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Study of Cashew Nut Shells Valorisation by Gasification

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During these last three years the production of cashew nuts is expanding across West Africa, and according to the USAID the sub-region produces 85 % of the world harvest. Furthermore, after the tourism, cashew nuts are one of the pillars of Casamance economy, (In Senegal, cashew nuts yield 35 million CFA francs a year). Cashew nut shells are a residue obtained from cashew shelling. This biomass residue is abundant, cheap and generates high energy content. Currently, cashew nuts shells are rejected by artisanal traders without being valued. They were often burned in open air and cause several socio-environmental problems. Therefore, the issue of energy recovery by thermochemical process arises to overcome this cashew nuts shells rejection and open air burning. Nevertheless, gasification technology is suitable for biomass residues conversion and remains an economical alternative for the valorisation of cashew nut shells in small scale industries. In order to evaluate the cashew net shells valorisation by gasification, several experiments were conducted on a char obtained from the pyrolysis of this biomass and using a fixed bed reactor. As gasifying agents, carbon dioxide, steam and the mixture of carbon dioxide and steam were used at different temperatures for the gasification of fine particles size (630 μm) and gross particles size (3,000 μm) CNS char. In order to compare the effect of each parameter studied, carbon conversion rate was calculated from gasification experiments results, by carbon mass balance, of the char carbon content and the produced gas carbon content. Kinetics parameters of CNS char gasification reaction were also determined, using a volume reaction model, in order to compare reactivity of the char, by the activation energy and pre-exponential factor comparison. From the results obtained, temperature has a positive effect on the kinetic of carbon conversion. The results obtained show clearly an improvement of CNS char reactivity with temperature increasing and using steam as gasifying agent. However, char particles size has no significant effect on the gasification reactivity.

1. Introduction

The increasing of energy demand coupled with the need to reduce greenhouse gas emissions, and the threat of exhaustion of oil reserves make us to consider an eventual recourse to the use of biomass waste as renewable energy source and efforts has been done in order to valorise vegeto-agricultural by-products such as peanut shells, sugarcane bagasse, nutshells, forest residues and sorghum stems. These raw materials are carbon neutral and homogenously distributed all over the word, which is a very important advantage for its utilization as an energetic vector. Therefore, the utilization of biomass energy can provide dual benefits: it can reduce carbon dioxide (CO_2) emission as well as increase fuel security when it is produced locally. Cashew nut shells are a residue obtained from cashew shelling, an abundant and cheap biomass residue, and could generate high energy. Currently, cashew nuts shells are rejected by artisanal traders without being valued. They were often burned in open air and cause several socio-environmental problems (Tippayawong et al. (2011). Thus, cashew nut shells (CNS), which have a high energetic content, are currently rejected, in Casamance (Senegal) or burned in open air, and causes several health problems, as pneumonia, and environmental problems as proliferation bushfire. Among different kinds of

biomass, CNS was studied for bio-oil production by flash pyrolysis (Melzer et al. 2013) but its gasification was not really investigated. The most gasification studies was investigated on the charcoal, obtained from the forest residues biomasse pyrolysis. The most parameters studied concern the gasification reactivity of biomass char and the effects of the operating parameters as reaction temperature, particle size, gasifying agent (carbon dioxide, steam, air or oxygene) as it was reported by several authors. The effects of the gasifying agent and the particles size on the char reactivity, was investigated by Guizani et al. (2013), using thermogravimetric analysis. High pressure gasification was investigated by Fermoso et al. (2009), using a pressurized thermo-gravimetric apparatus. Coetzee et al. (2013) studied the reactivity of large coal particle during steam gasification using also TGA analysis and various kinetic models such as the volume reaction model (VRM) was applied for their results. Dong et al. (2010) investigated the reactivity of biomass with CO_2, as gasifying agent, using also volume reaction model (VRM) and compared to shrinking core model and random pore model for their experimental data interpretation. Hyo et al. (2014) studied gasification of two types of char at high temperature at lab-scale tube furnace and used the several kinetics models to obtain the reaction rate constant.
This study aims to investigate the effects of gasification atmosphere, temperature and char particles size on the reactivity of cashew nut shells char gasification. Gasification tests were carried out on two char particles size (630 and 3,000 mm), at three reaction temperatures (950, 1,000 and 1,050 °C), using three gasifying agents (carbon dioxide, steam and the mixture of carbon dioxide and steam).

