

# KINETIC DESCRIPTION AND REACTION CONTROL INVESTIGATION WHEN GASIFYING A BIOMASS WASTE

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**Abstract** – Gasification is one of the most important methods in the harmless disposal of biomass. The gasification characteristics of biomass waste and an increasing number of biomass waste gasification plants provide the possibility of energy disposal with (heat or electricity).

In this study, the reactivity of biomass char was investigated at various temperatures and CO<sub>2</sub> concentrations in order to evaluate the diffusion coefficients and mass transfer according to the shrinking core model (SCM). Results show that the reaction control is based on mass diffusion showing that at the high temperature, 1000 °C, carbon conversion was not achieved. The chemically controlled reaction have been shown in comparing total reaction time, time for diffusion, diffusion coefficient and mass transfer coefficient. And according to this reaction control, the effects of reactant pressure on the kinetic parameters of the char reaction at temperatures 900, 950 and 1000 °C where chemical reactions alone controlled the conversion rates were computed and validated by the simple global model (an Arrhenius). The activation energies computed in our study were based in two models, the SCM and the volume reaction model (VRM).

**Keywords:** Biomass waste, Char, Gasification, Kinetic, Fixed bed reactor

## I. INTRODUCTION

Gasification currently provides high potentials in environmental and energetic problems due to the wide range of carbonaceous materials such as coal, biomass and wastes that can be fed in gasifying reactors. This process has been identified as the most favorable thermo-chemical biomass conversion process for renewable energy production due to the low sulfur and nitrogen contents of biomass [1]. Consequently, the produced biomass-fuel based offers some interesting potentials but they must be reformed into good and usable forms. The reforming of biomass fuel to high-heating value clean syngas is much desired [2]. Again, this process, under certain conditions is a good precursor for sustainable development. Indeed, apart from CO<sub>2</sub>, ashes with low TOC (Total Organic Carbon) can be recycled. As we have just shown previously, gasification is a thermo-chemical energy-production process which commonly takes place in a 800 - 1100 °C temperature range. As such, in a gasification reactor, several processes such as drying, pyrolysis, volatilization and char formation take place. Thus, the first chemical process which takes place inside a gasification reactor after drying reflects the pyrolysis of the material while volatiles are released and char is produced.

Gasification proceeds mainly through a two-step process: pyrolysis followed by gasification. The pyrolysis stage known as devolatilization/carbonization, is endothermic and produces volatile (hydrocarbons gaseous and liquid) and fixed carbon. Then, the hydrocarbons and the fixed carbon are converted into synthesis gas in the second step:

gasification. Relying on gasification reactions, one can with gasification agents (air/steam/carbon dioxide/oxygen) produce carbon monoxide and hydrogen. Depending on the nature of the gasification agent used and its flow, some of these reactions are accordingly important and can therefore influence the composition of the gas produced. Scott et al.[3] show that gasification reaction of char with some gaseous components is important through the gasification scheme. The kinetics of char gasification biomass needs to be determined accurately because it relatively depends on a lot of parameters such as reactor size, temperature distribution, biomass type, inhomogeneous distribution of the char, char particles size, and the gasification system operating parameters. A great effort has been made to develop kinetic models in order to predict the rate of conversion of char particles during gasification, i.e. the reactivity. Char particle gasification is mainly affected by char morphology, nature and content of ash-forming constituents, as well as diffusion of mass to and inside the particle [4]. While experimenting an analysis of the type of biomass reported in the literature leaving out elements such as reactor temperature, partial pressure or concentration of gasifying agent, sample geometry, char active sites and chemical composition of gasifying agent and other parameters. One realizes that depending on the type of biomass used, the kinetics obtained by applying a given model is different.

Bhat [5] gasified rice husk grain and powder char in carbon dioxide and steam at temperature between 750°C and 900°C. These authors applied the VRM and the SCM models to the experimental data obtained and demonstrated that the activation energies 200 kJ/mol and 180 kJ/mol respectively

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for rice husk grain and powder are in good agreement with those mentioned in the literature.

Also, Dong [1] investigated biomass char reactivity at various temperatures and pure CO<sub>2</sub> concentrations; they used the VRM, SCM, and RPM to interpret the experimental data and they found that the experimental data agreed better with the RPM than with the other two models.

Additionally, Feroso [6] compared the kinetic parameters of two biomass char at 1000 °C and 1400 °C during pure CO<sub>2</sub> gasification at 1 and 10 bars by using the VRM, GM (grain model or shrinking core model) and RPM models and they were also able to compute the reaction order. Consequently, they accordingly posited the capacity of the three models to predict the conversion of the char along the bed and at an internal spatial location within the particle.

Matsumoto [7], by analyzing various relationships, concluded that the random pore model (RPM) was the most suitable tool for a Japanese cedar char gasification reaction because of surface porosity, constant particle size and specific surface area profile, as well as the coincidence of gasification reaction rate. The later was experimentally computed from Arrhenius expression when using the random pore model; again, the gasification temperatures were 900 and 1000 °C..

## II. MATERIALS AND METHODS

### 1. Biomass char description

The chars were obtained by devolatilizing (pyrolysis process) the raw material in a rotary kiln during 20 min at 723 K under inert atmosphere. After the experiments, the chars obtained were collected and ground at 200 microns.

