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Investigation of parameters influencing gas production and gasification kinetics of Ziguinchor biomass

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This study presents the gasification of three types of biomass residues (wood, stem and shells) under CO_2 and water steam, using the different analyses X-ray fluorescence (XRF). Generally, the experiments are carried out using XRF installations and a fixed bed reactor system. The tests are carried out on wood, stems, and shells, because of their energy contents (Lower heating value LHV), and their high availability in the Ziguinchor region (Senegal). The solid residues obtained after pyrolysis were used to carry out the gasification tests. Thus, several gasification tests were carried out and the results were interpreted using the Arrhenius equation. Two kinetic models (Volume Reaction Model, and Shrinking Core Model) were used to explain the influence of experimental parameters (nature of biomass, reagent type, and temperature) on synthesis gas production. From the experimental results, it is found that the nature of the sample, the reagent, and the variation in temperature have significant effect on the char kinetics conversion. In addition to the differences in the chemical composition of the raw sample, ash and char density, an explanation on the parameters effects, which vary the conversion kinetics during the gasification tests is given. The purpose of this work is to understand the kinetic variations of raw materials in the fixed bed reactor during gasification.

Key words: Biomass residues, gasification, kinetic conversion, ash chemical composition.

INTRODUCTION

The impact of climate change has many implications for the world's natural system (lower agricultural yields, irregular rainfall patterns with serious human and agricultural consequences). To overcome this struggle cash on climate change, community and governmental initiatives (United Nations Framework Convention on Climate Change 1992, Kyoto Protocol signed in 1997, Intergovernmental Panel on Climate Change, and recently the "Conference of Parties" 2015-2023) and so many other bodies are being taught around the world. These aim to fight the limitation of the use of fossil resources through the development of renewable energies and for the control of energy demand. Even if awareness of this phenomenon may seem slow in view of

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the stakes on the planet, it is nonetheless real and is becoming more and more integrated into the world's energy landscape. However, developing and promoting renewable energies, and biomass, is becoming a priority because of the many environmental and energy benefits. In the logic of the use of biomass as a source of energy, it will be very difficult to take wood as a raw material, because its overuse may lead to an unfortunate cause of deforestation.

Given the low rate of electrification in rural areas, and given that the quantity of various increasingly important and unrecovered bio-resource waste delivered to the open air is considered a loss, it is more indicative that the thermochemical recovery of this diversity of biomass is a promising process. Processes known as "thermochemical conversion" are still explored in this research direction and development phase. They combine a thermal conversion (under the effect of heat) and a chemical conversion (reaction between two bodies). Then, gasification is a thermochemical conversion of a fuel, which consists in a thermal degradation of the char at a high temperature (> 600°C) to obtain a synthesized gases composed mainly of CO, H_2, and CH_4. These products can be used for electrification and/or cogeneration. The design and operation of a reactor requires an understanding of the gasification process, how its configuration, its size, its raw material preparation, and experimental conditions influence installation unit performance. A good understanding of the basic reactions is fundamental to the planning, design, operation, and process improvement of a gasification unit. In order to obtain a complete char conversion and an improved product yield, several experimental protocols have been presented in the literature. The work conducted by (Kamble et al., 2019; Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016) have different studies on the effect of temperature on biomass char conversion kinetics and have considered temperature as a fundamental parameter for the conversion of different biomasses. These authors indicated that the temperatures used have a positive effect on biomass conversion kinetics, that is, the higher the temperature (750 - 1350°C), the better will be the conversion kinetics of the biomass. Other researchers such as (Kamble et al., 2019; Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Schneider et al., 2021) presented the study of thermochemical conversion of biomass by evaluating the effect of the type of reagent on the conversion kinetics and that they point out that CO_2-char and H_2O-char reactions have different conversion kinetics effect, in addition the mixture of these reagents has a slowing conversion kinetics and that could be due to the competition effect between the different reagents. Finally, more advanced studies of the effect of char and ash chemical composition on conversion kinetics have been carried out by (Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Schneider et al., 2021; Wang et al., 2016; Zhang et al., 2017; Wu et al., 2022; Lv et al., 2004; Prestipino et al., 2018; Ling et al., 2022a; Wu et al., 2022b; Zhang et al., 2008; Yao et al., 2020; Parikh et al., 2007; Gao et al., 2017).

