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Comparison of the Gasification of Cashew Wood and Cashew nut Shells Chars with CO_2 and Steam

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Abstract

Cashew (biomass) is a fairly common plant in the tropics, while pyrolysis/gasification seems to be the best option for his recovery. Experimental gasification with carbon dioxide and steam in a fixe bed reactor studies are reported for a highly reactive South Senegal cashew wood, and cashew nut shells chars. Gasification tests were made in two atmospheres and at three different temperatures between 950°C, 1000°C, and 1050°C. The latter is done in order to investigate the effect of reactivity of these char samples. Gasification rate of carbon conversion at a given temperature is found to be dependent to the gasifying agent, suggesting the use of three models such as the volume reaction model (VRM) which is found to be the more suitable model compared to the shrinking core model (SCM) and the random pore model (RPM). The results show that in the presence of CO_2 and water vapor, the activation energies of the cashew wood is greater than those obtained for cashew nut shells. However, by using an empirical function computing time of reaction, the experimental results show that the kinetic reaction of the cashew nut shells with steam and CO_2 is faster compared to cashew wood; probably due to the nutshells liquid content (CNSL). In addition, results showed that char-steam reactivity is different to char-CO_2 reactivity.

Keywords: Comparison of the Gasification of Cashew Wood and Cashew nut Shells Chars with CO_2 and Steam

Introduction

The drop in global energy reserves combined with the increase in population and industrial development make biomass a renewable energy source that can replace fossil energy. This fuel resource was composed mainly of carbohydrate compounds and possessed a high energy content[1]. Energy from biomass resource can nowadays play an important role in the future energy systems of the world[1]. Designed in the 50's for the diversification and the reforestation of endangered areas, cashew plants are today in West Africa, financial resources due to strong Asian demand. This has the effect of boosting the sector and become an opportunity for small producers, investors.

According to Rongead, cashew has become the second main cash crop in West Africa in terms of export value behind cocoa and ahead of cotton, rubber, palm oil or banana. In Senegal, the cashew nuts production in 2015 was around 47,000 tons, and only 20 tons of cashew kernels were locally consumpted[2].

However, the cashew nut shells (CNS), generated in Senegal (Casamance) as an agricultural residues, are mostly burnt in open air or threw in abandon in bush, and dumped. Cashews can be used in a efficient way in order to develop the region and to reduce the nuts exportation in India. These residues in quantities and at low cost can be recovered effectively on site.

For the wide utilization of biomass, gasification is promising among many kinds of energy conversion technologies[3]. According to Kentaro *et al*., gasification has emerged as a clean and effective way to produce gas from biomass[4].

Given the diversity of processes for energy valorization of biomass, the expected result is a function of several parameters. Besides, according to Tingting L., et al[5] and Leteng L. and Michael S.[6], char-CO_2 reaction and char-H_2O reaction are both fundamentally important reactions occurring. In addition, Leteng and Michael in their studies showed that, the general char reactivity order was wood > miscanthus > straw[6].

The mechanisms of the char-CO_2 reaction and the char-H_2O reaction, and experimental temperature have been studied extensively by many authors[7-10], and they have equally worked on the char gasification mechanism in CO_2 or H_2O.

Given that several parameters have a direct effect on the mechanism of gasification, it is important to notice that temperature is the most important parameter because it has an effect on the other parameters such as the conversion rate, the calorific value, and the kinetic of gasification.

So, considering the great importance and potentiality of the new compounds that can be extracted from the shells (such as CNSL), this work analyzes gasification process performance in terms of the reaction temperature, gasifying agent, and char.