For the gasification tests, these chars (0.2 mm) were prepared at 873 °C under flowing N<sub>2</sub> at slow heating rates (approximately 14 °C.min<sup>-1</sup>) and at atmospheric pressure. According to the elemental analysis, the chemical formula of the raw biomass material that derives is determined and equal to CH<sub>1.42</sub>O<sub>0.68</sub>. Table 1 summarized the characteristics of the biomass (raw and coke materials) samples which include ultimate and proximate analyses. Table 1: Ultimate and proximate analysis of the biomass (raw material and coke) and its Lower Heating Value

Ultimate analysis (wt.% db)				
C	H	O	N	LHV (MJ/kg)
49.13	5.82	44.76	0.29	19
Ultimate analysis for the biomasse coke				
75.05	2.88	21.59	0.48	23.92
Proximate analysis (wt.% db)				
Volatile matter		Fixed carbon		Ash
77.3		21.8		0.9

The calorific value of the biomass raw material (pyrolysed at 450 °C) used in the gasification were determined using the correlation of Yin [8]. Indeed the use of two formulas below respectively based on elemental analysis and proximate analysis led to a value of HHV between 20.22 and 19.29 MJ/kg.

Using proximate analysis, the formula is :

$$\text{HHV} = 0.1905\text{VM} + 0.2521\text{FC} \text{ (MJ/kg)} \quad (\text{a1})$$

And by using ultimate analysis, the formula corresponding is:

$$\text{HHV} = 0.2949\text{C} + 0.8250\text{H} \text{ (MJ/kg)} \quad (\text{a2})$$

These two formulas have been validated through a large database from a relevant literature and allow us to work on our biomass olive stones biomass by using the eq. a1 and Oak wood (medium branch) using the eq a2.

The LHV is computed through the current mathematical formula (a3).

$$\text{LHV} = \text{HHV} - 9m_{\text{H}}h_{\text{fv}} \text{ (MJ/kg)} \quad (\text{a3})$$

Where  $m_{\text{H}}$  is the mass fraction of hydrogen in the fuel and  $h_{\text{fv}}$  is the water vaporization enthalpy ( $\approx 2.26$  MJ/kg).

### 1. Experimental set-up description

Gasification processes in a lab-scale fixed bed reactor, figure1 (I.D. 3.6 cm, L=56 cm), filled with mixture of sand particles of 0.2-0.8 mm and biomass char particles of 200 µm in order to avoid loss of material due to char biomass size, heat transfer inside bed particles, and minimizing the preferential gas passage.

Tars formed during the process and the excess of steam were separated from the gas flow by means of a thermoelectric cooler. The gas composition of the dried gases (H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO and CO<sub>2</sub>) was analyzed on-line, using a micro-GC dual channel.

The system was pressurized after reaching the desired temperature in N<sub>2</sub> to avoid any influence of pressure during the gasification process. After reaching the desired pressure and a stable mass, the gas was switched from N<sub>2</sub> to CO<sub>2</sub>. Once the gases passed through the injector, they enter into a column in which they were separated into its components in a time deviation equal to 160 seconds. The micro-GC was equipped with a molecular sieve, Molsieve 5 Å (for separating H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO), and a Plot Q (for separating CO<sub>2</sub>, CH<sub>4</sub> and water vapor); nitrogen was used as a gas carrier. The lower detection limit is 200 ppm and the upper limit 100% (full detection capacity).

The system was calibrated employing a standard gas mixture at periodic intervals defined according to the user. A constant nitrogen flow rate was introduced with the gasification agent. The nitrogen is detected by the microGC and is used to determine the flow rate of different syngas species by comparing the detected species mole fraction with the known nitrogen mole fraction.

The amount of gas generated during the experiments was calculated from a nitrogen balance, since the amount of nitrogen fed in and the composition of the evolving nitrogen are known.

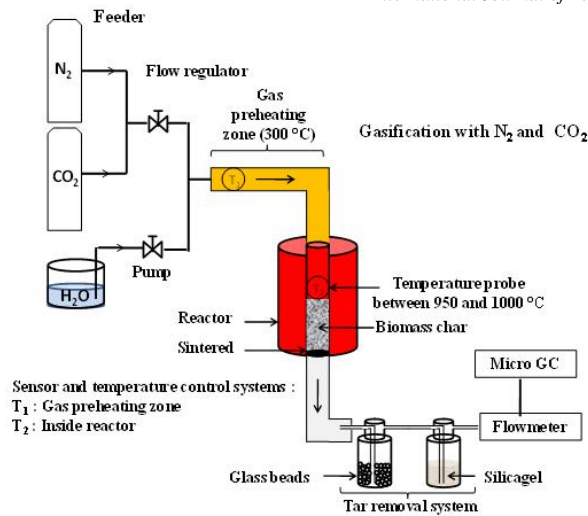


Fig.1 Schematic diagram of experimental apparatus (fixed bed reactor)

### 1. Experimental conditions

Since operating conditions are different from one experiment to another; our gasification was run under a fixed reactor bed. Commonly some authors ([9], [10] and [11]) saw that the reactor above remains the most widely used and offers various opportunities especially in terms of applications and product used. Reactor parameters are illustrated in Table 2.

**Table 2: Fixed bed reactor description**

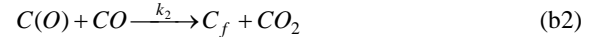
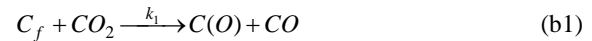
Description	Reactor parameters
Maximal pressure (bars)	3
Reactor power (kW)	1
Reactor height (mm)	560
Maximum bed height (mm)	95.93
Bed diameter (mm)	36
Freeboard height (mm)	464
Tube injection diameter (ext.) (mm)	19
Tube injection diameter (int.) (mm)	15

A nitrogen flow of 100 NL/h was started to remove any air from the system, while the heating system was heated. When the reactor temperature reached the target temperature of 900, 950 and 1000 °C, CO<sub>2</sub> mixed with nitrogen was introduced into the reactor and then was rapidly moved into the reaction zone in the middle of the electrical furnace to achieve a uniform temperature distribution within the reaction zone, taking this moment as time zero of the experiment. The total flow rate of the reactive gas introduced into the reactor during the gasification experiments was 100 NL/h, comprising CO<sub>2</sub> and N<sub>2</sub>. CO<sub>2</sub> concentration in the feed gas were fixed at 10, 40, 60 and 90 NL/h and led to CO<sub>2</sub> percentages comprise between 10%, 40%, 60% and 90%.

