Hydrogen Production by Gasification of Biomass from Copoazu Waste

Emilio Delgado, William Aperador, and Alis Pataquiva

***Abstract*—**Biomass is becoming a large renewable resource for power generation; it is involved in higher frequency in environmentally clean processes, and even it is used for biofuels preparation. On the other hand, hydrogen – other energy source – can be produced in a variety of methods including gasification of biomass. In this study, the production of hydrogen by gasification of biomass waste is examined. This work explores the production of a gaseous mixture with high power potential from Amazonas´ specie known as copoazu, using a counter-flow fixed-bed bioreactor.

***Keywords*—**Copoazu, Gasification, Hydrogen production.

I. Introduction

DUE to industrialization, population increase, globalization, among others, today´s world is immersed in the need for renewable energy sources. Demand is huge, just as serious environmental problems with outstanding and collateral consequences.

This relentless quest to transform the environment by humanity has brought visible consequences such as global warming and cycle of life disturbed due to animal and plants changes, and even, decreases of human welfare. These are strong reasons for reducing environmental impacts through the search of alternative sources that avoid affect life and habitats, reducing costs and increasing efficiency.

Nowadays, production and non-renewable fuels such as coal and oil accompanied by high pollutant loads caused by urban waste causing significant contributions of toxic emissions and environmental deterioration.

Most industrialization, most scarcity of oil increasing the global scientific community concern in this way, about future energetic emergencies. An emerging alternative is the biofuels production from renewable sources based on organic raw materials reducing, at the same time, atmospheric pollution.

In this work was studied an Amazonian fruit popularly known as copoazu that represents 144000 kg/crop in 20 Ha, producing 44,160 kg of waste/crop mainly conformed by fruit shells. In order to utilize the mentioned copoazu waste, a different alternative fuel is proposed.

Emilio Delgado is with Department of Mechatronic Engineering, University Militar Nueva Granada, Colombia, and Department of Industrial Engineering, University Escuela Colombiana de Ingeniería, Julio Garavito, Colombia (e-mail: arnoldo.delgado@unimilitar.edu.co).

William Aperador is with Department of Mechatronic Engineering, University Militar Nueva Granada, Colombia (e-mail: william.aperador@unimilitar.edu.co).

Alis Pataquiva is with Department of Engineering, University Jorge Tadeo Lozano, Colombia (e-mail: alisy.pataquivam@utadeo.edu.co).

Experiments were carried out a biomass gasification from copoazu waste to obtain a high energetic gaseous mixture, and subsequently it was employed a counter-flow fixed-bead reactor to produce biofuel. Chemical, physical and physicochemical tests were studied for products characterization.

II. Raw Material Characterization

A. Plant Species: Copoazu

Theobroma grandiflorum (copoazu tree) is a fruitful plant of the *Sterculiaceae* family; current name for a plant family find it in tropics whose components are mostly trees and shrubs easily recognized by their simple leaves and whole flowers, that born directly from the trunk and old braches.

Copoazu has an average weight of 1.2 kg ranging from 0.2–0.5 kg and its fruit consists in an elliptic capsule with obtuse and rounded ends with 15 – 40cm in length and 10 – 15cm in diameter. Hard shell with 2-4 mm in thickness, involves the Copoazu fruit that is woody and breakable easily. The cover with "ferruginous" villi with velvety appearance reveals a chlorophyll layer that indicates the mature fruit presence [1]. Copoazu yellow or white pulp has acid flavor and strong aroma, and envelops the seeds [2].

B. Determination of Physico-Chemical Analysis

Quantitative analysis (C,H, N,O) present in organic or inorganic samples were carried out by means of a quantitative elemental analysis technique using nitrogen, hydrogen and carbon analyzers.

Proximal analysis for determination of moisture, ashes, volatile materials, and fixed carbon in weight percent of a representative sample of solid fuel; were obtained using (ASTM-D3172-89(02)).

For calculating the humidity it was followed the procedure recommended by ISO 5068-1993 protocol, whereby the sample should be dried in an oven at constant temperature of 106°C.

