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Kinetic Study for Gasification Reactions of Corncobs Char

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***Abstract-* This study reports the carbon conversion rate calculated from the online gas analysis obtained from corncobs char gasification using carbon dioxide and water steam as reacting agent. Corncobs char is produced by the pyrolysis of corncobs in a muffle furnace at 450 °C for 45 min. The gasification tests is carried out at various temperatures 900 °C, 950 °C and 1,000 °C using carbon dioxide and water steam under isothermal conditions. The VRM (Volume Reaction Model), SCM (Shrinking Core Model) and RPM (Random Pore Model) were tested to interpret obtained experimental data. The kinetic parameters as activation energy (E) and pre-exponential (A) were determined from gas-analysis data by using the Arrhenius equation. From the results confrontation between experimental data and the results obtained from the models, it is found that RPM is more in agreement with the experimental data than the other two models. It is also obtained a values of activation energy of about 114.4 KJ/mol and pre-exponential factor 13.9 S^{-1} for Ψ equal to 12.3 for carbon dioxide and, respectively, 105.5 KJ/mol and 18.3 $S^{-1}$from Ψ = 8.68 for water steam gasification.**

Keywords- Conversion Rate ; Corncobs Char; Gasification; Kinetics.

1. INTRODUCTION

Renewable energies occupy a very important place in development strategy of a nation. Among renewable energies resources, we distinguish biomass energy formula. This study reports the work done on energy recovery from agricultural residues as biomasses by thermochemical conversion through gasification. Thermochemical conversion of biomass offers potentiality for transition from a fossil-fuel-driven global economy. Pyrolysis and gasification have been identified as the most favourable thermochemical processes of biomasses conversion for renewable energy exploitation due to their low sulphur and nitrogen contents. Biomass gasification products contain hydrogen, methane and carbon monoxide and so can be used as fuel in a gas turbine to generate electricity in rural areas [1]. In this context, pyro-gasification of such a biomass is possible for production of electricity starting from gas of synthesis resulting from pyro-gasification.

The economy of the most African countries rests on agriculture, making of Africa, an agricultural potential. This agricultural production generates waste which deserves to be developed. Maize production in the world is a production of 843 million tons in 2013-2014 (against 860 million tons and consumption of 866.7 Mt in 2011-2012). This makes the corn the most cultivated cereal in the world, ahead of wheat [2]. Indeed, it is shown that sub-Saharan Africa produces enough cereals without forgetting cotton. According to statistics of FAO for 2006, [3] average growth rates of sorghum, corn, millet, rice and cotton in West Africa were respectively 1.4 %; 2.9 %; 3.5 %; 1.8 % and 4.8 %. However, in terms of biomasses which may undergo beneficiation starting from these agricultural cultures, we have the corncobs knowing that the sheets, stems and straws are very often used for other applications useful for rural life. The Republic of Benin shows a considerable production rate of corncobs with a growth rate in production of maize in full evolution these last year's [4]. Benin generates an average of 1049.46450×10^3 tons of corncobs per year, starting from maize culture, according to crop years' from 2004/2005 to 2013/2014. All at once, Republic of Benin is characterized by a very weak rate of electrification in rural medium [5]. Consequently, this increased the interest in utilization of corncob as a renewable source of energy [6] [7]. Converting corncobs into gaseous is beneficial to countries which have no conventional energy resources and whose economies are tied to agriculture and local industries like Benin. In this context, the pyro-gasification of this biomass could be a solution for electricity production.

Kinetic parameters information are of particular importance for selection of gasification conditions as well as the logical design of a reactor for subsequent char gasification using carbon dioxide or water steam. This work presents a method for predicting reactivity of biomass char as a function of conversion, temperature and conversion time. The method is based on obtained experimental data from micro-chromatograph coupled to instrumented and equipped installation made of a fixed bed reactor. Several authors have worked on biomasses gasification with carbon dioxide using several kinetic models: The authors of the [8] have compared experimental results from a macro-thermal gravimetric reactor to those from a char particle model, which analyses reactivity versus conversion through the surface function F(x). The authors of the [9] have described changes surface area of char and its reaction rate with Random Pore Model (RPM) using Pressurized Drop Tube furnace (PDTF) at high temperature. The authors of the [10] used Uniform Conversion Model (UCM), Random Pore Model (RPM), Modified Random Pore Model (MRPM), Hybrid Random Pore Model (HRPM), Hybrid Modified Random Pore Model (HMRPM) and their own model. A semi-empirical gasification kinetic model was proposed by [11] on the basis of modifying random pore model to reconcile with gasification reactivity profile of biomass. The authors of the [12] studied CO_2 gasification kinetics of olive residue using the VRM and Langmuir-Hinshelwood model.

