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Thermal Pyrolysis of LDPE and LLDPE Films in Post-Consumer Packaging

Pirólise Térmica de Filmes de PEBD e PELBD de Embalagens Pós-Consumo

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Abstract

Thermoplastics are increasingly present in the daily life of society in the most varied applications. Among the thermoplastics, polyethylene is the one that presents the higher volume of worldwide production and consumption. However, a large part of its applications are for products with a short shelf life, especially the food packaging sector. This way, they become expressive constituents in the composition of urban solid waste, leading to large quantities often being deposited in landfills. Pyrolysis appears as a technology for recycling plastic waste, allowing the recovery of the monomers that originated it. Through this thermochemical process, the waste is converted into three different products: oil or, in some cases wax, non-condensable gases, and a solid fraction named char. Thus, the goal of this study is to contribute for the development of pyrolysis as a technology for the final treatment of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) waste from post-consumer packaging, through the analysis of the influence of the pyrolysis temperature in the chemical composition of the oil produced, as well as the discussion of possible applications. For this purpose, the waste was initially characterized through analyses of attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), thermogravimetry (TGA), differential scanning calorimetry (DSC), and X-ray fluorescence (XRF). The characterization experiments showed that the plastic waste is constituted of 4.07% ash, 0.52% fixed carbon, and 95.54% volatile matter, showing its great potential to produce pyrolytic oil. Thermal degradation of the waste initiated at around 410°C and continued through about 530°C, with maximum rate of thermal degradation at about 488°C. The pyrolysis process was carried out with 50g samples of post-consumer LDPE and LLDPE, previously agglutinated, with particle size ranging from 0.001mm to 4mm, in a horizontal quartz reactor, with an inert atmosphere of N_2, heating rate of 10°C/min, and residence time of 30 minutes. The experiments were conducted with experimental temperatures of 500°C and 700°C, in order to verify the influence of the temperature in the chemical composition of the oil obtained in the process. The analysis of the oil collected at 500°C by infrared spectroscopy revealed a specter similar to the one of commercial diesel. Through gas chromatography coupled with mass spectrometry, it was verified a composition constituted mostly by olefins (44%), from 8 to 35 carbon atoms, followed by paraffins (23.8%), and cycloparaffins (10%). There was also a considerable percentage of alpha-olefins, important for the petrochemical industry, and a percentage of aromatic compounds on a trace level. By varying the temperature to 700°C, an increase in the level of aromatic compounds to 16.6% occurred, accompanied by a decrease in the percentage of olefins, paraffins, and cycloparaffins. The oils obtained in both temperatures have potential

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for application in steam cracking or conventional catalytic cracking processes to obtain the raw materials of the petrochemical industry.

Keywords: Waste; Polyethylene; Pyrolysis.

Resumo

Os termoplásticos estão cada vez mais presentes no cotidiano da sociedade e nas mais variadas aplicações. Dentre os termoplásticos, o polietileno é o que apresenta o maior volume mundial de produção e consumo. Entretanto, grande parte de suas aplicações destina-se a produtos de curto tempo de vida útil, principalmente no setor de embalagens de alimentos. Tornam-se, assim, constituintes expressivos da composição do resíduo sólido urbano, levando a grandes quantidades depositadas frequentemente em aterros sanitários. Neste contexto, a pirólise surge como uma tecnologia para a reciclagem de resíduos plásticos, permitindo a recuperação dos monômeros que lhes deram origem. Através desse processo termoquímico, os resíduos são convertidos em três diferentes produtos: óleo ou em alguns casos cera, gases não condensáveis e uma fração sólida denominada carvão ou char. Assim, o objetivo do presente estudo é contribuir para o desenvolvimento da pirólise como tecnologia para tratamento final de resíduos de polietileno de baixa densidade (PEBD) e polietileno linear de baixa densidade (PELBD), provenientes de embalagens pós-consumo, através da análise da influência da temperatura de pirólise na composição química do óleo produzido, assim como a discussão de potenciais aplicações. Para tanto, os resíduos foram inicialmente caracterizados através das análises de espectroscopia por refletância total atenuada no infravermelho com transformada de Fourier (ATR-FTIR), termogravimetria (TGA), calorimetria exploratória diferencial (DSC) e fluorescência de raios-X (FRX). Os ensaios de caracterização mostraram que o resíduo plástico é constituído por 4,07% de cinzas, 0,52% de carbono fixo e 95,54% de matéria volátil, evidenciando seu grande potencial para a produção de óleo pirolítico. A degradação térmica do resíduo iniciou-se em torno de 410°C e se estendeu até cerca de 530°C, com máxima taxa de degradação térmica em cerca de 488°C. O processo de pirólise foi realizado com amostras de 50g de PEBD e PELBD pós-consumo, previamente aglutinados, com tamanho de partícula na faixa de 0,001mm a 4mm, em reator horizontal de quartzo, com atmosfera inerte de N^2, taxa de aquecimento de 10°C/min e tempo de residência de 30min. Os ensaios foram conduzidos com temperaturas experimentais de 500°C e 700°C, a fim de verificar a influência da temperatura na composição química do óleo obtido no processo. A análise do óleo coletado a 500°C por espectroscopia de infravermelho, revelou um espectro similar ao do diesel comercial. Através de cromatografia gasosa acoplada a espectrometria de massas, verificou-se uma composição constituída predominantemente por olefinas (44%), de 8 a 35 átomos de carbono, seguida de parafinas (23,8%) e cicloparafinas (10%). Evidenciou-se ainda um percentual considerável de alfa-olefinas, importantes para a indústria petroquímica, e percentual de compostos aromáticos a nível de traço. Ao variar a temperatura para 700°C, ocorreu um aumento no teor de compostos aromáticos para 16,6%, acompanhado de uma redução no percentual de olefinas, parafinas e cicloparafinas. Os óleos obtidos em ambas as temperaturas têm potencial de aplicação em processos de craqueamento a vapor ou craqueamento catalítico convencional para a obtenção de matérias-primas da indústria petroquímica.

