Effect of Temperature and Particle Size on the Yield of Bio-oil, Produced from Conventional Coconut Core Pyrolysis

Shirley J. Duarte, Jorge Lin, Dario Alviso, and Juan C. Rolón

Abstract—Thermochemical conversion processes can transform biomass in solid, liquid and gaseous fuels. Among these processes, pyrolysis allows a pyroligneous condensate, similar to fuel oil, called bio-oil. This research focused on conventional pyrolysis of Paraguayan coconut core, in order to determine the effects of temperature and particle size on the bio-oil yield; as well as to obtain physico-chemical properties of the biofuel under the selected operating conditions. Uncondensed gases generated during pyrolysis were analyzed as well as the bio-oil stability in a two month period at 40 ℃. The experiments were carried out using an electric oven, a fixed bed reactor and a vertical concentric condenser. The analysis of variance indicated that both factors have a significant influence on performance, and also indicates interactions between them. The liquid properties included water content of 53% w/w, pH 2.41, kinematic viscosity of 1.51 cSt, specific gravity of 1.0739 and higher calorific value between 14.75 MJ/kg to 10.88 MJ/kg. Uncondensed gases were composed mainly of CO and CO_2 with small amounts of CH_4 and C_3H_8, which were generated, up to 45 minutes after reaching pyrolysis temperature. Finally, stability tests indicated that bio-oil obtained is stable until the fourth day of storage at 40 ℃.

Index Terms—Chemical properties, fixed bed reactor, heating rate, stability.

I. INTRODUCTION

The growing awareness of the environmental problems that entails the use of fossil fuels, have made that the different governments be heading in the search for alternatives to these fuels. In this context, biofuels, or fuels derived from biomass, arise as an alternative to the use of non-renewable fuels, providing the advantages of reducing greenhouse gas emissions and secure supply of energy products [1].

Biomass comprises a heterogeneous group of organic materials from natural sources (animal or vegetable) or derived from human activities (agro-industrial waste and municipal waste), capable of being transformed into energy, biomaterials or other products of high added value. This is considered one of the greatest sources of renewable energy because its energy content comes from solar energy fixed by plants in photosynthetic processes [2].

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The use of biomass as an energy alternative has the advantages of being a potential substitute for fossil fuels.

A wide variety of solid, liquid and gaseous fuels can be produced from biomass, and environmental problems related to the disposal of organic waste can be solved. In addition, biomass can increase the profitability of crop processes and does not contribute to increase greenhouse gases, i.e., the net balance of CO_2 emissions is zero.

In predominantly agricultural countries, agro-industrial waste is considered as major source of biomass. In Paraguay, according to [3]; between 7 and 10 tons of coconut core and coconut shell per hectare per year is generated as agro-industrial sub products.

Currently, the core and shell coconut are used in boilers for heat generation. However, this method of traditional use is very inefficient because much of the energy is wasted in hot gases exhaust, it remains unburned or vaporized due to fuel moisture [4].

Through pyrolysis process is possible to obtain a liquid fuel with higher value-added, i.e. *bio-oil*. This fuel is manageable in combustion processes and generates lower toxic emissions compared to those of petroleum fuels. A mixture of combustible gases and carbonaceous solid residue can be used directly as fuel or can be transformed into activated carbon, with a higher value-added product [5].

Bio-oil is a biofuel obtained by condensation of the vapors coming from biomass sources pyrolysis.

Numerous studies such as those conducted by [6] and [7], demonstrate the influence of operational variables in the yield of bio-oil, using coconut core as feedstock. However in Paraguay, as far as we know there has not been conducted yet a detailed research about coconut core processing for the production of bio-oil and activated carbon.

In this paper the influence of pyrolysis temperature and particle size on the yield of bio-oil obtained from coconut core, variety *Acrocomia aculeate* is studied. Also, for selected operating conditions, the composition of the condensable gases during the reaction and the variations in the properties of the bio-oil obtained in a two months period are analyzed.

