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DETERMINATION OF THE PHYSICAL-CHEMICAL PROPERTIES OF SOLID WASTE FOR USE IN THE PYROLYSIS PROCESS[1]

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Abstract

Brazil is still very incipient in the use of Municipal Solid Waste (MSW) for the generation of fuels and electric energy. Law No. 12.305/10 establishes the National Solid Waste Policy (NSWP), considered efficient and adequate for solving the problems caused by MSW. However, NSWP is considered a process of high cost when compared to landfill. Due to the need to seek clean and renewable forms of energy, the pyrolysis process can be an alternative in the primary energy production. This is a thermochemical conversion process, which occurs at high temperatures and involves several chemical reactions, whose liquid organic aqueous fraction is called bio-oil. This work studied the physicochemical characteristics of some types of waste (food scraps, cardboard and paper) and their potential for power generation. The samples presented similar elemental composition and the moisture content for energy generation: 7 % for food scraps (FS), 6 % for cardboard and 4 % for paper.

Thermogravimetric analysis were performed to establish that the optimum temperature pyrolysis, in addition to determining the ash content, values above 20 % may cause loss of energy in the process or soot in the liquid fraction. The lowest heating value (LHV) presented typical values of biomasses, between 13 MJ/kg and 20/MJ kg. Considering the obtained results, these samples presented energetic potential for use in the pyrolysis process.

Keywords: Biofuel, Urban solid waste, Pyrolysis, Energy.

DETERMINAÇÃO DAS PROPRIEDADES FÍSICO-QUÍMICAS DE RESÍDUOS SÓLIDOS PARA UTILIZAÇÃO NO PROCESSO DE PIRÓLISE

Resumo

O Brasil ainda é muito incipiente no aproveitamento de Resíduo Sólido Urbano (RSU) para geração de combustíveis e energia elétrica. A Lei nº 12.305/10 institui a Política Nacional de Resíduos Sólidos (PNRS), considerada eficiente e adequada para a solução dos problemas causados pelo RSU. Porém, a PNRS é considerada um processo de alto custo quando comparado ao aterro sanitário. Devido à necessidade de buscar formas de energia limpa e renováveis, o processo de pirólise, pode ser uma alternativa na produção de energia primária. Esse é um processo de conversão termoquímica, que ocorre em altas temperaturas e envolve várias reações químicas, cuja fração aquosa orgânica líquida é denominada de bio-óleo. Este trabalho estudou as características físico-químicas de alguns tipos de resíduos (sobras alimentares, papelão e papel) e seu potencial na geração de energia. As amostras apresentaram composição elementar similar e o teor de umidade o para geração de energia: 7 % para sobras alimentares (SA), 6 % para papelão e 4 % para papel. Realizaram-se análises termogravimétricas para estabelecer qual a temperatura ideal de pirólise, além de terminar o teor de cinzas que valores acima de 20 % podem ocasionar perda de energia no processo ou fuligem na fração líquida. O poder calorífico inferior apresentou valores típicos de biomassas, entre 13 MJ/kg e 20 MJ/kg. Considerando os resultados obtidos, essas amostras apresentaram potencial energético para utilização no processo de pirólise.

Palavras-chave: Biocombustível, Resíduo sólido urbano, Pirólise, Energia.

INTRODUCTION

Concern over the destination of municipal solid waste generated by society is increasing, especially in large cities, the scarcity of areas for new landfills has become an administrative problem for the municipalities. The disposal of waste generates several problems: the dispersion of these debris makes it difficult to collect and transport, it poses risks to health and degrades the environment.

In Brazil, the way to solve the MSW problem was the adoption of Law No. 12.305/10, which establishes the National Solid Waste Policy (NSWP), considered efficient and adequate for solving national problems, however it faces the lack of investment, political, industrial and population culture in order to implement it. (BRAZIL, 2010).

The need to seek forms of clean and renewable energy due to global warming, limitations of areas for proper disposal of MSW, service to NSWP, and the search for alternative or complementary processes to those currently used as landfill, composting, biodigestion and incineration, has made researchers to study again the pyrolysis process, as it may be an alternative for energy production.

This is a thermochemical conversion process, which occurs at high temperatures and involves several chemical reactions, whose organic liquid aqueous fraction is called bio-oil (PÉREZ, 2004). Gases, water vapors, organic liquids, tar and mainly coal are the products resulting from the process (GONÇALVES, 2006). In the pyrolysis process the decomposition of the heaviest molecules occurs and their conversion to other low molecular weight. Moderate temperatures and pressures not much higher than atmospheric pressure are normally used. Currently the main objective of pyrolysis is to obtain liquid products that can be used as fuel or as raw material in the industry.

The knowledge of the residues composition and of their physico-chemical and thermal properties is fundamental for the definition of treatment systems, constituting a necessary planning stage when considering solutions for MSW. In the case of solid household waste, considering its heterogeneity and the diversity of its constituent materials, obtaining representative data and applying analytical methods to determine some parameters can be critical (GARCIA, 2017).