Palavras-chave: Resíduos; Polietileno; Pirólise.

1 Introduction

Polymers play an important role in modern society, being present in practically all daily activities. Due to the good relationship between their mechanical resistance and lightness properties, polymers started to replace conventional materials, such as wood, steel, paper, cardboard, and ceramics, in many applications.

Thermoplastic materials are an important class of polymers, popularly known as plastics. Driven by high commercial demand, plastic production has been increasing in recent years. In 2016, worldwide production was of 335 million tons and, in 2017, it reached 348 million tons of plastic (ASSOCIATION OF PLASTICS MANUFACTURES IN EUROPE (PLASTICSEUROPE), 2018).

Brazil has an expressive participation in the sector. With a production of 6.4 million tons of thermoplastic resins, and of 6 million tons of processed plastics, it produces more resin and processed plastics than every other Latin America country combined (ASSOCIAÇÃO BRASILEIRA DA INDÚSTRIA DO PLÁSTICO (ABIPLAST), 2019).

From an application point of view, in Brazil, short life cycle applications represent an important percentage of the national market, contributing with 31.1% of consumption. In this segment, the food packaging sector stand out, corresponding to 18.69% of the national market (ABIPLAST, 2019).

Short life cycle (up to one year) plastics represent a huge challenge for the sector (ABIPLAST, 2019). Although they are one of the biggest contributors for the large volume of plastic waste being generated, they are especially essential in the case of food packaging, contributing for food safety during transportation and product conservation, as well as complying to health agencies regulations.

In Brazil, according to the National Solid Waste Plan, plastic represents 13.5% of the gravimetric composition of urban waste (MINISTÉRIO DO MEIO AMBIENTE (MMA), 2012). Among the plastics most commonly found in municipal solid waste (MSW) of the big Brazilian metropolises, the low-density polyethylene (LDPE) and the linear low-density polyethylene (LLDPE) stand out. The presence of these plastics in MSW reflects its large consumption in the national market and its predominant application in products with a short life cycle.

In Brazil, recycled plastics represent 7.8% of the national market, and the main technique applied is mechanical recycling. In European countries and Japan, the situation is different, since energy recovery of waste, by incineration, and chemical recycling are preponderant (ABIPLAST, 2019; SPINACÉ, 2005).

Both mechanical recycling as well as incineration of plastic waste are limited processes. Mechanical recycling requires many steps of pre-treatment of the waste and presents quality loss of the final product after several cycles of reprocessing and heating, due to thermal degradation of the polymeric chains (AL-SALEM et al., 2017). Incineration, on the other hand, requires complex systems for the treatment of the gaseous emissions generated (FU et al., 2015).

Faced with the disadvantages shown both by mechanical recycling as well as energy recovery by incineration, chemical recycling proposes a different look over plastic waste. In this perspective, this waste are seen as materials constituted by monomers derived from petroleum and, therefore, can be converted back into its origin constituents, via chemical and thermochemical processes (AL-SALEM et al., 2017).

Among the chemical recycling process, pyrolysis of plastic waste has been intensely studied in recent years. Pyrolysis is a thermal decomposition process in an inert or oxygen-free atmosphere that promotes the breaking of the long polymeric chains of the materials and the formation of three products: oil, non-condensable gas, and a solid fraction named char. The yield, properties, and compositions of the products are influenced by the type of reactor used and by the conditions of the process: temperature, heating rate, residence time, pressure, and load characteristics (QINGLAN et. al, 2010).