Determination of volatile combustible material followed the ISO 562-1996 protocol.

The ash content in the sample was assessed by ISO 1171-1996. The fixed carbon content is obtained by difference between humidity percentage, ash and volatile materials from 100% following ASTM D3172 protocol. Calorific value was obtained using a calorimetric pump.

III. Biomass Processing

There are different methods of biomass processing defined by the different types of energy extraction, thus obtaining several products which are shown in Fig. 1. Biological products are degraded by microorganisms into simpler compounds; alcoholic fermentation and anaerobic digestion are the best known examples of this type of energy transformation. On the other hand, chemical processes in based on biomass processing by chemical reagents producing hydrolytic reactions to obtain high economic value product such as methyl and ethyl esters.

The thermo-chemical method is characterized by breakdown of cellular links by heat action, finding dependence between temperature and product quality, so as direct combustion, pyrolysis and gasification have different specific technologies of transformation [3].

This work is based on thermo-chemical method that uses gasification technology in order to obtain a gaseous mixture of high energy potential.

A. Biomass Gasification

Gasification is the thermal decomposition process which aims to obtain a gaseous mixture of methane, ethane, ethylene, hydrogen, and carbon monoxide and dioxide, among others. Solid materials were partially oxidized by pyrolysis to react with a restricted amount of gasifying agent such as air, water steam, carbon dioxide, oxygen, hydrogen or a mixture calorific value, as well as small amount of ashes and tars [4].

Currently the gasification of biomass and wastes has great interest in the potential for power generation over the use of conventional fuels and to other less efficient processes. The main advantage of gasification compared to other processes is to obtain a versatile fuel that can be used in equipment designed for gas or diesel can completely or partially replace conventional fossil fuels.[5].

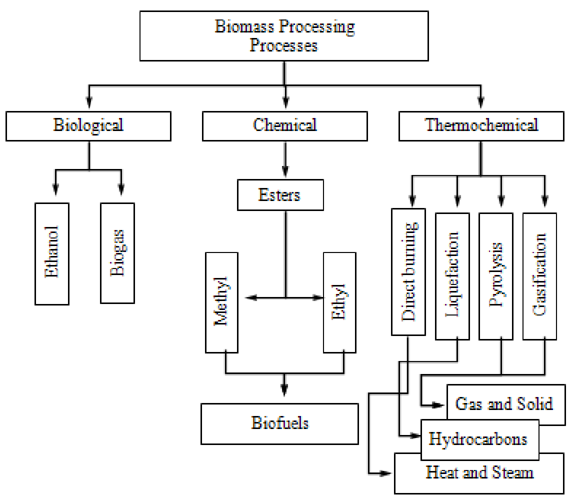

Fig. 1 Biomass Processing Processes

B. Variables in the Process

The operating conditions of the system, quality and composition of the material being worked and the type of leavening agent determines the physicochemical properties of the gas mixture obtained, therefore, one must understand and verifying each of the variables affecting the process, such as process temperature, pressure, gasifying agent and raw materials.

C. Gasification Equipment

Good equipment and materials selection is essential to asses operating conditions for evaluating the parameters that provide the appropriate design basis and scaling systems. Gasification equipment developed was fixed bed and counter-current reactors (see Fig. 2.) comprised by sensor system, control system, heat transfer system, collection system gas, supply systems and gas extraction.

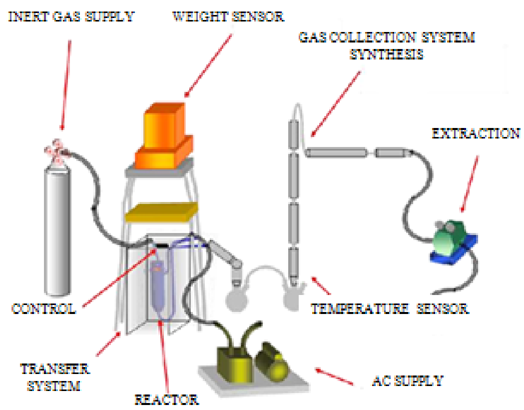

Fig. 2 Gasification equipment components

IV. Materials and Methods

Temperature was controlled during whole experimentation (WATLOW series 935 A). Water steam and air were the chosen gasifying agents and they were added to the process as follows: 8.82 ml of gasifying agent per each 5 g of biomass, copoazu waste for this study.

