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Abstract:

Experimental gasification studies are reported for highly reactive peanuts, palm and cashew nut shells chars from Ziguinchor area in order to aliment a local clay brick baking unit. The gasification tests were operated in a fixed bed reactor under steam and/or carbon dioxide at three different temperatures (950 °C, 1000 °C and 1050 °C), in order to investigate the experimental conditions of three samples at different particle size. The gasification of char conversion at different temperatures is found to be dependent on gasifying agent, nature of the sample, and can be explained by the Arrhenius equation, thus suggesting the use of three different models: Volume Reaction Model (VRM), Random Pore Model (RPM), and Shrinking Core Model (SCM) in order to interpret the carbon conversion data and to determine the kinetics parameters.

From the results obtained, temperature has a positive effect on the kinetic conversion. Further, the gasification under mixed atmosphere of steam and carbon dioxide showed that the reactivity of the different chars depends on the increase of steam concentration in the mixture. The gasifying char types has some effects in the determination of the kinetic parameters (activation energies obtained ranged between 110 - 126 kJ/mol for peanut shell, 104 - 125 kJ/mol for the cashew shell and 116 - 150 kJ/mol for the palm shell). By using different models, the experimental results shows that the kinetics reaction of the cashew shells char, and peanuts shells char, are faster than those from palm shells char. At the same time, results showed that the char-steam reactivity, char - CO_2 reactivity and their mixture (char-steam and char - CO_2) are different. The experimental measurements also show the influence of temperature on the Lower Heating Values (LHV) of the gas. The LHV of gas obtained are between (8- 12 MJ/Nm^3) and that, these values (LHV) are inversely proportional to the particles size of the biomass. While, based on the Europe Environment and Energy Management Agency (ADEME) standards on Lower Heating Value of gas, these gases obtained under all experimental conditions can be safely used to operate motor functioning with to gas.

Keywords:

Kinetic conversion of char, gasification of char, Char - CO_2 reactivity, Char - steam reactivity, Lower Heating Values

1. Introduction

Fixed bed reactor is known as a promising and effective way to transform biomass, such as vegetables and agricultural residues, into a more valuable combustible gas. However, the availability of biomass feedstock, and enhancement of the test parameters for gasification processes is becoming a big challenge for the Scientific Community. Therefore, technical processes need to be improved so that the biomass feedstock can be converted completely into a high quality gas synthesis that can be used directly for heat and power production. In order to optimize any biomass gasification process and to adjust process parameters to achieve complete conversion of the feedstock, a detailed knowledge of the way in which the experimental conditions influence the conversion mechanism is important. Gasification is a clean and efficient way to convert carbonated solid to gaseous products. Therefore, an investigation on the reaction mechanism of char-CO_2 and char-steam gasification during the reaction process [1], and the kinetic parameters can provide a basic work for a better understanding and a proper reactor design for the biomass gasification process [2].

Many researchers have worked on the char gasification mechanism in CO_2 and/or H_2O separately. According to Bai *et al*. [3], char-CO_2 reaction and char-H_2O reaction are both fundamentally important reactions. Thus, the mechanisms of the char-CO_2 reaction and the char-steam reaction have been studied extensively by [4]. These authors explain that, the mechanisms of the Char–CO_2 reaction and the Char–H_2O reaction have been considered to be essentially the same. The conversion level of char in the gasification step determines the overall efficiency of the gasifier.

Furthermore, the char conversion directly depends on its reactivity with gasifying agents such as oxygen, steam or carbon dioxide. There are several experimental parameters which may affect the gasification process and among them temperature is the most important parameter one [2]. Thus, Fermoso *et al*. [5], said that, the temperature was one of the most important parameter, which affect the performance of the gasification process. Furthermore, Taba *et al*. [6], have shown that, temperature is one of the most significant operating parameters, which have an effect on the gaseous composition, carbon conversion, gas yield, heating value, and finally char and tar yields, throughout the gasification reactions. This effect depends on the thermodynamic and endothermic behavior of the reactions. Yet, according to Huang *et al*. [7], the kinetics of char gasification play a key role since they provide valuable information of the proper design and operation of gasifier. It has been reported also by [8], that the rate of conversion of the gasification of char is one of the key factors to analyze the performance of gasifier. For this reason, the complexity of the gasification process, the differences in the char reaction can be due to the chemico-physical property of waste biomass, and experimental conditions.

Several kinetic models have been proposed to describe the relationship between the reaction rate and the reaction time. However, the utilization of the kinetic models was the subject of several recent studies. The aim of these models is to determine the kinetic parameters and also interpret the experimental results of char gasification under steam or CO_2 atmospheres.

Therefore, Tang *et al*. [9] concluded that, it is hard to establish a universal mathematical expression to correlate the gasification rate of an arbitrary char with the influencing variables. They gave some known kinetic models adapted to char gasification and highlighted that, the models are developed over a long period of research progress but each model is merely asserted from case to case.

In this context of discussion on parameters that affect the performance of the gasification process, we propose to investigate the effects of gasification temperature on the char conversion, the examination of reactivity of char samples, and gasifying agent during gasification process using isothermal half-reaction index reported by [3], and using kinetics models.

This comparison of the effect of these samples on the kinetics conversion has never been studied in the literature. The LHV (8- 12 MJ/Nm^3) of the gases obtained without catalyst with our samples and experimental conditions is new in the thermochemical conversion field. The results show that the char-CO_2 and char- H_2O reaction are different. It was also remarked that the temperature and the type of char sample are the most influential parameters in our experimental conditions. And, using volumetric reaction model (VRM), random pore model (RPM) and shrinking core model (SCM) kinetic models our tests data were interpreted and also kinetic parameters were determined.

2. Experimental study

2.1. Experimental samples

Palm shells from Ziguinchor, were provided by the Guirassy soap Company. In 2015, palm shell presents a calculated quantity of 97 700 tones (FAOSTAT 2015). The residues that are not used by the Guirassy soap Company, are discharged on the coast of Casamance river and burned in the open area, which represents a threat to the social and ecological environment. These cases are, considered ecological and environmental threats since, they have a good amount exploitable energy and a good calorific value (21.4 MJ/kg). This biomass is of interest to us because we intend to use it as raw material.