In this context, the general objective of this work is inserted, which is to contribute for the development of pyrolysis as a technology for the final treatment of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) waste. The choice of LDPE and LLDPE as the object of this study is justified by their important contribution in the composition of Brazilian municipal solid waste. Mainly, the specific objective of this study is to analyze the influence of the pyrolysis temperature in the chemical composition of the oil produced, as well as the discussion of possible applications.

2 Material and Methods

2.1 Raw material

The raw material used in this study consisted of a mix of post-consumer packaging, produced with films of low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), or even blends of both polymers. The waste was collected through collection points in commercial establishments and by the Uniciclar Recycling Cooperative, located in the municipality of São Leopoldo - Rio Grande do Sul. To separate the LDPE and LLDPE packaging from other thermoplastics, it was used the symbology present in the packaging itself and established by NBR 13,230 (ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS (ABNT), 2008).

2. 2 Agglutination of the material

To reduce the volume of the packaging and promote their agglomeration, they were subjected to the agglutination process in a KIE Agglutinator, model AK60, with 30CV power and 1760rpm rotation, in the Materials Recycling Laboratory from Education, Science and Technology Federal Institute Sul-Rio-Grandense (IFSUL) – Sapucaia do Sul Campus, as seen in Figure 1. The agglutinated material was used as reactor load in the pyrolysis experiments.

Figure 1 – Photograph of the inside of the agglutinator and the agglutinated product

Source: Authors (2019)

2.3 Granulometric Analysis of the Agglutinated Material

The granulometry experiment of the agglutinated LDPE and LLDPE waste was based on ASTM D1921-18 standard, which presents methods for the determination of the granulometric analysis of plastic materials in the shape of powder, granules, or pellets (ASTM, 2018). The methodology proposed by the standard was also used by Galdino (2014) for the analysis of particle size of ultra-high-molecular-weight polyethylene (UHMWPE) waste. To determine the particle size, it was used an electromagnetic sieve agitator from Produtest, model T, from Unisinos Cereals and Derivatives Technology Laboratory. For the experiment, a mass of approximately 50g and sieves of the Tyler series with 5, 8, 9, 20, 28, 35 and 42 mesh screens were used. With the data collected in this experiment, the retained and the accumulated mass fraction were calculated.

2.4 Preparation of the Samples for Characterization of the Raw Material

As can be seen in Figure 1, the agglutinated material is heterogeneous. In order to obtain greater homogeneity to characterize the material, it was necessary to reprocess it. Thus, the agglutinated material was transformed in pellets through the extrusion process, in an extruder from AX Plásticos from the Unisinos Polymers Laboratory.

Tests were carried out in different processing temperatures, feeding speeds, and screw rotation, in order to stabilize the extruded material. Thus, the following operation conditions were chosen: temperature of the heating zones of the extruder of 240°C, operation pressure of 11.5bar, feeding speed of 10rpm, and speed of the threads of 50 rpm.

The granulated material (pellets) obtained in the extrusion process was subjected to analyses of thermogravimetry (TGA), differential scanning calorimetry (DSC), and X-ray fluorescence (XRF).

To perform the analysis of the chemical composition of the waste through attenuated total reflectance infrared spectroscopy (ATR-FTIR), it was necessary to transform the granulated material into plastic film. The methodology applied in the production of the film was based in the ASTM D4703-16 standard, which describes molding practices by compression of thermoplastics into the shape of pellets or ground material, to obtain specimens. It was also used as a reference the method proposed by Andrade (2013) in a study to characterize recycled or virgin polypropylene compounds reinforced with coconut fiber and powder. The film was produced in an FKL automatic press, with capacity for 40 tons, from the Unisinos Polymers Laboratory.

2.5 Thermogravimetric Analysis (TGA) and Differential Thermogravimetry (DTG)

The thermogravimetric analysis was carried out in the equipment TGA 4000, from PerkinElmer, from the Unisinos Materials Characterization and Evaluation Laboratory (LCVMat). The equipment was programed to perform the analysis in the temperature range of 25°C to the maximum temperature of 1,020°C, with a heating rate of 10°C/min, in an inert atmosphere of nitrogen gas. The purpose of this analysis was to analyze the thermal behavior of the LDPE and LLDPE, and, through the data produced by the TGA, obtain its immediate analysis (content of volatile matter, fixed carbon, and ash). The immediate analysis was carried out by the methodology and equations presented in the ASTM E1131-08 standard (ASTM, 2010), whose scope is the analysis of the composition of materials through the TGA.