Nomenclature

dt	[s]	Time step
k	[m^{-1}]	Kinetic constant
m	[kg]	Mass
NS	[-]	Nut Shell
R	[$J/kg.K^{-1}$]	Universal gas constant
T	[K]	Temperature
X	[-]	Rate of carbon conversion
Y		Regression curve
w		Wood
Special characters		
α	[-]	Constant
δ	[-]	Constant
λ	[-]	Constant
ρ	[$g.cm^{-3}$]	Density
ψ	[-]	Particle parameter
Subscripts		
a		Activation
m		Number of the hydrogen atoms
n		Number of the carbon atoms
t		Time
RPM		Random Pore Model
SCM		Shrinking Core Model
VRM		Volume Reaction Model

Materials and Methods

Char samples: The samples used in this study consisted of two char samples, cashew nut shells, and cashew wood. These biomass residues come from Ziguinchor (the cashew nut shells comes from nut processing unit, and the cashew wood from the plantations), a city located in the south of Senegal. The char samples used for gasification tests were prepared by being washed several times with tap water and dried at 105°C during 48 hours in an oven. These samples were pyrolysed at 450°C during 15 minutes using a muffle oven. This pyrolysis temperature is selected based on the fact that in the case of cashew nut shells, the CNSL was released in the temperature ranging between 180-308°C[11].

The char obtained was ground and sieved into gross fraction with particles size <3000 mm.

Ultimate and proximate analyses of cashew nut shells, and cashew wood used and theirs chars are summarizes in Table-1.

The fixed bed reactor used for gasification tests is shown in Figure-1. The gasification of char samples with carbon dioxide and steam were conducted using a tubular fixed bed reactor (36 mm internal diameter and 350 mm height) which was equipped with a porous plate for bed support. Before each of the gasification test, 15 g of the char sample is mixed with 70 g of sand and placed in the reactor. Sand was used in order to improve heat transfer inside bed particles and for minimizing the preferential gas passage through the reactor. Afterwards, the reactor was electrically heated.

The gasification tests were carried out isothermally at 950, 1000 and 1050°C, using steam (90 NL/h) carried in by an inert flow of nitrogen at 10 NL/h.

Flow rates of CO_2 and N_2 were fixed using mass flow controllers while an HPLC piston pump adjusted the flow rate of water. After the gases were condensed and cleaned, the produced gas composition was measured by online gas analysis, using an SRA-Instruments gas analyzer (µGC).

Table-1
Ultimate analysis and proximate analysis, on dry basis, of cashew nut shells, and cashew wood

	Ultimate analysis (Wt. %)				**Proximate analysis (Wt. %)**				**LHV (MJ/kg)**
	C	**H**	**N**	**O**	**Moisture**	**Fixed Carbon**	**Volatile Matter**	**Ash**	**LHV**
Cashew wood	51.59	6.21	1.10	41.10	8.05	17.42	73.28	1.25	18.61
Cashew wood char	76.02	2.52	0.34	21.12	0.26	76.24	17.87	5.63	31.42
Cashew NS	58.10	7.30	0.62	35.12	---	15.80	81.40	2.60	21.29
Cashew NS char	83.40	4.03	0.96	11.60	---	65.70	27.20	7.50	27.31