The latter had different conclusions, according to some the chemical components of the ash have a significant effect on the biomass conversion rate. According to the study by Zhang et al., 2008, which compared the gasification reactivity of biomass samples under K-, Na-, Ca- and Mg-catalyzed steam, the results indicate that alkali metal-catalyzed char (K and Na) has a much higher reactivity than alkaline earth metal-catalyzed char (Ca and Mg). Secondly, despite the advantages of biomass fuel in reducing carbon emissions from the power sector, during the co-combustion process, many unexpected interactions between the ash-forming elements (such as K, Na, Ca, Si, Al, Cl, P, Mg and S, etc.) occur during the co-combustion process. It is inevitable that many ash-related problems, such as ash deposition, fouling and corrosion of heat transfer surfaces, could be due to the high alkali and alkaline earth metal content (Yao et al., 2020).

In this study, we are looking for a specific understanding of the kinetic sensitivity conversion of samples vs experimental conditions. To achieve the objectives, we seek to better understand the effect of the temperature, of the chemical composition of the ashes and samples on the kinetics gasification.

MATERIALS AND METHODS

Presentation of samples

Sorghum stems (St.sorghum), cotton stems (St.cotton), teak wood (W.teak), kaicédrat wood (W.kaicédrat), palm shells (Sh.palm) and peanut shells (Sh.peanut) were used. These samples were collected from the Ziguinchor region in southern Senegal. The samples were selected on the basis of their energy content (high heating values, Table 1) and their high availability in this area (in terms of recoverable quantity). The main properties of all these biomass samples were subjected to immediate and elementary analysis in accordance with ASTM D 3172-73 (84) and ASTM D 3176-84 standards (Zhang et al., 2008), the results are listed in Table 1.

Table 1 shows very good lower heating value (LHV) of our samples, which allowed us to select these samples in order of their energy content (LHV) among several other biomass. A variety of chemical component values of these biomass residues were also noticed. This noted difference can play a fundamental role during thermochemical conversion (Hu et al., 2022; Zhang et al., 2023). However, in order to characterize our biomass samples during gasification and to analyze their ashes, the tests were carried out using micro gas chromatography (μGC or micro-GC) and XRF, respectively. The results obtained from the ash analysis, in accordance with ASTM E 1755-1 (Zhang et al., 2008), are shown in Table 3.

The experimental protocol for the sample preparation, pyrolysis,

Table 1. Chemistries compositions of ash and of the samples.

Biomass	Elementary analysis (Wt. %)					Proximate analysis (Wt. %)			
Samples	C	H	N	S	O	CF	MV	Ash	LHV (MJ/kg)
Sh.peanut	49.8	8.50	1.30	0.40	40.00	19.60	65.40	5.7	17.98
W.teak	48.75	8.97	0.27	0.01	42.00	20.11	80.72	0.17	18.80
W.kaicedrat	50.12	7.01	0.50	0.02	42.35	17.27	82.00	0.73	18.80
Sh.palm	49.50	6.00	1.10	0.70	42.60	13.40	84.90	1.20	21.20
St.Sorghum	49.69	3.87	0.60	0.04	45.80	21.57	74.18	4.25	16.98
St.cotton	51.41	4.05	1.31	0.02	43.21	23.78	65.41	5.74	16.65