The aim of this work is to study the gasification reactivity profile of Benin's corncobs char by means of carbon dioxide and water steam gasification respectively by experimental way and to define convenient reactions model by exploring or comparing existent models on the basis of obtained experimental data.

2. MATERIAL AND METHODS

2.1. RAW MATERIAL CHARACTERIZATION

The corn cobs used for this study come from Benin (West Africa). The physicochemical properties of the studied corncobs and corncobs char are gathered in Tab.1.

Table 1: Determined physicochemical characteristics for corncobs sample and corncobs char

Performed analyses	Corncobs sample		Corncobs char
	Components	Values (%)	
Proximate analysis	Humidity	8	-
	Ash content	1.48	5.6
	Volatile matters	85.05	16.9
	Fixed carbon	13.47	78
Ultimate analysis	C	47.5	80.5
	H	5.96	3.2
	O	42.9	9.7
	N	0.63	0.82
Physicochemical analysis	Cellulose	35	
	Hemicellulose	31.4	
	Lignin	7.9	

Before every realized experiment, the tested corncobs sample is dried in a ventilated oven at 105 °C to constant mass.The determination of the ash content is carried out according to NF M 03-003 standard. The volatile matter index is given by TGA running at heating rate of 5 ºC/min, under inert atmosphere of helium with a gas output of 12 NL/h. Determination of the fixed carbon ratio is carried out according to NF M 03-006 standard. The ultimate analysis is carried out according to the NF EN 15104 while biomass physicochemical analysis is made according to Van Soest proportioning method. Corncobs char is obtained from isothermal pyrolysis carried out in a muffle furnace conditions of 450 °C and for 45 min.

2.2. Experimental Apparatus and Procedure

The diagram of the used experimental setup, for gasification of corncobs, is shown in Fig. 1. This schematically represented laboratory pilot plant belongs to University of Technology of Compiegne (France) and consists of a type of fixed bed reactor well instrumented and equipped. To investigate reaction kinetics of gasification of the corncobs char, the shown device below is used to follow the variation in conversion rates of contained carbon in the corncobs char during reaction with CO_2 or water-steam from analysis of the obtained carbon products.

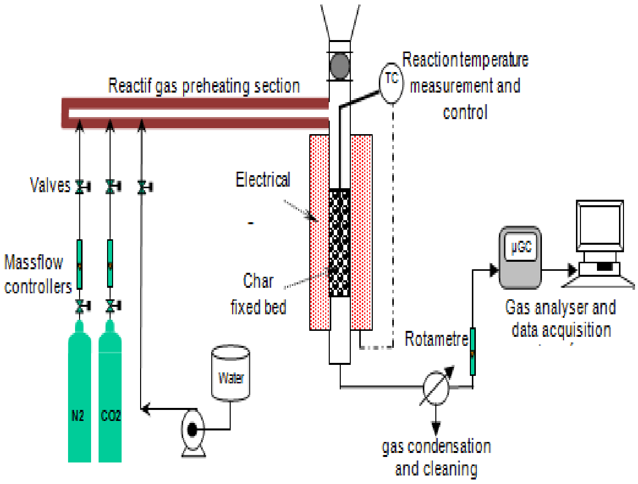


Figure 1: Diagram of the used experimental installation for gasification reactions of fixed bed type

In this context and in order to ensure temperature uniformity and avoid preferential flows in reacting bed, corncobs char (10 % wt) is mixed with sand quantity (90 % mass) having a mean diameter of the order of 300 µm in a cylindrical sample holder (provided with a sintered refractory steel at its lower end).