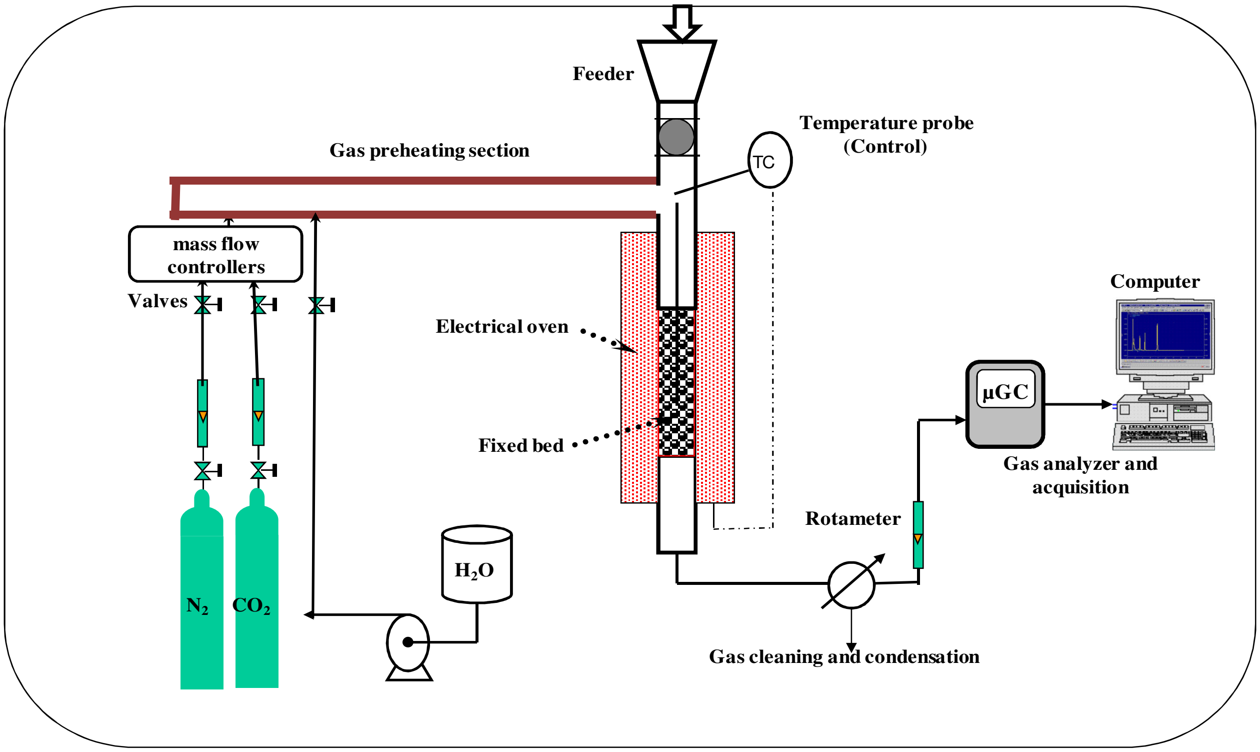

Figure-1
Synoptic representation of the fixed bed reactor system

Results and Discussion

During gasification process, ten sets of measurements were made. After seven sets of measurements, the repeatability was good, because the averaging error were in the magnitude of 2.1 %.

Effect of the temperature on char carbon conversion: The most important heterogeneous reactions described elsewhere for gasification facilities and, which take place during char gasification with carbon dioxide and steam, are described below.

$$C + H_2O \leftrightarrow CO + H_2 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

$$C + CO_2 \leftrightarrow 2CO \qquad (3)$$

These reactions (1, 2, and 3) are all endothermic reactions, according to the Le Chatelier principle. The products obtained in this reaction are favorable at high temperatures.

The ratio, carbon conversion (X) was evaluated with varying temperature between 950, 1 000, and 1050°C, and was plotted versus time in Figure-2 and Figure-3. The rate conversion can be calculated from the mass lost data during gasification by using the following equation:

$$X = \frac{m_0 - m_t}{m_0 - m_{ash}} \qquad (4)$$

Where m_0 is the initial mass of the sample (at the start of gasification), m_t is the sample mass at any given time (t), and m_{ash} is the mass of the remaining ash after gasification reaction is completed.

Observations in Figure-2 and Figure-3 show that for the same residence time, the rate conversion of carbon in temperature ranging from 1050°C is the higher; showing that experimental temperature has an influence on the char conversion. This correlation between temperature and gasification rate effects was also observed by Dong *et al.* [8] in CO_2 gasification, by Sansha *et al.*[12] in steam gasification, and by Guizani *et al.*[13] in mixture atmospheres gasification between steam and CO_2. A high gasification temperature enhances char gasification reactivity and cracks the tars produced during biomass gasification.