Peanut shells are agricultural residues abandoned in the crop fields obtained from the surrounding villages in the southern region of Senegal, Ziguinchor. They present an approximate LHV of 17 MJ/kg, and presenting an amount of 412 560 tones (FAOSTAT 2015). Thus, the use of this residue as an energy source would be a worthy contribution to the preservation of the environment. Furthermore, the energy production from these residues can solve the problems of energy from waste disposal.

Cashew nut shells are residues obtained, from cashew shelling. This biomass residue is abundant (231 760 tones FAOSTAT 2015), and generates high energy content (21.9 MJ/kg). Currently, artisanal traders rejected cashew nut shells without any valuation. They were often burned in open air and cause several socio-environmental problems. Therefore, the issue of energy recovery by thermo-chemical process arises as the best solution about this negative impact on the environment and on the population as well.

It should be noted that these three residues of biomass are seasonal. Thus, the palm shells are present all the year in Casamance and mostly from January to August. While, peanut shells are obtained during the dry season (corresponding to the harvest period), mainly during the period from November to May. Finally, cashew nut shells are obtained in abundance between the periods from April to July.

In order to prepare char samples for gasification tests, peanut shells, palm shells and cashew nut shells were pyrolysed, using a muffle oven at 450 °C under inert atmosphere (in presence of 50 NL/h N_2) and heating rate of 10 °C/min. Thus, char yields obtained is about an average to 39.97% of palm shell char, 38.39% cashew shell char and an average 36.84% peanut shell char.

The chars of these samples were ground and sieved into one average fraction of 0.63 mm, 3 mm, 12 mm and 30 mm. Results of proximate and ultimate analyses of these chars, obtained in compliance with standards are listed in Table 1.

Table 1: Ultimate and proximate analyses and waste production between 2014-2015

Biomass	**Palm Shell**	**Cashew N Shell**	**Peanut Shell**
Proximate analysis (Wt. %)			
FC	71.57±0.056	69.40±0.021	74.76±0.044
VM	21.81±0.043	27.00±0.041	14.82±0.053
Moisture	0.21±0.029	0.10±0.027	0.02±0.030
Ash	6.41±0.039	3.50±0.051	10.40±0.052
LHV (MJ/kg)	33.34±0.053	33.57±0.027	29.24±0.060
Elementary analysis (Wt. %)			
Carbon	86.50±0.025	85.40±0.028	81.22±0.048
Hydrogen	5.10±0.026	4.97±0.020	3.42±0.062
Oxygen	7.64±0.028	8.60±0.051	14.24±0.054
Nitrogen	0.56±0.052	0.96±0.038	1.02±0.043
Soufre	0.20±0.031	0.07±0.034	0.10±0.071
Waste quantity (tones)			
2014-2015	97 700	231 760	412 560

Agro-vegetable waste gains increasing attention around the world as they are a kind of renewable resource widely available cheap and environmentally friendly.

2.2. Experimental descriptions

The samples char gasification tests were conducted using a fixed bed reactor (36 mm internal diameter and 350 mm height) and equipped with a porous plate for bed support. Figure 1 shows a flow diagram of the system used. The main elements of the system consist of three sets: a gas analyzer, a gas condensation and cleaning system, and the fixed bed reactor.

After preheating the reactor, 15 g of char is mixed with 70 g of sand and charged in the reactor, under a nitrogen atmosphere, until reaching the desired temperature. Sand is used in order to improve heat transfer inside bed particles and for minimizing the preferential gas passage. The reactor temperature is controlled by means of a thermocouple, in contact with the sample bed and connected to a temperature controller. The gasification tests were carried out isothermally at 950 °C, 1000 °C and 1050 °C, using steam and CO_2 (90 %) and carried in an inert flow of 10 % of nitrogen. Flow rates of CO_2 and N_2 were fixed by the use of mass flow controllers while the flow rate of water was adjusted by an HPLC (High Performance Liquid Chromatography) piston pump. Before entering the reactor, N_2, CO_2, and H_2O cross a preheating section. The composition of the produced gas is obtained by online gas analysis, using an SRA-Instruments gas analyzer (µGC), after condensation and cleaning systems. For a reliability of our results, each test was repeated 4 times to guarantee the repeatability of the results and the average was represented.

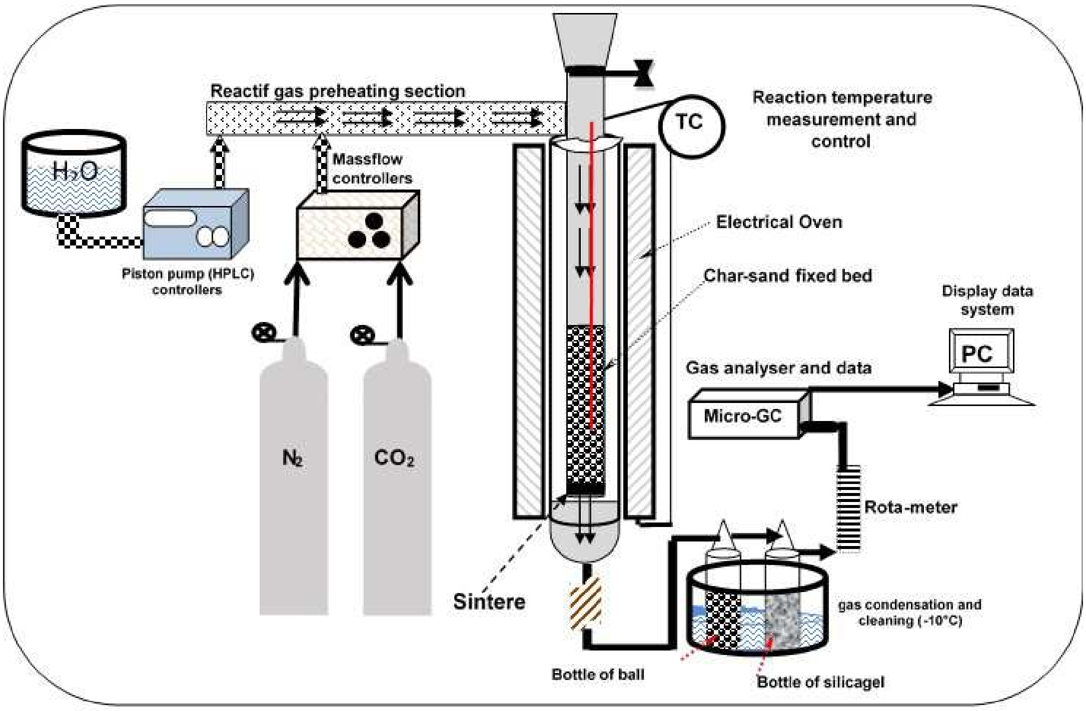

Figure 1: Simplified representation of the fixed bed reactor

The results are presented with uncertainties in experimental parameters to illustrate the repeatability of the tests obtained on gasification. From the comparison of the results from four trials (figures and tables), we can see that, a weak dispersion (error bars of 2-7%) is obtained according to the sample. This dispersion remains rather low for cashew shells, and palm shell char between 0 and 5%. However, for peanut shell chars, the observed experimental errors become more significant (3-7%). These errors can be caused by:

- uncertainties related to temperature fluctuations during gasification tests; they are greater for lower temperature (950 °C) ;
- uncertainties on measuring instruments (flow meters, balances, micro-GC...).

3. Results and discussions

The gasification char experiments were investigated at different conditions in a fixed-bed reactor. The results of char conversion rate are obtained by the following equation:

$$X_i = \frac{m_0 - m_{i+1}}{m_0 - m_{ash}} \qquad (1)$$

where, m_0: initial mass, m_{i+1}: the mass of the sample at time t, m_{ash}: the mass of ash remaining in the reactor.
The effect of the main operation variables such as temperature, particle size and type of the char used on the gasification process was studied, by evaluating and comparing the char kinetic conversion.
The char conversion, X, (equation 1) was defined as the total carbon contained in the produced gas (CO, H_2 and CH_4), with respect to the total carbon contained in the char's fixed bed. The amount of gas generated during gasification tests was calculated from nitrogen balance, since the amount of nitrogen fed in and the composition of nitrogen evolved are known.
In order to quantify the gasification reactivity of char sample, the isothermal half-reaction index $R_{0.5}$ reported by [3] was used.

$$R_{0.5} = \frac{X_{0-0.5}}{t_{0-0.5}} \qquad (2)$$

where, $X_{0\text{-}0.5}$ is char conversion data variation denoted by X = 0 to X = 0.5 and $t_{0\text{-}0.5}$ denotes the time required to reach a char conversion of X=0 to 50. So, the results obtained of the half reaction index (equation 2), are used to interpret the effect of temperature on char conversion.

3.1. Effect of temperature on the rate of carbon conversion

The gasification tests were carried out on chars of palm shell, peanut shell and cashew shell at temperature range of 950 °C-1050 °C. The results obtained using equation 2 shows the effects of temperature during char gasification with steam and/or CO_2, for particle size 3000 µm are shown in figure (2, 3 and 4). Figure (2, 3 and 4) show the char index $R_{0.5}$ as a function of gasification time at different temperatures for the particles size of 3000 µm. Char conversion is from the accumulated amount of carbon released as gaseous products including CO, CH_4 through the heat up and steams with char gasification, divided by the total amount of carbon in the fed char. Figures (2, 3 and 4) show that, the chars are sensitive to temperature variations, where an increase in temperature results in an enhancement in reactivity of carbon. We can see in these figures that the tendency of the half-reaction index obtained from 1050 °C is above that of 1000 °C. And the half-reaction index at 1000 °C is greater than that at 950 °C. The influence of gasification temperature on char kinetic conversion is very important, since all of steps of the char-CO_2, and/or char-steam reactions for syngas production are temperature dependent.

The amount of volatile matter, which is cracked from the solid, is a function of temperature. Several authors show that higher temperatures favor the production of syngas, such as [10-14] in their respective studies.