## IV. KINETIC MODEL DEVELOPMENT

The carbon dioxide gasification of char has been extensively studied by various authors. Several authors ([12],

[13]) showed that CO<sub>2</sub> gasification reaction proceeds by elementary trios that are:



where  $k_1$ ,  $k_2$  and  $k_3$  are the usual Arrhenius rate constants,  $C_f$  represents an active carbon site and  $C(O)$  a carbon-oxygen complex. The presence of CO produces an inhibiting effect by lowering the steady-state concentration of  $C(O)$  by the reaction (b2).

The gasification rate, in this case is complex and can be expressed as:

$$r_C = \frac{k_1 P_{CO_2}}{1 + (k_2/k_3) P_{CO} + (k_1/k_3) P_{CO_2}} \quad (1)$$

where  $P_{CO_2}$  and  $P_{CO}$  are the partial pressure of CO<sub>2</sub> and CO, respectively. When the CO concentrations are small and/or the inhibiting effect exerted by this species is not taken into account, a simple global model can be applied:



And the rate becomes :  $r_C = A \exp(-E/RT) P_{CO_2}^n$

The aim of the present work is to characterize the effect of CO<sub>2</sub> concentration, in a mixture CO<sub>2</sub>/N<sub>2</sub> on gasification of a biomass chars prepared from French's forest residue manufacturer (birch wood) at different reaction temperatures 900-1000 °C. The influence of the reaction time (diffusion and mass transfer coefficients) is investigated in order to determine reaction control type.

Regarding the literature, the majority of gasifiers operate at pressures of at least 1 MPa, due to the advantages of gasifying under pressure, such as savings in compression energy and reduction of equipment size [14]. Few studies have investigated the effect of pressure on the reaction rate and reactivity profile ([15], [8]). These studies reported different results for the effects of pressure.

A Model that takes into account reaction evolution between the external and internal surfaces (shrinking core model, SCM) is applied to represent the experimental data in kinetically controlled regime and to evaluate intrinsic kinetic parameters.

The ultimate goal of gasification as in most studies is to obtain more syngas with higher heating value. However various studies show that reaction kinetics produced effect on the yield and quality of syngas production.

In order to study reaction kinetic and reaction control type, gasification experiments with 900, 950 and 1000 °C and with 90 % CO<sub>2</sub> were performed. Finally, investigating pressure partial effects and based on eq 2 we are going to describe and validate the char biomass gasification.

The carbon conversion ratio,  $x$  illustrated by eq 3, relates to the ratio of carbon converted into gaseous carbon components. As the tar was removed from the gas by using (ice-water bath), the carbon in tar was not taken into account in the experiments. Therefore the carbon conversion can be calculated by:

$$x = \frac{12(CH_4 + CO_2 + CO)}{22.4 \times \%m_C} \times V_g \quad (3)$$

Where CH<sub>4</sub>, CO<sub>2</sub> and CO represent the percentages of the volume fraction of methane, carbon dioxide, carbon monoxide and hydrocarbons in the product gas, %m<sub>C</sub> is the percentage of mass fraction of carbon in the biomass fuel, and V<sub>g</sub> is the total dry gas produced (NL/h). From the concentration of nitrogen in the gas product and the total amount of nitrogen entering the reactor along, the total dry volumes of gas produced can be estimated using the following formula:

$$V_g = Q_r \frac{V_{N2,i}}{V_{N2,g}} \quad (4)$$

Where Q<sub>r</sub> is the rotameter graduation, V<sub>N2,i</sub> represents the volume fraction of N<sub>2</sub> entering the reactor and V<sub>N2,g</sub>, the volume fraction of N<sub>2</sub> in the gas products.

Once the carbon conversion ratio, x is obtained, one can define the rate of conversion namely reactivity or reaction rate by eq 5.

The reaction rate is defined as:

$$dx/dt = k(T, P_{CO2})f(x) \quad (5)$$

Where k is the constant rate based on gas temperature T, and the partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) and f(x) a function variation of the carbon conversion ratio x. Making the same assumption as in ([1], [12]) and according to various other authors, CO<sub>2</sub> remains constant during process so the reaction rate of char gasification can be expressed by using the Arrhenius equation as:

$$k = A \exp(-E/RT) \quad (6)$$

Where A, R, and E are the pre-exponential factors, universal gas constant, and activation energy, respectively. In the literature there are various models describing biomass char particles gasification. In this study, we applied the shrinking core model (SCM).

The SCM also called grain model is widely used and has been validated in several studies on biomass char [1]. Tilman et al. [16] have modified and validated the SCM in fluid particle reaction. This model assumes that gasification reaction happens only on surface of spherical particle, and the non-reacted core would shrink gradually in the reaction process. When reaction is the control step for small and large particles, shrinking core model can be written as,

$$dx/dt = k_{SCM} (1-x)^{2/3} \quad (7)$$

## V. RESULTS AND DISCUSSIONS

Measurements are based on the variation of the CO<sub>2</sub> concentration (fraction in the mixture). The experimental results obtained enable us to analyze the char residence time with the influence of CO<sub>2</sub> concentration, the temperature, and the partial pressure of CO<sub>2</sub> (see last paragraph).

### 1. Effect of CO<sub>2</sub> concentration in the conversion rate

The concentration of CH<sub>4</sub> due to CO<sub>2</sub> gasification reaction aims toward zero. Thus, based on the study done by Gautam [17] CH<sub>4</sub> concentration was almost negligible. Indeed this study, authors showed that methane concentration decreases with increasing temperatures and reaches negligible amount

after 900 °C. Therefore, CH<sub>4</sub> was switched off and gasification temperature was set to 1000 °C due to (for example significant uncertainties in gasification rate of char at high temperatures or the range of temperature in gasification process). Three tests were done by varying CO<sub>2</sub> fraction (compared to diluents fraction, N<sub>2</sub>) from a value of 0 up to a value of 90 % at constant temperature of 1000 °C.

