in affecting the reactivity of char for the subsequent gasification reaction.

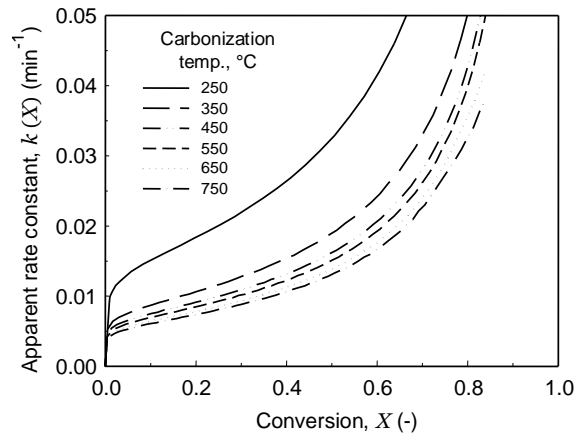


Fig. 6. Effect of char conversion on the calculated apparent rate constant of MVRM for chars prepared at various carbonization temperatures.

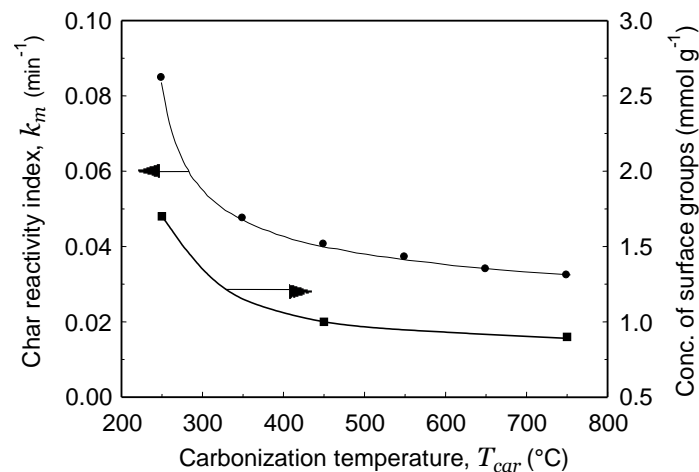


Fig. 7. Effect of carbonization temperature on char reactivity index ( $k_m$ ) and amount of surface functional groups of char prior to  $\text{CO}_2$  gasification at  $850^\circ\text{C}$ .

Porous properties of chars at the onset of gasification step were also determined, and it was found that both the surface area and pore volume of various chars were not greatly different varying from 500-550  $\text{m}^2/\text{g}$  and 0.24-0.26  $\text{cm}^3/\text{g}$ , respectively. From these data, it may be deduced that carbonization temperature has a direct influence on the chemical structure of char through the thermal decomposition of chemical components in biomass, with hemicellulose probably being the most reactive component [26]. This structural change would affect, to a greater extent, the type and number of active sites, giving solid chars with varying surface reactivities towards the gasification reaction. The highest reactivity of coconut shell char prepared at  $250^\circ\text{C}$  emphasizes the need to devolatilize this biomass in a low temperature region which falls fortuitously within the first peak of the DTG curve (see Fig.1). This inference is in accord with a recent technology known as *torrefaction* which is a mild pyrolysis treatment carried out in the low temperature range of  $200\text{-}300^\circ\text{C}$  to improve biomass properties for subsequent gasification and combustion processes [26].

The study of gasification kinetics for the most reactive char ( $T_{car} = 250^\circ\text{C}$ ) was also performed at 800 and  $900^\circ\text{C}$  and the calculated char reactivity index ( $k_m$ ) had the values of 0.0614 and  $0.1397 \text{ min}^{-1}$ , respectively. The effect of gasification temperature, in the range from  $800\text{-}900^\circ\text{C}$ , on the char reactivity index was then correlated via the well-known Arrhenius equation,

$$k_m = k_0 \exp\left(-E/R_g T\right) \quad (15)$$

where  $k_0$  is the pre-exponential factor,  $E$  is the activation energy,  $R_g$  is the universal gas constant, and  $T$  is the absolute temperature. The linear form of the equation is shown plotted in Fig. 8 for parameter estimation. By linear regression, the values of  $k_0$  and  $E$  were found to be  $820 \text{ min}^{-1}$  and  $20.25 \text{ kcal/mol}$  (or  $84.8 \text{ kJ/mol}$ ), respectively.

