



Original Article

Kinetic thermal behaviour and evaluation of physical structure of sugar cane bagasse char during non-isothermal steam gasification

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ABSTRACT

In the current study, the steam gasification reactivity, thermal behaviour and activation energies of sugar cane bagasse (SCB) chars prepared at 500, 800 and 900 °C were investigated via thermogravimetric analyser (TGA) under non isothermal conditions at different heating rates of 10, 15 and 20 °C min⁻¹. The physical structures of SCB chars as a function of pyrolysis temperature have been studied by using Brunauer–Emmett–Teller (BET) surface area technique. The achieved results explore that the gasification of SCB chars took place almost completely in one-stage process. The char reactivity is directly proportional to gasification heating rate and inversely to the pyrolysis temperature. The pyrolysis temperature significantly affected on the physical char structures. The activation energies were estimated by Vyazovkin and Ozawa–Flynn–wall methods. The Vyazovkin and Flynn–Wall–Ozawa methods show mean activation energies of 131.20–141.61 kJ mol⁻¹ for SCB 5, 195.40–203.17 kJ mol⁻¹ for SCB 8 and 246.84–252.66 kJ mol⁻¹ for SCB 9. Finally, Vyazovkin and Ozawa–Flynn–Wall methods are efficiently utilized to predict the experimental data and the reaction mechanism of SCB chars steam gasification.

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1. Introduction

Biomass is one of the most environmentally friendly fuels. It is a potential renewable energy resources to replace the depletion of fossil-fuel have attracted attention [1], which

allows energy generation from biological, by-product material and agricultural residues such as sugar cane bagasse (SCB) [2,3]. In comparison to other agricultural residues, bagasse is considered as a rich solar energy reservoir due to its very high yields. Bagasse offers the advantage of being a cheap, plentiful and low polluting fuel. In addition, chemical energy

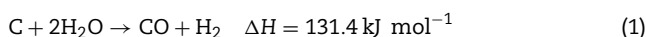
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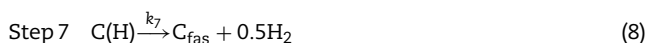
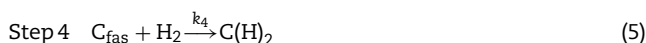
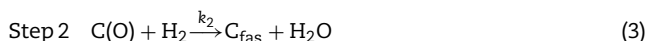
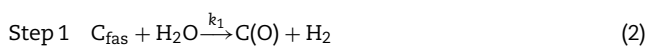
harvesting from bagasse is attractive since it is a renewable source of energy, and the combustion/gasification of sugarcane produces the same amount of CO₂ as it consumes during its growth so it has a neutral carbon [4]. By implementing thermo chemical upgrading of bagasse the energy efficiency can be increased significantly, resulting in energy saving and surplus energy products [5]. The biomass char is a solid carbonaceous residue with a high content of fixed carbon, which can be used as a potential resource in diverse industries, depending on their characteristics, directly as a fuel, fertilizer or precursor for activated carbon production, aluminium, copper, cement industries, for the production of chemicals and activation carbon [6,7].

Gasification can be divided into two main stages: pyrolysis and char gasification. Since char gasification determines the final conversion achieved in the process, the char gasification process is a much slower conversion process compared to the initial pyrolysis. Thus, it is dominant in the whole gasification process and is very much dependent on the development of a porous char structure in the pyrolysis stage [8-11]. Char gasification consists of a series of heterogeneous reactions (e.g. the steam reaction) of the carbon in the chars with the gasification agent (steam), and reactions among reactant and resultant gases. Hence, the char gasification directly depends on char reactivity with a gasification agent.

Steam gasification reaction (Eq. (1)) is endothermic. So, for practical applications of the steam-only gasification, it is necessary to produce heat from an external source [12].



Based on the active site concept [13,14], the steam gasification of char takes place according to two basic mechanisms indicated as the oxygen exchange mechanism and the hydrogen inhibition mechanism [13]. The steps to be considered are:



where k_i is the rate of the i th reaction.

The oxygen exchange mechanism consists of steps (1)–(3). The hydrogen inhibition mechanism may consist either of steps (1), (3) and (4), (5) or steps (1), (3) and (6), (7). For the oxygen exchange mechanism, hydrogen inhibition is due to the equilibrium of the dissociation reactions (1) and (2). For the first hydrogen inhibition mechanism, the formation of the C

(H)₂ complex is the reason of the inhibition. In the other case, a dissociative chemisorption of H₂ on the active sites occurs and in this way the active sites become not accessible for the oxygen transfer with steam.

Reactivity is one of the most important parameters determining fuels suitability for the use in the gasification process at industrial scale [15]. For this reason, the knowledge of the reactivity of char and its transformation stages during the reaction is vital for designing gasification reactors because char gasification defines the overall rate of conversion [16]. The kinetic analysis of char is important for the projections that involve gasification reactors because gasification is a slower process than pyrolysis. Additionally, gasification causes continuous changes in the char structure, and char reactivity therefore exhibits a tendency to change, depending on the time and the stage of reaction. Reactivity of the char quantified by kinetic parameters is also an important factor which can serve as an index for comparison of different coals and biomass to predict system performance. In thermal analysis activation energy mainly affects the temperature sensitivity of the reaction rate. Char reactivity, therefore, may be sufficiently characterized by its activation energy value alone [17]. The application of gasification process technologies involving biomass, petroleum coke and coal for power generation requires a proper understanding of the thermal properties and reaction kinetics of them.