2. Materials and methods

Cashew net shells (CNS) used in this study come from Casamance region in Senegal. In order to prepare char samples for gasification tests, CNS was pyrolysed, using a muffle oven, during 15 min at 450 °C under inert atmosphere. The char obtained was ground and sieved into two fractions: a fine fraction with particles size < 630 μm and gross fraction with particles size < 3,000μm. The proximate and ultimate analysis of the CNS used and the char obtained are listed in Table 1.
CNS char gasification tests were conducted using a tubular 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.

Table 1: Characteristics, on dry basis, of the cashew nut shells (CNS) and char

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)					
	VM	FC	Ash	C	H	O	N	Cl	S
CNS	81.6	15.8	2.6	58.1	7.3	34.4	0.62	<0.1	0.01
CNS Char	27.2	65.5	7.5	83.4	4.07	11.6	0.96	<0.1	0.03

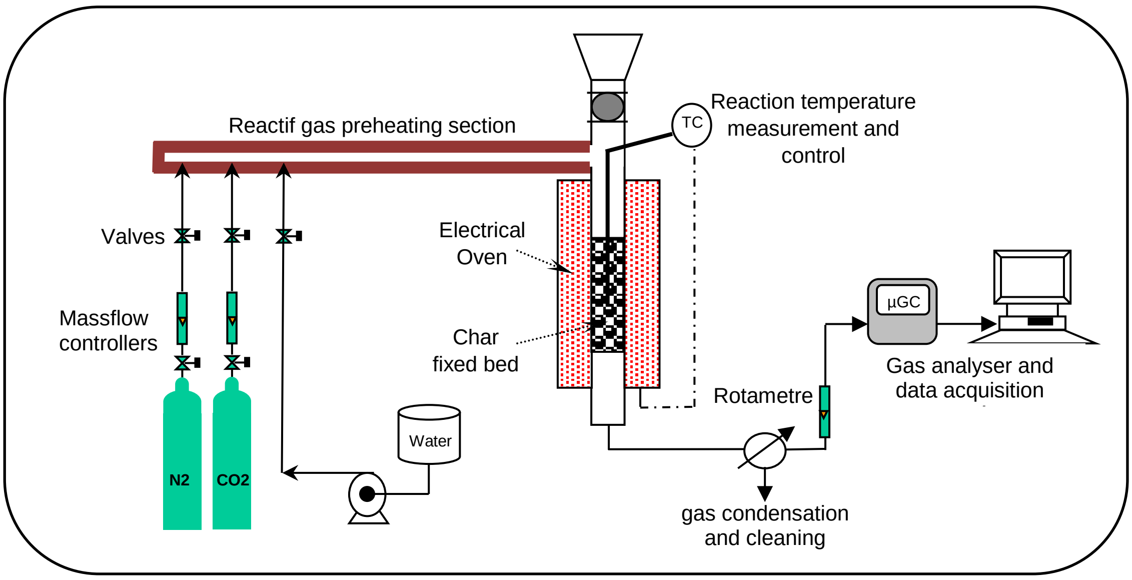

Figure 1: Simplified representation of the system the fixed bed reactor

After reactor preheating, 15 g of char is mixed with 70 g of sand and charged in the reactor, under a nitrogen atmosphere, until the desired temperature. Sand was 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, 1,000 and 1,050 °C, using carbon dioxide (90 nL/h) , steam (90 nL/h) and the mixture of steam and CO_2 (45 nL/h of each) and carried in an inert flow of 10 nL/h 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 piston pump. The composition of the produced gas is obtained by online gas analysis, using an SRA-Instruments gas analyzer (μGC), after gas condensation and cleaning.