Source: Authors

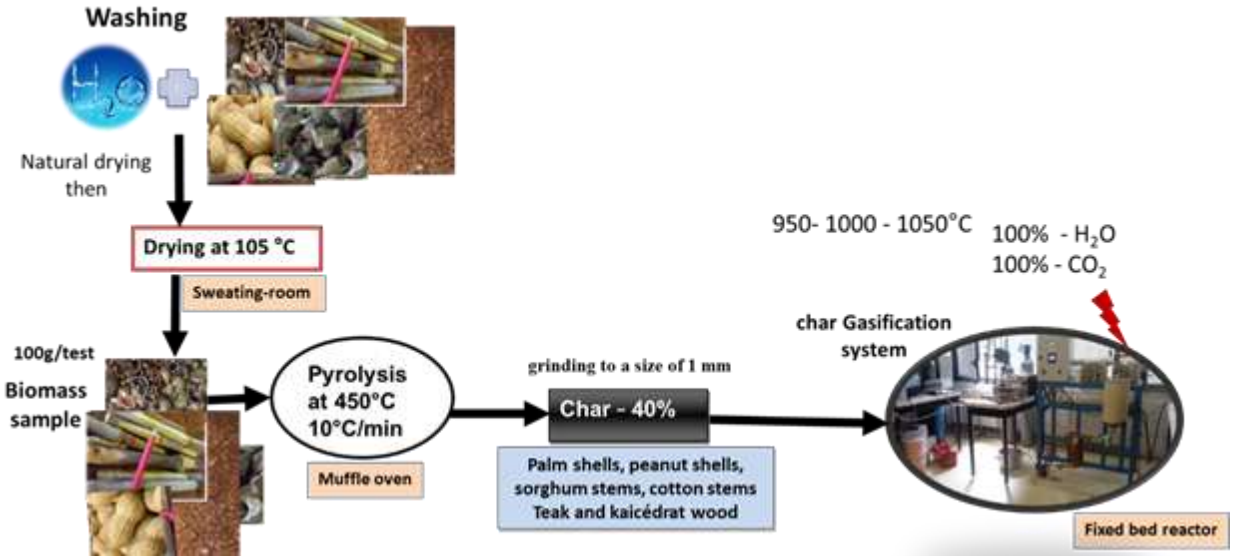

Figure 1. Simplified diagram of the experimental protocol.
Source: Authors

and gasification study is described in a simplified manner in Figure 1. In Figure 1, a sample washed with tap water was performed to reduce impurities. These mineral impurities have a significant influence on the thermochemical conversion process of the sample. After washing, the stems, wood and shells were dried naturally for 24 h and then steamed at 105°C for 24 h.

After this sample preparation, a mass of 100 g per test was used to carry out sample pyrolysis. The objective during the pyrolysis was to obtain a high proportion of char (carbon-rich solid) with a low porous surface. In order to achieve this, a temperature of 450°C is used with a heating rate of 10°C min^{-1}. The pyrolysis tests were carried out in a muffle furnace under an inert atmosphere. About 40% char was obtained. The char was crushed to an average size of 1 mm and the samples were then used for the gasification tests. Several gasification tests of the samples were carried out in a fixed-bed reactor at different experimental conditions (three temperatures, two reactive media, and five samples).

Fixed-bed reactor presentation

The fixed bed reactor system (36 mm internal diameter and 350 mm internal height) consists of a sample thermal conversion system and a gas analysis system. The reactor is simplified in Figure 2.

The operating principle of this fixed bed reactor is summarized as follows: the gasification temperature is controlled by a thermocouple. The flow rate of nitrogen and CO_2 is fixed by a mass flow regulator, and the water vapour is adjusted by a "Water 510 Doser" type pump. These reagents are first preheated to a temperature of 300°C before being injected into the reactor. The reactor is loaded with 15 g of char mixed with 70 g of sand. The sand plays the role of heat transfer, maintaining the temperature and limiting the preferential passage of gases. At the outlet of the reactor, there is a system for cleaning and condensing the gases. This system consists of two flasks immersed in a cold bath (≈ -10°C). At the outlet of the cleaning system, the gases are analyzed by gas phase micro-chromatography and the data are displayed on a computer.

The tests are repeated and the average is presented subsequently.