This assembly is placed in a vertical tubular reactor equipped with a heating element in order to ensure reactor's internal temperature. A temperature controller made of thermocouple and a sensor, placed in the middle of sample bed, is used to measure and control reactor's internal temperature. It is surmounted by a gas supply circuit. The amount of reactive and/or inert (N_2 or CO_2 or water steam) is fed to reactor. The water supply is provided and regulated by means of a volumetric pump Waters 510 which transfers water (in liquid form) towards a gas preheating zone where it instantaneously vaporized. The reactive gas (N_2 or CO_2 or water steam) passes through a preheating zone conferring temperature of 300 °C before reaching char / sand mixture bed inside reactor.

The reactive bed is preheated to the desired temperature under inert atmosphere of nitrogen N_2 at flow rate of 10 NL/h. The reactive gas flow was fixed to 40 NL/h for carbon dioxide and 1.5 ml/min for water steam. During gasification reactions, the nitrogen N_2 flow rate is reduced to 4 NL/h in reactor and serves as a reference to calculate the amount of non-condensable gases produced during the experiment. Meanwhile, the reactive gas supplied to the bed and assity to a mixture of 10 % N_2 (4 NL/h) and 40 NL/h of reactive gas. The product gases pass through a gas condensation and filtration system before gas analysis.

Finally, the gases are routed to a Micro Gas Chromatography (GC) analyser which tracks composition of the non-condensable gas fractions at reactor outlet. These described experiments are performed for three different temperatures: 900 °C, 950 °C and 1.000 °C.

3. RESULTS AND DISCUSSION

The kinetics model for reactions of corncobs char gasification reaction was performed by testing three different models (VRM, SCM and RPM) on the obtained experimental data using the described installation.

3.1. Experimental Results

Using the composition of the gasification product and the amount of N_2, used as a tracer gas, the carbon conversion amount during the reaction, at a given time (t), can be calculated by a simple of carbon mass balance. The conversion rate X is then defined by following formula [13]:

$$X = \frac{m_{c-converted}}{m_c} \qquad (1)$$

with $m_{c-converted}$ and m_c are respectively the mass of carbon converted and the initial mass of carbon (at the beginning of the gasification reaction).

From the formula (1) we plot conversion rate of corncobs char as a function of time, according to each reagent gas. In Fig. 2 and Fig. 3 showed the variation of conversion rate versus time obtained from corncobs char gasification for temperatures 900 °C, 950 °C and 1,000 °C, respectively with carbon dioxide and water steam. From these results, one can observe a significant gap in the conversion rate, as a function of time, from the temperature of 900 °C to 950 °C. Note that, the temperature exerts a considerable influence on kinetics of the gasification reactions, according to Arrhenius law. The study [14] observed the overlapping of the curves at high temperatures when he studied the effect of temperature on gasification of bituminous char in a WMR at 1.5 MPa under 2.5 % CO_2 gas stream. Conversion rate of corncobs char is very (< 4000 S). The work [15] varied the reaction temperature from 850 °C to 900 °C and observed that, at lower reaction temperature, the reaction completion requires longer reaction time. Also [16] observed the same overlapping phenomenon when they studied gasification of low melting coal at high temperature. Both previously studied reactions are endothermic and their different speeds.

3.2. Effects of the Reactive Gases

To study the effect of the reactive gas on the conversion rate, we carried forward in fig 4 the conversion rates obtained for the two extreme temperatures (900 °C and 1.000 °C) with the two reactive gases (carbon dioxide and water steam).The conversion with water steam is greater than that with carbon dioxide. Indeed, it was noticed that the sample mass loss in a CO_2 atmosphere is very small while at the same temperature the reaction rate of water steam is appreciable.

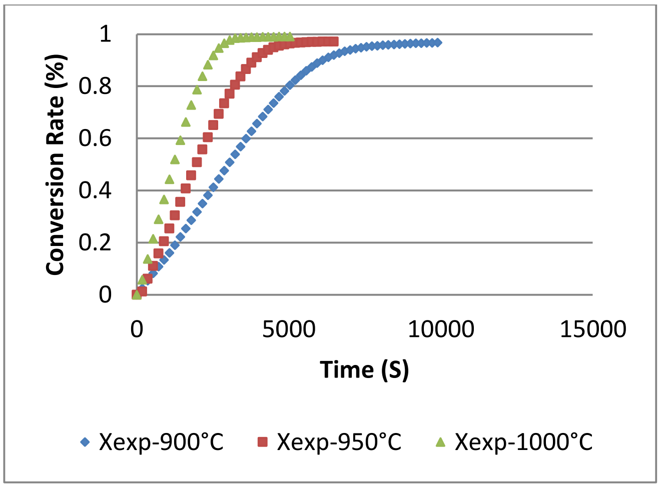


Figure 2 :Plot of X vs time at 900 °C, 950 °C and 1000°C from carbon dioxide gasification