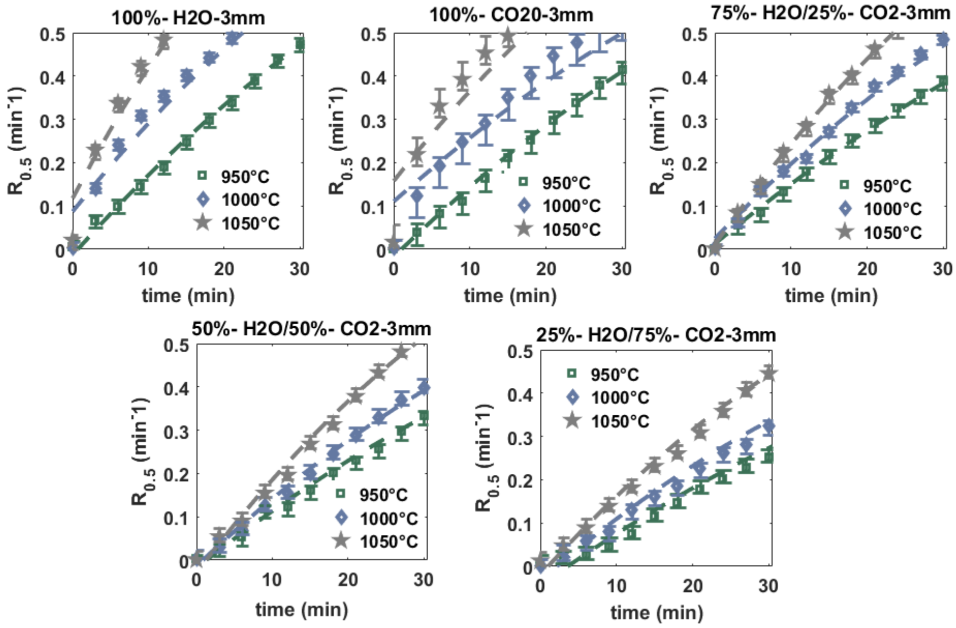

Figure 2: Effect of the temperature on the palm shell char reactivity

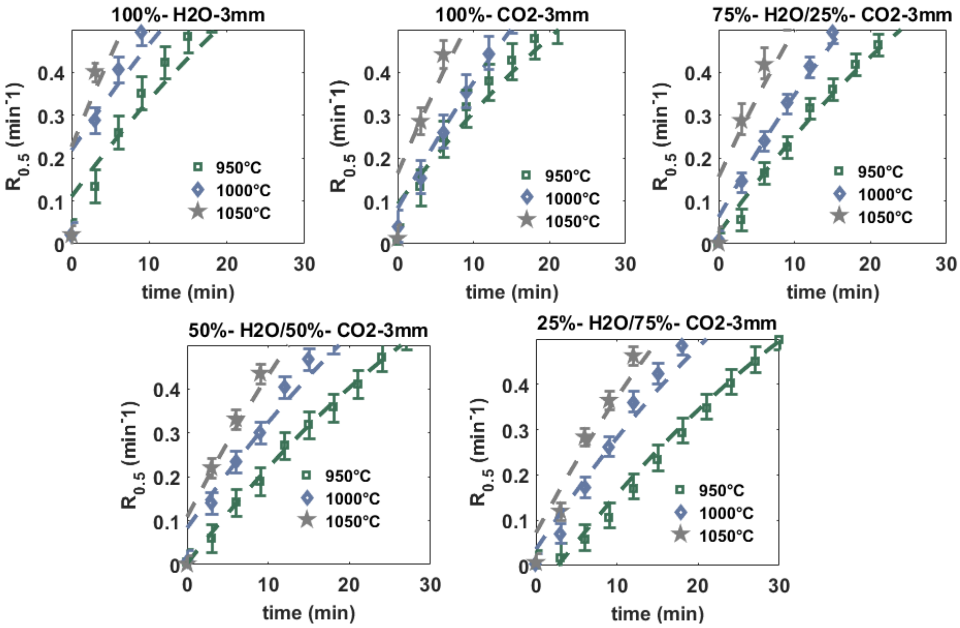

Figure 3: Effect of the temperature on the cashew nut shell char reactivity

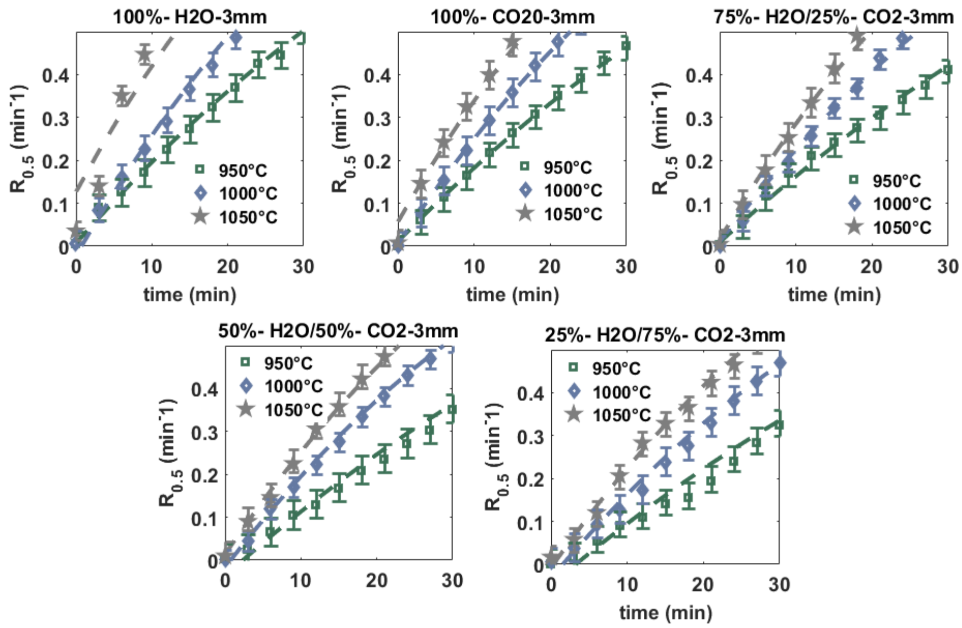

Figure 4: Effect of the temperature on the cashew nut shell char reactivity

This effect can be explained by the principle of Le Chatelier: that the products formed during the endothermic reaction are favored at high temperature. This result supports the choice of kinetic basing on activation energy used the models (volumetric reaction model, shrinking core model and random pore model). The models can be used to predict the conversion of the biomass char gasification and optimize the design and operation of the gasified [1]. Thus, some known kinetic models adapted to char gasification are listed below.

The volumetric reaction model (VRM) does not consider the structural changes of the char during gasification, assuming that the gasifying agents react with char at all active sites, which are uniformly distributed on both outside and inside surface particle [15]. The rate expression is thus given by:

$$\frac{dX}{dt} = k_{VRM}(1 - X) \tag{3}$$

$$\ln(1 - X) = k_{VRM}t \pm ct \tag{4}$$

where, k_{VRM} is rate constant corresponding at VRM and X is a char rate conversion.

This equation represents the physical and chemical profiles of the sample and several models represented it. Nevertheless, the profile of the conversion of carbon is a tendency of the Arrhenius equation.

$$k_{VRM} = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

Equation (4) can be further transformed as:

$$\ln(k_{VRM}) = \ln(k_0) - \frac{E_a}{RT} \tag{6}$$

where, k_0, E_a, R, and T are the pre-exponential, activation energy, universal gas constant, and the experimental temperature, respectively. In this expression E_a the activation energy, i.e. the energy that sample particle must acquire to be able to react. We note that $\ln(k_{VRM})$ is the logarithmic of the k corresponding to the VRM.

The shrinking core model (SCM) considers that the gasifying agents react on the surface of nonporous grains or in pore surfaces within the solid [15]. According to different assumptions, the reaction rates in the regime of chemical control can be expressed as:

$$\frac{dX}{dt} = k_{SCM}(1 - X)^{2/3} \tag{7}$$

$$3 \times (1 - X)^{1/3} = k_{SCM}\, t \pm ct \tag{8}$$

This model is able to predict a maximum for the reactivity as the reaction proceeds, as it considers the competing effects of pore growth during the initial stages of gasification, and the destruction of the pores due to the coalescence of neighboring pores during the reaction. The random pore model (RPM) can describe the behaviours of the systems, where the reactivity shows a maximum at the conversion levels of $x < 0.3$ or indicates a steady decrease with the increase of conversion.

$$\frac{dX}{dt} = k_{RPM}(1-X)\sqrt{(1-\psi\ln(1-X))} \tag{9}$$

$$\left(\frac{2}{\psi}\right)\left[\sqrt{(1-\psi\ln(1-X))}-1\right] = k_{RPM}t \pm ct \tag{10}$$

Some modification is made by introducing a new expression when equation (10) is multiplied by $\left(\psi^2/4\right)$, the following was obtained:

$$\left(\frac{\psi}{2}\right)\left[\sqrt{(1-\psi\ln(1-X))}-1\right] = k_{RPM}t \pm ct \tag{11}$$

$$\psi = \frac{2}{2\ln(1-X_{\max})+1} \tag{12}$$

According to (Liu *et al*. [16], the values obtained for Ψ_0 with eight chars are in a range of 2.2–7.7. We applied a mean of Ψ_0=4.6 in carbon burnout kinetics gasification for all char types. Thus, we have in our studies a mean of X_{max} of peanut shell char equal 0.153, of X_{max} of cashew nut shell char equal to 0.154, and a mean of X_{max} for palm shell char equal to 0.144. These values are used to calculate the dimensionless parameter (ψ) of each char.