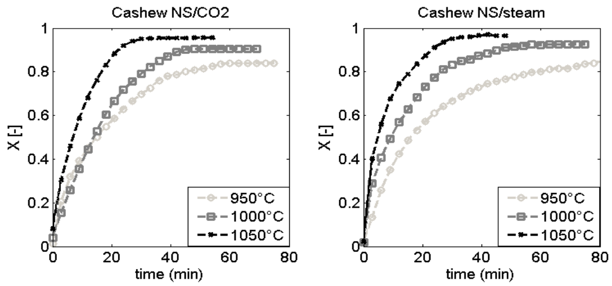

Figure-2
Influence of temperature on char carbon conversion ratio (cashew nut shells)

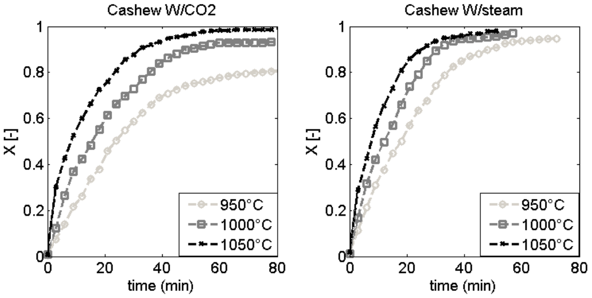

Figure-3
Influence of temperature on char carbon conversion ratio (cashew wood)

Effect of the temperature on the gas low heating value (LHV)

The low heating value of the dry gas produced is estimated using the following equation[14].

$$LHV = (30.0[CO] + 25.7[H_2] + 85.4 \times [CH_4] + 151.3[C_nH_m]) \times \frac{4.2}{1000} \quad (5)$$

Where [CO], [H_2], [CH_4], and [C_nH_m] are the gas fraction of CO, H_2, CH_4, and C_nH_m of the produced gas, respectively. In order to quantify the effect of the parameters affecting the lower heating value of the gas (LHV, in MJ/Nm^3), several tests were conducted on the cashew wood char, and cashew nut shells at three reaction temperatures and two atmospheres (CO_2 and H_2O carried in nitrogen flow). The values of the lower calorific value of the gas were determined (by equation (5)) and were reported in Table-2 below.

Table-2
Temperature influence in single atmosphere of steam or CO_2 on the gas LHV

Cashew nut shells				
Temperature (°C)		**950**	**1000**	**1050**
LHV (MJ/Nm^3)	CO_2	10.69	10.75	11.52
	H_2O	10.78	10.85	11.93
Cashew wood				
Temperature (°C)		950	1000	1050
LHV (MJ/Nm^3)	CO_2	8.10	10.47	10.72
	H_2O	8.94	10.77	10.92

We can note that the LHV of gas is about 10-12 MJ/Nm^3 for CNS, and 8-11 MJ/Nm^3 for cashew wood. In addition, high reaction temperature undergoes with better LHV gas value. We can conclude that temperature has a positive effect on the gas LHV value but also CNS has the best LHV value. However, at 1050°C, it is seen by Piyali and Anuradda[15] that there will be a decrease in the total liquid content in cashew nut shells, which is attributed to thermal cracking at this temperature. This is in accordance to the resulting higher gas content at this temperature as seen in Table-2. This value compared to the value (3.51 MJ/m^3) obtained by Tippayawong *et al.*[16] when gasifying CNS for thermal application in local processing semi-industrial factories based on fixed bed reactor technology, is about four times. Also some authors, Li, and Grace[17], gasifying several types of sawdust in a circulating fluidized bed reactor under air and steam, show that gas LHV increases with temperature from 973 K to 1073 K. Finally, based on Tippayawong *et al.* processing and the LHV ranging defined by McKendry, gas obtained in our case, can be considered as semi-rich and can be directly used for gas turbines, gas engines and other industrial application feeding[16,18].

Reagents effects on carbon conversion rate: Comparison using carbon conversion rate: Figure-4 below compares X, ratio for the two char samples when using carbon dioxide and steam.