The effect of pyrolysis conditions such as (heating rate, pressure, residence time and temperature) on the structure and gasification reactivity of biomass chars were investigated by several authors [7,9,11,18,19]. Among them, Fanfei Min et al. [11] investigated the effect of the pyrolysis temperature on the reactivity, physical and chemical structures of agricultural waste chars (corn straw and wheat straw) generated under various lower pyrolysis temperatures (500, 600, 700 and 800 °C). They reported that char gasification reactivity decreases with the pyrolysis temperature increases. The char particles generated under high pyrolysis temperatures had many smaller pores with thinner cell walls, larger surface areas, and some melting. Raphael Idem et al. [18] studied the effect of the pyrolysis temperature on the char characteristics of flax straw, they found that the pyrolysis temperature has a significant impact on the micro-structure of chars and has a stronger influence on the char reactivity compared to pyrolysis residence time in the isothermal regime. They also found that the degree of porosity and graphitization increased with an increasing pyrolysis temperature. The chars formed at pyrolysis a lower temperature were found to be more reactive than the chars produced at a higher pyrolysis temperature.

Edreis et al. [19] studied the effect of gasification heating rate and the kinetic thermal behaviour of sugar cane bagasse chars prepared at 500, 800 and 900 °C during CO₂ gasification, they found that the gasification of SCB chars occurred in one-stage process. They also found that the maximum rate of mass loss and its corresponding temperature are directly proportional to pyrolysis temperature and gasification heating rate.

The information and understanding of behaviour, kinetics, char reactivity and its variation during gasification are essential for proper designing of gasification reactors. These play an important role in the large-scale gasification process.

Table 1 – The proximate, ultimate analyses and atomic ratios of SCB and its char samples.

Sample	Proximate analysis (w%) ^a				Ultimate analysis (w%) ^b				Atomic ratios		
	M	Ash	VM	FC	C	H	O ^c	N	S	H/C	O/C
SCB 9	0.73	16.68	6.93	75.66	74.49	1.83	22.29	1.11	0.25	0.29	0.22
SCB 8	1.19	13.61	9.72	75.48	51.52	1.96	46.05	0.35	0.11	0.47	0.67
SCB 5	2.33	10.35	23.04	54.28	47.39	4.51	47.54	0.45	0.10	1.14	0.75
SCB	7.317	4.411	76.93	11.33	46.95	6.06	46.78	0.13	0.08	1.55	0.74

^a As received basis.
^b Dry ash basis.
^c Calculated by difference.

Table 2 – Sugar cane bagasse ash analysis (wt%).

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	V ₂ O ₅	Ni ₂ O ₃	TiO ₂	P ₂ O ₅
0.70	4.41	17.04	54.62	1.52	4.41	7.54	7.32	0.06	0.02	0.87	1.41

To these ends, thermogravimetric analysis (TGA) is useful, popular and simplest. It provides information on activation energy and kinetic model [20]. TGA can be carried out under isothermal or non-isothermal conditions. The non-isothermal method used in this study has become a common analytical technique in recent decades due to a high sensitivity to experimental noise compared to the isothermal methods. In the present work and under this condition (non-isothermal) our study provides a novel result for estimation of kinetic thermal behaviour and reactivity.

The Vyazovkin method based on the Coats-Redfern approximation and Ozawa-Flynn-Wall method based on the Doyle's approximation were applied in order to determine the activation energies, find the optimum mechanism for char reaction and to describe the reactive behaviour of the samples. The literature on Sudanese sugar cane bagasse char H₂O gasification does not provide an understandable relationship between pyrolysis conditions and char reactivity. This remains a relatively unexplored area of research. Based on these points, the aims of this study are:

- (1) To investigate the non-isothermal steam gasification thermal behaviour of sugar cane char produced at different temperatures.
- (2) To characterize (reactivity and physical structures) the sugar cane chars as a function of pyrolysis temperatures.
- (3) To estimate the activation energy and find the optimum reaction mechanism of the samples.

2. Experimental methods

2.1. Raw material

The raw material used in this study is sugar cane bagasse (SCB), it is a by-product of sugar industry which came from Sudan (Elgnuied Sugar Factory).

The SCB was air dried to moisture less than 10%. This material was crushed, ground and sieved to a particle size between

180 and 450 μm . The proximate, ultimate analyses and atomic ratios are given in Table 1, however, the ash composition of SCB was presented in Table 2.

