Evaluation of the pyrolysis and co-pyrolysis process of palm shell and waste tyres in a co2 atmosphere

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Abstract

In this manuscript, the effect of various mixture proportions of a lignocellulosic material (palm shell) and waste tyres (a material not easily degraded in natural environmental conditions) subjected to a thermochemical process known as pyrolysis, on the distribution of the different fractions of the reaction products, was analyzed. The mixtures consisted of 20%-80%, 50%-50% and 80%-20% of palm shell and used tyre respectively, which were subjected to a co-pyrolysis, a simultaneous thermochemical decomposition of two biomass sources, and the resulting liquid and solid fractions were characterized. The experiments were carried out using a 0.5 mm-particle size under 500 °C for each pyrolysis run. The raw materials are characterized by proximate and elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR) in addition to Thermogravimetric Analysis (TGA).

Solid and liquid products were also characterized by FTIR, and their calorific value was also determined. The distribution of fractions was made by weight difference between the fractions and the mass fed. The pyrolysis run that obtained the best properties was the mixture of 80% waste tyres and 20% palm shells with a calorific value of 21,117 kJ/kg, obtaining three types of products with the following mass proportions: solid 23.5%, liquid 18.6% and gas 57.9%. It can be concluded that the solid product obtained has a great energy potential, superior than that of dry wood, which is 19,000 kJ/kg.

Keywords: Pyrolysis, fuels, tyres, biodegradable, pollution, resources, biofuels, lignocellulosic, polymer.

I. Introduction

Nowadays, the relationship between energy and quality of life is evident [1], therefore, in view of the high consumption of fossil fuels (non-renewable resource), obtaining fuels from new alternative energy sources is necessary, using residual biomass and economically viable urban waste that contribute to mitigate the adverse environmental implications of fossil fuels [2].

In the scientific literature, there is a large number of previous works in which the energy from waste materials, such as lignocellulosic materials, is investigated. These include biodegradable materials such as palm shell residual biomass that is obtained during palm oil extraction process. Oil palm is the most productive oleaginous plant on the planet; one hectare sown produces between 6 and 10 times more oil than other species. Colombia is the fourth largest producer of palm oil in the world and the first in America. Municipal solid waste and other low-grade fuels, as well as high energy concentration materials such as rubber and plastic [3] are also produced.

The residues that negatively stand out by their characteristics include Waste Tyres which represent a serious environmental risk because rubber is an artificial polymer and is not biodegradable [4]. Additionally, when this material agglomerates, it lends itself as a shelter for rodents, insects and other animals that can transmit diseases. Another negative feature is that they generate visual pollution, for example, in Bogotá approximately 2,050 tyres are discarded every day, which end up invading public space. This problem generates approximately little more than 800,000 tyres annually [5]. It is certainly a problem whose impact increases more and more every day, and that is the main reason why tyre rubber is used in this project, because in addition to complying with the necessary energy characteristics, it also contributes to the environment by recycling and reducing the contamination that tyre rubber can generate [6].

Thermochemical transformations are an attractive method to recycle tyres, which have been the subject of renewed interest in multiple investigations. Pyrolysis of tyres can produce oils, coals and gases, in addition to steel wires, which have the potential to be recycled. Liquids (oils) from this process have been found to be a mixture of paraffins, olefins and aromatic compounds that have a high gross calorific value (GCV) of around 41- 44 MJ/kg, which would encourage its use as substitutes for conventional liquid fuels [1, 7-15].

The advantage of pyrolysis when compared to other thermochemical transformation processes is that it allows to obtain three types of products (solid, liquid and gas phase). The liquid product is important because it is easy to store and transport, and therefore it is necessary to establish the best operating conditions to maximize its production while minimizing the environmental impact [16]. It has been found that liquid products from biomass are unstable due to their tendency to react with oxygen and the amount of water present, while the pyrolysis of tyres produces liquid fractions of greater stability [17]. Different sources and systems of energy production have been used by people through the stages of society development [18]. These systems and sources of energy production include, for example, stubble (lignocellulosic material) from rural areas, as well as firewood. Wood is used to generate electricity, and there is a sustainable forestry industry that allows the forest to be renewed and its wood exploited [19].