Further attempt was also made to find the correlation between the char reactivity index and porous properties of some activated carbons produced by  $\text{CO}_2$  gasification. Two series of experiments were carried out by activating various chars at  $850^\circ\text{C}$  for 60 and 120 min. under the flow of carbon dioxide. The char reactivity index ( $k_m$ ) for each activated carbon produced was estimated from Eq. (12) and Eq. (8), knowing the activation time ( $t$ ) and values of the kinetic model constants ( $a$  and  $b$ ) for each char, as listed in Table 3. Table 5 lists the values of char conversion ( $X$ ) calculated from Eq. (8), char reactivity index ( $k_m$ ) calculated by integrating Eq. (12) up to the value of calculated  $X$ , along with the corresponding porous properties of derived activated carbons. The plotted results obtained from Table 5, as shown in Fig. 9, shows that surface area of activated carbon increased with increasing  $k_m$  and passed through a maximum at  $k_m$  around  $0.02 \text{ min}^{-1}$ . Since  $k_m$  can be alternatively considered as a measure of reaction extent, this type of correlation is found to resemble that of surface area versus char burn-off, as reported in the literature for many different biomasses [27-29]. Figure 9 further shows that for  $k_m$  smaller than  $0.02 \text{ min}^{-1}$ , both total pore volume and micropore volume increased with increasing char reactivity. However, at higher  $k_m$  a slight drop in micropore volume was observed, whereas the total pore volume was still rising. This implies that for a relatively high reactivity index (correspondingly high char conversion), new micropores are still created but more mesopores are also formed at the expense of micropores [28]. Therefore, the small decrease in carbon surface area for a twofold increase in the reactivity from  $0.02$  to about  $0.04 \text{ min}^{-1}$  is ascribed to the coalescence of adjacent micropores at a high reactivity index, giving less surface area per unit mass of activated carbon.

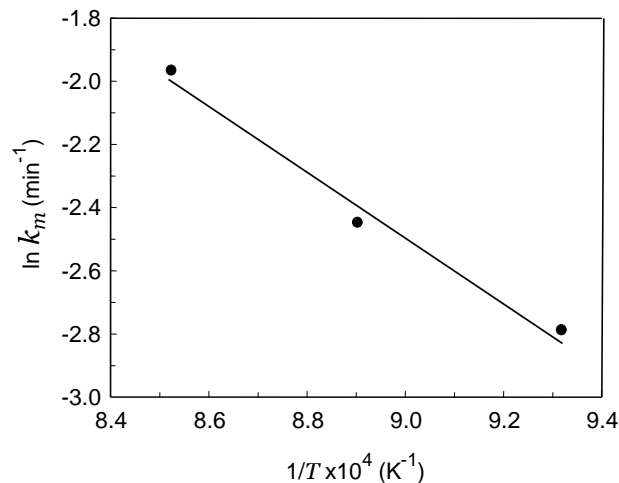
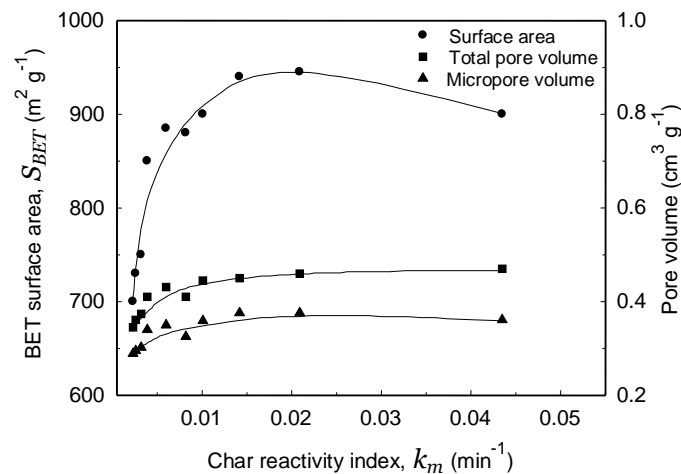


Fig. 8. Arrhenius plot of char reactivity index ( $k_m$ ) for  $\text{CO}_2$  gasification of char prepared at carbonization temperature of  $250^\circ\text{C}$ .

Table 5. Correlation between char reactivity index and porous properties of produced activated carbons.