The value of parameter (ψ) is mainly dependent on the type of the solid fuel and the char formation condition. Additionally, the structural parameter can be calculated by means of maximal conversion degree of solid, X_{max}, for which maximal reaction rate is observed. From these results, the dimensionless parameter (ψ) for cashew nut shell char, for palm shell char and for peanut shell char, was equal to ψ_1 = 3.001; ψ_2 = 2.900, and ψ_3 = 3.000, respectively. For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a chemical and structural composition of sample dependent. In the suite, the results obtained with these models, are used to study the kinetics of sample structure evolution and the effect of mixture volume composition of the reactant.

3.2. Effect of sample structural evolution on the kinetics conversion

For the purpose of studying the effect of the sample nature on conversion kinetics during gasification, the gasification tests were carried out under the same experimental conditions. Then, the results of the comparative study of the conversion kinetics of palm, cashew and peanut shells chars are represented in figure 5. We note ln(kVRM), ln(kRPM) and ln(kSCM) were respectively the logarithmic of the k corresponding to the VRM, RPM and SCM. It is clear that the regression lines of the kinetic parameters of the plots follow well the evolution of the Arrhenius equation. We can see in this figure 5, that the coefficient of the trend of the cashew char is smaller than that of the peanut shell. On the latter we obtain a smaller slope, in comparison to the coefficient for the palm shell char. Since, the slope of the equation used corresponds to ($-E_a/R$), with R the perfect gas constant; the activation energy (E_a) obtained from the cashew nut shell char is smaller than the one obtained from the peanut shell char, and the latter one in turn has a smaller E_a than that of the palm shell char. Starting from the remarks made by [17], we can conclude that the cashew nut shell char is more reactive than the peanut shell char, which is in turn more reactive than the palm shell char. This effect could be due to the different reasons of these chars composition. The characteristics of the char that affected the reaction rate are essentially: the structural properties, which include the surface area and porosity, the intrinsic reactivity, depending on the surface chemistry and catalytic effect of the ash compounds. The latter conclusion may also be due to the char pores as the structure opens, which allows the gasifying reagent greater contact with the char carbon, and which increases the kinetic char conversion.

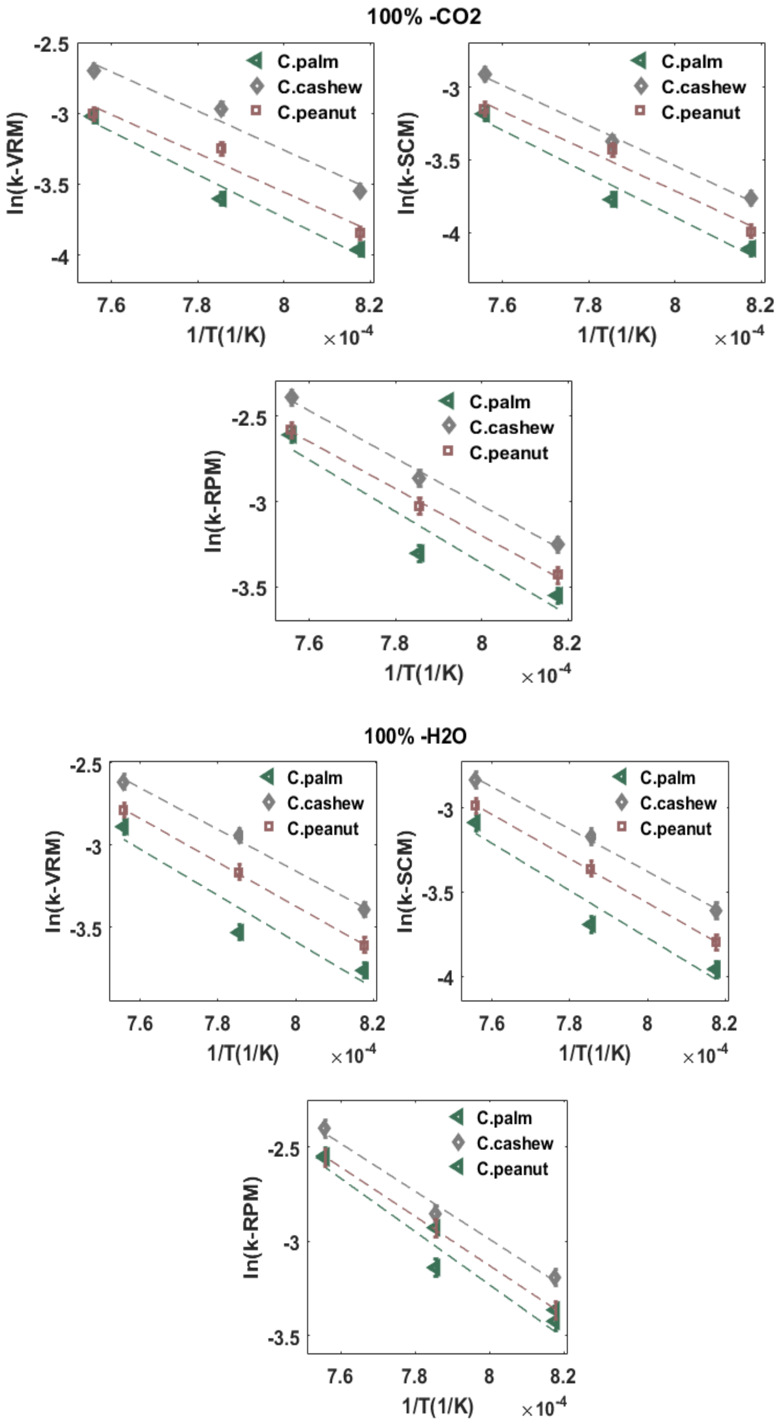

Figure 5: Reactivity of the three chars plot of ln(k) depends on (1/T)