At a global level, companies and governments are making intense efforts to present biofuels and transgenics as environmentally friendly alternatives that would help combat climate change by replacing a portion of oil consumption [20], resulting in less environmental pollution.

It is necessary to implement and investigate on new characteristics of biomass for the benefit of the environment and to advance in the scientific developments required by this area. This investigation is aligned with the above because it represents an alternative that intends to make significant contributions for both lines of research at Universidad Libre: Mechanical Engineering and Alternative Energy Program.

In this work, the characterization of the raw materials was carried out using physicochemical tests, such as proximate and ultimate analyses. Subsequently, these materials were subjected to TGA tests for the determination of the appropriate working temperature. After completing the pyrolysis process, the samples were characterized again by FTIR analysis, percent determination of solid, liquid and gas fractions obtained by the mixtures and measurement of calorific power of the solid phase.

II. Materials and methods

The following scheme was followed to conduct the project.

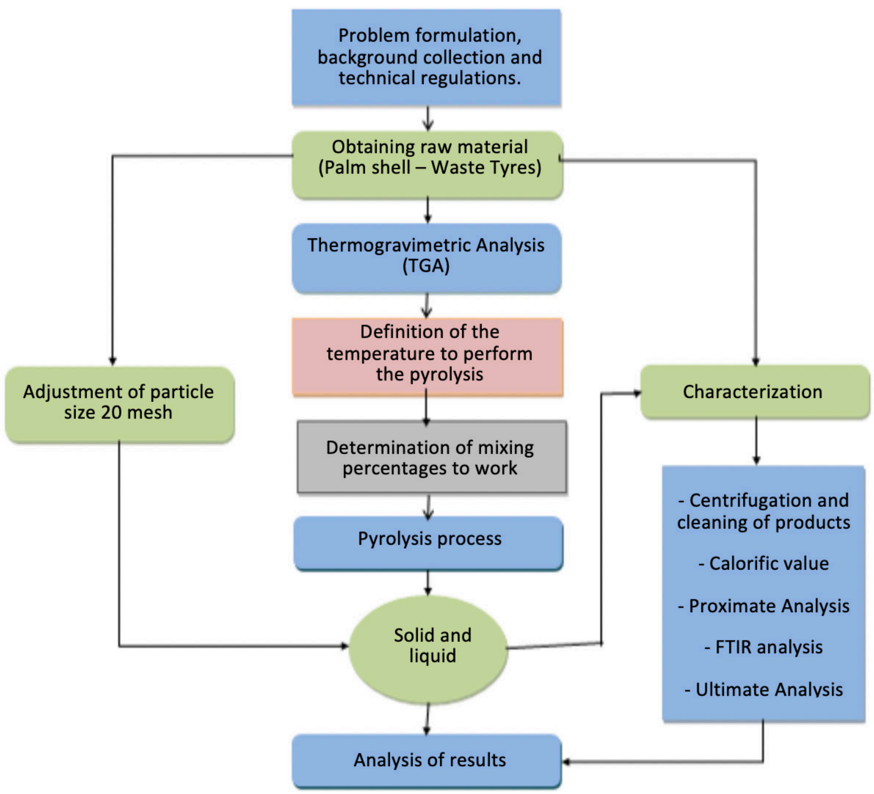

Figure 1. Methodological scheme

Tyre samples were obtained from the Biollantas Company with a particle size of 0.5 mm; samples of palm shell were obtained through the National Federation of Biofuels (Fedebiocombustibles). Samples of raw materials were characterized by proximate analysis, ultimate analysis, Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and calorific value. Once this stage was completed, both raw materials were mixed at different proportions in a mechanical stirring system for 20 minutes according to the amount of raw material used, and then subjected to pyrolysis in a 1-liter capacity fixed bed reactor, coupled to a vapor condensation system. In all pyrolysis reactions a constant mass of 200 g, and a constant flow rate of inert gas (CO_2) of 40 cm^3/s, were used. This flow rate is required to keep the system free from oxygen for the duration of the test. Mixtures of 20%-80%, 50%-50% and 80%-20% of palm shell and used tyre respectively were used in each pyrolysis run. The liquid product was cooled and weighed to be characterized by FTIR; the solid product was evaluated for its calorific value and the functional groups were determined by FTIR.