The plot in figure 2 shows the effect of CO<sub>2</sub> concentration in a mixture of CO<sub>2</sub>/N<sub>2</sub> as a gas carrier on the char conversion. As shown by the curves, the char conversion increases due to the increment of the CO<sub>2</sub> concentration, and according to the reaction  $C + CO_2 \rightarrow 2CO$ , led to an increasing of CO production.

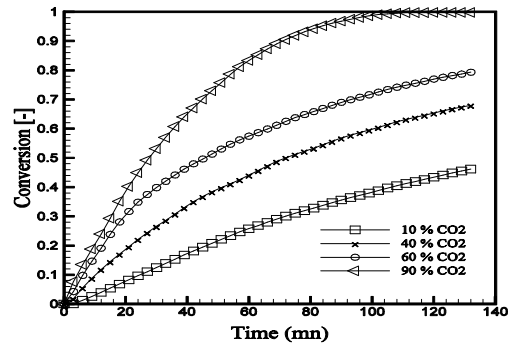


Fig.2 Effect of the CO<sub>2</sub> concentration in carbon conversion at 1 000°C

In order to highlight the influence of the inert gas on the conversion rate, we have compiled the table 3 below.

Table 3 shows that when CO<sub>2</sub> concentration increases, biomass char conversion increases. Indeed for each fixed time, there is an increase in biomass char conversion. Therefore, the less the concentration of inert gas (N<sub>2</sub>) was, the more biomass chars are converted. When the CO<sub>2</sub> concentration increases, particles residence time decreases and more biomass char is converted to over a relatively short time i.e. curves with lower CO<sub>2</sub> concentrations reach conversion rates close to 1 for higher time. Therefore in presence of a high temperature (paragraph below) and a less inert concentration, more chars biomass are converted in a relative short time during the test.

Table 3: Influence of CO<sub>2</sub> concentration on the conversion rate at T=1000°C

Time (min)	CO <sub>2</sub> concentration			
	10 %	40 %	60 %	90 %
15	0.054	0.145	0.238	0.293
30	0.125	0.265	0.398	0.531
45	0.194	0.368	0.496	0.701
60	0.258	0.441	0.574	0.833

### 2. Temperature effects

Since gasification is an endothermic process, the gas composition product is sensitive to temperature change. The effect of temperature on gas product composition (corresponding results have not been illustrated here) shows that the concentration of H<sub>2</sub> and CO increases with increase

in temperature. Higher temperature provides more favorable conditions for cracking and steam reforming of methane. Hence, when temperature increases, the methane concentration in the gas product decreases (correlated by Gautam [17] study) and this contributes to the increase in concentrations of hydrogen. The CO<sub>2</sub> concentration decreases with increase in temperature because higher temperature favors endothermic formation of CO via Boudouard reaction. H<sub>2</sub> and CO productions are favorable at high temperature while CH<sub>4</sub> and CO<sub>2</sub> productions are preferred at medium-low temperature.

The heating rate had a marked influence on the gasification reactivity of the fuel char, independently of its nature. With the increase of the heating rates, temperature increases faster and individual reactions do not have enough time to reach completion, or equilibrium, and they overlap with the adjacent higher temperature reaction [18]. So, by plotting temperature versus time we are able to evaluate the heating rate which is equal in our experiment to 13.55 °C/min. In order to have an explication of gas yields (CO and CO<sub>2</sub> formation) in high temperature gasification, we plot the ratio CO/CO<sub>2</sub> versus time for reactor temperature between 900, 950 and 1000 °C in presence of inert gas (see figure 3).

Some authors ([19], [20]) reported that CO and CO<sub>2</sub> are formed from competing parallel routes. CO production route is favored at high heating rates and at high reactor temperatures. However CO<sub>2</sub> route is favored in the presence of gasification agent and high reactor temperatures. Our conclusion is little bit different from Ahmed and Gupta [18] conclusions whose gasification agent uses steam and is confirmed from the results of CO/CO<sub>2</sub> ratio shown in figure 3. The current trends observed during the tests show that the maximum conversion remains in high temperatures, i.e. the curve corresponding to 1000 °C decreases more rapidly than the curves corresponding to 950 and 900 °C, respectively.

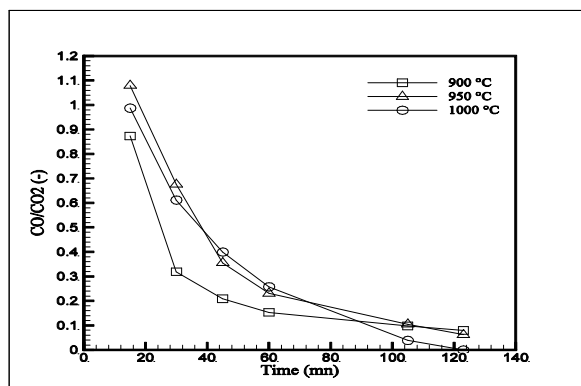


Fig.3: CO/ CO<sub>2</sub> ratio after CO<sub>2</sub> gasification at a reactor temperature of 900, 950 and 1000°C

A temperature above 900 °C is necessary to establish a good conversion, corresponding to the activation of the oxidation of CO reactions. And for reactor temperatures between 950 and 1000 °C, the rates of consumption of biomass char are between 67.34 % and 74.88 % respectively in a residence time of 129 min and almost equal to 50 % (49.64 % and 56.82 % respectively in 60 min). The oxidation of biomass char leading to the formation of CO is completed

with a long residence time. The CO content will then depend only on the oxidation of CO<sub>2</sub>. At a temperature of 1000 °C, the reduction reactions are little activated, resulting in lower levels of CO concentrations compared to a combustion case due to the CO<sub>2</sub> gasification (figure 3 shows high CO<sub>2</sub> concentration). Close to a residence time of 105 min, CO is decreasing with the reactor temperature. This result is logical since a rise in temperature will promote the oxidation reactions of CO to CO<sub>2</sub>. Indeed, we noticed an increase of CO<sub>2</sub> concentration with increasing temperature gasification (see figures 3-4).