Moreover, the following remarks may be the reasons for the difference noted on the conversion kinetics of our samples:

- the strong presence of ash (on average 2.64 g) in the case of the peanut shell char; these ashes are 0.43 g for the cashew shell char and 0.35 g for the palm shell char;
- the density of the cashew shell char is lower (0.39 kg/L) than that of the palm shell char (0.69 kg/L). Thus, on the basis of the thermal diffusivity equation (which is a function of the density), we can, as a first approximation, say that the cashew shell char will have a faster conversion speed than that of the palm shell char.

The palm shell has a harder structure, more resistant than the others samples (cashew shell, and peanut shell). This latter can contribute to the resistance of its char with respect to heat transfer and therefore low reactivity of the peanut. The remarks made in our study can be well correlated with the remarks of [18], which show that during the gasification tests of beech wood and maritime pine, the pine (soft wood) was more reactive than beech (hard wood). The char samples were extremely different in the gasification reactivity, although these chars were derived from the biomass main composition. The difference in the gasification reactivity clearly indicated that the mineral matter inherent in main compositions of biomass, have a strong activity for the char gasification, consistent with the relative abundance at the ash chemical composition.

3.3. Effect of the volume composition of the mixture of the reactant on the char kinetics conversion

To study the influence of the nature of gaseous reactants on reactivity, we carried out gasification tests of the char samples resulting from the pyrolysis of the different biomasses under H_2O (steam), CO_2 or under CO_2/steam mixtures in the following proportions: 75% / 25%, 50% / 50% and 25% / 75%. The plots obtained from these tests are grouped together in figures 6, 7 and 8 respectively for the palm, cashew, and peanut shell chars. From the results of ln(k_{VRM}) as a function of (1/T) for different proportions of reactive gases, we can see that we obtain a better reactivity of the chars samples with the steam compared with CO_2 and this whatever biomass used. It can also be seen that these chars are less reactive with the mixtures (CO_2/H_2O) than when these reagents (H_2O or pure CO_2) are used separately, and that this reactivity increases with the increase in the proportion of steam in the mixture. The competition between the H_2O and CO_2 for the active sites during gasification remains a controversial issue in the literature.

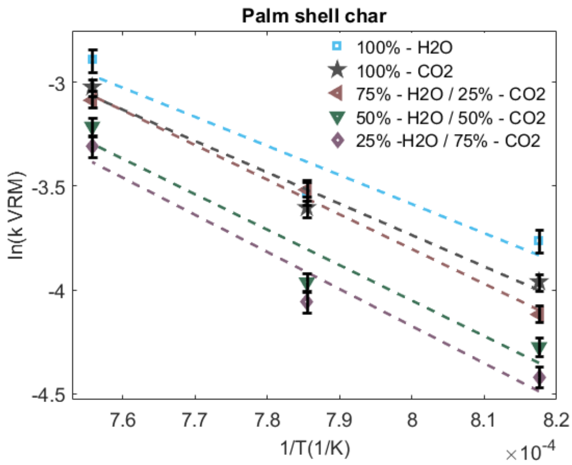

Figure 6: Ln (k_{VRM}) as a function of 1/T in the case of the char palm shell gasification under five atmospheres

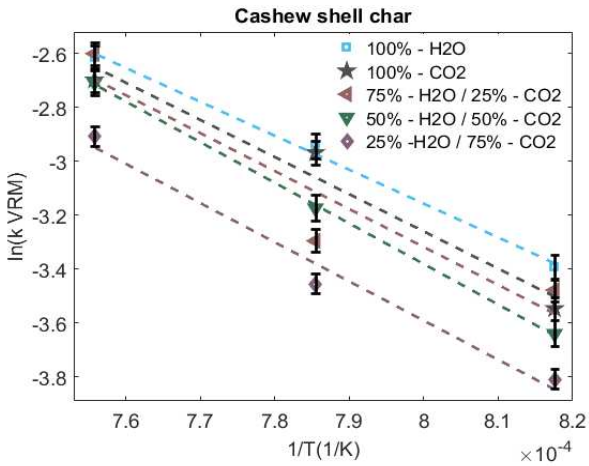

Figure 7: Ln (k_{VRM}) as a function of 1/T in the case of the char cashew shell gasification under five atmospheres

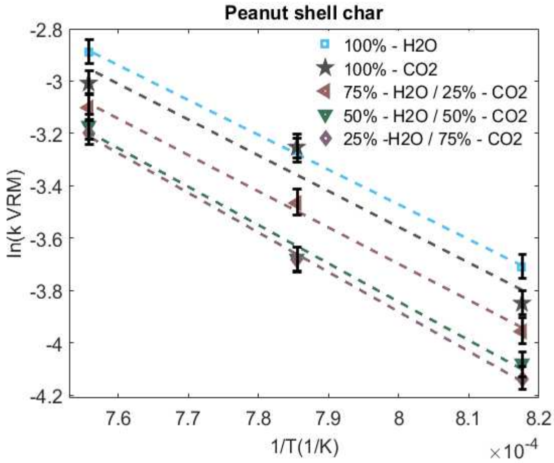

Figure 8: Ln (k_{VRM}) as a function of 1/T in the case of the char peanut shell gasification under five atmospheres