2.2. Char preparation

The chars were prepared by devolatilization of SCB in a horizontal tube furnace (46 mm internal diameter, 600 mm length) under pure nitrogen atmosphere (99.99% purity) at a flow of nitrogen 1 L/min for required time (20 min) at a designed temperature 500, 800 and 900 °C, which further denoted as SCB 5, SCB 8 and SCB 9, respectively. After the furnace was heated to the desired temperature, about 1 g of SCB in a ceramic container (50 mm \times 30 mm \times 10 mm), it was placed on the outlet side of the tube and then the N₂ was purged into the furnace. When there was no oxygen in the tube, the container was pushed rapidly to the central section (heating zone) of the tube. After a given residence time, the container (resulting char) was immediately moved out of the heating zone, cooled in a nitrogen flow to room temperature and stored in desiccator to prevent moisture absorption. Proximate analysis of samples was carried out in the TGA-2000 (Navas Instruments, Spain) using the American Society for Testing and Materials (ASTM) D5142. The ultimate analysis was determined in a Euro-CA 3000 (HEKA tech, Italy) elemental analyser. The relevant data are presented in Table 1.

2.3. H₂O gasification of SCB chars

H₂O gasification of SCB chars were carried out by using thermogravimetric analyser (TGA, NETZSCHSTA 449/F3). The TGA was coupled with a steam generator through heated transfer line set to 150 °C to prohibit condensation. Experiments were performed with inert sample atmosphere consisting of 75 H₂O: 25 N₂ at a total flow rate of 100 ml min⁻¹. In each experiment, the samples (5–6 mg) were heated at constant rates (10, 15 and 20 °C min⁻¹ up to 150 °C and held at this temperature in order to evaporate water. The steam flow started only when the furnace reaches a minimum temperature of 150 °C, which

is achieved during the automatic pre-heating phase of the furnace. A non-isothermal (dynamic) temperature programme for the TG experiments with reactive H₂O and ramping up with a constant heating rate 10, 15 and 20 °C min⁻¹ to the final gasification temperature of 1100 °C. The furnace chamber was purged several times with nitrogen to ensure an inert sample atmosphere at the beginning of the experiment. Once this was done, the temperature programme started and automatically completed by the control system.

2.4. Characterization of physical structure

The influence of pyrolysis temperature on the physical structure of the char samples such as BET surface area, micro volume, total volume and average diameter pores were measured by nitrogen adsorption/desorption isotherms (195.8 °C) using Micrometrics TriStar 3000 V6.07A apparatus. The system operates by measuring the quantity of nitrogen adsorbed onto or desorbed from a solid sample at different equilibrium vapour pressures. Prior to analysis, all the samples were first oven-dried at 110 °C and then degassed for at 150 °C under final pressure of 1.33 × 10⁻⁴ Pa at least 24 h. Brunauer-Emmett-Teller (BET) [21] and Barrett-Joyner-Halenda (BJH) [22] theories were used to determining the BET surface area and the pore size distribution of the samples, respectively. The micropore volume was obtained by applying the Dubinin-Radushkevich (DR) equation [23], to P/P₀ = 0.20. The total pore volume was determined from the quantity of gas adsorbed at a relative pressure of 0.97, by assuming that pores are filled with liquid adsorbate.

2.5. H₂O gasification kinetic study

Generally, for all kinetic studies, the rate of conversion is expressed by the following basic rate equation.

$$\frac{dx}{dt} = kf(x) \quad (9)$$

where k is the reaction rate constant and $f(x)$ refers to the reasonable model of the reaction mechanism. Eq. (9) expresses the rate of the conversion, dx/dt , at a constant temperature as function of the reactant concentration loss and rate constant. The conversion x is defined as

$$x = \frac{w_i - w_t}{w_i - w_f} \quad (10)$$

where w_t is the weight of the sample at a given time t (min), w_i and w_f refer to values at the initial and the end of the weight loss the sample (mg).

The rate constant k is generally given by the Arrhenius equation (Eq. (11)):

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (11)$$

where E is the activation energy (kJ mol⁻¹), A the pre-exponential factor (min⁻¹), R the universal gas constant (8.314 JK⁻¹ mol⁻¹), T is the absolute temperature (K) and t is the reaction time (min).

By combining Eqs. (9) and (11), the reaction rate can be written as follows:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (12)$$

For non-isothermal process (dynamic TGA process), by substituting the heating rate β , $\beta = dT/dt$, into Eq. (9) yield:

$$\frac{dx}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(x) \quad (13)$$

Eqs. (12) and (13) are the fundamental expressions of analytical methods to determine kinetic parameters on the basis of TGA data.

The integral form of Eq. (13) can be shown as follows:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (14)$$

The Ozawa-Flynn-Wall method [24,25] and Vyazovkin method [26] are the two most common model-free methods of determination of kinetic parameters, and both of them are used in this study to estimate activation energy of sugar cane bagasse chars during H₂O gasification process at the conversion rate range from 10% to 90%.