According to the Brazilian Association of PET Packaging Manufacturers (ABEPET, 2014) in Brazil most of the urban waste is composed of organic material, followed by paper and cardboard. It is observed that the presence of metals, mainly of aluminum in the municipal waste is reduced, due to the high value added to discarded cans, favoring their separation for sale (ABEPET, 2014).

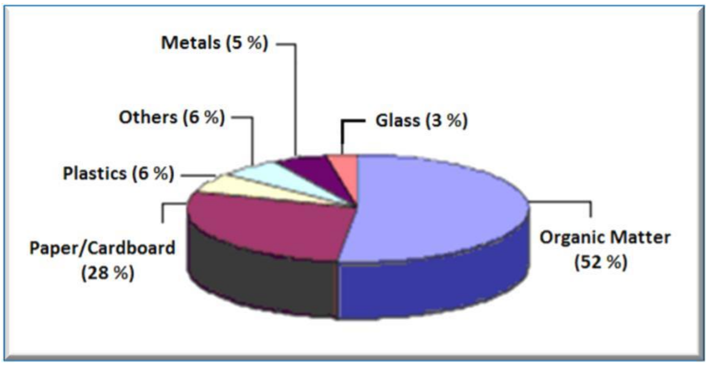

Figure 1. Total composition of municipal waste in percentage in Brazil - Source: ABEPET (2014).

The elemental chemical analysis of the MSW defines the elements content that form part of the fuel chemical composition, such as carbon, hydrogen, nitrogen, sulfur, oxygen and other minor components. This composition is determined experimentally and represents an essential information for analysis of the combustion process, involving the calculation of the amount of air required for combustion, the quantity and type of gases generated and energy released in the combustion process. This information can also be used to estimate the calorific value of the fuel (SILVA, 2004).

The immediate analysis defines the content, usually as a percentage of fixed carbon mass, volatile matter, ash and moisture. These parameters are directly related to fuel utilization and are important for the furnace design and the required quantities of primary and secondary air as a function of the percentage of volatiles present in the fuel. Also the volatile content has an important role during the ignition and the initial stages of the combustion of solid fuels (SILVA, 2004).

The energy contained in the biomass and the different wastes is the amount of heat released by the combustion of a unit of mass in this material (MJ/kg). In the residues used for energy purposes, variations occur due to intrinsic characteristics such as calorific value, density and moisture that affect energy efficiency (LIMA, 2010).

This work studied the potential of energy generation of some types of waste (food scraps, cardboard and paper) through its chemical and physicochemical characteristics.

MATERIALS AND METHODS

Samples were prepared in Fuels and Lubricants Laboratory (LCL) by the following unit operations: separation, grinding, drying and milling process to a granulometry smaller than 60 mesh.

The unused food scraps stored in trays at the IPT restaurant are weighed and discarded separately by the restaurant staff. After weighing, the foods were selected using the highest number of varieties of meat, vegetables, fruits and cereals (Figure 2). Foods were weighed and dried for 24 hours in an oven at 105 °C. After the drying period, the samples were milled and sieved to obtain a powder with granulometry below 60 mesh, to meet the standards requirements used in the physicochemical characterization.

Figure 2. Preparation of food scraps samples.

For the paper samples preparation draft paper was used of the LCL and in the carbdoard samples preparation, boxes of cardboard were selected. The pieces of paper and the cartons samples were cut with scissors into small square pieces of approximately 1 cm x 1 cm (Figure 3).

Figure 3. Preparation of paper and cardboard samples.

- *Characterization of raw material and obtained products*

After the samples preparation, the physicalchemical tests (immediate analysis and elemental analysis) and calorific value and thermogravimetric analysis (TGA) were performed.

- *Determination of moisture total (U) and residual (u) content (ASTM E1756 -08 (15))*

FS samples were tested for moisture content, organic matter and volatiles. The moisture content test was performed by drying the oven samples at 105 °C. The samples were then triturated, homogenized and sieved in a 9.5 mm mesh for the organic matter test by the muffle method at 440 °C. After the organic matter test, the sample was again placed in the muffle at 550 °C for the volatile content test.

- *Determination of carbon, hydrogen and nitrogen (C, H, N) (ASTM D5373-16)*

The combination of the high oven temperature (900 °C to 1050 °C) and the pure oxygen flow result in the combustion of a known mass sample. All the material contained in the sample undergoes an oxy-reduction process and the contained carbon, hydrogen and nitrogen are released as CO2, water vapor and N2, respectively.

- *Determination of ash content (ASTM E1755-15)*

Ash content is the approximate content of the amount of minerals and inorganic materials in a sample. It is usually considered as impurity or contaminant. The sample is ignited until only ash and carbon remain. The carbonaceous residue is reduced to ash by heating in muffle with air circulation with a capacity to reach 950 °C.