RESULTS AND DISCUSSION

In order to study the effect of temperature on char

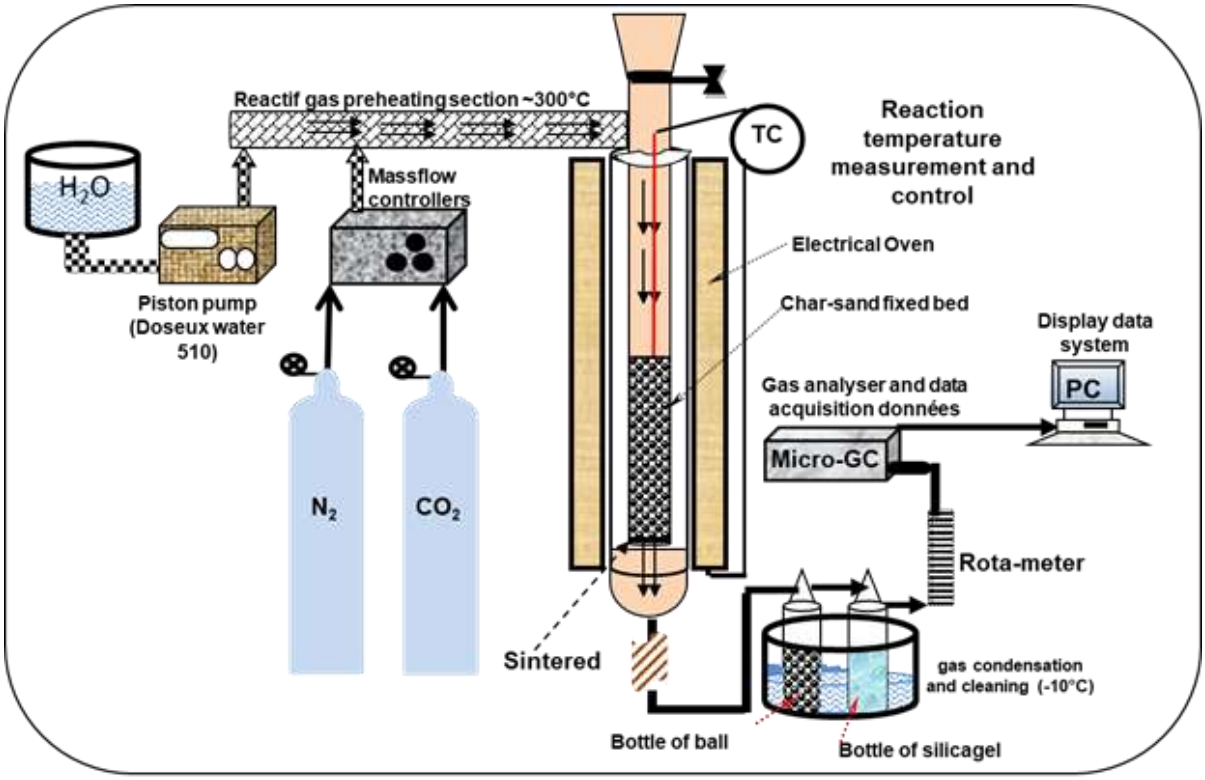

Figure 2. Simplified representation of the fixed bed reactor system.
Source: Authors

conversion, several gasification tests were carried out on the wood char, stem and shells samples at 950, 1000 and 1050°C.

Effect of gasification temperature on conversion

In order to evaluate the effect of temperature, the half-reaction index ($R_{0.5}$) described in (Guizani et al., 2013) is used:

$$R_{0.5} = \frac{X_{0-0.5}}{t_{0-0.5}} \quad (1)$$

where $t_{0.5}$ is the half-conversion time of the char (50%).
To better see the effect of temperature on the gasification reaction rate of the chars resulting from the pyrolysis of the different samples, we plotted the variation of this half-conversion rate of Equation 1 as a function of time using the half-conversion rate data (from X=0 to X=0.5). The result obtained is as shown in Figures 3 and 4. In Figures 3 and 4, we can see that the variations in the trend of the half-conversion rate of the char at a temperature of 1050°C is above those obtained at 1000 and 950°C. Similarly, the trend of the conversion rate at 1000°C is also above those obtained at 950°C. It is clear that the char kinetic conversion rate from “kaicacedrat” wood, teak wood, peanut shells, palm shells, cotton, and sorghum stems during the gasification process under CO_2, or under steam is improved at high temperature (that is, the higher the temperature the better the conversion of the char), thus reflecting the fact that temperature has a positive effect on the reactivity of the char. it is concluded that the reaction temperature has a precursor effect on the reactivity of the char.
Similar conclusions were made by (Jayaraman et al., 2017; Pandey et al., 2022; Porada et al., 2017; Mularski et al., 2020; Pinto et al., 2016; Yu et al., 2021; Gao et al., 2017; Almeida et al., 2019). This effect of temperature could be due to the endothermic reaction phenomenon char-CO_2 or char-H_2O. Indeed, during this reaction according to chemical principles, the production of synthesis gas is favorable at high temperature. Further, this temperature effect during the gasification of char under steam or CO_2 can be interpreted by the Arrhenius correlation.

On the basis of this Arrhenius equation, we used the "Volumetric Reaction Model (VRM)" and the "Shrinking Core Model (SCM)" to study the effect of the nature of the char on the conversion kinetics.

Char nature effect on conversion kinetics

The char kinetic conversions have been the subject of many studies as they are of crucial importance in