For Ozawa-Flynn-Wall method, based on the Doyle's approximation [27] is used for temperature integration and Eq. (14) is rearranged into,

$$g(x) = 0.00484 \frac{A}{\beta} \exp\left(-1.052 \frac{E}{RT}\right) \quad (15)$$

By rearrangement and taking the logarithm of Eq. (15) the following formula is obtained,

$$\ln \beta = \ln\left(\frac{AE}{Rg(x)}\right) - 5.331 - 1.052 \frac{E}{RT} \quad (16)$$

For Vyazovkin method based on the Coats-Redfern approximation [28] is used for temperature integration and Eq. (14) is transformed into,

$$g(x) = \frac{A}{\beta} \cdot \frac{RT^2}{E} \cdot \exp\left(-\frac{E}{RT}\right) \quad (17)$$

Similarly, by taking logarithm, Eq. (17) is further rearranged as,

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(x)}\right) - \frac{E}{RT} \quad (18)$$

Then, the activation energy, E , can be determined from the slope of the line $(-E/R)$ determined by plotting $\ln \beta$ vs. $1/T$ for Ozawa-Flynn-Wall method or $\ln \beta/T^2$ vs. $1/T$ for Vyazovkin method basing on the same conversion at different heating rates.

3. Results and discussion

3.1. Thermal effects on chemical compositions of SCB Chars

The data from the proximate and ultimate analyses of SCB and its chars are listed in Table 1. As can be seen, pyrolysis temperature has a clear effect on the chemical compositions of the chars. Char is formed mostly from the thermal decomposition of lignin and some extractive part of biomass, whereas the volatile matter is transformed into the gas phase and minerals in the biomass are left as ashes. From Table 1 it can be seen that more volatile matters have been released out of the char particles in higher pyrolysis temperatures. Less volatile matters are left in the particle form with 23.04, 9.72 and 6.93 wt% for SCB 5, SCB 8 and SCB 9, respectively. At the same time, a higher pyrolysis temperature resulted in a higher fixed carbon content. The fixed carbon content of the char is the carbon that found after volatile matters are evaporated from the biomass char. Therefore, at a higher pyrolysis temperature more volatiles have been removed, which resulted in less volatile matters and more fixed carbon in the char particle with 75.66, 75.48 and 54.28 wt% for SCB 5, SCB 8 and SCB 9, respectively. The carbon content increased rapidly, while the hydrogen and oxygen content were decreased when the pyrolysis temperature increased. Losses in hydrogen and oxygen could be due to the scission of weaker bonds within char structure affected by higher temperatures. As a pyrolysis temperature increases the atomic ratios of H/C and O/C decrease continuously from 1.55 and 0.74 for pure SCB to 0.29 and 0.22 for SCB 9, respectively. This means that the chars become gradually more aromatic and carbonaceous ranging from lignite to anthracite with an increasing temperature [29].

At high pyrolysis temperatures (SCB 8 and SCB 9), the H/C ratio decreases significantly compared to the O/C ratio, suggesting direct dehydrogenation and demethylation of the chars at high temperatures.

3.2. TG–DTG curves analysis and behaviour

Fig. 1 shows the derivative mass loss (DTG) curves for SCB 5, SCB 8 and SCB 9 chars at different heating rates (10, 15 and 20 °C min⁻¹), respectively. Fig. 1 was also given to show the effect of both the pyrolysis temperature and gasification heating rate.

The characteristic results of the maximum mass loss rates and its corresponding temperature were presented in Table 3. From Fig. 1 it can be observed that the gasification of SCB chars took place almost completely in one-stage process as it has been shown by the presence of only one peak in DTG curves. From Fig. 1 it was observed that there was a lateral shift for the maximum rate of mass loss and its corresponding temperature when the heating rate increased. The same results were found in the literature by different researchers [20,30]. This shift can be explained by large variances between the temperature inside the furnace and that of the sample when the heating rate changed. This could be due to an inefficient heat transfer from furnace to sample which obviously increase with the heating rate [20,30]. From Fig. 1 it was observed that