The proximate analyses performed on the raw material were carried out according to the ASTM-D 3173, 3174, 3175 and 3172 standards for the determination of humidity, volatile material, ashes and fixed carbon, respectively. The ultimate analysis (determination of the amounts of carbon, hydrogen, oxygen, nitrogen and sulfur) was determined in an elemental microanalyzer Thermo Finnigan Flash 1112 Series, with carbon being the predominant element in raw materials, and sulfur the lowest in percentage.

The calorific value test was performed on a Parr 1341 Plain Oxygen Bomb Calorimeter pump, according to DIN 51900.

Regarding the thermogravimetric analysis (TGA), the appropriate temperature was determined in order to carry out the pyrolysis process in the reactor under a CO_2 atmosphere, with a heating rate of 10 °C/min in a STA 7200 Thermal Analysis System- HITACHI, according to ASTM D 7582.

In the pyrolysis tests, an air purge was first performed by supplying an amount of CO_2 equivalent to 10 times the volume of the reactor before starting to heat at a heating ramp of 10 °C/min, until it reached a temperature of 500 °C, where it remained for 2 hours. Then the heating was stopped and the inert flow was kept constant until room temperature was reached, to proceed to carefully collect samples of solid and liquid products, establishing by difference the amount of gaseous product formed.

III. Results and analysis

Table 1 shows the values obtained through the proximate analysis; the left side shows the results for palm shell and the right side shows the results for Waste Tyres.

Table 1. Proximate analysis for palm shell (left side) and waste tyres (right side).

Parameter	Result	ASTM standard
Humidity	8.17	D-3173-03
"Carbon (C) % Mass"	47.52	D-4239-08
"Hydrogen (H) % Mass"	6.37	D-5865-04
"Oxygen (O) % Mass"	45.21	D-5865-04
"Nitrogen (N) % Mass"	1.14	D-5865-04
"Sulfur (S) % Mass "	0.2	D-5373-08

Parameter	Result	ASTM standard
Humidity	0.69	D-3173-03
"Carbon (C) % Mass"	74.24	D-4239-08
"Hydrogen (H) % Mass"	6.46	D-5865-04
"Oxygen (O) % Mass"	3.92	D-5865-04
"Nitrogen (N) % Mass"	2.62	D-5865-04
"Sulfur (S) % Mass "	1.49	D-5373-08

Table 2 shows the calorific value data of raw materials and solid products. It is observed that the mixture of Waste tyres at 80% and palm shell at 20% was the one that generated the largest energy power and the mixture in equal proportions of raw materials showed the least calorific power. This is due to the fact that a large percentage of used tyres are preserved, which alone have the highest calorific value of pyrolysis runs in the solid portion.

Table 2. Calorific values in each pyrolysis run.

"Mixing percentage (%)"	Mass (g)	Temperature Difference (°C)	"Calorific Value (MJ/kg)"
"Palm Shell 20 Waste Tyres 80"	200	2.526	21.117
"Palm Shell 50 Waste Tyres 50"	200	2.445	20.44
"Palm Shell 80 Waste Tyres 20"	200	2.481	20.548
Waste Tyres 100	200	3.322	27.771
Palm Shell 100	200	2.201	18.4

Figures 2 and 3 present the results from a TGA performed to determine the temperature conditions in the reactor.

Hemicellulose is known to be the least stable of the three constituents of lignocellulosic materials [21, 22], the weight loss recorded between 200 °C and 350 °C, is caused by the degradation of this constituent, generating CO, CO2 and some volatiles. Cellulose decomposes at a temperature ranging between 350 °C - 400 °C [23]. Lignin is the most stable component of lignocellulosic materials and exhibits a very slow decomposition between 200 °C and 500 °C [24], generating a large amount of charred material, between 25% and 37%.

When performing the TGA analysis, it was determined that the appropriate temperature for the 5 pyrolysis runs should range between 450 °C - 550 °C. For palm shell, as shown in Figure 2, starting at 400 °C the raw material begins to lose a considerable amount of weight and after 500 °C the material shows the greatest decomposition.