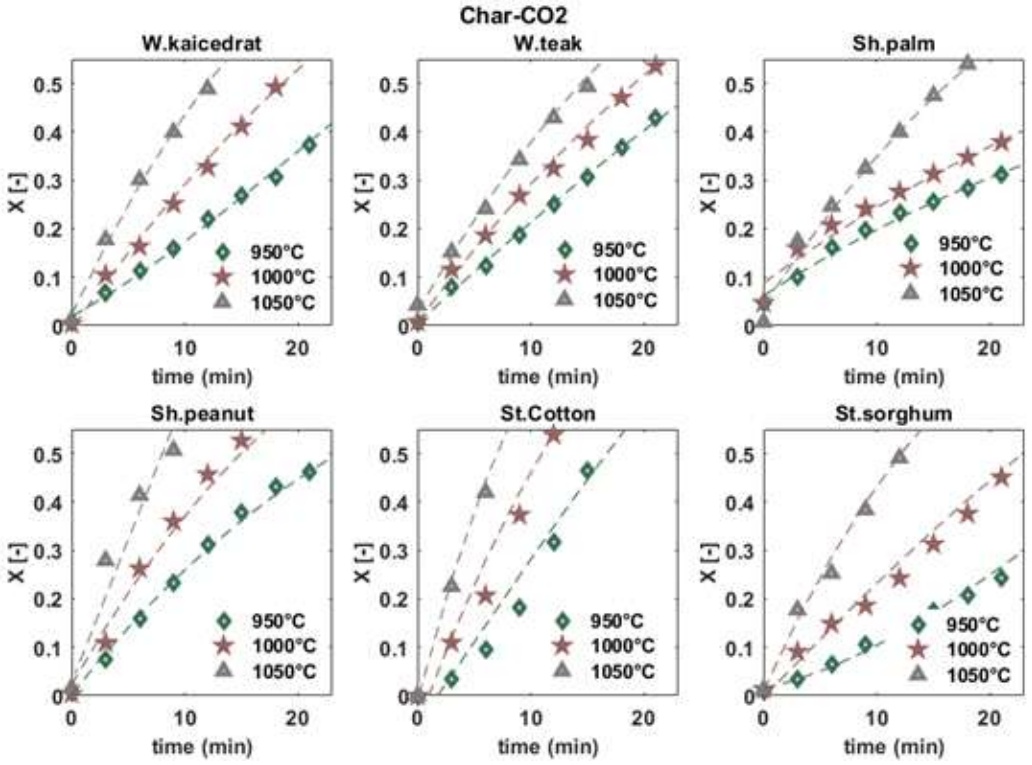

Figure 3. Influence of temperature on conversion kinetics with CO_2 presence.
Source: Authors

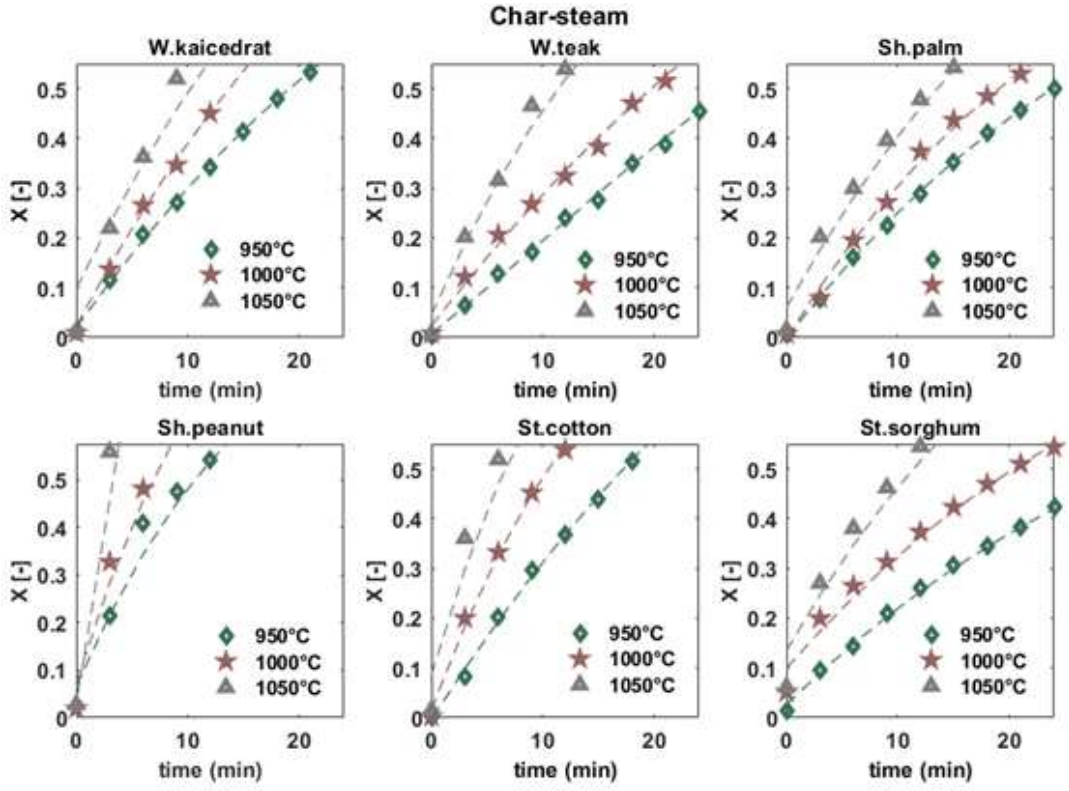

Figure 4. Influence of temperature on conversion kinetics with steam presence.
Source: Authors

describing the evolution of char conversion (Li et al., 2017; Hernowo et al., 2022; Ansoumane et al., 2018; Zuo et al., 2015). The gasification kinetics of the char remains complex, when it is linked to several parameters defining the structure and char composition; for example the nature of the char (granulometry, porosity, chemical composition, dispersion of minerals in the char, etc). This complexity of the gasification kinetics of the char is at the origin of the varying properties of the char and is also a function of the process used to form the char. Therefore, it is still difficult to establish a universal mathematical expression to describe the gasification kinetics of the char, however we will use the most widely used models in the literature. Models are developed as research progresses, but each model is valid and practical on a case-by-case basis (Zuo et al., 2015). It has been described in the literature (Schneider et al., 2021; Wang et al., 2016) that each model gives its own interpretation of the kinetics of the char during thermochemical transformation.