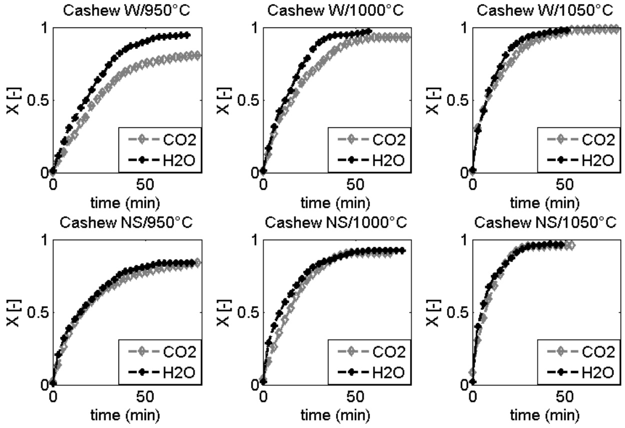

Figure-4
Influence of reaction agent on the carbon conversion rate

These graphs saw that char gasification with steam and CO_2 were rather different. The reaction rate in all samples follows the order: pure steam (fastest) > pure CO_2 (slowest). In order to confirm this observation, an empirical function was used to estimate the reactivity of char-steam and char-CO_2 gasification process.

Comparison using the empirical function: An empirical function defined by Susanna *et al.* was used to examine the reactivity of char-CO_2 and char-steam[7].

$$F(X) = [(1 - X_t)(\delta X_t + \lambda)]\exp(-\lambda X_t^{\alpha}) \quad (6)$$

Where: X_t is the instantaneous carbon conversion rate, δ, λ, and α, constants defined by finite values. We have tested different constants value to determine the effect of the reactivity. Finally, the better values obtained for δ, λ and α respectively are 31, 4 and 2.1. Using the ratio, X, the values of the function F(X) were obtained and the trends are shown in Figure-5.

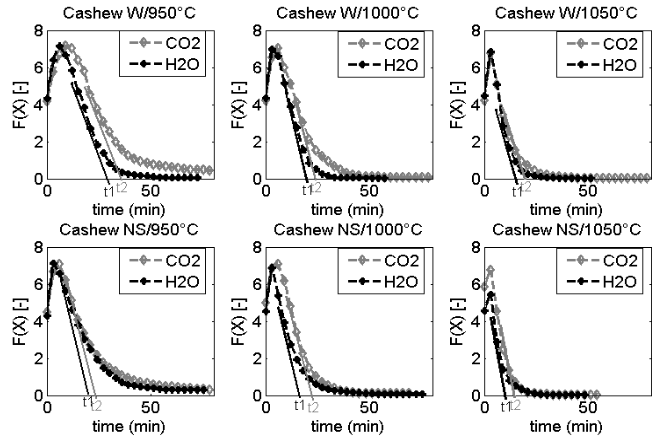

Figure-5
Influence of CO_2, H_2O reagents on carbon conversion rate using the empirical function

Figure-5 shows that the residence time, t_2 (corresponding to X=60%), obtained with CO_2 is greater than residence time, t_1, obtained with steam. Furthermore, the ratio, t_2/t_1 was between 0.84-2. Thus, char-steam gasification reaction is 0.84-2 times faster than char-CO_2 gasification reaction. Same trends were described by Susanna *et al.*[7] and explained by Roberts and, Harris[19].

When comparing CNS and cashew wood char, we can notice an inversion in F(X): F(X) is higher with CO_2 compared to water vapor in CNS char; also the latter has the smaller residence time.

The nutshell liquid components (anacardic acid, cardol and methyl derivatives), are expected to affect positively the char reactivity.