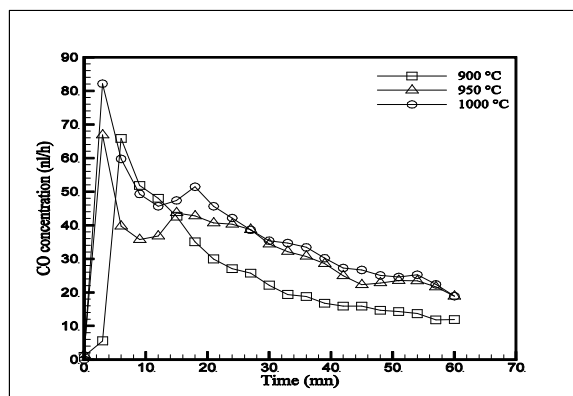


Fig.4: Evolution of CO concentration for gasification temperatures of 900, 950 and 1000 °C

From figure 3 we note that for CO<sub>2</sub> concentration fixed at 100 %, biomass char conversion remains best at 1000 °C and occurs on a shorter residence time compared to other tested temperatures of 900 and 950 °C. For low residence time, the conversion rate decreases with temperature (figure 5). Figure 5 shows also that the complete carbon conversion was not achieved. The time required to achieve the complete carbon conversion was around 262 min at 900 °C, whereas this time was 147 min at 1000 °C. Although the gasification temperature of 1000 °C resulted in the highest carbon conversion rate, however the use of high temperature was not beneficial from economical and operational points of view. Moreover, high temperatures could shift the reaction to the diffusionally-controlled regime, where a good insight into the char morphology and its microstructure is required to study the overall gasification performance [21].

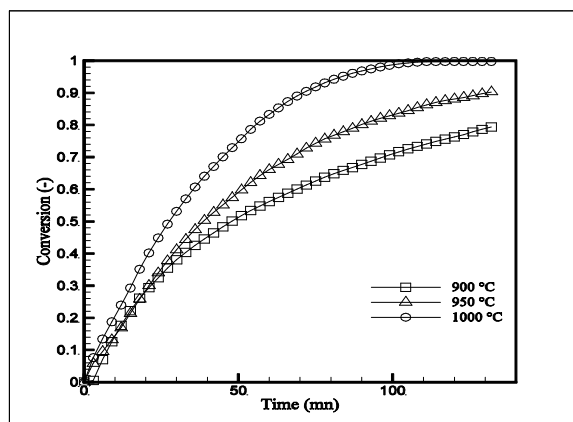


Fig.5: Evolution of carbon conversion for gasification temperatures of 900, 950 and 1000 °C

In this part of the study of concerning the effects of the inert fraction on conversion rate and the effect of temperature on the inert fraction, the results show that a temperature of 1000 °C and a fraction of 90% CO<sub>2</sub> have favorable impact on the biomass char gasification.

**2. Gasification kinetics with 90% of CO<sub>2</sub>**

As it was established above, the CO concentration rapidly increases but then decreases faster as the reaction time increases. As it can be seen in figures 3 and 4, the CO production increased with the increase of the reaction temperature, implying that higher temperatures favored the reaction. Keeping in mind these observations and the fact that

at above 900 °C, rates of mass transfer and pore diffusion are lower than those of chemical reactions [11], we are going to compute the biomass char reactivity. In order to quantify the kinetic parameters of the model by using the values of char conversion, the experimental mathematical figure of  $-\ln(1-x)$  vs. time for VRM was fitted in figures 6a and 6b. The results obtained from the VRM model for all temperature were used in figure 9 for determining the constant reactions ( $k_{VRM}$ ).

Figure 7 shows the plot of the function  $3[1-(1-x)^{1/3}] = f(t)$  or x, conversion rate, as a function of time for different temperatures range (900 °C, 950 °C and 1000 °C) for the SCM model.

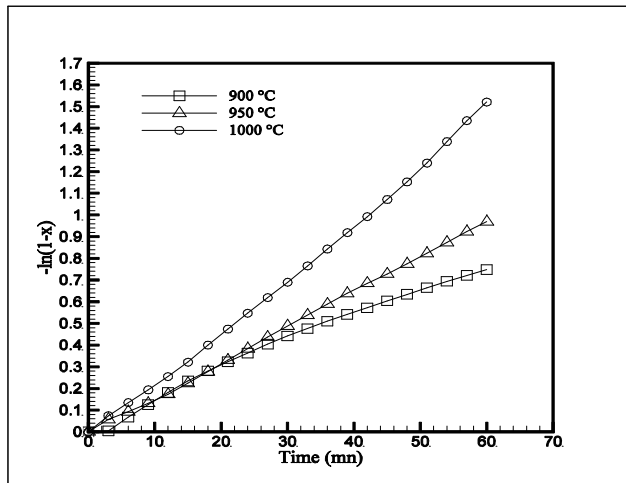
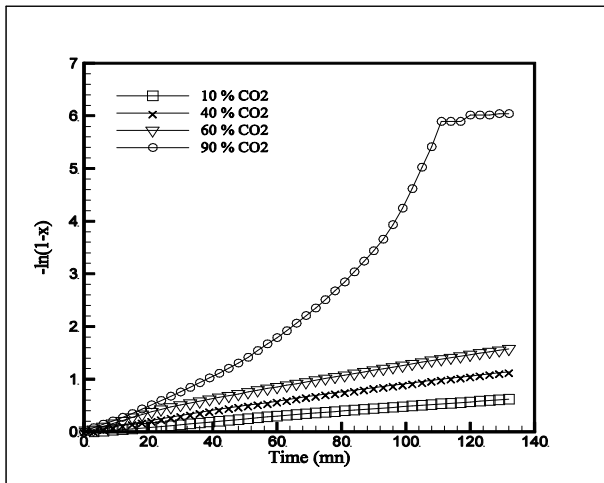