The Volumetric Reaction Model (VRM) defined by Equation 2 is used to describe the chemical evolution of the conversion of char particles (Zhang et al., 2017; Prestipino et al., 2018; Yao et al., 2020). These authors stipulated that with VRM, the reaction is uniform for a given particle size. They added that with this model, the porosity of the particles increases linearly with the conversion of the char.

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

The Shrinking Core Model (SCM, Equation 3) consists of a reaction that first occurs on the outer surface of the particle and then continues progressively inside the particle (Jeong et al., 2014). For this model, the particle porosity remains constant and the particle size decreases with the conversion kinetics of the char (Yang and Chen, 2015).

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

We have seen that an increase in temperature leads to an increase of the conversion speed of the char. Thus, to evaluate the effect of the nature of the biomass on the reactivity of the gasified chars, the kinetic parameters were determined using the two models described earlier.

These different models made it possible to determine the rate constants k of the Volumetric Reaction Model (kVRM), and k of the Shrinking Core Model (kSCM) for each reaction temperature used (950, 1000 and 1050°C). The principle of determining the reaction rate constant as a function of temperature is based on the use of the results of the variation of the conversion rate (X=0 to X=0.5) as a function of time. The results are as shown in Figure 5.

From these results, we can see that the experimental data were well represented by both models (VRM and SCM), with quite high regression coefficients (R^2> 0.9). Table 2 summarizes the kinetic parameters obtained for each sample during their gasification.

In addition, there was no significant difference in the kinetic parameters calculated using the two different models, as the difference between the results was less than 3%. The results also show that the increase in gasification temperature is linearly correlated with the increase in char conversion kinetics (Figure 5). Further, we have activation energies of the reaction of our samples ranging from 100 to 135 kJ/mol (Table 2). It was that the chemical composition of the char corresponding to the different samples influences the kinetic parameters of the gasification of the char under H_2O or CO_2. Also, it was noted that the sorghum stem char is more reactive than the cotton stem char, which is in turn more reactive than the teak wood char, then latter in turn becomes more reactive than the “kaicédrat” wood char, the latter remains more reactive than the peanut shell char, which is finally more reactive than the palm shell char in general in a reaction environment.

This effect could be due to the difference in the chemical composition of the raw material, and the chemical composition of the ash (Table 3). Then, the biomass char generally contains a wide variety of predominantly metallic species (Zhang et al., 2008; Jeong et al., 2014; Fermoso et al., 2009; Lahijani et al., 2013).

Research shows that the mineral composition of the char has a strong impact on the processing, application and environmental, technological concerns associated with these fuels (Zhang et al., 2008; Skodras et al., 2015; Qian et al., 2015; Yang and Chen, 2015). For biomass, the variability in the mineral content of plants can be considerable, as it depends on genetic and environmental factors or origins, it also depends on physico-biological differences between crops (Xie et al., 2012). The results obtained from the analysis of the ash raw material are listed in Table 2.

It clearly shows that the composition of the biomass ash is different from one biomass to another. The sample ashes are mainly composed of K, Na, Mg, Al, Fe, Ca and P, in the form of oxides, silicates and chlorides. We paid particular attention to the contents of alkali metals, alkaline earth metals and silicon in the biomass ashes and their roles in controlling the char reactivity during the gasification. According to the study carried out by Zhang et al. (2008), comparing the gasification reactivities of biomass samples under steam catalyzed by K, Na, Ca and Mg, the results indicate that the alkali metal-catalyzed char (K and Na) has a much higher reactivity than that catalyzed by alkaline earth metals (Ca and Mg). With K being the most active chemical species for carbonized gas, hence, we can say that the difference in the reactivity of our samples could be due to this