II. PYROLYSIS OF COCONUT CORE

Sundaram & Natarajan (2009), investigated the influence of pyrolysis temperature, heating rate and grain size in the performance of pyrolysis products [6]. The study was carried out using a fixed bed reactor, at temperatures between 400-600 ℃, constant rate of heating of 20 ℃/min, 40 ℃/min and 60 ℃/min and particle size in the range of 0.15 to 1.80

mm. They observed that, for a rate of 60 °C/min, the yield of liquid and gas increased from 38% to 43% and 30% to 33% respectively when the final pyrolysis temperature of 400 °C is increased to 600 °C, while the yield of the solid decreases from 32% to 22%. The yield of liquid and solid increased significantly when increasing particle size. Concerning the heating rate, heating rates low, produce low yields of the liquid, increasing as the rate increases. Furthermore, they observed that the heat capacity of bio-oil obtained was similar to that of Gasoil.

The selected operating conditions encountered in the study are: final pyrolysis temperature of 550 °C, grain size ranging from 1.18 to 1.8 mm and heating rate of 60 °C/min. With a maximum liquid yield than 45%.

Joardder *et al.* (2011), carried out the pyrolysis of coconut core in pirotubular fixed bed reactor, analyzing the effect of bed temperature, particle size and reaction time on the yield of bio-oil [7]. Test were performed in a pyrolysis temperature range of 400-600 °C, particle sizes between 0.6 to 6 mm, reaction times up to 125 min and flow of inert gas (N_2) constant at 6 L/min. The authors concluded that:

1) When the final pyrolysis temperature varies from 400 °C to 600 °C, the liquid yield initially increased, reaching a maximum value at the temperature of 450 °C, above which the performance returns to decline.
2) Performance liquid decreases with increasing of grain size (unlike studies by [6], in which the performance of bio-oil increases when increasing grain size).
3) For certain conditions, the yield of bio-oil is maximum when the reaction time is 100 min, below this value, the reaction is incomplete and thus the yield is lower, whereas above this value the yield remains almost constant.
4) Best performance was 34.3% for the operating conditions of: 450 °C temperature, grain size 0.6 mm, reaction time of 100 min and nitrogen gas flow of 6 L/min.

III. METHODOLOGY

A. Characterization of the Coconut Core

The coconut core used in this study was obtained from the eastern region of Paraguay (Paraguari).

Sarubbi (2014), characterized the coconut core, respect to its approximate analysis and higher heating value, according to Mexican Norm B-030, B-036, B-157 and the ASTM D3175 [8]. The results are presented in Table I.

TABLE I: APPROXIMATE ANALYSIS AND HIGHER HEATING VALUE [8]

Parameter	Value	Unit of measure
Ash	1.75	(%w/w)
Volatiles	75.25	(%w/w)
Humidity	5.1	(%w/w)
Fixed carbon	17.9	(%w/w)
Higher heating value	4604.73	(cal/g)

B. Experimental Design

The influence of the independent variables (pyrolysis temperature and particle size) on the dependent variable (performance in bio-oil) was determined.

The selected approach corresponds to factorial design 3^2. Factor A was the pyrolysis temperature in three levels: 450

°C, 500 °C and 550 °C. Factor B was the particle size in three levels: 2 – 1.4 mm; 850 − 600 μm; 425 − 300 μm.

C. Number of Experiments and Randomization

The total number of possible combinations of independent variables levels is 9 (three temperature levels multiplied three particle size levels). Experiments were performed three times each; therefore, the total number was 27. In Table II, are showed the randomized results, using Microsoft Office Excel 2007 Software.

TABLE II: DISTRIBUTING TESTS FOR THE DIFFERENT OPERATING CONDITIONS

		A Factor		
		-1	**0**	**+1**
B Factor	**+1**	3	13	19
		14	5	20
		23	16	8
	0	10	12	17
		7	18	21
		26	1	4
	-1	15	11	2
		27	9	6
		25	24	22

D. Experimental Procedure
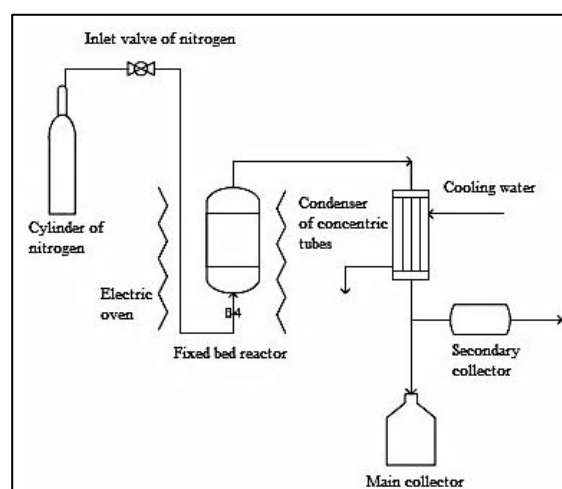
Fig. 1 presents a diagram of the process.

Fig. 1. Process flow diagram.