- *Determination of high heating value (HHV) (ASTM D5865-13)*

HHV is the amount of energy released when a unit mass of a fuel is burned at the calorimetric pump at constant pressure and under specific conditions with all the formed water condensed in the liquid state. For lower heating values (LHV), it is necessary that all the generated products, including water, to be in the gaseous state. HHV is computed from temperature observations before, during, and after combustion and its result is calculated by the equipment software and printed at the end of the analysis. The LHV is established according to Equation 1.

$$LHV = HHV - (0.2122xH) \quad (1)$$

LHV = lower calorific value, in MJ/kg.

HHV = higher calorific value, in MJ/kg.

H = hydrogen content, in mass %.

- *Thermogravimetry (TGA) (ASTM E1131:2014)*

TGA was used to study the changes that the heating can provoke in the raw materials, aiming to establish the temperatures in which the processes of decomposition and oxidation begin. For the TGA determination the following analysis conditions were used: TGA-isotherm of 10 °C/min up to 950 °C; N2 flow rate: 10 mL/min. For the TGA determination the Thermogravimetric Analyzer TA, model Q50 was used.

RESULTS AND DISCUSSION

Table 2 presents the results of the physicalchemical tests of the samples. The tests were performed on a dry basis. As expected, the result obtained from the FS presented the highest value, because the MSW presented a high water content. Samples of food scraps, cardboard and paper have similar composition for the elemental analysis (CHNSO), except for food scraps nitrogen (2 % to 4 %), immediate analysis (volatile matter and fixed carbon), whereas ashes content had higher values for paper (13.8 %), then cardboard (8.3 %) and food scraps (4.5 % on average). The lower calorific value (LHV) presented higher value for the food scraps.

Table 2. Results of the physicalchemical analysis of the raw material.

Sample	U (%)	C (%)	H (%)	N (%)	Ash (%)	HHV (MJ kg^{-1})	LHV (MJ kg^{-1})
FS	7	45 a 49	6 a 7	2 a 4	4.5	19 a 21	18 a 20
Cardboard	6	41	6	0,2	8.3	16	15
Paper	4	39	6	0,2	13.8	14	13

Table 3 presents the results obtained by the TGA technique. The paper and cardboard samples had similar mass loss behaviors, where the largest mass loss (about 60 %) occurred at the second thermal event at a mean temperature of 411 °C. The food scraps sample had the same behavior, where the highest loss also occurred in the second thermal event, but at a higher temperature 595 °C and with a loss of mass around 70 %. As for the solid residue generated, it can be noted that the results of the paper and cardboard samples did not show repeatability, however it is possible to deduce that the residual value is in the range of 20 %, considering the results of previous losses.

Table 3. Results of the thermogravimetric analysis (TGA).

Materials	1º Mass loss			2º Mass loss			3º Mass loss			Residue (%)
	Initial temp. (ºC)	Final temp. (ºC)	Loss (%)	Initial temp. (ºC)	Final temp. (ºC)	Loss (%)	Initial temp. (ºC)	Final temp. (ºC)	Loss (%)	
Cardboard	17.2	121.4	5.5	173.5	414.3	64.0	641.7	753.3	4.3	5.4
	24.8	137.5	4.9	192.5	418.1	59.3	604.8	756.4	5.2	21.5
Paper	28.5	113.8	3.0	191.5	406.7	64.0	556.4	709.9	7.8	17.8
	19.06	110.0	4.7	213.3	406.7	62.4	588.6	719.4	8.7	12.2
FS	25.7	143.2	2.8	149.8	595.3	69.2	712.8	919.4	5.2	20.7
	21.9	145.1	3.0	152.7	595.3	69.3	735.5	900.4	5.4	18.7

CONCLUSION

Samples of food leftovers showed typical HHV values of biomass samples between 22.6 MJ/kg (5401 Kcal/kg) and 16.9 MJ/kg (4044 Kcal/kg), according to the results presented in the study of Mendonça (2008). These values can be explained by the presence of cellulose, hemicellulose and lignin in plant origin foods, therefore they are similar to biomasses. The presence of a small amount of vegetable oil used in food preparation also contributes to the increase in calorific value.

The Brazilian solid residue consists of a fraction of organic material (about 50 %), which would make the process potentially more productive by mass of total residue. Considering the potential for biogas energy generation and energy conservation through the recycling of non-organic fraction materials, it is possible to make solid household waste an attractive and viable material for the country.

According to the obtained results, it can be verified that household residues can be used in the energy production, since the value of calorific value is similar to the value of sugarcane bagasse, widely used as solid fuel.

During the preparation stage of the residue sample, it was observed that the sample heterogeneity requires more detailed studies in the separation and segregation of the organic fraction, removing inorganic materials that contaminate, reducing the energetic potential of the organic residue.

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