ISSN 2229-5518

Modeling Of Pyrolisis Reactions Of Coconut Hulls, Wood Waste, And Straw: Application For Predicting The Molar Composition Of Gasification Gas

Latif FAGBEMI, Farid ADAMON, Malahimi ANJORIN, Aristide Comlan HOUNGAN

Abstract— This study proposes the coupling of numerical and experimental methods for predicting the molar composition of gas mixtures produced from biomass gasification. It considers the different gasification stages, namely: drying, pyrolisis, combustion and the main reduction reactions. This proposed method is based on several experimental results from the pyrolysis of three different biomasses which have the physico-chemical characteristics representative of multiple biomasses and on the reaction kinetics of the main reduction reactions, namely the Boudouard reaction and water-gas reaction. The results predicted by this method correctly approximate the experimental results obtained in wood to oxygen gasification.

.

Index Terms— Molar composition, biomass gasification, physico-chemical characteristics, pyrolysis reactions

1 INTRODUCTION

IN recent decades, several efforts of experimental, analytical and numerical research have been developed to describe the different methods and phenomena observed and recorded during the gasification process. These various studies have contributed to predict the molar composition of gasification gas as well as to the true understanding of the different stages of the gasification process. For the prediction of the molar composition of gas as a function of operating parameters, besides the GUMZ model [1], which is based on reactions assumed to be at thermodynamic equilibrium, we have also the sequential model [2] which considers all the stages of the gasification process. If the GUMZ model doesn't achieve the pursued objectives, the sequential model gives better results, confirmed by industrial data. However, this model requires a database on the molar composition of pyrolysis gas as well as on the thermal degradation products of these biomasses, namely the weight percentage of gas and carbon, all of which bring challenges in the use of this model. In order to find a solution to render this model more flexible, the present study offers, from experimental studies of three types of biomass, a parameter prediction numerical model of the above-noted (gases and degradation products) for pyrolysis, which is the most important stage in gasification. This model completes the sequential prevision model of the molar composition of gasification gas. Three types of biomass were selected to cover the range of biomass densities; weak (straw), medium (wood) and strong (coconut hulls). Finally, a computer program was created to facilitate using the model.

2 EXPERIMENTAL METHODS AND MATERIALS

2.1 Experimental setup

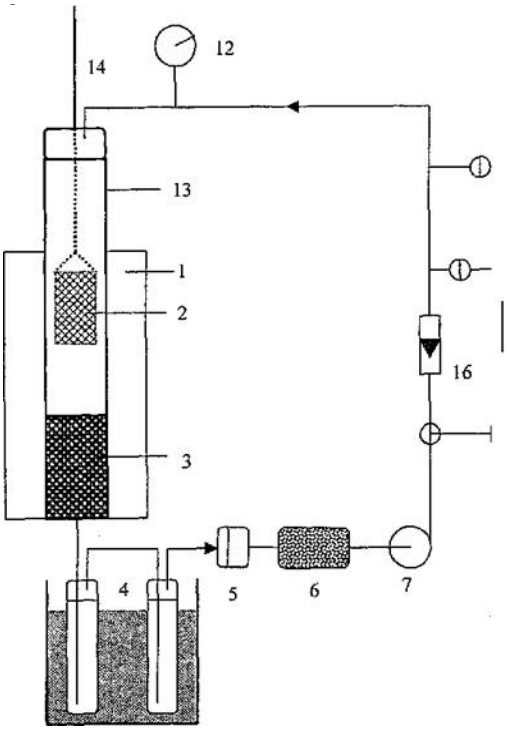
The experimental setup is illustrated below in figure 2. The experiments were conducted in a quartz reactor of 1.20m in length and 6 cm in diameter. Heating is provided by a tubular furnace with temperature regulation. Gas products in the furnace are extracted by a circulation pump located at the base of the reactor. This gas mixture is successively passed through two condensers, a filter, and a calcium chloride layer to retain water. During pyrolysis, non-condensable gas accumulates in an expansion balloon which is empty at the beginning of the experiments.