Fig.6 a) Variation curve of  $-\ln(1-x) = f(t)$  over a period of 132 min in VRM model and b) Shape of the VRM curve linearized in gasification at different temperatures

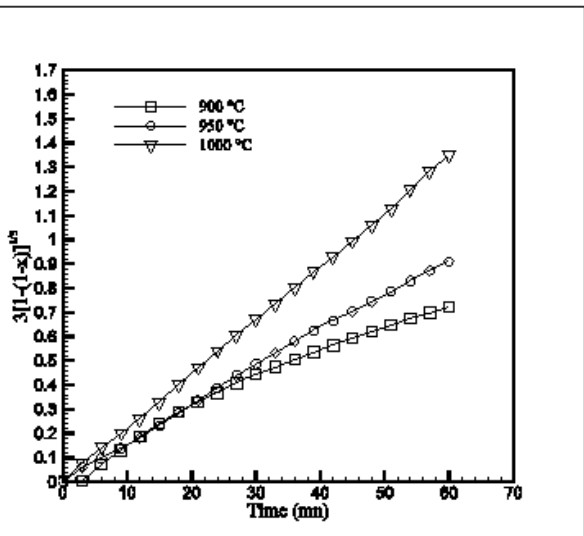
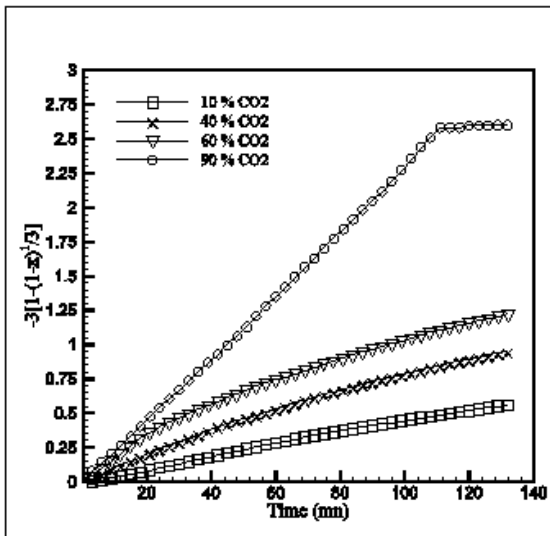


Fig.7 a) Variation curve of  $3[1-(1-x)^{1/3}] = f(t)$  over a period of 132 min in SCM model and b) Shape of the SCM curve linearized in gasification at different temperatures

The results obtained from the two models for all temperature were used in Fig. 9 for determining the reaction constants ( $k_{VRM}$  and  $k_{SCM}$ ). The latter can be obtained from the slopes of each graph of Fig. 6b and 7b. Compared to the VRM model, the SCM model has the smallest gaps, especially at 1000 °C. In addition, there is a good agreement tendency in the fits illustrated by fig. 6a and 7a.

**a) Reaction control for spherical particle**

Due to the fact that carbon conversion was not completely achieved at 1000 °C, therefore we are going to highlight the type of reaction control, by evaluating the diffusion coefficients and mass transfer in the case of SCM model (table 4). Thus, for a gasification reaction at a temperature of 1000 °C, and CO<sub>2</sub> concentration of 90 NL/h parameters were calculated. Table 4 resumes the estimated values for a spherical particle.

**Table 4: Reaction rate, diffusion and masse transfer coefficients for spherical char biomass gasification (SCM)**

Reaction control type	Temperatures		
	900 °C	950 °C	1000 °C
Mass transfer coefficients (m.s <sup>-1</sup> )	1.9210 <sup>-06</sup>	3.0410 <sup>-06</sup>	3.8710 <sup>-06</sup>
Reaction rate constant (s <sup>-1</sup> )	9.5910 <sup>-08</sup>	1.5210 <sup>-07</sup>	1.93010 <sup>-07</sup>
Mass diffusion coefficients (m <sup>2</sup> .s <sup>-1</sup> )	3.2010 <sup>-12</sup>	5.0710 <sup>-12</sup>	6.4510 <sup>-12</sup>

Furthermore, we measured reaction times for the three different temperatures (900, 950 and 1000 °C) in order to have more details on reaction control type using the SCM model.

The time computed here means the time to reach any stage of conversion and the total time required to complete particle conversion is equal to the sum of time required to complete film reaction alone, plus time required to complete ash reaction alone and time required to complete reaction alone when taking account to the simultaneous action of these three resistances for the shrinking core model.

The time for complete disappearance of a particle or time required for complete conversion for small particles in the stokes regime are shown in table 5 below [22].

**Table 5: Conversion time expression, Shrinking-core model [22]**

Particle shape	Film diffusion control	Ash diffusion control	Reaction control
Sphere	$\frac{t}{\tau} = X$	$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X)$	$\frac{t}{\tau} = 1 - (1 - X)^4$
	$\tau = \frac{\rho R}{3bk_g C_g}$	$\tau = \frac{\rho R^2}{6bD_e C_g}$	$\tau = \frac{\rho R}{bk'' C_g}$

For example, for ash-free particles which shrink with reaction, only two resistances, gas film and surface reaction,

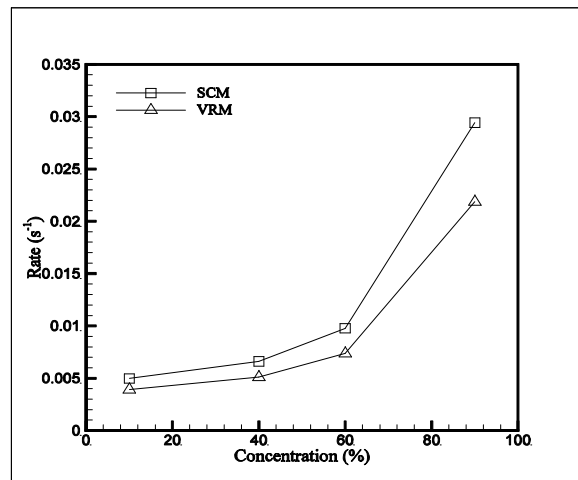
need to be considered. Because these are both based on the changing exterior surface of particles.