The set up consists of an electric oven, a nitrogen balloon, a fixed bed reactor, a vertical condenser of concentric tubes and two condensate collectors. The reactor consists of a stainless steel tube AISI 304 of 19 cm length; 3.81 cm outer diameter and 3.54 cm inner diameter; and at the end of it, two segments of wire mesh Tyler No. 300, in order to support the bed. Inside the furnace, the reactor is vertically supported to a

pipe section of the same material as the reactor, through which nitrogen gas is transported. The condenser consists of two concentric tubes of 3.81 cm and 2.54 cm diameter and 30 cm length. The condensate collector or main collector collects most of the condensate formed in the process. The collector B is located at the exit of the exhaust line of non-condensable gases and its objective is to retain the condensate escaping.

The reactor was charged with 90 g of coconut core dried at 105 °C for 24 hours (moisture: 0.74 %w/w). The charge was introduced into the furnace before each experiment. The system purging was performed with nitrogen gas at 2 L/min flow rate for a 10 min period.

The pyrolysis was carried out under a non-linear heating rate, with 16.5 °C/min average rate, for a period of 45 min, studying the performance of pyrolytic liquid, as well as the char and that of non-condensable gases, for three particle sizes of coconut core.

During pyrolysis process, nitrogen gas flow was kept constant, performing two functions: to maintain the anaerobic conditions and to flush fluid for the products that are formed by controlling the gases residence time. A similar procedure was made by [7].

E. Pyrolysis Products Yields

Bio-oil yield: calculated as the percentage of the coconut core mass fraction of the feed that is condensed as bio-oil, using Equation (1).

$$\eta_{bio-oil} = \frac{Weight_{bio-oil}}{Weight_{coconut\ core}} \times 100 \qquad (1)$$

Char yield: calculated as the percentage of the coconut core mass fraction, which is converted to a solid carbonized (char), using Equation (2).

$$\eta_{char} = \frac{Weight_{char}}{Weight_{coconut\ core}} \times 100 \qquad (2)$$

Effluent gases yield: calculated from the mass balance, using Equation (3).

$$\eta_{bio-oil} + \eta_{char} + \eta_{gases} = 100 \qquad (3)$$

F. Bio-oil Characterization

The characterization of bio-oil, obtained using the best conditions established prior by a correlational study, from the variance analysis *ANOVA*, was conducted.

Higher heating value: it was determined using a calorimeter pump by measuring the increase in temperature of water caused by the combustion of 1 g sample and using energy balance Equation (4)

$$HHV = \frac{C_B \times \Delta T}{m_s} \qquad (4)$$

where:
- *HHV*: is the higher calorific power.
- C_B: is the constant of the calorimetric bomb used.
- ΔT: is the increase in temperature of the water mass.
- m_s: mass of the sample.

Viscosity: it was performed using ASTM D 445 method, designed for measuring kinematic viscosity of liquid petroleum fuels. This method uses an Ostwald viscometer and distilled water as reference liquid. Oasmaa and Peacocke (2001), found that small deviations in temperature causes greater measurement errors in tests conducted at 20 °C, compared to those performed at temperature 40 °C [9]. Therefore, the latter was selected as the reference temperature for measurement.

Relative density: it was determined by taking standard ASTM D4052 method that uses a Gay-Lussac pycnometer at 25 °C average temperature of Paraguay.

pH: it was determined by direct measurement using a pHmeter.

Water content: it was performed using Karl-Fisher method. The analysis was carried out in National Institute of Technology, Standardization and Metrology (INTN-Py).

G. Analysis of Chemical Composition of the Effluent Gases Analysis

For the analysis of non-condensable gases issuing the pyrolysis process, the operating conditions used were those defined as the most favorable in the ANOVA analysis. An infrared spectrometer coupled to Fourier transform (model DX Gasmet 3000) was used. Once the system reached 100 °C composition data was collected each 5 minutes, for a period of 45 minutes. The element H_2, was not detected due to limitations of the instrument.

H. Stability Study

The stability study was carried out storing 10 samples of bio-oil in an oven at 40 °C. Each sample consisted of 40 mL of biofuel, arranged in an Erlenmeyer matrass of 100 mL with lid and stored for a period of time showed in Table III, after which it was removed and analyzed viscosity and pH values were analyzed.