2.2 . Experimental procedure

Can be described by the following operations:
- A sample of 20 to 30g of lignocellulosic material, in a metal basket, is first placed in the top part of the unheated reactor;
-The furnace is heated to the experimental temperature, ranging from 400°C to 1000°C;
-The reactor, purged with air, is then filled with an inert gas (helium);
The metal basket containing the sample is then immersed in the reactor's heated area and the circulation pump is turned on and starts the pyrolysis reaction.
In the experiments, the wood samples are cut into 3 to 5 mm thick pieces, the coconut hulls are broken into small fragments and the straw is cut into about 10 cm long pieces.
At the end of pyrolysis, a gas sample is analyzed with a gas chromatograph. The carbonaceous residue is weighed and the initially accumulated gas product volume in the balloon is measured by a flow meter. The amount of water produced is determined by the difference in the initial mass of calcium chloride and its final mass at the end of the experiment.

3 RESULTS AND DISCUSSION

The analysis and discussion of the results obtained from these experiments are conducted by FAGBEMI and all [3]. The following tables (1, 2, and 3) summarize these results for the three types of biomass depending on pyrolysis temperatures. The data is more or less consistent with the results obtained on wood by ANTONINI [5] and P.O. Morf [6].



LEGEND

1 Oven
2 Basket
3 Packing
4 Cold traps
5 Filter
6 CaCl2 Dryer
7 Circulation pump
8 Gas-meter
9 Gas expansion _hag
11 Vacuum pump
12 Pressure gauge
13 Quartz reactor

Fig. 1. Schematic diagram of the test rig

Table n°1: : Experimental results of gas mass composition from wood pyrolysis and degradation products

Temperature in °C	400	450	500	550	600	650	700	800	900
CO mass %	34.3	34.2	39.7	40	41.5	44.3	50 .2	50.3	56.1
CO_2 mass %	50.9	43.1	36.6	29.2	23	22.3	16.7	9	6.5
H_2 mass %	4.3	11.9	7.6	8.6	10.8	14.7	15.5	20.8	25.3
CH_4 mass %	7.3	7.1	12.8	14.9	17.5	16.7	16.1	14.2	12.1
Gas mass %	19	18	14.4	17	21.4	28.4	32.8	44.7	46.7
Carbon mass %	31.8	29.2	23.1	24.1	21	23.8	22.3	21.3	17.6
ater mass %	25.1	27	25	28	26.8	23.3	26.1	22.5	20.8

Table n°2: Experimental results of gas mass composition from pyrolysis and straw degradation products

Temperature in °C	500	600	700	800	900
CO	37.7	35	41	48	53.3
CO2	40.7	31	15.8	8.4	4.5
H2	7.4	16.8	19.2	24.6	23.4
H4	10.8	12.5	13.7	15.4	9.1
Gas mass %	25	29.2	35.2	44.2	55
Carbon mass %	35	33.8	30.3	29.3	27
Water mass %	18.2	22.5	15.3	14.9	10.7

Table n°3: Experimental results of gas mass composition and decomposing products from coconut hull pyrolysis.

Temperature in °C	400	450	500	600	700	800
CO	30.6	34.7	35	38.1	40.1	49.2
CO2	53.3	49.9	46.3	28.7	17.9	9.8
H2	0.8	2.6.	5.4	12.4	23.4	23.8
CH4	5.6	10.2	13.3	16.8	18.6	17.2
Gas mass %	13.5	15.1	17.9	21	30.4	36.3
Carbon mass %	33.2	30.4	29	26.5	25.2	23.8
Water mass %	32.4	33.6	31.4	33.9	32	28

3.1. Digital model of the mass composition of pyrolysis gas

Estimation of gas mass composition and pyrolysis of various degradation products with different biomass types depending on reaction temperature is made by the NEWTON method from the experimental data obtained at the end of pyrolysis. Indeed, the NEWTON method, by André FORTIN [4], is a polynomial interpolation method. Therefore, it allows obtaining a polynomial equation, which is a function of the selected variables. Moreover, it should be noted that all programs of this document are written in the MATLAB 7.0 interface. The application in the MATLAB 7.0 language of the NEWTON method was used to write a program

We were able to find a function that can now enable us to estimate the gas mass fraction constituting the resulting gas mixture of the pyrolysis of waste and degradation products stated above, knowing the pyrolysis temperature.