3. Results and discussions

The effect of the main operation variables as temperature, particle of the char size and nature of the gasifying agent on the CNS char gasification was studied, by the evaluation and the comparison of the char carbon conversion. The carbon conversion, X, (Eq(1)) was defined as the total carbon contained in the produced gas (CO, CO_2 and CH_4), with respect to the total carbon contained in the char 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.

$$X_t = \frac{m_{initial} - m_t}{m_{initial} - m_{ash}} \tag{1}$$

Where X_i, $m_{initial}$, m_t and m_{ash} are respectively the carbon conversion rate, the initial mass of carbon of the sample used, the carbon mass of the produced gas and the mass of the sample ash.

3.1 Effect of temperature on the coal gasification

Regarding the endothermic effect, reaction temperature is one of the most important operating parameters affecting the performance of gasification. In order to evaluate the effect of this parameter on the reactivity of the char, several tests were carried out on two particles size of the char particles (<630 μm and < 3,000 μm). Three gasifying agent were tested (CO_2, steam and the mixture of the two gasifying) agent at three reaction temperatures (950, 1,000 and 1,050 °C). The results obtained from these tests, traduced by the variation of the carbon conversion (Eq(1)) versus time, are summarized on Figure 2.

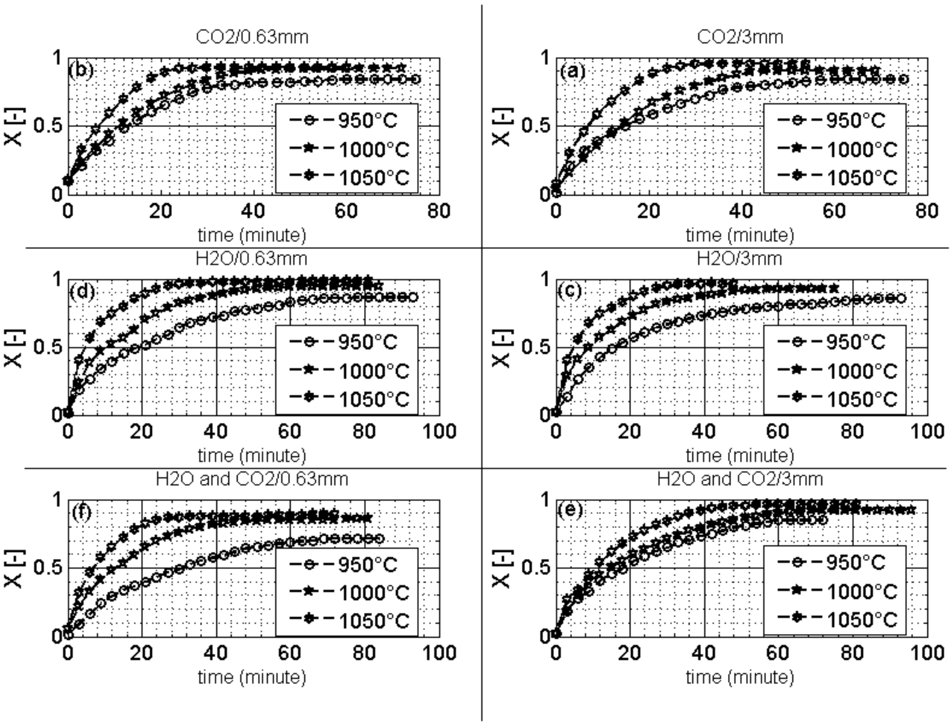

Figure 2: Influence of temperature on reactivity of CNS char with CO_2 (a and b), steam (c and d) and with CO_2 and steam mixture (e and f)