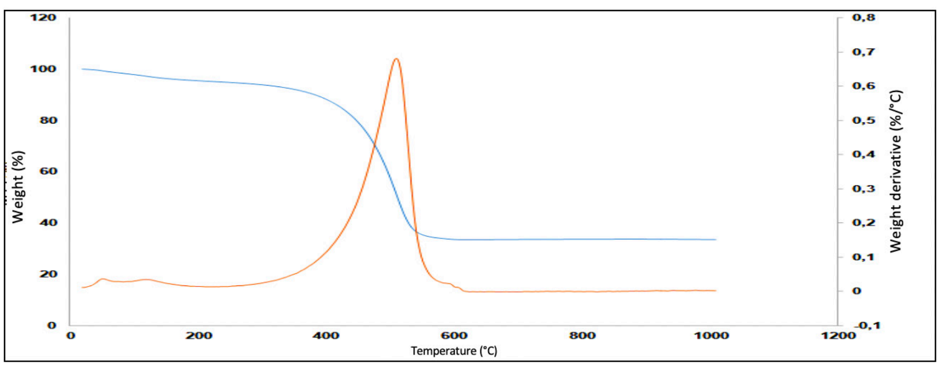

Figure 2. Palm shell weight loss by TGA

Hemicellulose is the least stable of the three constituents of lignocellulosic materials, the weight loss recorded between 200 °C and 350 °C, is caused by the degradation of this constituent, generating CO, CO2 and some volatiles. Cellulose decomposes at a temperature ranging between 350°C - 400 °C [23]. Lignin is the most stable component of lignocellulosic materials and exhibits a very slow decomposition between 200 °C and 500 ° C [24], generating a large amount of charred material between 25% and 37%. The waste tyres decomposition exhibits three main stages of degradation, which are defined by their maximum peaks. The first stage is between 50 °C and 100 °C, water loss occurs in this area. The second stage occurs between 250 °C and 350 °C, at this point the decomposition of volatile compounds as well as low molecular weight hydrocarbons occurs. The third stage is between 350 °C and 520 °C, finally in this stage the decomposition of butadiene occurs, at which point the decomposition of waste tyres is complete, as shown in Figure 3.

According to the studies, 500 °C was determined as the temperature to carry out the pyrolysis runs because at this point the palm shell loses most of its weight fraction and the decomposition of waste tyres is complete.

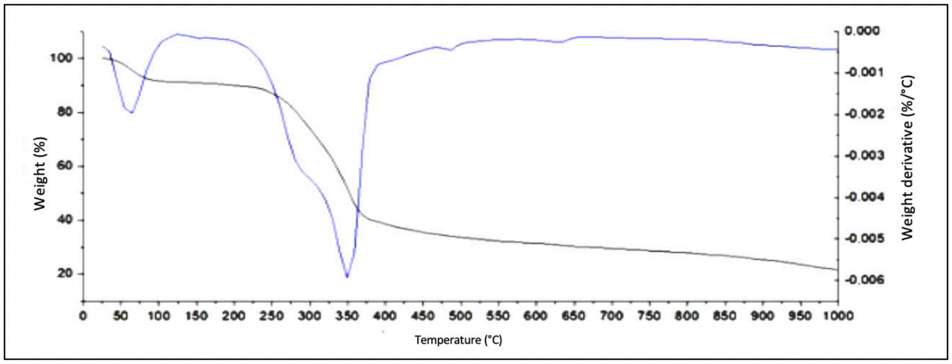

Figure 3. Waste tyres weight loss by TGA.

The weight fractions obtained in each pyrolysis test performed are shown in Table 3.

Table 3. Weight fractions obtained in each pyrolysis run.

"Mixing percentage (%)"	Weight (g)	Solid percentage (%)	Liquid Percentage (%)	Gas percentage (%)
"Palm Shell 20 Waste Tyres 80"	200	23.5	18.6	57.9
"Palm Shell 50 Waste Tyres 50"	200	34.625	17.715	47.66
"Palm Shell 80 Waste Tyres 20"	200	22.285	14.875	62.84
Waste Tyres 100	200	19.75	21.4	58.85
Palm Shell 100	200	22.23	11.874	65.895

The analysis of the solid, liquid and gas fractions is performed based on 200 g of sample that was the standard in each of the pyrolysis runs. After each thermochemical decomposition, the fractions obtained were weighed (see the table above for the corresponding data). The results shown in Table 3 indicate that the liquid fraction obtained is not significantly affected by the percentage in the initial mixture between the palm shell and the tyres used. The largest amount of liquid fraction was obtained from the mixture consisting of 80% waste tyres and 20% palm shell with a value of 18.6%

For the mixture composed of 50% of each component, the amount of liquid generated was only 2.4% lower.