- BIOMASS : straw

When the pyrolysis temperature is greater than500°C, the mass fractions of the gas constituting the resulting pyrolysis gas mixture are calculated according to the following polynomial function: $aT^4 + bT^3 + cT + dT + e$, where (a, b, c, d, e) c (R*x R*x R*x R*x R*) the values of a, b, c, d, e are summarized in the table 4 below for each gas species.

Table 4 : a, b, c, d, e coefficients values

	a	b	c	d	e
CO	$2.08x10^{-9}$	$-6.688X10^{-6}$	$7.9598x10^{-3}$	-4.09238	+799.94
CO_2	$-7.3X10^{-9}$	$2.12x10^{-5}$	$-2.2594x10^{-2}$	10.3627	-1685.9
H2	$-8.17X10^{-9}$	$2.2912x10^{-5}$	$-2.38627x10^{-2}$	10.97512	-1867.6
CH_4	$-3.79X10^{-9}$	$1.0004x10^{-5}$	$-9.8079x10^{-3}$	4.24514	-673.42
H_2O	$-1.2x10^{-8}$	$3.425x10^{-5}$	$-3.6185x10^{-2}$	16.731	-2832.3
Carbon	$-3.58X10^{-9}$	$1.0108x10^{-5}$	$-1.05408x10^{-2}$	4.78678	-762.94
Gas	10^{-9}	$2.8X10^{-6}$	$-0.278x10^{-2}$	1.223	- 179

- BIOMASS: Coconut hulls

The pyrolysis changes of the coconut hulls consist of two main parts : When the pyrolysis temperature is between 400°C and 500°C , the mass fractions of the gas forming the gas mixture are calculated according to the following polynomial function: $aT^2 + bT + c$, where (a, b, c) c (R*x R*x R*). The table 5 below summarizes the values of the a, b, c coefficients

Table 5: a, b, c, coefficients values

	a	b	c
CO	$-7.6x10^{-4}$	0.728	-139
CO2	$-4x10^{-5}$	-0.034	73.3
H2	$2x10^{-4}$	-134	22.4
CH4	$-3x10^{-4}$	0.347	-85.2
H2 O	$-6.8x10^{-4}$	0.602	-99.6
Carbon	$2.8x10^{-4}$	-0.294	106
Gas	$2.4x10^{-4}$	-0.172	43.9

When the pyrolysis temperature is greater than 500°C, the mass fractions of the gas forming the gas mixture are calculated according to the following polynomial function: $aT^3 + bT^2 + cT + d$, where (a, b, c, d) c (R*x R*x R*x R*), the values of the a, b, c, and d coefficients are shown in the table 6 below.

BIOMASS: Wood waste

The pyrolysis changes of the wood waste also consist of two main parts :

When the pyrolysis temperature is between 400° C and 700° C, the mass fractions of the gas forming the gas mixture are calculated according to the following polynomial function: $aT^6 + bT^5 + cT^4 + dT^3 + eT^2 + fT + g$, where (a, b, c, d, e, f, g) c (R*x R*x R*x R*x R*x R*x R*), the values of the a, b, c, d, e and f coefficients are shown in the table 7 .

Table 6: a, b, c, d coefficients values

	a	B	C	d
CO	$1.37x10^{-6}$	$-2.521x10^{-3}$	1.5574	-284.7
CO2	$-6.83x10^{-7}$	$1.5694x10^{-3}$	-1.28081	379.73
H2	$-2.43x10^{-6}$	$4.574x10^{-3}$	-2.7501	540.7
CH4	$-2.5x10^{-7}$	$3.65x10^{-4}$	-0.139	22.8
H2 O	$3.83x10^{-7}$	$-9.094x10^{-4}$	0.67681	-127.53
Carbon	$-2.17x10^{-/}$	$4.506x10^{-4}$	-0.32319	105.07
Gas	$-1.63x10^{-6}$	$32.49x10^{-4}$	-2.0596	439.2

- When the pyrolysis temperature is between 700° C and 500° C, the mass fractions of the gas forming the gas mixture are calculated according to the following polynomial function: abT2 + bT + c, where (a, b, c) c (R*x R*x R*). The table 8 below summarizes the values of the a, b, c coefficients.