Particle diameter determination used a disc type mill for grinding material; subsequently a sieving process was performed to obtain the chosen diameters (20 and 100) for which were retained the greatest fraction of copoazu waste (0.59 and 0.18 respectively).

Study levels of bed height were height 1 (3 cm) and height 2 (5 cm).

A. Methods

1) Operation of the Gasification Equipment

Procedure used for each test followed the sequence shown below in Fig. 3.

Copoazu waste (15 g) based on copoazu shell was placed in the presence of gasifying agent. A mass loss sensor was installed, as well as the level sensor bubble type to verify the alignment in horizontal plane.

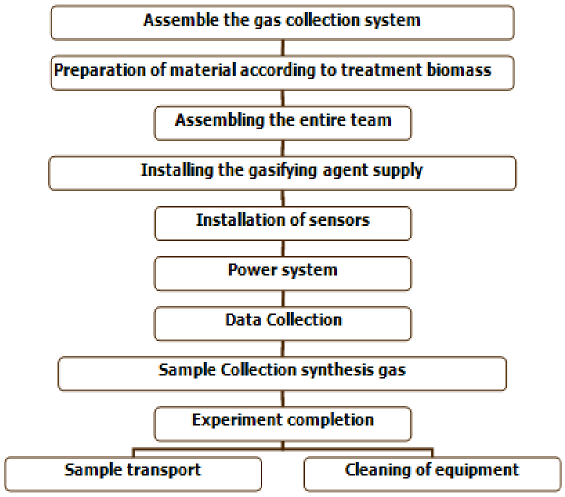

Fig. 3 Operation flow diagram of gasification equipment

Subsequently, the gas suction pump was activated with 150 - 200 mmHg of pressure and the income nitrogen flow was 0.5 L/min for 2 minutes. After that, the flow was decreased and weighed. The cooling flow in heat exchangers was allowed to ensure a heating rate of 10°C/min, increasing the set point value until 1000°C after 120 min.

After gasifying agent entrance, the gas suction pump was turned off for sampling and collected samples were reserved at 4°C. Next, flow energy into the oven was finished and reactor was removed from the oven and present char was quantified.

2) Chromatography Analysis

After gasifying test, chromatographic analysis of product gases were carried out, with the aim of calculating the samples mass composition.

Mass quantification (H_2, CO, CO, O_2, N_2) was developed using a Thermal Detector of Conductivity (TDC); additionally, CH_4, C_4H_6 and C_2H_4 were quantified by Flame ionization detector (FID).

B. Statistical Analysis

Essays were performed using a 2k factorial design, which is useful in the early stages f experimental work with many factors to be studied. This design allows the determination of influence of each factor in the measured response and suggests a lower number of runs per study.

TABLE I
APPLIED TREATMENTS IN THE DESIGN OF EXPERIMENTS

No Treatment	Treatment	Description			
1	C1M2H1A2	Copoazu	Mesh 100	height 1	Air
3	C1M1H1A2	Copoazu	Mesh 20	height 1	Air
5	C1M1H2A2	Copoazu	Mesh 20	height 2	Air
6	C1M1H1A1	Copoazu	Mesh 20	height 1	Water
11	C1M2H1A1	Copoazu	Mesh 100	height 1	Water
12	C1M2H2A2	Copoazu	Mesh 100	height 2	Air
13	C1M2H2A1	Copoazu	Mesh 100	height 2	Water
14	C1M1H2A1	Copoazu	Mesh 20	height 2	Water

Factors such as the selected levels for experimentation were defined before (see number 4) and different treatments were applied (See Table I) in order to make combinations that correspond to a fully randomized factorial design, involving four factors with 2 levels.