Table 2: The kinetic parameters

Models	E_a (kJ.mol^{-1})	A (min^{-1}) x E^{+3}	R^2	Reactifs	Samples
VRM	116.80±0.023	2.08±0.023	0.919±0.023	H_2O	**Palm Shell char**
SCM	116.07±0.031	1.71±0.031	0.951±0.031		
RPM	117.53±0.035	3.19±0.035	0.942±0.035		
VRM	126.00±0.051	4.36±0.051	0.975±0.051	CO_2	
SCM	124.44±0.040	3.20±0.040	0.968±0.040		
RPM	125.80±0.023	6.22±0.023	0.918±0.023		
VRM	139.30±0.045	14.62±0.045	0.995±0.045	H_2O/ CO_2-75/25	
SCM	138.69±0.052	12.92±0.052	0.998±0.052		
RPM	139.23±0.051	21.83±0.051	0.994±0.051		
VRM	142.42±0.034	15.39±0.034	0.936±0.034	H_2O/ CO_2-50/50	
SCM	141.37±0.025	13.85±0.025	0.951±0.025		
RPM	142.21±0.024	22.88±0.024	0.997±0.024		
VRM	148.96±0.037	25.54±0.037	0.952±0.037	H_2O/ CO_2-25/75	
SCM	147.28±0.043	22.58±0.043	0.988±0.043		
RPM	149.59±0.026	46.32±0.026	0.955±0.026		
VRM	104.81±0.030	1.01±0.030	0.995±0.030	H_2O	**Cashew nut Shell char**
SCM	103.45±0.027	0.78±0.027	0.997±0.027		
RPM	105.72±0.031	1.31±0.031	0.989±0.031		
VRM	114.84±0.018	2.39±0.018	0.975±0.018	CO_2	
SCM	115.31±0.012	1.89±0.012	0.968±0.012		
RPM	115.44±0.028	3.22±0.028	0.918±0.028		
VRM	117.26±0.036	2.85±0.036	0.884±0.036	H_2O/ CO_2-75/25	
SCM	116.96±0.057	2.40±0.057	0.949±0.057		
RPM	117.54±0.050	4.51±0.050	0.989±0.050		
VRM	121.04±0.042	3.12±0.042	0.979±0.042	H_2O/ CO_2-50/50	
SCM	120.99±0.008	2.30±0.008	0.923±0.008		
RPM	121.38±0.009	3.94±0.009	0.913±0.009		
VRM	125.47±0.011	5.90±0.011	0.999±0.011	H_2O/ CO_2-25/75	
SCM	124.37±0.024	4.87±0.024	0.999±0.024		
RPM	125.68±0.037	8.97±0.037	0.989±0.037		
VRM	110.63±0.054	1.29±0.054	0.999±0.054	H_2O	**Peanut Shell char**
SCM	109.28±0.048	0.94±0.048	0.999±0.048		
RPM	109.80±0.036	1.52±0.036	0.999±0.036		
VRM	113.70±0.050	1.70±0.050	0.955±0.050	CO_2	
SCM	112.91±0.046	1.40±0.046	0.973±0.046		
RPM	114.38±0.047	2.44±0.047	0.998±0.047		
VRM	115.25±0.047	1.61±0.047	0.996±0.047	H_2O/ CO_2-75/25	
SCM	114.65±0.039	1.34±0.039	0.984±0.039		
RPM	115.40±0.054	2.21±0.054	0.995±0.054		
VRM	121.92±0.039	2.64±0.039	0.992±0.039	H_2O/ CO_2-50/50	
SCM	120.41±0.053	1.98±0.053	0.992±0.053		
RPM	121.67±0.061	3.97±0.061	0.991±0.061		
VRM	125.92±0.050	3.74±0.050	0.998±0.050	H_2O/ CO_2-25/75	
SCM	124.59±0.048	3.26±0.048	0.995±0.048		
RPM	125.92±0.038	5.97±0.038	0.997±0.038		

Thus, these results could be explained by a CO_2 inhibiting effect on the reactivity of the char in the presence of water vapor.

On the other hand, several others [2,19,20] highlight, as in our case, the reasons for the effect of the conversion kinetics of the char under mixture of steam and / or CO_2.
Thus, in this same sense, the authors [2,19-21], estimate that conversion kinetics under carbon dioxide is about 2-5 times slower than that with water vapor. These show that steam and carbon dioxide affect the structure of the char differently during gasification. Umemoto *et al*. [21] go further by introducing the effect of the size of H_2O molecules, and CO_2, and explain that CO_2 does not diffuse small pores while the H_2O diffuses them [22]. These are in agreement with the conclusion of [22], that the different from the dominating effects of H_2O, CO_2 plays an increasingly more crucial role in the char structural changes during gasification step. And this could therefore be a reason that impacts the reactivity of chars for CO_2-rich mixtures. Moreover, this can also be explained by the inhibitory effect of CO on the production of H_2 advocated by [4].
The kinetic conversion of char gasification follows the order: pure H_2O (fastest) > pure CO_2 > CO_2 / H_2O mixture (slowest). The relationship between $\ln(k_{VRM})$ or $\ln(_{SCM})$ and $\ln(_{RPM})$ models vs (1/T) considering structural changes of the char reaction as the rate-controlling step is shown in figures (6, 7 and 8). If a linear regression is for every point in figures (6, 7 and 8), then, according to Eq. (6), the average apparent activation energy and pre-exponential factor of steam and/or CO_2 gasification of palm, cashew, and peanut shell chars are calculated by the slope and intercept of the fitting straight-line. The values are shown in Table 2.
All values of activation energy of SCM for sample were much smaller than the corresponding values of VRM and RPM. It can be seen that the values of activation energy obtained with three models are almost varied for each char, and only a slightly lower value of E_a was obtained for the cashew shell char. With the SCM model, the porosity of the particle remains constant and the particle size decreases with coke conversion [11]. Thus, the RPM model is used, because its description of the reaction of the solid is based on the assumption of reactivity occurring with pore size variation. In addition, the VRM model is used to describe the chemical evolution of coke particle conversion [18]. Thus the difference noted by the kinetic parameters obtained from these three models teaches the influence of pores, of the chemical conversion and particle size on the sample conversion kinetics. As shown in Table 2 the experimental results obtained on cashew shell char, are in agreement with those reported by [12], who also have determined the kinetic parameters of peanut shell char, and they obtained values of 103.45- 125.68 kJ/mol. The activation energy values obtained for palm shell char are slightly similar to those reported by [23], who obtained values of 116.07 - 149.59 kJ/mol according to the different gasification conditions. The activation energy obtained for the cashew nut shells char gasification is comprised between 103.45- 125.68 kJ/mol, as a function of gasifying agents.