Table 8: a, b, c, coefficients values

	a	b	c
CO	*2.85x10~4*	*-0.4265*	*209.1*
CO2	*2.6x10~4*	*-0.467*	*216.2*
H2	*-4x10 5*	*0.113*	*-44*
CH4	-10 5	-0.004	23.8
H2 O	9.5x10 5	-0.1785	104.5
Carbon	*-1.35x10-*	*0.1925*	*-46.3*
Gas	*-4.95x10 4*	*0.8615*	*-327.7*

Table 7: a, b, c, d, e, f coefficients values

	a	b	c	d	e	f	g
CO	2.8x10 12	-9.447x10 9	1.31975x10 5	-9.7673125x10	4.03721125	-883.2503	79901.1
CO2	-1.32x10 12	4.102x10 9	*-5.2598x10 6*	*3.562765x10-*	*-1.3447317*	*268.047725*	*-21974.9*
H2	*-3.18x10 1*	*1.0708x10 8*	*-1.494725x10*	*1.10687x 10 2*	*-4.5845795*	*1006.6542*	*-91496.5*
CH4	*3.3x10 12*	*-1.0971x10*	*1.510195x10 5*	*-1.1016642x10*	*4.4911695*	*-969.91507*	*86667.65*
H2 O	*-2.99x10 1*	*1.01975x10*	*-1.4364875x10*	*1.0695456x10*	*-4.4383891*	*973.182125*	*-88049.2*
Carbon	*-7.5x10 12*	*2.4775x10 8*	*-3.386375x10*	*2.4511162x10*	*-9.9070287*	*2119.601*	*-187462.*
gas	*-2.63x10 1*	*8.7755x10 9*	*-1.2131375x10*	*°.8908312x10 2*	*-3.6415451*	*789.895075*	*- 70830.4*

3.2 Comparative study and analysis

Simulations on wood at a temperature of 800^{0}C (Table 1) for pyrolysis and gasification (Table 9) were conducted to assess the gap between digital and experimental values obtained for the molar composition of pyrolysis and gasification products from wood waste for example. The tables below summarize the differences

Table 9: Comparative study of digital and experimental values of the gas composition of wood pyrolysis at 800°C.

Gas constituting the gas mixture resulting	Numeric values (mass fractions)	Experimental values (mass fractions)	Gap observed in absolute value
CO (%)	50.3	50.3	0
H2 (%)	20.8	20.8	0
CH4 (%)	14.2	14.2	0
CO2 (%)	8.99	9.0	0.01

By integrating the functions found above to the sequential model [2], we have written a program in the MATLAB 7.0 interface whose objective is to predict the molar composition of gasification gas for several types of biomass (wood waste (average density), coconut hulls (high density) and straw (low density)).

The application of this model gives the results summarized in the table below compared with the results obtained in a gasifier using wood waste.

Table 10: Comparative study of digital and experimental results for the composition of the gas from wood waste gasification at 800^{0}C, on the fluidized pilot bed

Gas constituting the gas mixture resulting from	Fluidized bed results (mass fractions)	Digital results (mass fractions)	Observed gap
CO (%)	41.9	46.33	4.43 (10.5%)
O2 (%)	24.8	24.90	0.10 (0.4%)
H2 (%)	26.4	21.61	4.79 (18%)
CH4 (%)	6.8	7.14	0.34 (5%)