The analysis of functional groups present in the structure of raw materials and liquid and solid products was carried out in IR Prestige 21 SHIMATZU equipment, according to ASTM WK 24875; the results of this analysis are shown in Figures 4 and 5.

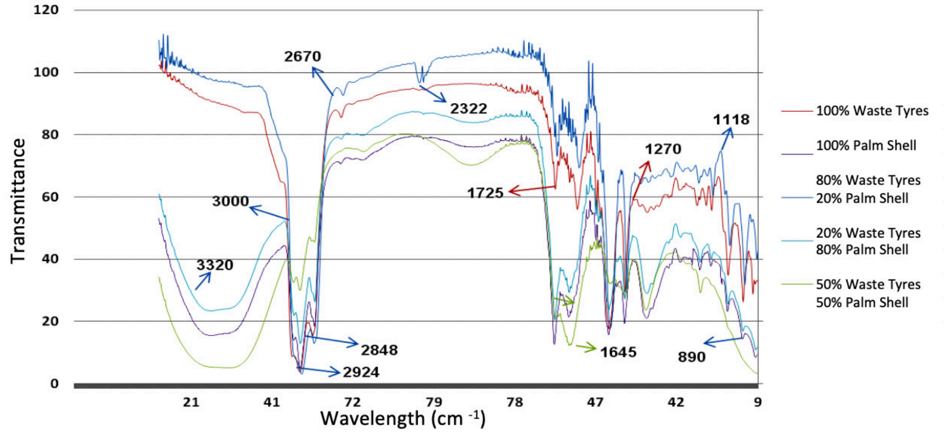

Figure 4. FTIR analysis of liquid products

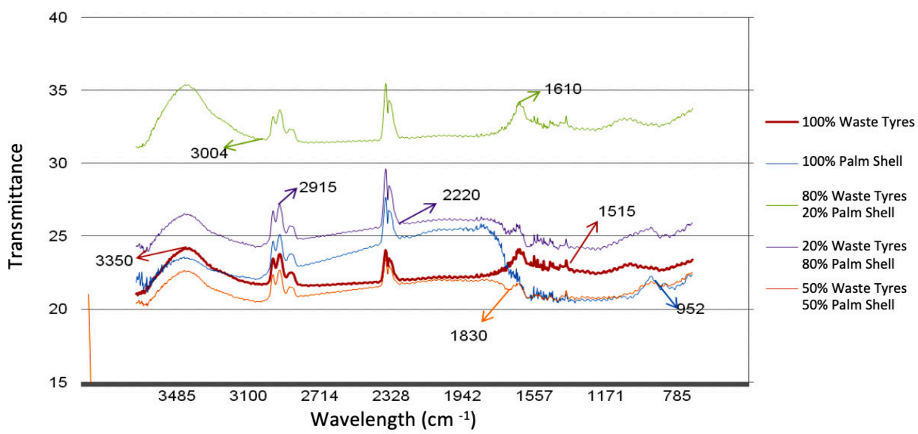

Figure 5. FTIR analysis of solid products

Table 4. FTIR spectrum

Wavelength Range (cm-1)	Wavelength (cm-1)	Functional group	Structure
3375-3320	3320	O-H Wide stretch and associated vibration	Phenol
2938-2920	3000	C-H Symmetric stretching in aromatic methoxy, methyl and methylene groups	Methoxy Aromatics
2270- 1900	2135	C≡C Stretching, Vibration	Alkyne
1880-1800	1876	C=C Stretching, Vibration	Alkyl
1740-1720	1725	C=O Stretching in unconjugated ketones	Ketone
1700-1590	1645	C=C Stretching, Vibration	Alkyl
1520-1500	1514	C=C Stretching and vibration of the aromatic ring	Aromatic
1490-1400	1450	C-H deformation and asymmetric vibration	Alkenes
1375-1366	1373	C-H Deformation	Alkyl
1300-1150	1270	CO-O Stretching	Carboxylic acid
1100-900	1055	CH3 Oscillating vibration	Aromatic (Methylbenzene)
900-600	890	C-C skeletal vibration	Alkane

According to the information shown in Figures 4 and 5, from the analysis carried out in Table 4, it can be concluded that the mixtures obtained from the palm shell and waste tyres, are mostly made up of functional groups associated with alkenes, aromatics and ketones.