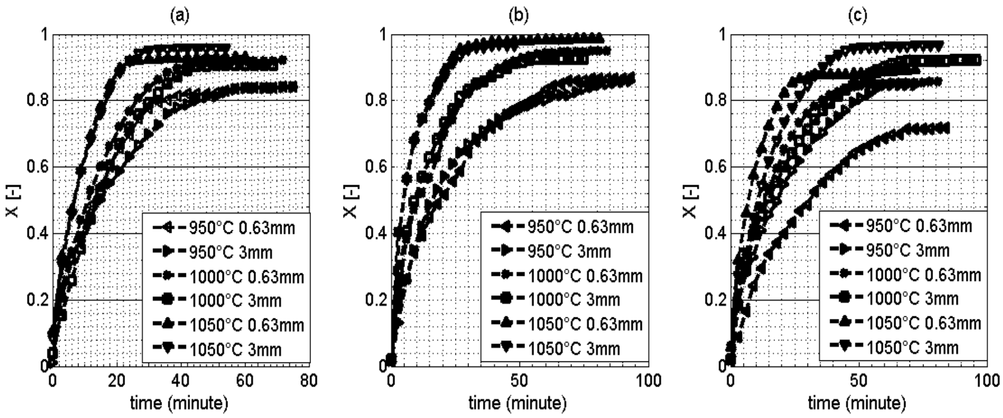

Figure 3: Influence of particle size on reactivity (a=CO_2, b=H_2O, and c= CO_2/H_2O)

From the results obtained, one can observe clearly that the carbon conversion of CNS char during its gasification with steam, CO_2 or with the mixture of the two gasifying agent is improved with the reaction temperature increasing, traducing an enhancement of the char reactivity. High temperatures improve reaction kinetics parameters and so the enhancement of the char conversion rate as it was also observed by several authors. Ye et al. (1998) point out that the gasification rate increases with increasing reaction temperature for H_2O and CO_2 reaction with char. The results obtained by Dong et al. (2010) showed an increase of CO production with the temperature increasing, traducing that higher temperature favoured the reaction. Quinglong et al. (2012) observed also that reaction temperature is an important factor with regard to the composition of final syngas. Coetzee et al. (2013) indicated that the reactivity was found to be a temperature sensitive. And, Fermoso et al. (2009) explained that temperature is one of the most important operating parameters affecting the performance of gasification.

3.2 Effect of particle size on rate of carbon conversion

In order to evaluate the effect of the particles size on the gasification reactivity of the CNS char, several tests were carried out on two char particles size (<630 μm and 3,000 μm). The results obtained from these tests, traduced by the evolution of the carbon conversion rate versus time, for each reacting agent at the three temperatures and the two char particles size tested are given on Figure 3. From these results, one can observe that there is no significant difference between the results obtained on the two particles size CNS char tested, especially when carbon dioxide or steam were used alone, for the three temperatures tested. This result was also obtained by Ye et al. (1998) for the South Australian coal gasification with carbon dioxide and steam, which means that the gasification reactions occur homogeneously throughout the particle and are controlled by chemical kinetics. The same observations, concerning the char particles size effect on the steam gasification reactivity, were also obtained by Hanson et al. (2002) for char particles size of 0.5 and 2.8 mm and Coetzee al. (2013) for the two chars particles size 5 et 10 mm.
CNS char particles size could have an effect on the gasification reactivity when a mixture of carbon dioxide and steam is used as the gasifying agent, especially at low temperature (950 °C). This effect could be explained by the char reactive surface development during gasification which improves the conversion rate of carbon.

3.3 Kinetics parameters determination

In order to better evaluate the effect of the gasifying agents and the char particles size on the gasification reactivity, kinetics parameters of these reactions were calculated for each situation, using the volume reaction model (VRM), according to the relation 2, for the determination of the rate constant (k_{VRM}) for each temperature tested. The pre-exponential factor (k_0) and activation energy (E_a) were obtained from ArrheniusEq(3), from the plot of ln(k_{VRM}) versus 1/T.

$$\frac{dX}{dt} = k_{VRM}(1 - X) \tag{2}$$

$$k_{VRM} = k_0 \exp^{-\frac{Ea}{RT}} \tag{3}$$

The Arrhenius equation plot results are given in Figure 4, however the pre-exponential factor and the activation energy obtained from these plots, for each test conditions, are regrouped in Table 2.