While reading table 9, we see that whatever the pyrolysis model, the digital values obtained agree with experimental data. This proves the accuracy of the method used, in addition to its importance in the determination of the volume fractions of pyrolysis products, at any temperature. For the composition of the gaseous gasification mixture, the gap shown in table 10 is a little larger for CO and H_2; this is justified by approximations carried out in the kinetics of secondary reactions proposed by the sequential model [2], by not taking into account in this model the pyroligneous extract cracking (tar). However, note that our results are close to better experimental results in of wood gasification with oxygen, thus making it an important tool to forecast the molar composition of gasification for different biomass gas depending on their density with temperature

Conclusion

A digital model to predict the molar composition of pyrolysis gas was proposed for different types of biomass and a wide temperature range. This model relies on many experimental results obtained from the biomass pyrolysis. It has overcome the shortcomings of the sequential model to predict the molar gas composition of gasification by the determination of the appropriate polynomial functions for mass composition of gases and products from pyrolysis decomposition. The introduction of the functions thus determined in the sequential model for molar composition prediction achieves results closer to those obtained in a wood gasifier. Finally, a calculation program is proposed to predict the molar composition of gasification gas valid for several types of biomass.

References

[1] GUMZ, "Gas produces and blast furnaces," Edition Wiley- New-York, (1975).

[2] R. CAPART, L. FAGBEMI, M. GELUS, "An experimental study of wood pyrolysis: a basis for predicting the gas production from the FRAMATOME process," Proceeding of the 1986 International Congress on renewable energy sources (Madrid 1986). S. TEROL (413-425).

[3] L. FAGBEMI, L. KHEZAMI, R. CAPART, "Pyrolysis products from different biomass: application to the thermal cracking of tars, applied Energy," Vol.69, pp. 293- 306, 2001.

[4] André FORTIN, "Analyse numérique pour ingénieurs," deuxième édition, (2001).

[5] P.O. Morf, "Secondary reactions of tar during thermochemical biomass Conversion," Thèse de Doctorat (Doctoral Thesis), Swiss Federal Institute of Technology Zurich, (2001).

[6] Gérard ANTONINI Mourad HAZI, "Etude ADEME / PROCEDIS, Partiel: Etat de l'art des procédés existants, faisabilité de traitement d'un déchet par Pyrolyse ou gazéification" (ADEME/PROCEDIS Study, part 1: State of the art of existing processes, feasibility of waste treatment by pyrolysis or gasification), (2004).

- FAGBEMI Latif received the Ph.D. degrees in chemical process Engineering from Compiègne University (FRANCE)
  He is currently Assistant Professor of biomass energy, fluid mechanic at Polytechnic School of Abomey-Calavi – University of Abomey-Calavi (BENIN). His principal research interests are applied mechanics and Biomass energy in Laboratory of Energetics and Mechanics Applied (L.E.M.A)
  e-mail: latiff08@yahoo.fr

- Farid ADAMON received the M.Sc. in
  He is currently thesis student of biomass energy at Polytechnic School of Abomey-Calavi – University of Abomey-Calavi (BE-

NIN). His principal research interests are applied Biomass energy in Laboratory of Energetics and Mechanics Applied (L.E.M.A)

- Malahimi Anjorin received the M.Sc. in Moscow and Ph.D. degrees in Heat Transfer from INPL of Nancy (FRANCE)
  He is currently Assistant Professor of Heat and Mass transfer, fluid mechanic at Polytechnic School of Abomey-Calavi – University of Abomey-Calavi (BENIN). His principal research interests are applied mechanics and Heat and Mass Transfer in building Material and Biomass energy in Laboratory of Energetics and Mechanics Applied (L.E.M.A)
  e-mail : malahimianjorin1@yahoo.fr

- Comlan Aristide HOUNGAN received the M.Sc. in Benin and Ph.D. degrees in Energetics and Environment from Agro Paris-Tech /ENGREF of Nancy (FRANCE)
  He is currently Assistant Professor of Heat and Mass transfer, fluid mechanic at the Technological Institute of Lokossa – University of Abomey-Calavi. His principal research interests are applied mechanics and Heat and Mass Transfer in building Material and biomass energy in Laboratory of Energetics and Mechanics Applied (L.E.M.A) . e-mail: hounaris@yahoo.fr