3.4. Effect of temperature and particle size on gas performance

In order to study the performance of our gases treated and in order to highlight the effect of temperature, and the particle size on the Lower Heating Values (LHV) gases the following correlation (13) of Xie *et al*. [14] was used.

$$LHV = \left(30{,}0[CO] + 25{,}7[H_2] + 85{,}4[CH_4] + 151{,}3[C_nH_m]\right)\left(4{,}2/1000\right) MJ/Nm^3 \qquad (13)$$

where, [CO], [H_2], [CH_4], and [C_nH_m] the molar ratio of CO, H_2, CH_4, and C_nH_m in the produced gas respectively. According the equation (13), high CO, H_2, and CH_4 content of hot reducing gases would be beneficial for the char gasification process [24]. Using this equation (13), maximum peaks were listed according to the experimental conditions and the type of sample. The trends in the results obtained from equation (13) were grouped in figure (9) giving the variation of the LHV of the gases produced as a function of the experimental conditions. The analysis of the results obtained, we can notice that the differences between the regression lines of the LHV values of the gases obtained at different particles sizes remain important. We can also see that the LHV of the gases are improved with the increase of the temperature and decrease when the char particles size increases; which is in perfect agreement with the conclusions of [5, 25]. Our results are in agreement with thoses of researchers [10,14, 26-28], who have also noticed that the temperature has a positive effect on the conversion of char.
The values of the lower heating value (LHV) of the gases obtained from our various tests vary from 9 to 12 MJ/Nm^3 for gasification under CO_2, and from 7 to 11 MJ/Nm^3 under water vapor, compared to the LHV of the natural gas which is 36 MJ/Nm^3. Thus, in view of the composition of the gases and the value of the LHV of the gases recorded during the gasification of our various samples, we can conclude that these synthesis gases can be used for the production of electricity and/or heat. According to the following applications:

- our gases can be burned in a boiler for electricity generation using a steam turbine;
- they (our gases) can also be used in a gas turbine (TAG) or a gas engine, because, according to the Europe Environment and Energy Management Agency (ADEME), such gases must have a heating value greater than 4 MJ/Nm^3 to operate a TAG;

- always in the same motive and based on the study done by [29], working on the gasification of cashew nuts to supply a local food processing plant, with a fixed bed gasification system, and finding LHV of 3.51 MJ/Nm^3, we can promote use of our gases for the operation of an internal combustion engine. Moreover, according to ADEME this type of engine, is the most interesting in the use of gas producer gas.

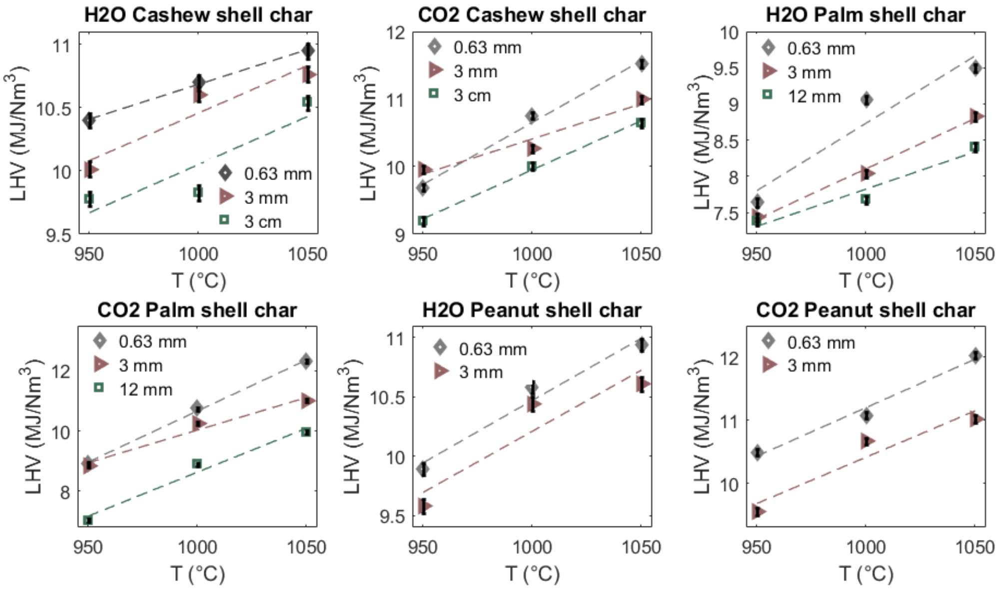

Figure 9: Gas PCI versus Temperature for Different Particle Sizes

However, the choice between an engine solution and a turbine is not obvious and there is no established rule. Thus, internal combustion engines are less demanding than gas turbines in terms of gas quality and are more efficient than single gas turbines. On the other hand, solutions in the combined cycle are much more competitive but obviously much more complex according to ADEME (2001).

Then, in relation to our initial objective, we are able to advise the use of synthesis gas from the gasification of the char of palm shells, peanuts and cashew, for the supply of fuels of clay brick firing unit for the production of terracotta bricks.

4. Conclusion

In this paper, several experimental data have been obtained on char gasification in fixed bed. Thus, gasification tests, mainly conducted on palm, peanut, and cashew nut shell char, give the following conclusions:

The gasification of the three samples under different atmospheres (100 % -H_2O, 75 % -H_2O / 25 %-CO_2, 50 % -H_2O / 50 % -CO_2, 25 % -H_2O / 75 % -CO_2, and 100 % -CO_2) and at different temperatures (950 - 1050 °C) enables to validate the results from the literature that clearly show the positive effect of temperature on char kinetics conversion. The activation energies obtained ranged between 110 - 126 kJ/mol for peanut shell, 104 - 125 kJ/mol for the cashew shell and 116 - 150 kJ/mol for the palm shell. The results using kinetics models indicated that char reactivity order was cashew nut shells (fastest) > peanut shell > palm shell (slowest).

However, it is found in these tests that the kinetic conversion of char gasification reaction follows the order: pure H_2O (fastest) > pure CO_2 > CO_2 / H_2O mixture (slowest). And, the gasification, under mixed atmosphere of steam and carbon dioxide, showed that the reactivity of the different chars depend on the increase of volume composition of steam in the mixture. Furthermore, based on the quantity of these biomass residues and on the gas quality obtained (7 to 12 MJ/Nm^3), it would be a great advantage for Senegal, which currently remains very dependent on fossil fuels and is facing a serious problem of power outages in production, and at the supply of electricity to users.

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