V. RESULTS AND DISCUSSION

In the experiments a wide range of results were obtained, and the most relevant will be discussed to follow:

A. Results Related to Gases Mixture Products

By the gas chromatography technique, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, N_2 andO_2 were quantified and evaluated the effect of a particular gasifying agent in the productions of these gases, and their influence on the calorific value of the gaseous mixture. Two different bed heights were studied: height 1 (3 cm) and height 2 (5 cm), with tow diameter: mesh 20 (diameter of 0.0833 cm) and mesh 100 (diameter of 0.0147cm). Finally gasifying gases were water steam and air, and material was copoazu waste.

Experiments were conducted in triplicate for obtaining an estimate of experimental error and calculate the effect of the factors in each assay [6].

To follow, results from gaseous chromatography of water steam as de gasifying agent.

1) Results of Gaseous Mixture from Using Water Steam as Gasifying Gas

In order to evaluate the effect of water steam there were used these gasification treatments: 6, 11, 13, 14 that were varied in height of the bed and in diameter particle of copoazu waste.

During experimentation with water steam, it was possible identify the gas mixture that is the main product of this study. At the moment in which copoazu shells carbonized, they react with steam to form the gaseous product that was analyzed using gas chromatography.

Some chromatograms obtained from the process of gasifying with water steam (see Fig. 4) and the percentages of the gases that form the mixture (see Fig. 5).