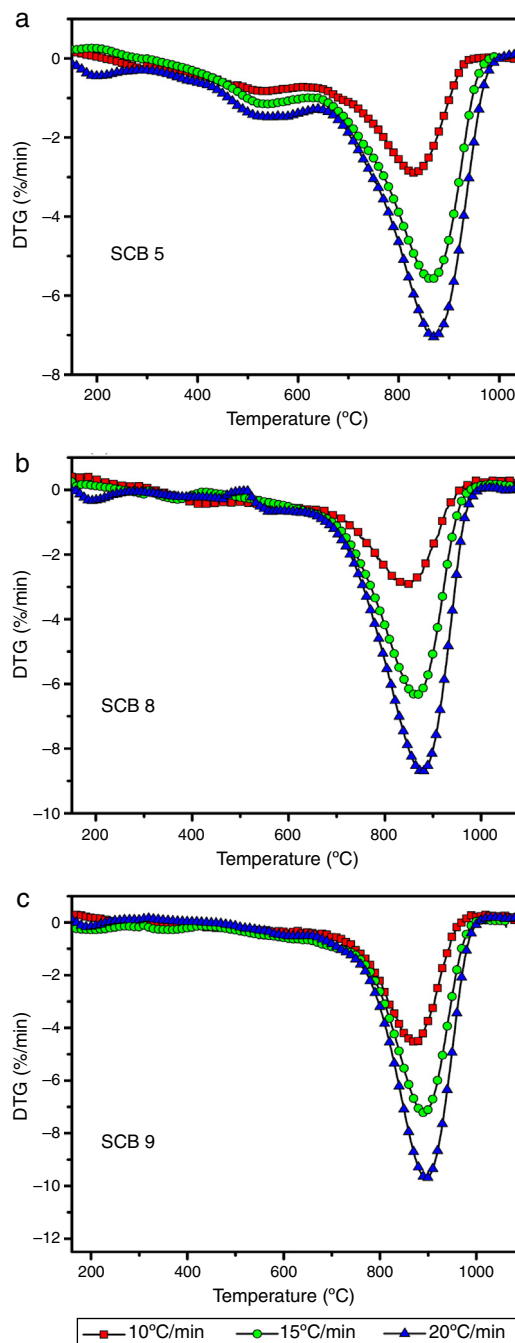


Fig. 1 – DTG curves of SCB chars during non-isothermal H₂O gasification (a) SCB 5, (b) SCB 8 and (c) SCB 9.

the maximum rate of mass loss was directly proportional to pyrolysis temperature.

From Table 3 it can be observed that the maximum rate of mass loss and its corresponding temperature (DTG_{max} ; T_{max}) increased randomly from (2.8% min⁻¹; 832.2 °C), (5.6% min⁻¹; 863.8 °C) and (7.1% min⁻¹; 871.3 °C) for SCB 5 to (4. % min⁻¹; 872.5 °C), (7.3% min⁻¹; 892.5 °C) and (9.8% min⁻¹; 896.6 °C) for SCB 9 under heating rate of 10, 15 and 20 °C/min, respectively. It can be concluded that the maximum rate of mass loss and its corresponding temperature are directly proportional to pyrolysis temperature and gasification heating rate.

Table 3 – Characterization of the maximum rate of mass loss and its corresponding temperature.

β	$10^\circ\text{C min}^{-1}$		$15^\circ\text{C min}^{-1}$		$20^\circ\text{C min}^{-1}$	
	T_{max}	DTG_{max}	T_{max}	DTG_{max}	T_{max}	DTG_{max}
SCB 5	832.2	2.8	863.8	5.6	871.3	7.1
SCB 8	848.3	3.0	866.3	6.4	877.1	8.7
SCB 9	872.5	4.6	892.5	7.3	896.6	9.8

β : heating rate ($^\circ\text{C min}^{-1}$); T_{max} : maximum temperature (min); DTG_{max} : maximum rate mass loss ($\%\text{min}^{-1}$).

3.3. Char conversion and reactivity measurements

The char conversion and index reactivity profiles were measured using TGA analysis data. The carbon conversion profiles of SCB chars versus reaction time were presented in Fig. 2. It seems that, the carbon conversion was significantly influenced by the pyrolysis temperature and gasification heating rate. The time required for complete carbon conversion increased by increasing pyrolysis temperature and decreasing gasification heating rate. This could be due to the high volatile matters and lower fixed carbon in the char produced in the lower temperature.

Generally, to evaluate the overall gasification reactivity of char, R_i was used as reactivity index which is defined as follows [31,32]:

$$R_i = \frac{0.5}{t_{0.5}} \quad (19)$$

where $t_{0.5}$ is the time required to reach the carbon conversion of 50% (min). Fig. 3a and b shows the profile effects of pyrolysis temperature and gasification heating rate on the index reactivity of SCB chars, respectively. It can be seen that, the char reactivity is directly proportional to gasification heating rate and inversely to the pyrolysis temperature. This means the chars produced at lower temperature was found to be more reactive than the chars formed at higher temperature, the same results were obtained in previous studies [7,18,33]. The results indicated that the pyrolysis temperature and gasification heating rates have a significant influence on the char conversion and reactivity. Similar results were also found by previous study [7].

3.4. Physical structures of char

The physical structures such as BET surface area and pore characteristics of SCB char obtained at different temperatures were listed in Table 4. The devolatilization of biomass materials established porosity in the chars, resulting in particles with an essentially micro-macro pore structure. The surface area values varied significantly at different pyrolysis temperatures. In contrast to pore volumes and BET surface areas of SCB char. The results show that the BET surface area, micro pore volume total pore volume and average pore diameter were increased with increasing pyrolysis temperature. It can be concluded that the pyrolysis temperature significantly affected on the physical char structures. It can be observed that the BET surface values increased gradually from $211\text{ m}^2\text{ g}^{-1}$ for SCB 5 to $286\text{ m}^2\text{ g}^{-1}$ for SCB 9.