Table III shows the storage periods employed for the different samples.

TABLE III: STORAGE PERIODS FOR BIO-OILS SAMPLES

Sample number	Storage days	Sample number	Storage days
Sample 1		Sample 7	
Sample 2	0	Sample 8	28
Sample 3		Sample 9	
Sample 4	4	Sample 10	42
Sample 5		Sample 11	
Sample 6	11	Sample 12	57

IV. RESULTS AND DISCUSSION

A. Performance in % w/w for the Mass Fraction of Bio-oil, Char and Non Condensable Gases

The yields of the different fractions (bio-oil, char, incondensable gases) obtained from the pyrolysis process at different operating conditions are presented in Table IV (A, B and C). The measurements have a standard deviation less of 1.65.

In Table IV A, B and C it is observed that for all possible combinations of factors in each experiment, bio-oil yields were greater than 32% w/w. This value is higher than the one obtained by conventional pyrolysis [5].

The char average yield was about 35% w/w, which is considered for its usage as briquettes of higher heating value, considering that the calorific power would be between 7500 −

9000 cal/g.

TABLE IV-A: PERFORMANCE OF THE DIFFERENT FRACTIONS OBTAINED (*BIO-OIL*) FOR THE DIFFERENT OPERATING CONDITIONS

| | | Yields of the differents pyrolysis products | | |
| | | Bio-Oil | | |
	Temperature (°C)	450	500	550
Grain Size	Large (2 mm>p>1.4 mm)	35.52	36.80	36.22
	Medium (850 μm>p>600 μm)	36.23	36.54	38.17
	Small (425 μm>p>300 μm)	36.00	32.33	35.40

TABLE IV-B: PERFORMANCE OF THE DIFFERENT FRACTIONS OBTAINED (*CHAR*) FOR THE DIFFERENT OPERATING CONDITIONS

| | | Yields of the differents pyrolysis products | | |
| | | Char | | |
	Temperature (°C)	450	500	550
Grain Size	Large (2 mm>p>1.4 mm)	36.50	35.53	34.09
	Medium (850 μm>p>600 μm)	36.85	35.73	34.17
	Small (425 μm>p>300 μm)	36.43	35.23	33.63

TABLE IV-C: PERFORMANCE OF THE DIFFERENT FRACTIONS OBTAINED (*INCONDENSABLE GASES*) FOR THE DIFFERENT OPERATING CONDITIONS

| | | Yields of the differents pyrolysis products | | |
| | | Incondensable gases | | |
	Temperature (°C)	450	500	550
Grain Size	Large (2 mm>p>1.4 mm)	27.98	27.68	29.68
	Medium (850 μm>p>600 μm)	26.92	27.73	27.66
	Small (425 μm>p>300 μm)	26.82	32.44	30.72

The non-condensable gases mass fractions issuing the process are non negligible due to its chemical composition, rich in CO, CO_2; H_2 and CH_4. It can be used in others process of chemical conversion.
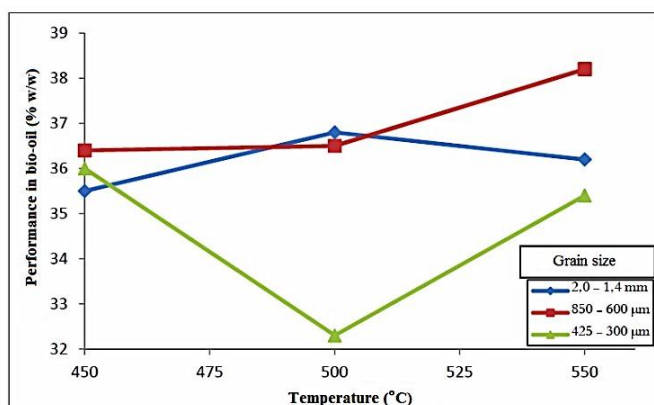

Fig. 2. Yield average in Bio-oil for different combination of temperature and grain size.

B. Influence of Temperature and Particle Size in Bio-oil Performance

Fig. 2 shows the yield average as function of the pyrolysis temperature and the grain size levels.

A preliminary analysis suggests that higher yields are obtained at 550 °C, whereas a tendency for the effect of grain size on yield is not observed. The existence of interaction between factors is also observed, resulting in nonparallel yield curves.