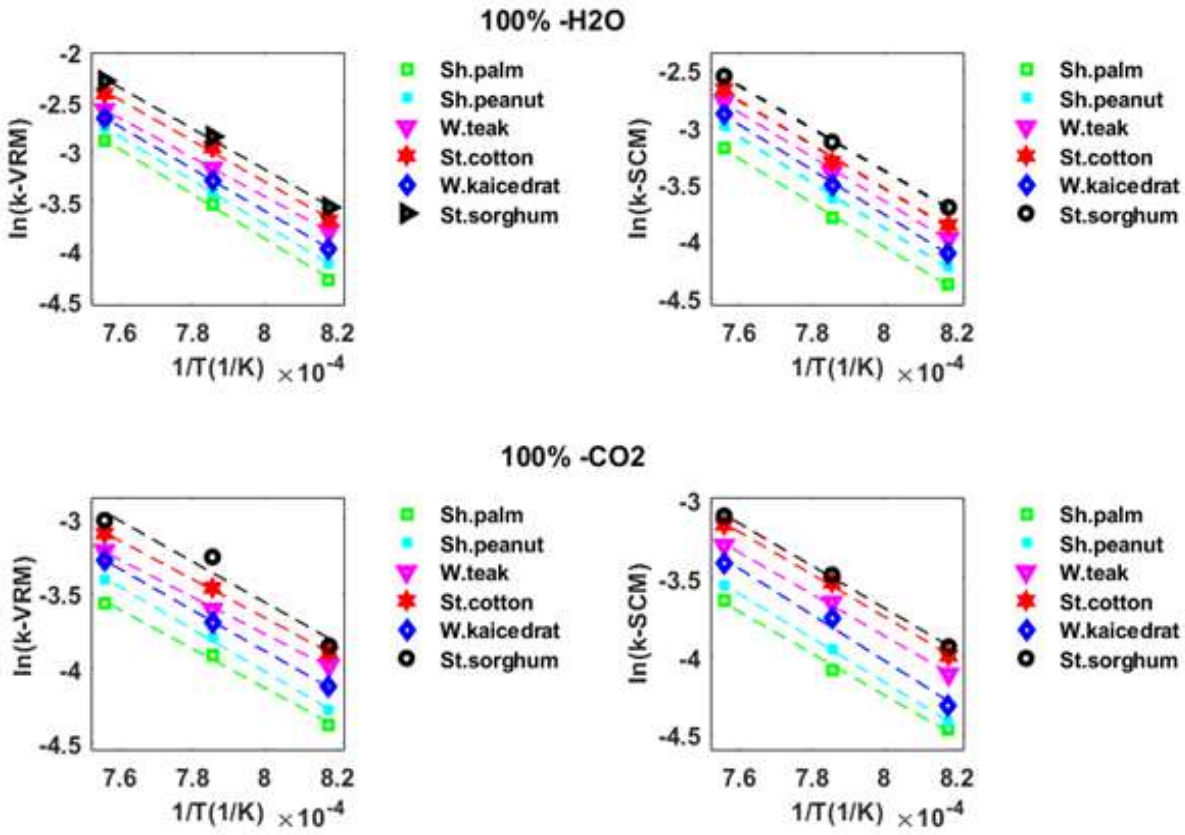

Figure 5. Reactivity of the chars samples (plot of Ln(k) versus f(1/T).
Source: Authors

difference in the chemical composition of the raw material and the ashes.

In all processes of gasification biomass, ash must be collected and disposed of in an acceptable manner. Depending on the specific process and the properties of the biomass ash, some will produce particulate residues solidifies. Numerous uses have been proposed for ash, ranging from the manufacture of building materials (bricks, concrete and asphalt agglomerates) to agricultural products (fertilizer supplements). Any potential value of a given ash is related to the quantity produced and its physical and chemical properties.

Sample gas performance

In order to know the performance of the gases obtained from our samples as a function of the experimental conditions, we used the equation described by (Xie et al., 2012; Kong et al., 2022).

$$LHV = (30\times[CO] + 25.7\times[H_2] + 85.4\times[CH_4] + 151.3\times[C_nH_m]) \times \left(4.2/1000\right) MJ/Nm^3 \quad (4)$$

The results obtained from Equation 4 are listed in Table 4. In this table of variation of gas LHV values as a function of temperature and reaction medium, we can see that the higher the temperature, the better the gas LHV value. This effect could be due to the principle described by Le Chatelier. According to the latter, in char-CO_2 or char-H_2O reaction (endothermic reaction), the production of gases is favourable at high temperature. We note that the LHV values of wood gases (8.06-11.95 MJ/Nm^3) are approximately equal to those of stems (7.78-12.17 MJ/Nm^3) and shells (8.93-12.14 MJ/Nm^3). Therefore, given the seasonality (stems are available from January to April and shells can be available all year round) of biomass residues and the fight against deforestation, it may be recommended to substitute white or red wood with unused biomass waste (burnt in the open air) such as sorghum stems, cotton stems, palm, and peanut shells for energy purposes.