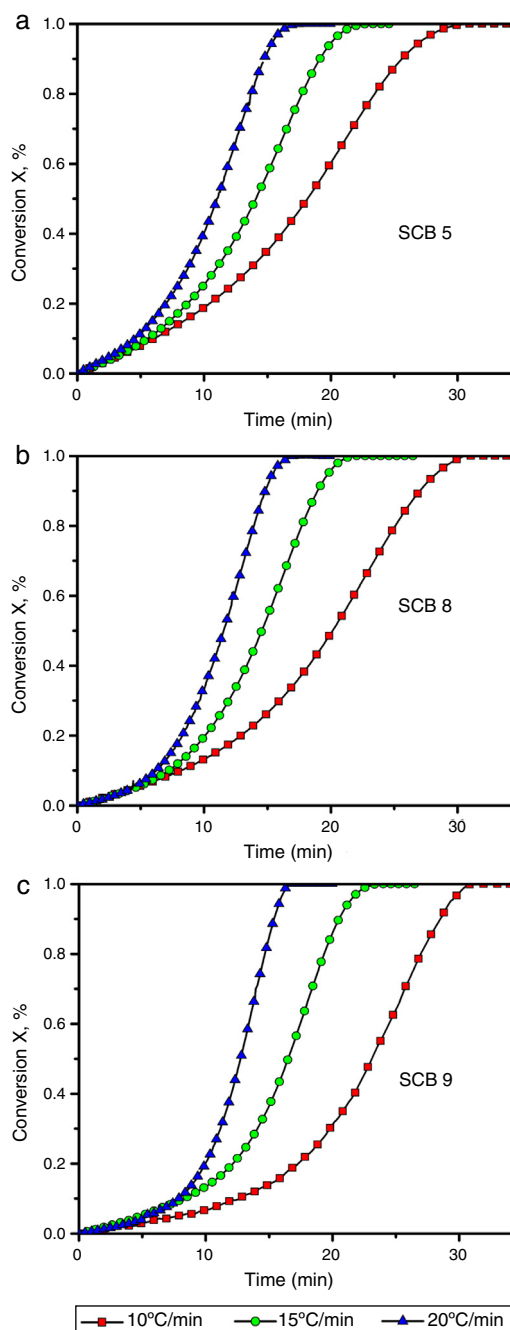


Fig. 2 – Carbon conversion of SCB chars versus reaction time during non-isothermal H_2O gasification (a) SCB 5, (b) SCB 8 and (c) SCB 9.

Table 4 – SCB chars physical structures characteristics.

Sample	BET surface area (m ² /g)	Micro pore area (m ² /g)	Micro pore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Average pore diameter (NM)
SCB 5	211.46	113.51	0.0519	0.1367	3.971
SCB 8	264.08	148.14	0.0680	0.1681	4.382
SCB 9	286.10	177.15	0.0816	0.1832	4.847

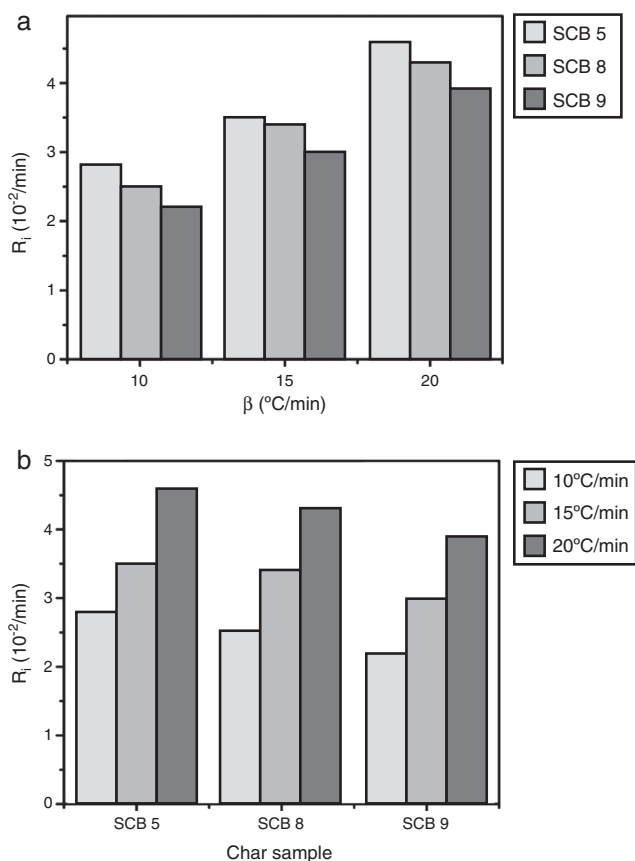


Fig. 3 – Effects of gasification heating rate (a) and pyrolysis temperature (b) on the reactivity of SCB chars during non-isothermal H₂O gasification.

In general, surface area of biomass char increases with the pyrolysis process due to the generation of porosity. The result of the carbonization step at a high temperature will damage the development of porous structures in the char and the walls of the pores become so thin that they collapse and this leads to decline the existing surface area. It can be concluded that the pyrolysis temperature significantly affected on the physical char structures. At 900 $^{\circ}\text{C}$, the pore and BET increases could be due to the lignin decomposition.