Where  $D_e$  (m<sup>2</sup>/m solid.s) is the effective diffusion coefficient of gaseous reactant in the ash layer;  $k_g$  is the mass transfer coefficient between fluid and particle;  $\rho$ , the molar density of reactant in the solid ;  $C_g$ , gaseous reactant concentration;  $b$ , stoichiometric coefficients for the reactant ;  $k''$ , reaction rate constants;  $k_g$ , mass transfer coefficient of the gas film (mol/m<sup>2</sup>.Pa.s);  $R$ , radius of particle (m), and  $X$ , fraction of reactant converted, the conversion (-).

Table 4 shows that the reaction control is based on mass diffusion showing that at the high temperature, 1000 °C, carbon conversion was not achieved. Furthermore, beyond 1000 °C, one can get control of the reaction kinetics for the SCM model.

For these different reaction temperatures, time were found to be 36, 29 and 26 min, respectively for 900, 950 and 1000 °C. This explains the fact that the SCM model is less suitable for such orders of temperature magnitude compared to VRM model which gives reasonably good values of the kinetics (control type).

The following figure (fig. 8) summarizes the reaction rates of different models according to the concentration.



**Fig. 8 Reaction rate variation for the three models based on CO<sub>2</sub> concentration at 1000 °C**

The value of the activation energy determined using fig. 9 (126.21 kJ/mol) in the VRM model for biomass char sample (size 200 μm) is in a good agreement with Ollero [23] value (126.10 kJ/mol) found for a olive residue char (45-150 μm) at CO<sub>2</sub> gasification (800 - 950 °C).

Therefore, De Micco [24] and ([25], [26]) show that gasification reaction with CO<sub>2</sub> is normally controlled by the chemical reaction and occurs nearly uniform throughout the interior surfaces of the char particles, for char particles smaller than 300 μm and temperatures below 1273 K. This remark supports the values obtained in the table 6. If the chemical reaction kinetic is the slowest process, the char particle reduces its density by increasing its porosity and leaving its external diameter almost unchanged.

Base on the linear characteristic of eq. 6 and temperature operation we can determine the values of E and  $k_0$ . The curves  $\ln(k) = \ln(k_0) - E/(RT)$  for the two models are presented in fig.9.

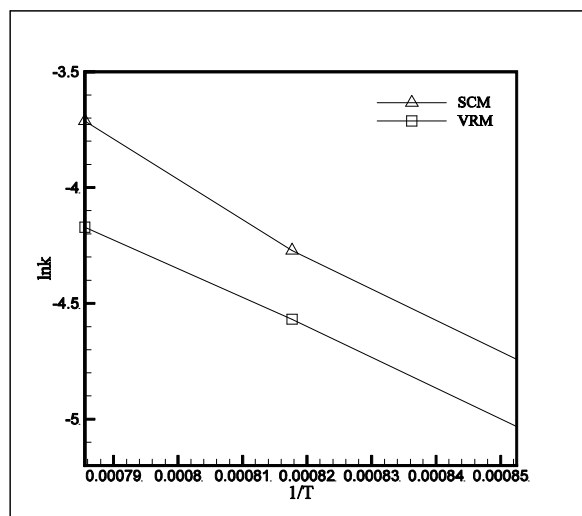


Fig. 9 Arrhenius plot for biomass char at 1000 °C for the two models

Table 6: Summary of the kinetic parameters of the biomass char sample during CO<sub>2</sub> gasification

Models	Equations	R <sup>2</sup>	E (kJ/mol)	k <sub>0</sub> (min <sup>-1</sup> )
VRM	$\ln k = (-15169.9/T) + 8.3888$	0.9997	126.21	$2.64 \cdot 10^5$
SCM	$\ln k = (-15974.4/T) + 8.6805$	0.9796	132.91	$3.53 \cdot 10^5$

VRM model fits the experimental data better than SCM ( $R^2 = 0.9796$ ) model, since it displayed a significant fit and has the highest  $R^2$  value (table 6).

As observed, the model describes adequately the experimental data for low conversion levels. As observed in the table 6, similar activation energies and reaction orders were estimated by applying the two models described before. Activation energy estimated for gasification of the biomass char by SCM model is higher than the activation energy obtain from VRM.

Finally, based on table 6 we can determined for each of the three operating temperatures the activation energy corresponding to the different models used in the present work (see table 7).

We note that the activation energy remains almost constant at the desired temperatures for the same sample, only the reaction rate varies with temperature.

Table 7: Summary of biomass char kinetics according to temperature range

Temperatures	VRM		SCM	
	k <sub>VRM</sub>	E	k <sub>SCM</sub>	E
900 °C	0.00873	127.469	0.0075	132.490
950 °C	0.01396	128.121	0.0114	133.813
1000 °C	0.0102443	127.433	0.0219	132.416

## b) Reaction order and CO<sub>2</sub> partial pressure effect

In our experiments we maintained constant partial pressure of CO<sub>2</sub> while increasing the partial pressure of N<sub>2</sub>, diluent. And by varying reaction temperature (900-1000 °C), we are able to compute partial pressure effects on the measured reaction rates.