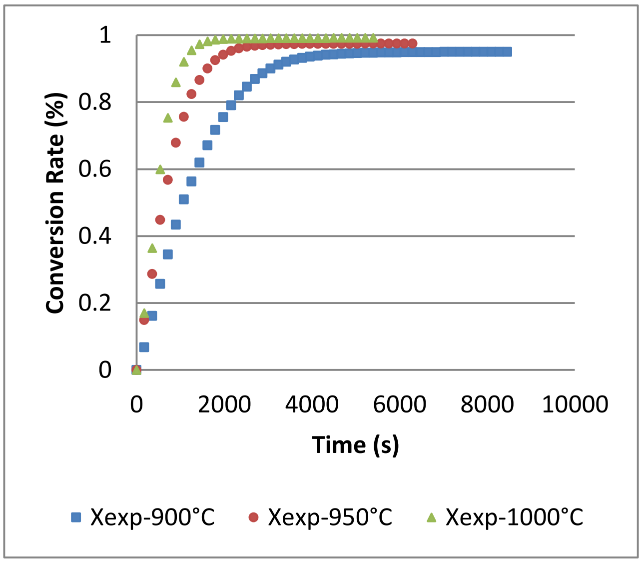


Figure 3: Plot of X vs time at 900 °C, 950 °C and 1000°C from steam gasification

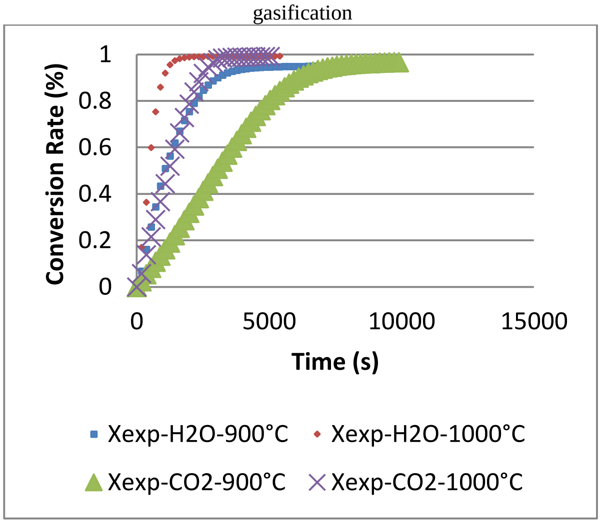


Figure 4: Reactive gases effects on the conversion rate versus time for 900 °C and 1.000 °C

3.3. Determination of Kinetics Parameters

To determine the kinetics parameters, three models were tested in order to find the one which best simulates the experimental results giving the kinetics of corncobs char of gasification reactions.

The rate of conversion is expressed as:

$$\frac{dx}{dt} = kf(x) \qquad (2)$$

Where k is the reaction rate constant based on the gas temperature T and the partial pressure of reagent gas, f(x) is the term which expresses the reactivity dependence on conversion and can take a number of different forms [17]. Assuming that the concentration of carbon dioxide remains constant during the test, the reaction rate of gasification can be represented by means of Arrhenius equation as:

$$k = Ae^{\frac{-E}{RT}} \qquad (3)$$

Where A, E and R, are respectively, the pre-exponential factor, activation energy and universal gas constant.

Three models were applied for studying the reactivity of rice husks charcoal:

VRM (Volume Reaction Model) [18]: It assumes a homogeneous reaction throughout a char particle and the reaction rate is described as follows [19] (fig. 5-A and fig.5-D):

$$\frac{dx}{dt} = k_{VRM}(1 - X) \qquad (4)$$

SCM (Shrinking Core Model): It assumes that the reaction initially occurs at the external surface of char and gradually moves inside. At the intermediate conversion of the solid, there is a shrinking core of non-reacted solid [20] (fig. 5-B and fig. 5-E) and its reaction rate is:

$$\frac{dx}{dt} = k_{SCM}(1 - X)^{2/3} \qquad (5)$$

RPM (Random Pore Model): It considers the overlapping of pore surfaces which reduces the area that is available for reaction [21] (fig. 5-C and fig. 5-F). It can predict the maximum value of the reactivity as the reaction proceeds because it simultaneously considers the effects of pore growth during the initial stages of gasification and the destruction of pores due to the coalescence of adjacent pores. The reaction kinetic is described as follows:

$$\frac{dx}{dt} = k_{RPM}(1 - X)\sqrt{[1 - \Psi\ln(1 - X)]} \qquad (6)$$

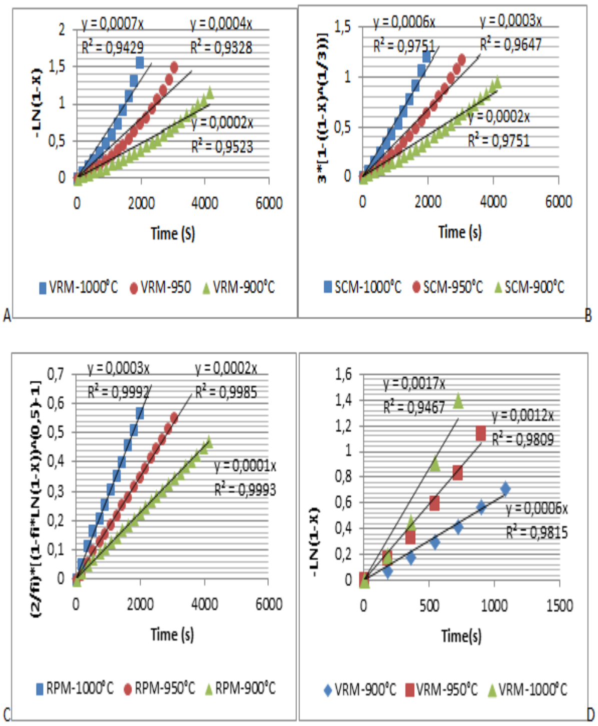
$$\Psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \qquad (7)$$

WithΨ, $L_{0,}\ \varepsilon_0, S_0$ are respectively the pore length, the solid porosity and the surface area that is related to the pore structure of the non-reacted sample.

In this study we have written a program in MATLAB 7.0 [22] allows us to find the useful values of Ψand k having the experimental conversion rate depending on the input reaction time. The graphs of Fig. 5 show the application of the three different models to our acquired experimental data from gasification using respectively carbon dioxide and water steam. The reaction constants of the three different models were obtained from the slope of each of the graphs depending on whether carbon dioxide or steam gasification. As different curves showed it, we observed more dispersion of points for VRM model, much less for SCM model rather linearity for RPM model.

Ψ values found in this study for corncobs char gasification with carbon dioxide and steam are respectively of 12.3 and 8.6. These found values of Ψ for RPM model agrees well with the set conditions by [23] in using this same RPM model. In our case, the maximum value of conversion rate (Xm), according to their work, is 0.34 for gasification with carbon dioxide and 0.32 for gasification with steam. These values are very low than 0.393 found in their work through application of the following formula:

$$X_m = 1 - e^{\frac{2-\Psi}{2\times\Psi}} \qquad (8)$$



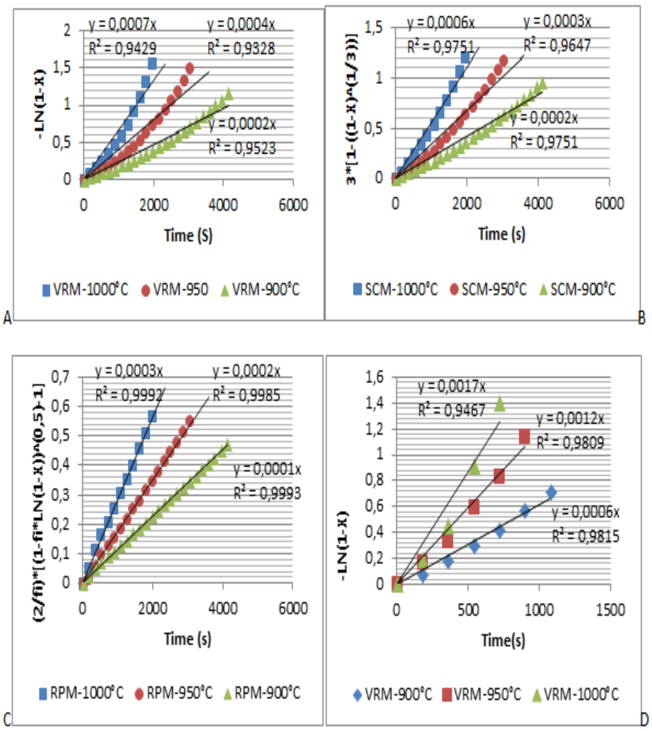


Figure 5: Plots of linearized VRM-SCC-RPM during gasification of corncobs char using respectively CO2 (A, B and C) and steam (D, E and F) at 900 °C, 950 °C and 1,000 °C.

For each model, kinetic parameters were determined corresponding standard deviations and summarized in Tab. 2.

Table 2: Obtained kinetics' parameters using the three tested models: VRM, SCM and RPM

T (°C)	Gasification with CO_2					
	K_{VRM}	R^2	K_{SCM}	R^2	K_{RPM}	R^2
900	$2.7*10^{-4}$	0.97	$2.3*10^{-4}$	0.99	$1.1*10^{-4}$	0.99
950	$4.8*10^{-4}$	0.97	$3.9*10^{-4}$	0.98	$1.8*10^{-4}$	0.99
1000	$7.6*10^{-4}$	0.97	$6.1*10^{-4}$	0.98	$2.8*10^{-4}$	0.99
(E, A)	E(KJ/mol	$A(S^{-1})$	E(KJ/mol	$A(S^{-1})$	E(KJ/mol	$A(S^{-1})$
Values	127.8	134.5	120.8	55.5	114.5	13.92

T (°C)	Gasification with steam					
	K_{VRM}	R^2	K_{VRM}	R^2	K_{VRM}	R^2
900	$6.7*10^{-4}$	0.99	$5.9*10^{-4}$	0.99	$3.6*10^{-4}$	0.99
950	$12.7*10^{-4}$	0.99	$10.6*10^{-4}$	0.99	$5.8*10^{-4}$	0.99
1000	$19.6*10^{-4}$	0.96	$15.8*10^{-4}$	0.98	$8.5*10^{-4}$	0.99
(E, A)	E (KJ/mol	$A(S^{-1})$	E (KJ/mol	$A(S^{-1})$	E (KJ/mol	$A(S^{-1})$
Values	133.6	610.2	120.7	144.9	105.5	18.3

3.4. *Comparative Study Of The Conversion Rates*

The accuracy of a prediction model can be assessed by computing its Estimated Standard Error (ESE), labelled here σ_{CSt} and defined according to the following equation [24]:

$$\sigma_{CSt} = \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{X_{pred}-X_{exp}}{X_{pred}}\right]^{2}}{N-2}} \qquad (9)$$

Where X_{pred} and X_{exp} are respectively the predicted model and experimental char conversion rates, and N is the number of data points of conversion (X)-(t) time (t) data. Tab. 3 and Tab. 4 allow comparing the ESE values of the two tested kinetic models (SCM and RPM) respectively obtained with carbon dioxide and steam gasification.

Table 3: Estimated Standard Error (ESE) for testing the accuracy of kinetic model prediction for CO_2 gasification

Gasification temperature (°C)	Number of data points (N)	Estimated Standard Error (σ_{CSt}) for CO_2		
		SCM	RPM	VRM
900	56	0.14192281	0.05580422	0.18554094
950	37	0.22106105	0.11793458	0.2530101
1,000	29	0.14264105	0.03124638	0.18720104

Table 4: Estimated Standard Error (ESE) for testing the accuracy of kinetic model prediction for steam gasification.

Gasification temperature (°C)	Number of data points (N)	Estimated Standard Error (σ_{CSt}) for steam gasification		
		SCM	RPM	VRM
900	48	0.12635741	0.06515244	0.08379707
950	36	0.23386689	0.06071291	0.05820845
1,000	31	0.46662136	0.02653453	0.10111024

Based on values of regression coefficients (R^2) in Fig. 5 and ESE in Tab. 3 and Tab. 4, without forgetting dispersion of data in function of time, it is noted that kinetic's experimental data for corncobs char gasification, respectively with carbon dioxide and water steam, are best described by RPM model when the temperature is higher than 900 °C. The recorded trend, for the predictive capability of the tested models, is an increasing order corresponding to that following: SCM < VRM < RPM.