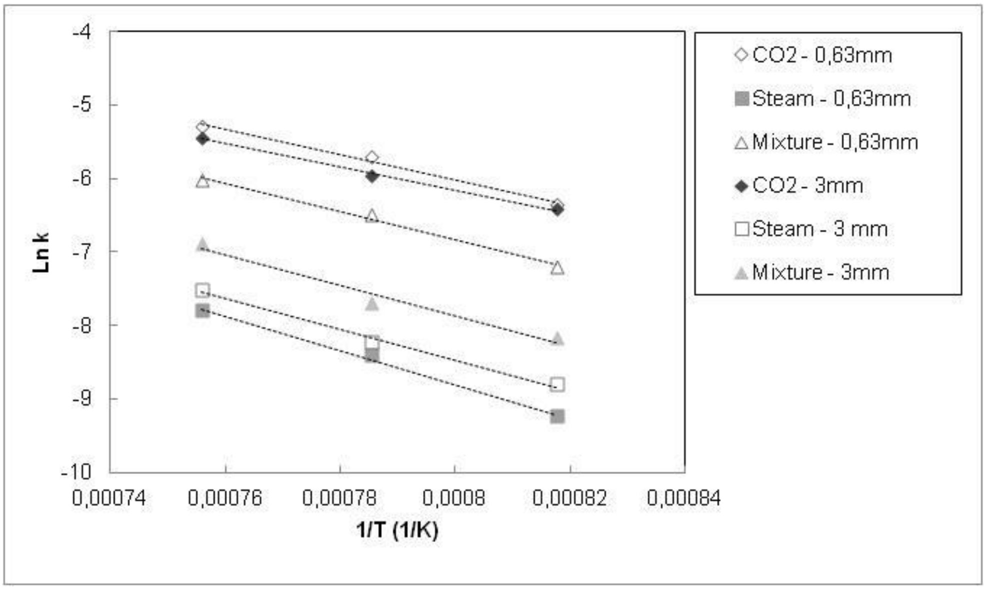

Figure 4: Arrhenius plots of CNS char gasification reaction with the various gasifying agents

Table 2: Kinetic parameters of CNS char gasification

Gasifying agent	E_a(kJ/mol)	K_0 (s^{-1})	R^2	Particles size
CO_2	144.91	2.64E+3	0.9937	
Steam	187.17	9.90E+3	0.9988	630 μm
Mixture (CO_2/steam)	164.79	5.37E+3	0.9979	
CO_2	142.51	1.95E+3	0.9984	
Steam	182.28	1.11E+4	0.9959	3,000 μm
Mixture (CO_2/steam)	174.40	4.77E+3	0.9845	

From these results, we can notice that the experimental data were very well represented by the Volume Reaction Model (VRM) with high regression coefficients (R^2 > 0.99) and so this model could describe the evolution of char particles along the gasification process.
The activation energy obtained for the CNS char gasification is comprised between 145 and 185 kJ/mol, function of the gasifying agents and char particles size, which is in concordance with the results obtained by Dong et al. (2010). From the results obtained and regarding kinetics parameters, one can observe clearly that CNS char reactivity is improved by steam gasification, traduced by a high pre-exponential factor and low activation energy, compared with gasification with carbon dioxide. The mixture gives an intermediate reactivity between the gasification with carbon dioxide and steam.

4. Conclusions

The reactivity of cashew nut shells char gasification with the reacting agents: carbon dioxide, steam and the mixture of CO_2 and steam were evaluated at various temperatures (950 - 1,050 °C) and for two different particles size (630 and 3,000 μm). Temperature increasing showed an improvement of CNS char carbon conversion for the three reacting agents and the two chars particles size used. High temperatures improve syngas production, mainly carbon oxide and/or hydrogen, with high carbon conversion rate.
The results obtained showed also that the char particles size has no effect on the carbon conversion rate, during its gasification with carbon dioxide or with steam, for the two particles size studied. However, an effect of the char particles size was observed when a mixture of carbon dioxide and steam was used as gasifying agent, especially at low temperature. Finally, reactions kinetics parameters showed a best reactivity of CNS char with steam, compared with its reactivity with carbon dioxide or with the mixture of the two gasifying agents.

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