C. Statistical Analysis of the Differences in Yield Obtained

The ANOVA analysis reveals whether the observed differences are significant, or are due to random errors during the experiments and also if there are interactions between the factors. The ANOVA analyses of two factors, carried out using Microsoft Office Excel 2007 software, are presented in Table V.

TABLE V: ANALYSIS OF VARIANCE RESULTS

Origin of variations	Sum of squares	Degrees of freedom	Medium of the squares	F	Critical value for F
Grain size	28.1261	2.0000	14.0630	18.6085	3.5546
Temperature	8.4924	2.0000	4.2462	5.6187	3.5546
Interaction	23.0557	4.0000	5.7639	7.6270	2.9277
Inside the group	13.6032	18.0000	0.7557		
Total	73.277355	26			

In Table V is observed that for grain size and temperature factors, the value calculated for the F test exceeds the critical value, which indicates that within 5% error; the observed differences in performance Bio-oil due to each the factors are significant.

It is also noted that the interactions between the variables are significant, which corroborates what was observed in Fig. 2.

As the results of variance analysis indicates that the observed differences are significant we selected the operating conditions, corresponding to a grain size between 850−600 µm; and pyrolysis temperature of 550 °C.

D. Physicochemical Characterization of Bio-oil Obtained Using the Best Conditions

The results of the physical-chemical characterization are presented for the Bio-oil obtained at 550 °C and with a grain size between 850 − 600 µm.

1) Organoleptic analysis

The bio-oil obtained has a dark brown color, with a sour smell, similar to that of smoke.

Initially two phases were present, the upper phase (about 20% volume with slightly cloudy color) and the lower phase (with a darker appearance). Phase separation is indicative that water content in bio-oil is high, generally more than 30-35%. However, after 2-3 hours there was spontaneous mixture of both phases, showing slight micelles (deep black) within the liquid.

Centrifugation tests, were performed at 5000 rpm for a period of 15 minutes, however, no clear phase separation was observed. Therefore, the physicochemical properties were determined to the mixture previously homogenized.

2) Physico-chemical properties

The results of the physicochemical characterization of the bio-oil are summarized in Table VI.

TABLE VI: PHYSICO-CHEMICAL PROPERTIES OF BIO-OIL OBTAINED BY CONVENTIONAL PYROLYSIS OF THE COCONUT CORE OF THE VARIETY ACROCOMIA ACULEATA

Analysis	Results	Unit of measure
Kinematics viscosity at 40 °C	1.51	cSt
pH	2.41	-
HHV pure bio-oil	14.75-10.88	MJ/kg
HHV bio-oil + methanol	14.58 ± 0.83	MJ/kg
Relative density at 25 °C	1.0739 ± 0.0005	-

In Table VII, the properties of water content, viscosity and density are presented. Experiments were conducted at the National Institute of Technology, Standardization and Metrology (INTN).

TABLE VII: PHYSICO-CHEMICAL PROPERTIES OF BIO-OIL OBTAINED REALIZED BY THE INTN

Analysis	Results	Unit of measure
Kinematics viscosity at 40 °C	1.64	cSt
Water content	53	%
Density at 25 °C	1.06993	g/mL

As it can be observed, moisture content is very high compared to typical values of bio-oil samples, whose values varies in the range of 15-30% [10].

Considering that moisture from biomass used was 0.74%, the high water content would suggest the presence of secondary reactions of dehydration between the pyrolysis products. This assumption is supported by the presence of a carbonaceous residue in the pipeline that connects the reactor with the condenser, immediately at the furnace exit. The solid could be due to condensation and dehydration of bio-oil in this region, due to lack of insulation.

The high water content directly affects the other properties analyzed. In the case of viscosity, the bio-oil obtained has a fluid consistency, with a kinematic viscosity slightly higher than twice that of water value at the same temperature, which is lower compared to values presented by [10] who proposed typical viscosity values of bio-oil in the range of 10-100 cSt at 40 °C.

There are differences between the viscosity obtained in the laboratories of the Chemistry Faculty at the UNA and the one determined by the INTN. This discrepancy might be due to the reactions of bio-oil aging, since the tests at INTN were realized on the fourth day of its obtainment.

The pH measurement obtained is in agreement with the expected values for samples of bio-oil, due to its high content of volatile acids [9]. However, it is expected that the presence of high water content increase the corrosive properties, especially at elevated temperatures [10].