For temperatures higher or equal to 900 °C, the kinetic constant of the steam reaction is 1.3 times greater than that for Boudouard reaction. Thus, the apparent kinetic parameters, as determined by RPM model which better fits obtained experimental data, are:

- For Boudouard reaction : E=114.4 KJ/mol and A=13.9 S^{-1}
- For vapogazeification: E=105.5 KJ/mol and A=18.3 S^{-1}

With those obtained kinetic parameters, one can have now access to a model based on the RPM one which allows us simulating reactions' kinetics of corncobs charcoal during gasification.

A comparative study was also carried out between the experimental conversion rates and that obtained directly from the model as shown Fig. 6 and Fig.7.

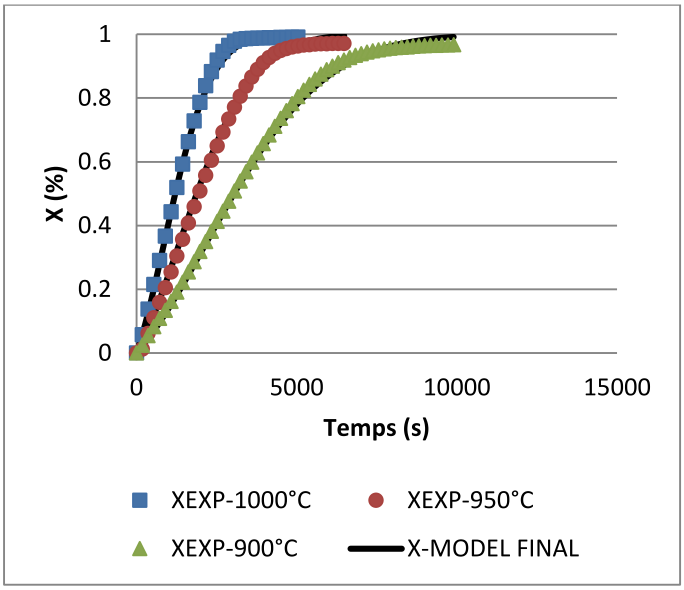


Figure 6: Comparative study of the experimental conversion rate with that achieved by RPM model at cited temperatures in legend using carbon dioxide.

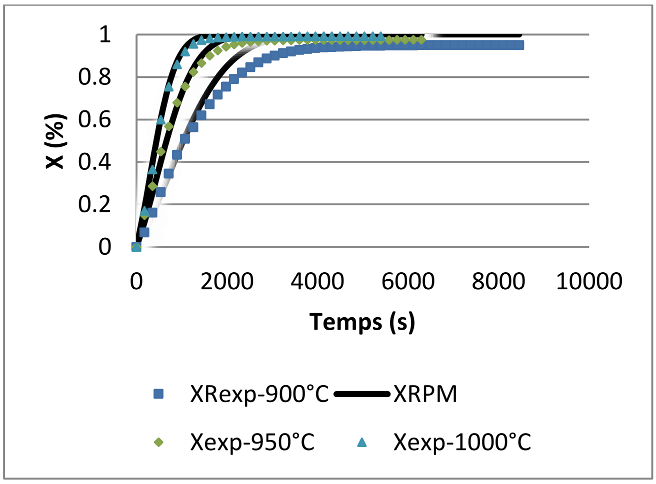


Figure 7: Comparative study of the experimental conversion rate with that achieved by RPM model at cited temperatures in legend using water steam.

The RPM model better simulates the reaction of coal corncobs gasification with carbon dioxide than steam. However, the gap between the experimental data and those from the model gradually decreases and as one progresses to higher temperatures. The reaction with the water vapor is faster than that with carbon dioxide.

CONCLUSION

A set of tests, on kinetic models, was carried out to find the one that best simulates the gasification reactions of corncobs charcoal under carbon dioxide and water steam atmospheres respectively. It was shown that VRM model and RPM model give better results than SCM with experimental data. But, it shows that the RPM model gives a better prediction of experimental data. The increase in temperature causes an increase in reaction's rate more sensitive from 900°C to 950°C. The reaction was subjected to a double control: chemical reaction and internal distribution.

Using the RPM model, different kinetics' parameters have been determined for each corncobs charcoal and validated respectively for Ψ=12.3 under carbon dioxide atmosphere and Ψ=8.68 under water steam atmosphere.