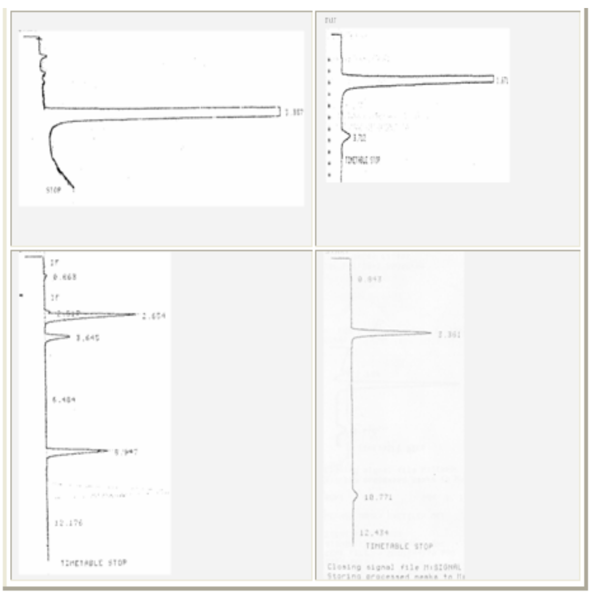

Fig. 4 Chromatograms of water steam as gasifying agent

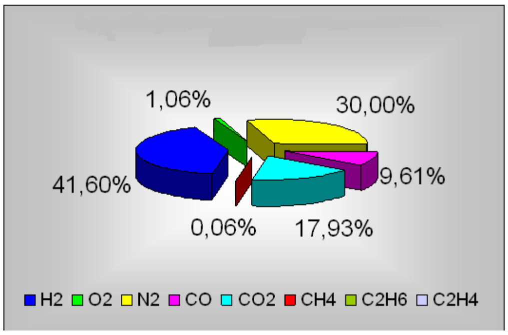

Fig. 5 Productgaseous mixture composition. Treatment 6

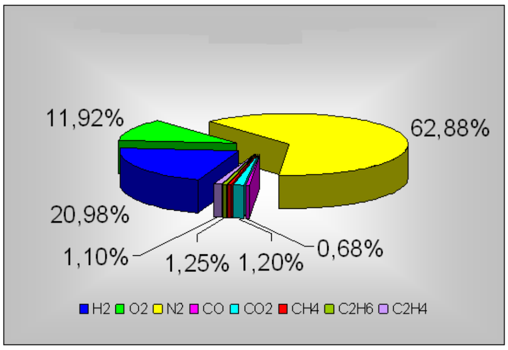

Fig. 6 Product gaseous mixture composition. Treatment 11

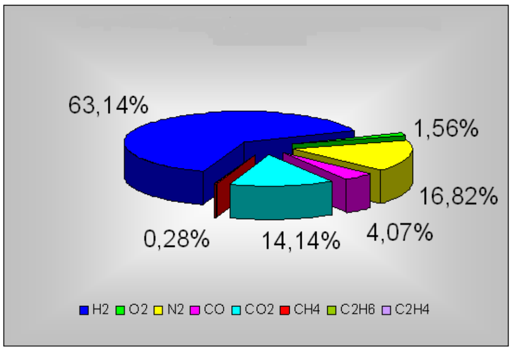

Fig. 7 Product gaseous mixture composition. Treatment 14

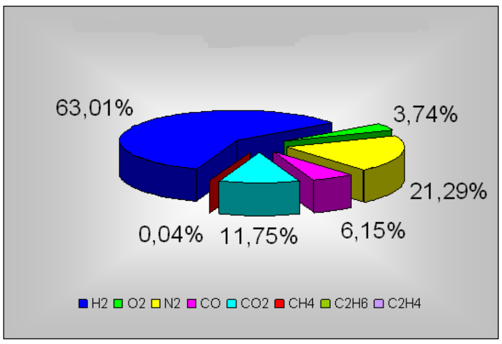

Fig. 8 Product gaseous mixture composition. Treatment 13

Fig. 7 shows the gas composition obtained by the gasification process for the combined treatment with copoazu mesh 20 particles diameter, height of bed 2 and water steam as gasifying agent.

As shown the presence of N_2 (16,82%) CO_2 (14,14) and H_2 (63,14) represent the major composition of the mixture, there are relatively small amounts of CO (4-07%), CH_4(0,28%) O_2 (1,56%) and a 0.01% C_2H_6 and C_2H_4. Percentage of H_2obtained as a result of this treatment shows the inclination of the reaction towards hydrogen production.

Fig. 8 represents the composition of the gas mixture to be applied which involves copoazu with a particle diameter given by mesh 100, height of bed 2 and water steam as a gasifying agent.

With this treatment, high values in the hydrogen were observed (63.01%), and N_2(21.29%) and O_2(3.74%) concentrations favor the increasing concentrations of CO (6.15%) and CO_2 (11.75%). Both CH_4 (0.04%) and C_2H_6 and C_2H_4 (0.08%, each) do not represent a significant contribution in the composition of the mixture.

Compositions of the product gas mixture from the application of treatment involving copoazu such as diameter particle given by mesh 20, bed height 1 and water steam as a gasifying agent; are shown in Fig. 5.

The results shows a considerable concentration of H_2 (41.60%) and N2 (30%), important amounts of CO_2 (17.93%) and CO (9.61%) compared to O_2 (1.06%). Finally CH_4, C_2H_2 and C_2H_6 present small percentages less than 1%.

Composition of different collected gases by the treatment 11 is shown in Fig. 6. Diameter particle of mesh 100, bed height and water steam as a gasifying agent are the parameter for this treatment.

High concentration ofN_2 (62.88%), and avery significant amount of H_2 (20.98%) and O_2(11.92%) are obtained. The low concentrations of other components such as CO(0.68%), CO_2(1.20%) C_2H_4(1.10%) and for the mixture consisting of $CH_4$and C_2H_6 (1.25%) are shown as well for this treatment.

B. Product Analysis of Gas Mixture

During experimentation there was a marked difference in the composition of mixtures, mainly due to the use of a particular gasifying gas. Water steam considerably favors the production of a combustible gas due to high concentrations of hydrogen, which increase significantly the calorific value of the obtained gaseous mixture. On the other hand, analysis shown that the use of air as gasifying agent do not shown significant concentrations of components considered as combustibles. Chromatographic results revealed N_2 and O_2 concentrations similar to the atmospheric air when used air as gasifying agent.

Thus, gasifying agent has a crucial importance in the development of the gasification process of copoazu waste based on shells. During experimentation, it was observed that rich gaseous mixture and low retention time are obtained when water steam is used as gasifying agent, due to high reactivity of carbonized copoazu in water steam atmospheres.