Carbonization Temperature (°C)	Activation Temperature (°C)	Activation Time (min)	Calculated Conversion, $X$ (-)	Char Reactivity Index, $k_m$ (min <sup>-1</sup> )	$S_{BET}$ (m <sup>2</sup> /g)	$V_{mic}$ (cm <sup>3</sup> /g)	$V_{mes}$ (cm <sup>3</sup> /g)	$V_T$ (cm <sup>3</sup> /g)
250	850	60	0.927	0.0435	900	0.360	0.111	0.471
350	850	60	0.500	0.0060	885	0.351	0.080	0.431
450	850	60	0.422	0.0039	850	0.340	0.070	0.410
550	850	60	0.388	0.0032	750	0.302	0.072	0.374
650	850	60	0.355	0.0026	730	0.295	0.066	0.361
750	850	60	0.333	0.0023	700	0.289	0.056	0.345
450	850	120	0.924	0.0209	945	0.384	0.076	0.460
550	850	120	0.851	0.0142	940	0.376	0.074	0.450
650	850	120	0.775	0.0101	900	0.359	0.086	0.445
750	850	120	0.726	0.0082	880	0.325	0.086	0.411

Fig. 9. Relationship between char reactivity index ( $k_m$ ) and porous properties of coconut shell char gasified at 850°C with CO<sub>2</sub>.

#### 4. Conclusions

The CO<sub>2</sub> gasification kinetics of coconut shell chars, prepared at various carbonization temperatures in the range of 250-750°C, was studied in a thermogravimetric analyzer by following the sample weight remaining as a function of time at a fixed temperature of 850°C. The kinetic analysis showed that coconut-shell char conversion increased with increasing reaction time such that the gasification rate increased with the extent of reaction. Of the various kinetic models tested, the modified volume-reaction model (MVRM), coupled with a power-law equation for describing the conversion-time data, was found to best predict the gasification kinetics of coconut shell chars. Due to the increasing apparent rate constant of the MVRM with conversion, the char reactivity index was defined as the conversion-averaged value of the rate constant up to fractional conversion of 0.99 and was used to represent the reactivity of each respective char. Based on this reactivity index, it was found that the reactivity of char towards carbon dioxide gasification decreased with increasing carbonization temperature, with the char prepared at the lowest carbonization of 250°C giving notably the highest reactivity. It was presumed that thermal decomposition at this low temperature region could promote a large number of surface active sites, resulting possibly from the thermal decomposition of hemicellulose, which is the most reactive chemical component in biomass. The char reactivity index correlated well with porous properties of activated carbon produced from the char gasification, showing the maximum in surface area at the reactivity index of 0.02 min<sup>-1</sup>. The drop in surface area at higher reactivity index is due possibly to the merging of neighboring micropores. To generate more useful kinetic information, it is recommended that the kinetic experiments be further performed to cover a

broad range of gasification temperatures, say from 800-1000°C for all chars, so that a general correlation could be developed that enables the prediction of char reactivity as a function of both carbonization and gasification temperatures.

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## References

- [1] A. Aygun, S. Yenisoy-Karakas, and I. Duman, "Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties," *Micropor. Mesopor. Mater.*, vol. 66, 189-195, 2003.
- [2] Y. Ngernyen, C. Tangsathitkulchai, and M. Tangsathitkulchai, "Porous properties of activated carbon produced from eucalyptus and wattle wood by carbon dioxide activation," *Korean J. Chem. Eng.*, vol. 23, 1046-1054, 2006.
- [3] G. Chattopadhyaya, D. G. Macdonald, N. N. Bakhshi, J. S. Soltan, and A. K. Dalai, "Preparation and characterization of chars and activated carbons from Saskatchewan lignite," *Fuel Proc. Tech.*, vol. 87, 997-1006, 2006.
- [4] J. F. Gonzalez, J. M. Encinar, C. M. Gonzalez-Garcia, E. Sabio, A. Ramiro, J. L. Canito, and J. Ganan, "Preparation of activated carbons from used tyres by gasification with steam and carbon dioxide," *Appl. Surf. Sci.*, vol. 252, 5999-6004, 2006.
- [5] C. Bouchelta, M. S. Medjram, O. Bertrand, and J. P. Bellat, "Preparation and characterization of activated carbon from date stones by physical activation with steam," *J. Anal. Appl. Pyrol.*, vol. 82, 70-77, 2008.
- [6] K. Sun and J. C. Jiang, "Preparation and characterization of activated carbon from rubber-seed shell by physical activation with steam," *Biomass Bioenerg.*, vol. 34, 539-544, 2010.
- [7] W. H. Li, Q. Y. Yue, B. Y. Gao, Z. H. Ma, Y. J. Li, and H. X. Zhao, "Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions," *Chem. Eng. J.*, vol. 171, 320-327, 2011.
- [8] W. M. A. Wan Daud, W. S. Wan Ali, and M. Z. Sulaiman, "The effects of carbonization temperature on pore development in palm-shell-based activated carbon," *Carbon*, vol. 38, 1925-1932, 2000.
- [9] B. Cagnon, X. Py, A. Guillot, and F. Stoeckli, "The effect of the carbonization/activation procedure on the microporous texture of the subsequent chars and active carbons," *Micropor. Mesopor. Mater.*, vol. 57, 273-282, 2003.
- [10] W. Li, K. Yang, J. Peng, L. Zhang, S. Guo, and H. Xia, "Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars," *Ind. Crop. Prod.*, vol. 28, 190-198, 2008.
- [11] N. Tancredi, T. Cordero, J. Rodriguez-Mirasol, and J. J. Rodriguez, "CO<sub>2</sub> gasification of eucalyptus wood chars," *Fuel*, vol. 75, 1505-1508, 1996.
- [12] M. Kumar, and R. C. Gupta, "Influence of carbonization conditions on the gasification of acacia and eucalyptus wood chars by carbon dioxide," *Fuel*, vol. 73, 1922-1925, 1994.
- [13] A. C. Lua, and J. Guo, "Preparation and characterization of chars from oil palm waste," *Carbon*, vol. 36, 1663-1670, 1998.
- [14] C. Tangsathitkulchai, Y. Ngernyen, and M. Tangsathitkulchai, "Surface modification and adsorption of eucalyptus wood-based activated carbons: Effects of oxidation treatment, carbon porous structure and activation method," *Korean J. Chem. Eng.*, vol. 26, 1341-1352, 2009.
- [15] M. J. Antal, and G. Varhegyi, "Cellulose pyrolysis kinetics: The current state of knowledge," *Ind. Eng. Chem. Res.*, vol. 34, 703-717, 1995.
- [16] D. Vamvuka, E. Kakaras, E. Kastanaki, and P. Grammelis, "Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite," *Fuel*, vol. 82, 1949-1960, 2003.
- [17] B. Cagnon, X. Py, A. Guillot, F. Stoeckli, and G. Chambat, "Contributions of hemicellulose, cellulose and lignin to the mass and porous properties of chars and steam activated carbons from various lignocellulosic precursors," *Bioresour. Technol.*, vol. 100, 292-298, 2009.