REFERENCES

[1] International Energy Agency (IEA), "Biomass energy: data, Analysis and trends, " 1988.
[2] International Energy Agency (IEA), "World Energy Outlook,"2010.
[3] Blein Roger and *al.*, "Agricultural potentialities of West Africa (CEDEAO)," 2008.
[4] Direction of the statistics of the ministry for Agriculture, the breeding and of Sins of Benin (MAEP), "Evolution of the vegetable production of 1995-2013, " 2013.
[5] Yatopa Adrien Bio and *al.*, "Project to develop the Benin starting from the renewable sources of energies: Identification and cartography of the potentialities and matched renewable sources of energy of the possibilities of exploitation," final report/ PNUD, 2010.
[6] Beagle E.,"Rice husk conversion to energy," Agricultural Services Bulletin, 31. Rome, Italy, FAO, 1978.
[7] Luan TC and Chou TC, "Recovery of Silica from the gasification of rice husks/coal in the presence of a pilot flame in a modified fluidized bed, " Industrial and Engineering chemistry Research 29 (9), 1990.
[8] L. Van de Steene and *al.*, "Gasification of Wood chip particles: Experimental and numerical study of char-H_2O, char-CO_2 and char-O_2 reactions,"Chemical Engineering Sciences 66, 2011, 4499-4509.
[9] Kajitani S. and *al.*, "Gasification rate analysis of coal char with a pressurized drop tube furnace," Fuel 81, 2002, 539-546.
[10] Jason Kramb and *al.*, "Modeling biomass char gasification kinetics for improving prediction of carbon conversion in a fluidized bed gasifier, " Fuel 132, 2014, 107-115.
[11] Y. Zhang and *al.*, "Proposal of a semi-empirical kinetic model to reconcile with gasification reactivity profiles of biomass char, " Fuel 87, 2008, 475–481.
[12] Ollero P and *al.*, "The CO_2 gasification kinetics of olive residue, " Biomass and Bioenergy, 24, 2003, pp. 151-61.
[13] François-Xavier Collard, New strategies for catalytic gasification of biomass: Influence of metal impregnated on pyrolysis mechanisms, Thesis-GPI / UTC, 2012.
[14] Moors JHJ, "Pulverized char combustion and gasification at high temperatures and pressures, " Phd. Dissertation, Eindoven Tech.Univ., The Netherlands, 1998.
[15] Everson RC and *al.*, "Properties of high ash coal-char particles derived from inertinite-rich coal: II. Gasification kinetics with carbon dioxide," Fuel, 87, 2008, pp. 3403-8.
[16] Tang L. and *al.*, "Gasification reactivity of coal with lower ash melting point at high temperature, " J East China Univ Sci Technol, 29, 2003.
[17] Di blasi C, "Combustion and gasification rates of lignocellulosic chars, " Prog Energy combust Sci 35(2), 2009, pp. 121-40.
[18] Seo D. K. and *al.*, "Gasification reactivity of biomass chars with CO_2, "Biomass and Bioenergy, 34(12), 2010, pp. 1946-1953.
[19] Ishida M. and Wen C. Y., "Comparison of zone-reaction model and unreacted-core shrinking model in solid-gas reactions, " Chem. Eng. Sci. Vol 26, 1971, pp. 1031-1041.

[20] Szekely J. and Evans J. W, “A structural model for gas-solid reactions with a moving boundary, ” Chem. Eng. Sci, Vol 25, 1970, pp. 1091-1107.

[21] Fermoso J. and *al.*, “High pressure gasification reactivity of biomass chars produced at different temperatures, ” Journal of Analytical and Applied Pyrolysis, 85 (1-2), 2009, pp. 287-293.

[22] Adrian B. and Moshe B., “MATLAB for engineer, ” Versions 6 and 7, Pearson Education, 2004, (ISBN 2744070254).

[23] Jian-Liang Zhang and *al.*, “A modified Random Pore Model for kinetics of char gasification, ” BioResource 9 (2), 2014, pp. 3497-3507.

[24] Lane D. M., “Standard error of the estimate, Online Statistics Education: A multimedia Course of study, ”Ch. 14, 2012, Available at: http://onlinestatbook.com/2/regression/accuracy.html.