Fermoso [6] investigated the effect of the total and partial pressures of CO<sub>2</sub>. They have shown that an increase in the total pressure of the system during the gasification tests results in a decrease in the reaction rate. They also observed that the reaction rate increases proportionally when increasing the partial pressure of CO<sub>2</sub>. Also they found that the apparent reaction order with respect to CO<sub>2</sub> partial pressure was 0.33 and 0.35 for gasification at 1 and 10 bars, respectively.

Renganathan [27] shows that pressure has a negative effect on CO<sub>2</sub> gasification, increasing the carbon formation and decreasing the CO<sub>2</sub> conversion.

The partial pressure of CO<sub>2</sub>,  $P_{CO_2}$ , is obtained from the equation of state as follows:

$$P_{CO_2} = y_{CO_2} P_{tot} = (n_{CO_2}/n_{tot}) P_{tot} \quad (8)$$

Multiplying by the molar volume and by the time the numerator and denominator of the above equation, we get:

$$P_{CO_2} = Q_{CO_2}/Q_{tot} P_{tot} \quad (9)$$

where  $y_{CO_2}$ ,  $n_{CO_2}$ ,  $n_{tot}$ ,  $P_{CO_2}$  and  $P_{tot}$  are the molar fraction, number of mol of CO<sub>2</sub>, total number of mol of gas, partial pressure of CO<sub>2</sub> and total pressure of the gas, respectively. From the relationship between  $k_{VRM}$  and  $P_{CO_2}$ , the reaction order (n) with respect to CO<sub>2</sub> gasification was calculated as 0.43, as shown in fig. 10.

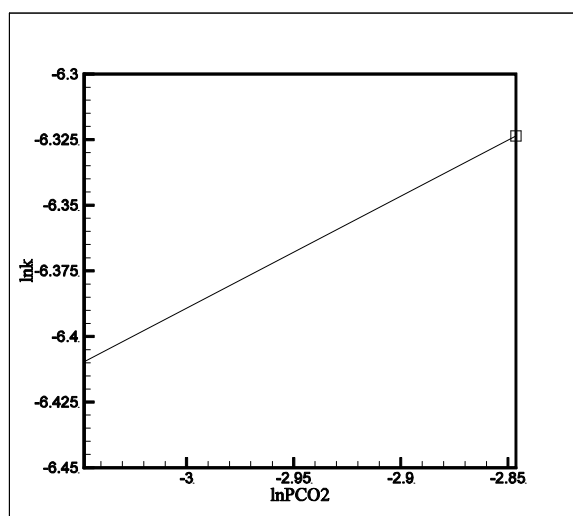
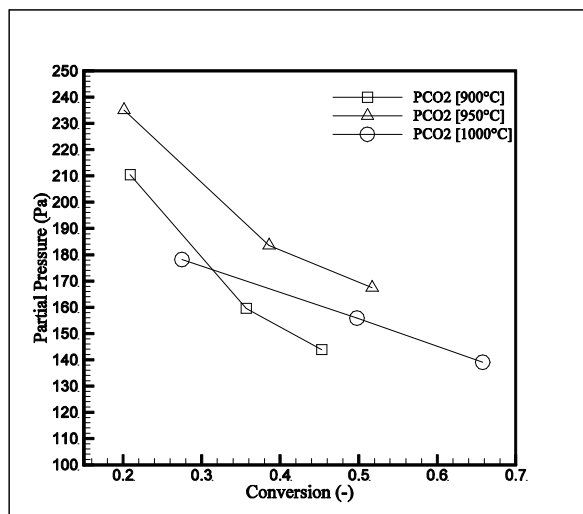


Fig. 10 Log plot of  $k_{VRM}$  vs. CO<sub>2</sub> partial pressure

From fig. 10 we notice that at high CO<sub>2</sub> concentrations, the conversion rate is better when increasing the partial pressure of CO<sub>2</sub>. For these concentrations, the partial pressure is independent of the conversion rate (fig. 11).



The reaction rate increase proportionally when increasing the partial pressure of CO<sub>2</sub>.



**Fig.11 CO<sub>2</sub> partial pressure versus carbon conversion ratio**

In addition, to better illustrate the effect of temperature, we plot the variation of the partial pressure of CO<sub>2</sub> in the rate of conversion for the highest concentration (90%) for temperatures 900, 950 and 1000 °C. The curve (fig. 11) shows that when the temperature is high, the partial pressure of CO<sub>2</sub> is low and the conversion rate becomes better. This result is in agreement with the work of Renganathan [27] which shows that pressure has a negative influence on CO<sub>2</sub> gasification when increasing the carbon formation and decreasing the CO<sub>2</sub> conversion at high temperature.

## VI. CONCLUSION

Biomass chars gasification pyrolysed at 450 °C submitted to CO<sub>2</sub>/N<sub>2</sub> ratio under chemical control conditions was satisfactorily described by SCM model. The results showed that:

- The more we increase the concentration of CO<sub>2</sub> which correspond to a decrease on N<sub>2</sub> concentration the more we split the point (coordinates) giving the minimum starting temperature gasification;
- in a chemically controlled reaction, process undergoes three steps: chemical adsorption to the solid surface, surface reaction step and the desorption from the solid surface. Therefore, the chemically controlled reaction has been shown in comparing total reaction time, time for diffusion, diffusion coefficient and mass transfer coefficient.
- Activation energies were calculated for the two models. For SCM, the activation energy obtained is closed to those obtained by [1], the result is in good agreement with result obtained by Ollero [23].

At this stage of work, our results suggest that it is better to gasify biomass char (pyrolyzed at 450 °C) with high temperatures at around 1000 °C, CO<sub>2</sub> flowrate between [60-90] NL/h, and CO<sub>2</sub> partial pressures of between 5000 and 8000 Pa. Finally the

computation of the kinetic parameters using eq 2 is very suitable for this char gasification with CO<sub>2</sub>; again, mass diffusion controls the kinetics.

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