Concerning the higher heating value, numerous tests were performed to determine this property, however, the high moisture content produces poor combustion, resulting in a large dispersion between the values obtained. In fact, in most of the tests, combustion of bio-oil did not occur. To overcome this problem, we add 10% (volume) of methanol in the bio-oil, with a significant improvement in the combustion process.

The results indicate that, despite the high water contents; the higher calorific value of bio-oil is comparable to typical values for samples from other biomass sources [10]. However, it was lower than the one reported by [11], who conducted the pyrolysis of coconut core of India obtaining values of 19.75 MJ/kg in samples of bio-oil with 10% humidity. However, the reported density values are similar to those obtained in the present study.

3) Comparison between the physicochemical properties of the bio-oil and the fuel oil

The Ministry of Industry and Trade, through resolution 1336/2013 establishes the technical specifications for the Fuel Oil commercialized in Paraguay. Comparing the properties of bio-oil obtained with these specifications can observe the following:

• The higher calorific value of bio-oil is considerably lower than the fuel oil, equaling at approximately 36.3% of the energy released by the fuel oil during the combustion of the same amount of mass.

1) Therefore, in order to get the same amount of energy, it is necessary to use a greater volume of bio-oil.

2) The bio-oil is less viscous, with the kinematic viscosity (measured at 40 °C) approximately 463 times lower than Fuel Oil. This is favorable, since the low viscosity is beneficial for pumping and injection processes, thereby avoiding the need for prior heating, such as for the fuel oil.

3) Given the low pH of the bio-oil, the same will be much more corrosive than fuel oil, which implies that for the handling and usage is required corrosion resistant materials.

E. Chemical Analysis of Non-condensable Gases

In Fig. 3, is observed the results of chemical analysis of the incondensable gases generated in the pyrolysis conventional process of the coconut core, variety *Acrocomia aculeata*. These results were obtained using a final temperature of pyrolysis of 550 °C, particle size between 850 μm and 600μm; and a heating rate average equal to 16.5 °C/min.
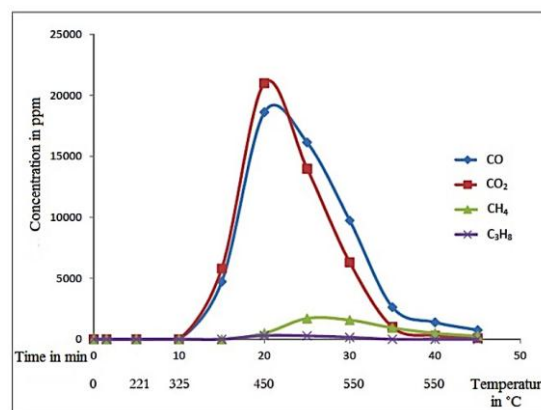

Fig. 3. Chemical analysis the incondensable gases generated in the pyrolysis conventional process.

During the process is expected that the release of hydrogen gas would occur at temperatures near 500 ℃ by breaking C-H bond and the formation of H-H bond, according to [12] and [13]. However, it was not possible to verify this due to limitations of the instrument used.

The results indicate that the major gaseous products of conventional pyrolysis of coconut core are CO_2 and CO, whereas CH_4 and C_3H_8 are produced only in trace amounts.

This is in agreement with the results obtained by [12].

Ethylene and propane gases were present at very low concentrations compared to other major components. Traces of NO and NO_2 were also detected and the presence of Acetylene and N_2O was discarded.

Fig. 3 shows that the formation of gas begins after ten minutes of the heating process. CO and CO_2 are the first species formed during the process. At that moment the furnace temperature was approximately 300 ℃ and the gases formed probably due to the onset of decomposition of hemicellulose described by [14].

The formation of CO and CO_2 reaches a maximum peak at 20 minutes, when the oven temperature is 450 ℃. This is in agreement with values presented by [13]. The CO_2 is produced mainly of cracking and reforming of the carboxyl groups, present mainly in the hemicellulose. While CO formation would have two sources: first, the carbonyl and carboxyl cracking in cellulose and hemicellulose groups, and second, the secondary reactions between the generated volatiles.

F. Stability or Aging Study

The stability study was performed for the bio-oil obtained to a pyrolysis temperature of 550 °C and particle size between 860 µm and 600 µm.