- [18] M. Ishida, and C. Y. Wen, "Comparison of zone-reaction model and unreacted-core shrinking model in solid-gas reactions," *Chem. Eng. Sci.*, vol. 26, 1031-1041, 1971.
- [19] J. Szekeley, and J. W. Evans, "A structural model for gas-solid reactions with a moving boundary," *Chem. Eng. Sci.*, vol. 25, 1091-1107, 1970.
- [20] S. K. Bhatia, and D. D. Perlmutter, "A random pore model for fluid-solid reactions: I. Isothermal, kinetic control," *AIChE J.*, vol. 26, 379-386, 1980.
- [21] S. Kasaoka, Y. Sakata, and C. Tong, "Kinetics evaluation of the reactivity of various coal chars for gasification with carbon dioxide in comparison with steam," *Int. Chem. Eng.*, vol. 25, 160-175, 1985.
- [22] S. A. Scott, J. F. Davidson, J. S. Dennis, P. S. Fennell, and A. N. Hayhurst, "The rate of gasification by CO<sub>2</sub> of chars from waste," *Proc. Combust. Inst.*, vol. 30, 2151-2159, 2005.
- [23] M. F. Irfan, M. R. Usman, and K. Kusakabe, "Coal gasification in CO<sub>2</sub> atmosphere and its kinetics Since 1948: A brief review," *Energy*, vol. 36, 12-40, 2011.
- [24] D. M. Lane, "Standard error of the estimate," *Online Statistics Education: A Multimedia Course of Study, Ch. 14*, 2012. Available at: <http://onlinestatbook.com/2/regression/accuracy.html>
- [25] H. P. Boehm, "Some aspects of the surface chemistry of carbon blacks and other carbons," *Carbon*, vol. 32, 759-769, 1994.
- [26] M. J. C. Van der Stelt, H. Gerhauser, J. H. A. Kiel, and K. J. Ptasinski, "Biomass upgrading by torrefaction for the production of biofuels: A review," *Biomass Bioenerg.*, vol. 35, 3748-3762, 2011.
- [27] T. Yang, and A. C. Lua, "Characteristics of activated carbons prepared from pistachio-nut shells by physical activation," *J. Colloid Interface Sci.*, vol. 267, 408-417, 2003.
- [28] S. Junpirom, D. D. Do, C. Tangsathitkulchai, and M. Tangsathitkulchai, "A carbon activation model with application to longan seed char gasification," *Carbon*, vol. 43, 1936-1943, 2005.
- [29] J. V. Nabais, P. Carrott, M. M. L. Ribeiro Carrott, V. Luz, and A. L. Ortiz, "Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor," *Bioresour. Technol.*, vol. 99, 7224-7231, 2008.