Conclusion

In this study of thermochemical conversion under H_2O or CO_2 of wood residue, stems and shells, the conversion kinetics of the samples increase with temperature. The latter remains a determining parameter for the thermochemical valorization of bio-resources. It was also concluded that, based on two kinetic models (VRM and

Table 2. Kinetic parameters of char gasification under CO_2 or H_2O.

Sample	Reactive	Model	E_a (kJ/mol)	K_0 (min^{-1}) xE^{+4}	R^2
Sh.peanut	CO_2	SCM	111.81	1.40	0.973
W.teak			109.21	3.36	0.964
W.kaicedrat			108.81	0.62	0.986
Sh.palm			134.24	3.20	0.968
St.Sorghum			101.95	0.89	0.998
St.cotton			102.01	1.01	0.985
Sh.peanut	CO_2	VRM	112.70	1.06	0.995
W.teak			108.28	1.67	0.998
W.kaicedrat			107.18	0.95	0.998
Sh.palm			127.41	2.36	0.975
St.Sorghum			100.97	1.35	0.942
St.cotton			101.84	2.39	0.996
Sh.peanut	H_2O	SCM	108.08	1.14	0.999
W.teak			103.03	2.18	0.999
W.kaicedrat			105.16	1.14	0.999
Sh.palm			116.07	1.71	0.951
St.Sorghum			100.58	0.27	0.905
St.cotton			101.45	0.88	0.997
Sh.peanut	H_2O	VRM	110.63	1.29	0.999
W.teak			103.53	2.24	0.993
W.kaicedrat			104.02	0.90	0.995
Sh.palm			116.80	2.08	0.919
St.Sorghum			100.15	1.03	0.975
St.cotton			100.87	1.11	0.995

Source: Authors

Table 3. Biomass ash chemical compositions obtained from our samples using XRF.

Sample	Chemical compositions (Wt. % of ash mass)							
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Cl
Sh.peanut	0.20	4.76	8.21	23.11	22.69	11.07	6.07	0.12
W.teak	12.82	5.56	6.50	16.47	25.76	20.84	4.57	1.08
W.kaicedrat	10.31	12.72	4.97	19.50	23.30	18.09	1.78	0.01
Sh.palm	6.21	15.34	11.30	34.02	20.23	11.42	8.23	3.01
St.Sorghum	15.08	4.13	2.38	17.43	30.57	6.14	15.11	2.15
St.cotton	12.43	6.40	5.82	18.21	28.07	26.09	3.80	0.08

Source: Authors

SCM), the conversion reactivity of our samples follows the kinetic order: (more reactive) St.sorghum > St.cotton > W.teak > W.kaicedrat > Sh.peanut > Sh.palm (less reactive).We found activation energies of the reaction of our tanks between 100 and 135 kJ/mol. This difference in the conversion kinetics of the char may be due to the difference in the chemical composition of the material itself and the chemical composition of the ashes. The values of the lower calorific value of the gases obtained vary from 7 to 12 MJ/Nm^3 and are a function of the experimental conditions. This agrees with what is reported in the literature. The gases obtained with the experimental

Table 4. Effect of temperature on the LHV value of gases (MJ/Nm^3).

Sample		Reactive	950°C	1000°C	1050°C
LHV of gas (MJ/Nm^3)	Sh.peanut	CO_2	9.55	11.08	11.61
		H_2O	9.58	11.48	12.03
	W.Teak	CO_2	8.06	10.66	11.07
		H_2O	9.23	11.10	11.95
	W.kaicedrat	CO_2	9.01	9.91	10.36
		H_2O	9.54	10.14	10.81
	Sh.palm	CO_2	8.93	9.48	11.32
		H_2O	9.76	10.24	12.14
	St.Sorghum	CO_2	7.78	9.08	9.78
		H_2O	8.22	9.49	9.78
	St.Cotton	CO_2	9.03	10.75	11.04
		H_2O	10.81	11.37	12.17

Source: Authors

conditions of this study can be used to operate an engine or a gas turbine. By comparing LHV values from these different samples, we can conclude that residues of cotton stalks, sorghum, palm shell and peanuts can act as a substitute for the wood used. This distorts the comparison of the LHV values of the gases found. This study therefore focuses on the control of wood cutting and the use of residues of agricultural biomass (cotton stems, sorghum stems and peanut shell) and plant biomass (palm shell) for energy purposes.

It would be desirable to test these samples in a semi-industrial unit under the same experimental conditions. Finally, it would also be necessary to make tests of the mixtures of mass stems, shells, etc., to know the effect of the various conditions on the kinetics of conversion.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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