3.5. Activation energy determination

In the present study, to determinate the activation energy on the conversion fraction during the major gasification process, nine conversion values varying from 10% to 90% were employed at three heating rates of 10, 15 and 20 $^{\circ}\text{C}/\text{min}$. The regression lines with the correlation coefficients (R^2)

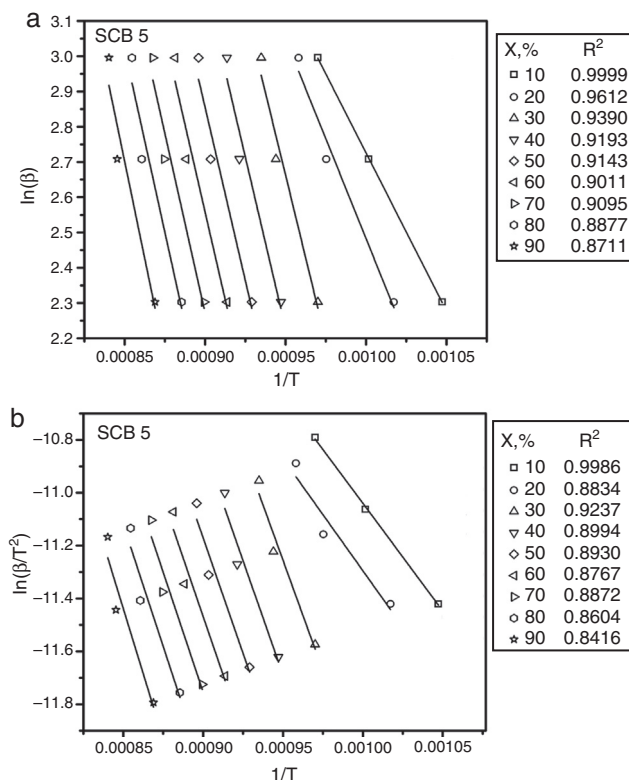


Fig. 4 – Plots of $\ln[\beta/T^2]$ and $\ln[\beta]$ versus $1/T$ with correlation coefficients values of SCB 5 obtained by (a) Vyazovkin method; (b) Ozawa-Flynn-Wall method.

of SCB 5, SCB 8 and SCB 9 based on the Vyazovkin and Ozawa-Flynn-Wall methods were shown in Figs. 4-6, respectively. As shown in Figs. 4-6 the fitted lines are almost parallel, which indicates to the possible single reaction mechanism in all conversion levels. For all cases it was found that the lowest values of R^2 were achieved at higher conversion value of 90% and also at higher pyrolysis temperature (SCB 9). The lowest values of R^2 obtained by SCB 9 are 0.7029 and 0.6619, which were achieved by Vyazovkin and Ozawa-Flynn-Wall methods, respectively. The activation energies of SCB 5, SCB 8 and SCB 9 obtained by Vyazovkin and Ozawa-Flynn-Wall methods were listed in Tables 5-7, respectively. The mean values of activation energy obtained by Vyazovkin method were 131.20, 195.40 and 246.84 kJ mol^{-1} for SCB 5, SCB 8 and SCB 9, respectively. While, Flynn-Wall-Ozawa method shows the following values 141.61, 203.17 and 252.66 kJ mol^{-1} for SCB 5, SCB 8 and SCB 9, respectively. It is obvious that the values of the activation energies obtained by Flynn-Wall-Ozawa method were higher than the values of the activation energies obtained by Vyazovkin method. It can be seen that for both methods and at all

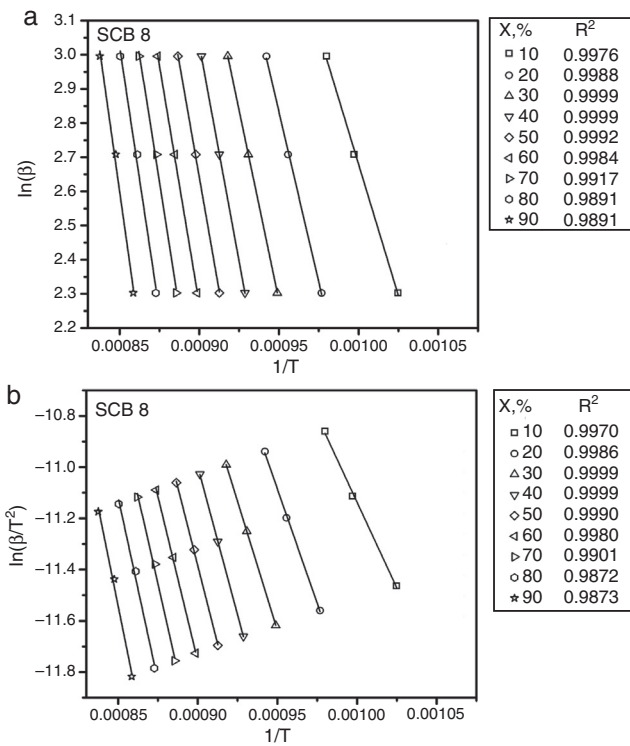


Fig. 5 – Plots of $\ln[\beta/T^2]$ and $\ln[\beta]$ versus $1/T$ with correlation coefficients values of SCB 8 obtained by (a) Vyazovkin method; (b) Ozawa-Flynn-Wall method.