1) Longitudinal analysis of the variation of pH

The results of measuring the pH of the stored samples are showed in Fig. 4.
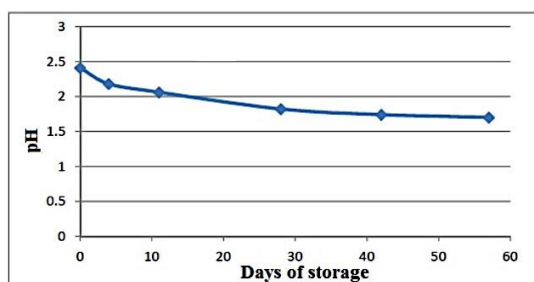

Fig. 4. PH evolution of bio-oil samples stored at 40 °C.

Fig. 5. Phase separation in the bio-oil, after 11 days storage at 40 °C.

It can be observed that the largest decrease in pH occurs in the first month of storage, from 2.41 (day 0) to 1.82 (day 28), while in the second month only a slight decrease is observed up to day 42, after which it remains almost constant. This could suggest that the main reactions that cause the instability of bio-oil are given during the first month of storage.

The decrease of pH may be due to increased concentration of carboxylic acids, product of the oxidation reactions of alcohols and aldehydes described by [15].

2) Longitudinal analysis of the variation of the kinematic viscosity

Concerning the kinematic viscosity, the samples analyzed on the fourth day of storage showed an increase of approximately 10% of its initial value (1.51 cSt to 1.67 cSt). However, on the eleventh day of storage phase, separation of the samples was found (see Fig. 5), which prevented for following days the determination of this property by Ostwald viscometer.

In order to analyze the viscosity of bio-oil samples having phase separation, Lu *et al.* (2009) recommends the use of rotational viscometers [10]. However, given the low viscosity of bio-oil obtained, is required a minimum of 200 mL to obtain reliable results. This amount was not available when conducting the analysis.

According to [15], the viscosity increase is due to polymerization reactions between the compounds present in the bio-oil, while phase separation could be due to advanced polymerization reactions, esterification reactions that transformed the carboxylic acids of polar character, to esters of character non polar and dehydration reactions, which increase the water content and causes the destabilization of the emulsion. Yu *et al.* (2007) studied the aging of bio-oil samples obtained from corn crop residue [16]. The bio-oil obtained had a moisture level of 15.2% and phase separation occurred after 30 days of storage, also at 40 ℃. Stabilization tests conducted by adding methanol and ethanol, concludes that the phase separation was inhibited, with a minimum 10% methanol (by volume).

G. Additional Stability Tests of Methanol/Bio-oil Mixtures 10% v/v and 20% v/v

Additional tests were performed with the addition of 10% v/v and 20% v/v methanol to bio-oil samples and 80 °C for 48 hours storage. Phase separation was also observed in the samples, however, is noted that the separation was less pronounced with increasing percentage of methanol.

Finally, an addition of approximately 30 - 40% methanol was tested. In this case no phase separation was observed after three months storage at room temperature.

V. CONCLUSION

The results of analysis of variance (ANOVA) indicate, with 95% confidence that the variables pyrolysis temperature and grain size significantly affect performance in bio-oil.

The findings suggest the presence of interactions between the study variables, observable by plotting the average response for each combination of treatments in which the yield curves versus temperature were not parallel for the different grain sizes studied. This result was compared by ANOVA.

Best performance in bio-oil was approximately 38% using the pyrolysis temperature of 550 ℃ and grain size comprised between 850 and 600 microns.

The bio-oil, showed a water content significantly higher

than desired, which affects the other properties analyzed. The main affected properties were viscosity and higher calorific value, both below reference levels. Also, the bio-oil showed a very lean combustion condition considerably improved by the addition of 10% methanol.

The higher heating value of the bio-oil was variable, presenting a range of values between 14.75 MJ/kg to 10.88 MJ/kg.

The higher heating value of the bio-oil / methanol mixture was on average 14.58 MJ / kg.

It was observed that, at equal amount of mass, the higher calorific value of bio-oil equivalent to 36% of fuel oil, value which totals 40% if the comparison is done per unit volume. While the viscosity turned out approximately 463 times lower.

Storage of bio-oil has the disadvantage of phase separation and the low pH forces the use of materials resistant to corrosion, such as stainless steel or corrosion resistant polymers.

The condensable gases were composed mainly of CO and CO_2 with low amounts of methane and propane, until after 45 minutes of heating.

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