Aromatic compounds were evidenced by vibration bands from 1520 cm-1 to 1500 cm-1 and 1100 cm-1 to 900 cm-1, attributed to this class of organic structures. Stretches presented between 1740 cm-1 to 1720 cm-1 together with the vibrations manifested at 1300 cm-1 and 1350 cm-1 are associated with oxygen-containing keto structures to carboxylic bonds. These results have been reported in similar works [25]

The analysis and formula determination of the mixed compounds was carried out by ultimate analysis of carbon, hydrogen, oxygen, nitrogen and sulfur.

Table 5 and Table 6 show the procedure to obtain the empirical formula of raw materials. The CHONS elemental analysis was carried out by "Calderon Asistencia Técnica Agrícola Ltda" laboratory, to which the raw material samples were supplied.

Table 5. Procedure to find the empirical formula in palm shell.

Element	Result	Atomic mass	Molar fraction	Normalized to moles of C
C	47.52	12	3.96	1
H	6.37	1	6.37	1.6085
O	45.21	16	2.8256	0.7135
N	1.14	14	0.0814	0.0205
S	0.2	32	0.0062	0.00156

The empirical formula is obtained by dividing the weight present in the sample by the atomic mass of the element, to find the molar fraction, which is then normalized to moles of carbon.

Then, the resulting empirical palm shell formula is:

$$CH_{1.6085}N_{0.0205}S_{0.00156}O_{0.7135}$$

Table 6. Procedure to find the empirical formula of waste tyres

Element	Result	Atomic mass	Molar fraction	Normalized to moles of C
C	74.24	12	6.1866	1
H	6.46	1	6.46	1.0441
O	3.92	16	0.245	0.0396
N	2.62	14	0.1871	0.0302
S	1.49	32	0.0465	0.00751

To determinate the empirical formula of waste tyres, the above procedure is performed, then the resulting empirical formula of the waste tyres is:

$$CH_{1.0441}N_{0.0302}S_{0.00751}O_{0.0396}$$

IV. Conclusions

1. From the results shown in tables 5 and 6, it can be established that the empirical formulas for the Palm Shell and the Waste tyres are:

$$CH_{1,6085}\,N_{0,0205}\,S_{0,00156}\,O_{0,7135} \qquad \text{Palm Shell}$$

$$CH_{1,0441}\,N_{0,0302}\,S_{0,00751}\,O_{0,0396} \qquad \text{Waste Tyres}$$

These empirical formulas refer to the CHONS elemental analysis, which represent the characterization of each biomass based on the carbon present in each raw material.

2. The temperature at which the different pyrolysis runs were performed was determined to be 500 °C according to the analysis of Figures 2 and 3.
3. Regarding the percentage of liquid product obtained in relation to the mixing percentages, the result allows us to determine that when 100% waste tyres were pyrolyzed, the fraction of liquid products was 21,4% and for the different mixtures, the highest proportion of liquids reached was 18,6% corresponding to a mix ratio of 80% waste tyres and 20% palm shell.
4. The liquid proportions did not exceed 25% in any case, which allows us to conclude that if more liquid fraction is desired, another type of reactor, one that allows for a shorter contact time, must be used.
5. When measuring the calorific powers obtained in the solid phase, which are shown in Table 3, it is observed that the highest result was obtained in the mixture of 20% palm shell and 80% used tyres with a value of 21.117 (MJ/kg).
6. The solid product obtained has a great energy potential, superior than that of dry wood, which is 19,000 kJ/kg being an alternative in rural areas.
7. Based on the ultimate analysis, the empirical formulas of raw materials were successfully obtained.

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