Comparative studies of the reactivity of char samples: Comparison based on experimental data of the carbon conversion rate: The experiments show that, with carbon dioxide at several temperatures, cashew nut shells char is more reactive than cashew wood char (same trends were obtained when using steam as gasification agent). During gasification and at temperature between 1000 and 1050°C, the conversion rate curve of the cashew nut shell char is above the conversion trend obtained with char from cashew wood. And at 950°C we obtain inversion; this trend can be due to the remaining cashew nut shell liquid which can cause apparition of porosity in the cashew nut shell char. Also, the reactivity of the corresponding char will depend on the given parent fuel, the pyrolysis conditions and the residence time which is not sufficient to reduced the reminding Cashew NSL. Moreover, Piyali, and Anuradda[15] have shown that the oil content is still high (42%) at 500-550 °C. So considering our pyrolysis temperature, gasification reaction will be directed at high temperature (between 500 and 600°C). Therefore, when gasifying with CO_2, the rate conversion become better when using cashew nut shells char compared to cashew wood char. Also during char gasification with steam, the reactivity effect of the two different samples is insignificant.

In order to highlight char samples reactivity, the same empirical function is also used (by computing the time when carbon conversion was equal to 60%).

Comparison based on the empirical function: The results obtained were presented in Figure-6. Regarding the slope of the different curves obtained, gasification reactivity follows the order: char cashew nut shells > char cashew wood (slowest).

In a heat transfer point of view: The difference obtained in the reactivity can be explained in a physical point of view. Indeed, density, ρ of the char from cashew nut shells, was 0.38 g/cm^3, and 1.07 g/cm^3 for cashew wood, since matter with small density drives better heat than those with high density.

In chemical point of view: Cashew nut shells and cashew wood do not have the same chemical composition (Table-1). This difference in the chemical composition could be the cause of the difference in the reactivity observed under the same experimental conditions. Also, by computing the O/C ratios, we notice a positive correlation between the O/C ratios in char and char reactivity. However, more and wide tests on char types are needed to make general conclusions about this trend (effect).

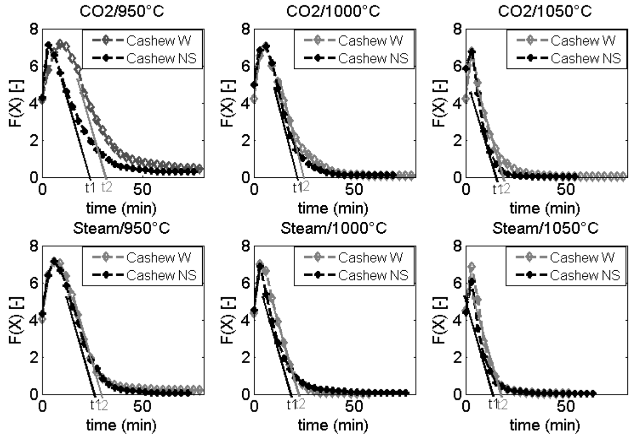

Figure-6
Influence of char sample on carbon conversion rate (empirical function)

In addition, it is well known that gasification occurs on exposed edges of the graphitic planes found within carbon chars and that the basal plane is unreactive[20]. At low temperatures, the unsaturated carbon atoms and the unsaturated edge carbon atoms that have high adsorptive capabilities can react with CO_2 adsorbed directly[20]. According to Erich, and Lalit[20], this reaction requires more energy and the higher concentration of the oxygen complexes on the carbon surface will decrease the C–C bond energy and thus decrease the activation energy of the reaction (Table-3).

Kinetic parameters: The evaluation of the gasifying agents on char reactivity is done by estimating the kinetics parameters using the three models (volume reaction model (VRM), shrinking core model (SCM) and the random pore model (RPM)), according to relations 4, 5 and 6. The latter let us determining the rate constant (k_{VRM}, k_{SCM} and k_{RPM}) for all temperatures tested. The pre-exponential factor, k_0, and the activation energy, E_a were calculated from Arrhenius equation (equation (11)), by plotting ln(k_{VRM}, k_{SCM} and k_{RPM}) versus 1/T (Figure-7-9).