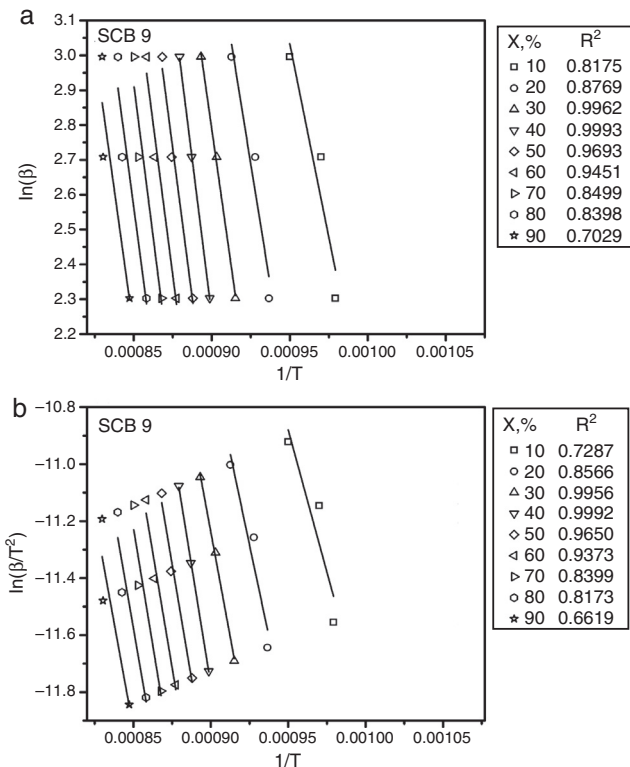


Fig. 6 – Plots of $\ln[\beta/T^2]$ and $\ln[\beta]$ versus $1/T$ with correlation coefficients values of SCB 9 obtained by (a) Vyazovkin method; (b) Ozawa-Flynn-Wall method.

Table 5 – Activation energies (kJ mol^{-1}) of SCB 5 obtained by Vyazovkin and Flynn-Wall-Ozawa methods.

Conversion (x) (%)	Vyazovkin	Flynn-Wall-Ozawa
10	67.63	70.90
20	70.49	89.54
30	138.90	148.61
40	143.90	153.76
50	145.16	155.29
60	146.83	157.17
70	150.67	161.09
80	153.21	163.79
90	164.00	174.37
Mean	131.20	141.61

Table 6 – Activation energies (kJ mol^{-1}) of SCB 8 obtained by Vyazovkin and Flynn-Wall-Ozawa methods.

Conversion (x) (%)	Vyazovkin	Flynn-Wall-Ozawa
10	111.30	121.56
20	148.44	157.57
30	167.72	176.36
40	192.48	200.23
50	203.31	210.82
60	213.46	220.74
70	227.66	234.49
80	238.55	245.10
90	255.66	261.66
Mean	195.40	203.17

Table 7 – Activation energies (kJ mol^{-1}) of SCB 9 obtained by Vyazovkin and Flynn-Wall-Ozawa methods.

Conversion (x) (%)	Vyazovkin	Flynn-Wall-Ozawa
10	165.83	175.48
20	214.09	220.61
30	243.90	249.32
40	278.94	282.93
50	266.78	271.58
60	268.53	273.46
70	273.91	278.76
80	261.10	266.80
90	248.48	255.04
Mean	246.84	252.66

conversion levels, the activation energies are directly proportional to the pyrolysis temperature. As the value of activation energy represents the minimum energy required to break the chemical bonds between the atoms, which means the lower value of activation energy, as well as, the higher reaction. It is a factor demonstrating of the reactivity of an overall reaction rate. So, the char prepared at a lower temperature is more reactive than that obtained at a higher temperature. Finally, Vyazovkin and Ozawa-Flynn-Wall methods were successfully utilized to predict the reaction mechanism of SCB char's gasification.

4. Conclusions

The results established that as pyrolysis temperature increases the atomic ratios of H/C and O/C decrease con-

tinuously from 1.55 and 0.74 in SCB to 0.29 and 0.22 for the char prepared at 900 °C, respectively. At higher pyrolysis temperatures (800 and 900 °C), the H/C ratio decreases significantly compared to the O/C ratio, suggesting direct dehydrogenation and demethylation of the char at high temperatures. The peak of weight loss rate in the DTG curves shifted to a higher temperature with heating rate. The maximum rate of mass loss and its corresponding temperature are directly proportional to pyrolysis temperature and gasification heating rate. The char reactivity is directly proportional to gasification heating rate and inversely to the pyrolysis temperature. The char BET surface area and pores characteristics are directly proportional to the pyrolysis temperature. The Vyazovkin and Flynn–Wall–Ozawa methods show mean activation energies of 131.20–141.61 kJ mol⁻¹ for SCB 5, 195.40–203.17 kJ mol⁻¹ for SCB 8 and 246.84–252.66 kJ mol⁻¹ for SCB 9. For both methods and at all conversion levels, the activation energies are directly proportional to the pyrolysis temperature. Finally, Vyazovkin and Ozawa–Flynn–Wall methods were effectively useful to predict the reaction mechanism of SCB char's gasification.

Conflict of interest

The authors declare no conflict of interest.

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