Production of high levels of hydrogen in the gaseous mixture, suggests copoazu waste as fuel in the gasification process. However, low concentrations of other gases such as C_2H_6, C_2H_4, CO and CH_4 suggest a define directionality into reaction mainly due to the rapid removal o produced gases during reaction favoring the formation of other gases in the mixture.

Statistical analysis of results determines the incidence of interaction between remaining factors in the process. Due to low amounts of gases of interest when air is used as gasifying agent, this was excluded from statistical analysis.

VI. ANOVA ANALYSIS

A randomized 2^2 factorial design was chosen because it gives the analysis of effects caused by interactions between bed height and particle diameter producing valid conclusions about experimental conditions. Detailed treatments that were susceptible of statistical analysis are shown in Table II.

TABLE II
STATISTICAL ANALYSIS OF EMPLOYED TREATMENTS USING WATER STEAM AS GASIFYING AGENT

No Test	No Treatment	Description			
1	13	Copoazu	Mesh 100	height 2	Water
2	11	Copoazu	Mesh 100	height 1	Water
10	14	Copoazu	Mesh 20	height 2	Water
11	6	Copoazu	Mesh 20	height 1	Water

Percentages average obtained from H_2, CO and CO_2 content in the mixture are presented in Table III, IV and V respectively. CH_4, C_2H_6 and C_2H_4 concentrations were ignored due to low concentrations obtained from gas chromatography results. Both N_2 and O_2 were not taken into account been irrelevant for this study.

Variance analysis was performed using MINITAB statistical software.

TABLE III
H_2 PERCENTAGE IN GASEOUS MIXTURE

% H2	WATER VAPOR	
	Mesh 20	Mesh 100
Height 1	36,76	14.71
Height 2	52.30	48.93

TABLE IV
CO PERCENTAGE IN GASEOUS MIXTURE

% CO	WATER VAPOR	
	Mesh 20	Mesh 100
Height 1	6.86	0.26
Height 2	5.02	6.24

TABLE V
CO_2 PERCENTAGE IN GASEOUS MIXTURE

% CO2	WATER VAPOR	
	Mesh 20	Mesh 100
Height 1	14.54	1.91
Height 2	16.44	12.99

Table VI shows the summary o variance analysis obtained for H_2, CO and CO_2 all of them present in higher concentrations in the gas mixture.

TABLE VI
VARIANCE ANALYSIS OBTAINED FOR H2, CO AND CO2 (ANOVA)

Source of variation	GL	%H2		%CO		%CO2	
		Adj ms	P	Adj ms	P	Adj ms	P
Bed height (H)	1	1650,34*	0.04	13,146	0.120	112,30*	0.032
Particle diameter (DP)	1	430,69	0.064	17,245	0.082	172,33*	0.013
H*DP	1	232,7	0.150	44,014*	0.014	56,33	0.1
Error	7	89,13		4,189		15,69	

* Significative value a $\alpha= 0.05$
FD: freedom degree.
Adj ms: square sum adjustment.
P: significance level.

Corresponding values for H_2 percentage indicate that bed height is the most significant factor evaluated because **P** values is lower than 005. Likewise, there is no interaction between particle diameter and bed height (see Fig. 8) where the significance level of the interaction is 0.15. This fact indicates that use of fixed-bed height should favor H_2 concentration regardless of which particles diameter is used.