The first adopted model is the VRM; this model assumes a homogeneous reaction throughout a char particle[21].

$$\frac{dX}{dt} = k_{VRM}\,(1 - X) \qquad (7)$$

The random pore model considers the overlapping of pore surfaces, which reduces the area available for reaction (Levenspiel),

$$\frac{dX}{dt} = k_{RPM}\,(1 - X)\sqrt{(1 - \psi \ln(1 - X))} \qquad (8)$$

Shrinking core model assumes that the reaction initially occurs at the external surface of char and gradually moves inside[21].

$$\frac{dX}{dt} = k_{SCM}\,(1 - X)^{2/3} \qquad (9)$$

Also, for $k_{(VRM,\ SCM,\ or\ RPM)}$, they all meet the Arrhenius equation:

$$k = k_0 \exp\left(-E_a/RT\right) \qquad (10)$$

And using the natural logarithm, equation (10) can thus be transformed into equation (11):

$$-\ln(k) = -\ln(k_0) + \frac{E_a}{RT} \qquad (11)$$

The results obtained by several models, are given in Figures-7-9. The pre-exponential factor and the activation energy obtained from the plots of these figures, for each test conditions (temperature and reagent), are shown in Table-3. These results show that the experimental data were very well represented by the VRM, SCM, and RPM models, with high regression coefficients (R^2>0.9). The activation energy obtained in VRM, RPM and SCM models are respectively comprised between 112-146 kJ/mol, 114-143 kJ/mol, and 113-143 kJ/mol, depending on char sample gasification and the gasifying agents.

The activation energies (Table-3) for the three chars when gasifying with steam and CO2 are close to the values published by 22, 23 which were 29–209 kJ/mol. Also, Gangil[24], in their review, for biomass char gasification with steam, reported 40-240 MJ/mol for the activation energy.