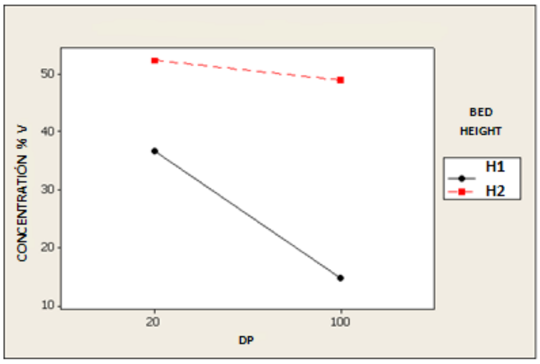

Fig. 9 Interaction between factors for H_2

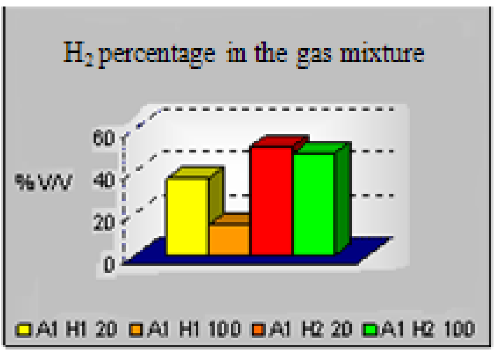

Fig. 10 H_2 percentage in the gas mixture

Comparing the H_2 percentage of H_2 (see Fig.9.) a marked difference in the production of this gas is evident when bed height 2 is used. This fact can be attributed to the lower mass loss during pyrolytic gasification stage, result in gina greater proportion of carbonized available for reaction with the gasifying agent.

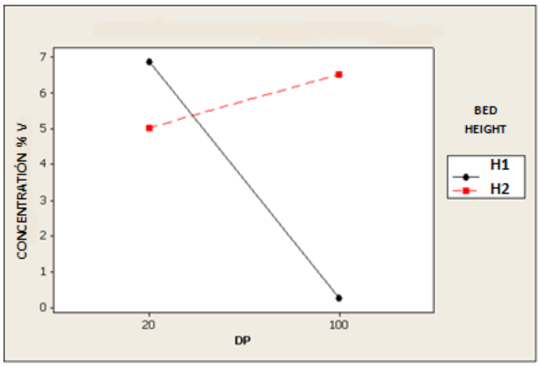

Fig. 11 Interaction between factors for CO

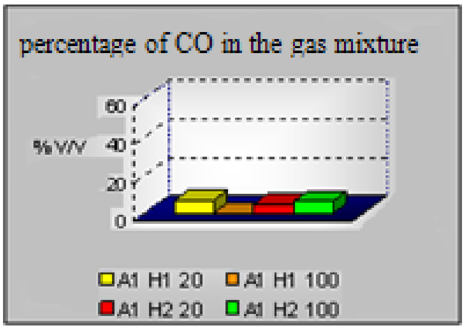

Fig. 12 CO percentage in the gas mixture
*ANOVA analysis taken

Levels of significance for CO production (see Table VI) indicate that only the interaction between factors bed height and particle diameter (P=0.014) have a significant impact on the production of this gas. The individual effects of each factor are not significant (see Fig. 11).

Highest values of CO are obtained by applying thetreatment6 (see Fig. 12) which relates the height of bed1 with the particle diameter given by the mesh20 and treatment 13 in which height bed2 with the particle diameter of100 mesh are combined. The lowest value of CO is obtained by using a bed height to100 mesh particle diameter.

VI. Conclusion

Thermo-chemical conversion processes of biomass are presented as an alternative of energy generation for those areas not connected to the national grid electricity as the Colombian Amazon, where there is high dependence on agriculture. The implementation of gasification systems contributes to these lf sustainability of the processes and competitive advantage sunder an environmental point of view over other system so electricity or heat.

Physicochemical properties of biomass play an important role in the gasification process since the thermal decomposition of material is determined by the elements that constitute it. Different material compositions generated at different temperatures and reaction times favor the production of the product of interest such as the case of hydrogen; and various types of biomass under the same conditions result indifferent products.

The selection process of gasifyer type to implement a system of energy production by thermo-chemical conversion of biomass must be careful and specific: equipment has accomplishing technical and environmental requirements because it plays an important role when selecting an alternative of renewable energy supply affecting directly the process efficiency.

According to the results obtained from experiments it can be concluded that under given conditions (equipment design, temperature and pressure) copoazu waste gasification yields positive results for the production of a biofuel gas composed mostly of hydrogen that can be used to generate electricity or heat in the Colombian Amazon.

Acknowledgment

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