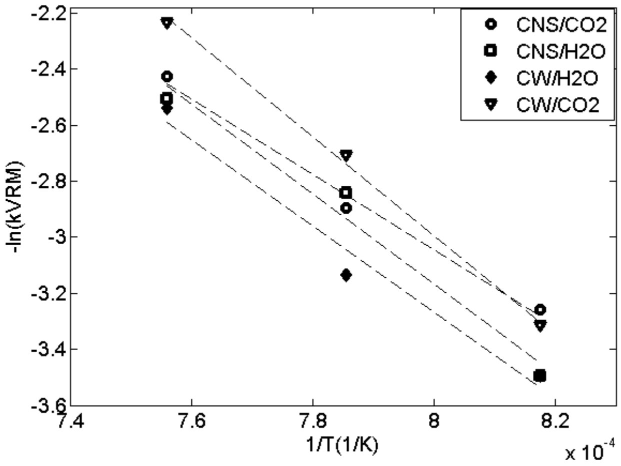

Figure-7
Arrhenius plots using VRM model

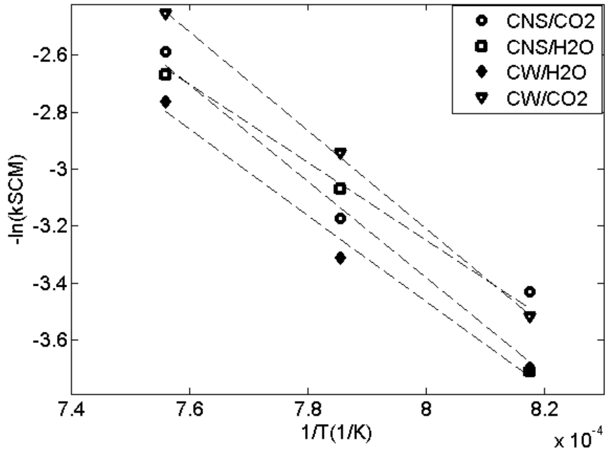

Figure-8
Arrhenius plots using SCM model

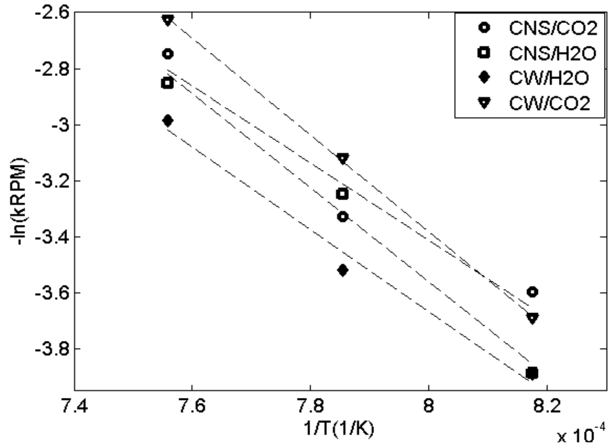

Figure-9
Arrhenius plots using RPM model

Table-3
Kinetic parameters of cashew nut shells and cashew wood chars

Models	**E_a (kJ/mol)**	**k_0 (min^{-1})**	**R^2**	**Char samples**
$\mathrm{VRM}_{\mathrm{CO2}}$	111.72	2.20E+3	0.990	Cashew nut shells
$\mathrm{SCM}_{\mathrm{CO2}}$	113.38	2.10E+3	0.942	
$\mathrm{RPM}_{\mathrm{CO2}}$	114.04	1.91E+3	0.946	
$\mathrm{VRM}_{\mathrm{steam}}$	133.28	0.15E+5	0.997	
$\mathrm{SCM}_{\mathrm{steam}}$	140.35	0.25E+5	0.974	
$\mathrm{RPM}_{\mathrm{steam}}$	139.57	0.19E+5	0.987	
$\mathrm{VRM}_{\mathrm{CO2}}$	127.55	8.15E+3	0.973	Cashew wood
$\mathrm{SCM}_{\mathrm{CO2}}$	125.32	5.39E+3	0.985	
$\mathrm{RPM}_{\mathrm{CO2}}$	121.55	3.07E+3	0.984	
$\mathrm{VRM}_{\mathrm{steam}}$	146.07	4.66E+5	0.999	
$\mathrm{SCM}_{\mathrm{steam}}$	143.29	3.89E+5	0.999	
$\mathrm{RPM}_{\mathrm{steam}}$	143.30	3.28E+5	0.999	

Conclusion

In this paper, kinetic studies of gasification char of cashew nut shells, and cashew wood with CO_2 and steam were made in a fixed bed reactor at several temperatures (950°C, 1000°C, 1050°C) in order to interpret the experimental reactivity of the different chars. Parametric tests, varying the reaction temperature, gasifying agent (steam and CO_2), and char samples (cashew nut shells, and cashew wood), have been performed to determine their effects on the gas produced, gas LHV, and carbon conversion rate.

The results obtained in this study confirm that temperature have an influence on char gasification reactivity (endothermic reaction). Furthermore, the syngas heating value ranged from 8 to 12 MJ/Nm^3: 10-12 MJ/Nm^3 in cashew nut shells char and 8-11 MJ/Nm^3 in cashew wood char gasification. Comparing LHV value in the three different temperatures, we conclude that high reaction temperature and fuel parent combined to pyrolysis conditions lead to better LHV gas value. It is also found in these tests that the conversion rate of gasification reaction follows the order: pure steam (fastest) > pure CO_2 (slowest).

The activation energies obtained are 112–140 kJ/mol for cashew nut shells char, and 121–146 kJ/mol for cashew wood chars. The results using an empirical function indicated that the char reactivity order was cashew nut shells > cashew wood. Furthermore, the observation shows, based on the same mass, cashew nut shells provides more syngas than cashew wood. This remark confirms the high value of the LHV obtained in cashew nut shells compared to cashew wood.

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