2.6 Differential Scanning Calorimetry (DSC)

The analysis by Differential Scanning Calorimetry aimed to determine the melting point, temperature ranges of waste degradation, and verification of possible contaminations of the samples collected with other thermoplastics. The analysis was carried in the equipment TGA 4000, from PerkinElmer, from Unisinos’ LCVMat. The equipment was programed to perform the analysis in the temperature range of 25°C to the maximum temperature of 1,020°C, with a heating rate of 10°C/min, in an inert atmosphere of nitrogen gas.

2.7 X-ray Fluorescence (XRF)

The XRF analysis was carried out to identify the chemical elements that constitute the LDPE and LLDPE waste. The equipment from Schimadzu was used, model EDX-720, constituted of a Rhodium X-ray tube, from Unisinos’ LCVMat. The result provided by the equipment was qualitative and, therefore, identified only the presence of major (above 50%), minor (between 5% and 50%), and trace level (below 5%) elements.

2.8 Pyrolysis System

The pyrolysis experiments were carried out in Unisinos' LCVMat, in a horizontal tubular quartz reactor, operating in batch mode, which presents the following dimensions: 8cm in diameter and 60cm in length. The tubular reactor remains attached to the inside of a muffle furnace, which reaches a maximum temperature of 1,200 °C, as shown in Figure 2.

Figure 2 – Photography illustrating the horizontal tubular reactor used in the pyrolysis experiments in this work (on the left) and the material inside the reactor (on the right)

Source: Authors (2019)

The heating of the reactor occurs through the electrical resistances of the muffle furnace, surrounding the reaction system. The maximum experimental temperature (reactor setpoint), heating rate, and residence time of the sample were set up using the controllers coupled to the furnace.

To monitor the temperature, there are two type K thermocouples: the first measures the temperature of the muffle furnace, while the seconds is located inside the tubular reactor and stays in direct contact with the sample of the polymer during the pyrolysis experiment. The sample of the agglutinated material, previously weighed, was inserted in a 410 stainless steel crucible prepared to not undergo changes when subjected to the operational variables, which was introduced on the inside of the tubular reactor.

The FieldChart Novus software was used to monitor and collect temperature data measured by the thermocouples of the reactor and the muffle furnace, allowing the control of the heating rate throughout the process.

The reactor operated in an inert atmosphere, using nitrogen as the carrier gas. The gas flow was controlled through the rotameter installed in the N^2 supply line.

The flow of condensable gases and vapors from the reactor outlet was aligned with the cooling system, maintained at a temperature of around -10°C. The condensation of vapors produced in the process allowed the collection of the liquid pyrolysis fraction, analyzed in this study. The incondensable gases were purged through the laboratory's exhaust system. The remaining solid product in the reactor was collected in the crucible, in which the sample was initially inserted, in order to be used in later studies.

2.9 Pyrolysis Experiments

The operational conditions of the pyrolysis experiments were defined based on data from previous studies, present in the literature; as well as at the temperature of maximum degradation rate of the thermoplastics, determined by differential thermogravimetry (DTG); and in the results of the pyrolysis pre-tests. Thus, the experiments were conducted with 50g samples of the mixture of LDPE and LLDPE, under a heating rate of 10°C/min, inert atmosphere with nitrogen flow of 150ml/min, and residence time of 30 minutes. The samples were heated at temperatures of 500°C and 700°C, in order to verify the influence of the temperature in the composition of the pyrolytic oil.

2.10 Preparation of the Samples of Pyrolytic Oil

At the end of each pyrolysis run, the oil obtained in the process (Figure 7) was diluted in dichloromethane, according to the methodology proposed by Onwudili et al. (2009), for the analysis of the composition of the oil obtained in the pyrolysis of low-density polyethylene and virgin polystyrene. After dilution in dichloromethane, the samples were placed in test tubes and kept under refrigeration until the analyses were performed.

2.11 Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR)

Infrared spectroscopy had as an objective the qualitative analysis of the chemical composition of the raw material and the pyrolytic oil, through the interpretation of its spectrum and the identification of the main functional groups present in its chemical structure.

To perform the analysis, an spectrometer was used from Agilent Technologies, model Cary 630 FTIR, with attenuated total reflectance accessory, employing a zinc selenide crystal (ZnSe), from the Unisinos Toxicology and Molecular Biology Laboratory. The spectra were obtained in the range of 600cm^{-1} to 4000cm^{-1}, with 16cm^{-1} resolution and 32 scans.

The infrared spectroscopy of the LDPE and LLDPE waste was carried out through the analysis of the film product, as previously described in item 2.4.

To analyze the oil, aliquots of the samples diluted in dichloromethane were transferred with a Pasteur pipette to watch glasses, remaining in the fume hood for a 30-minute interval, to promote the evaporation of the solvent, before the analysis was carried out.

2.12 Gas Chromatography—Mass Spectrometry (GC-MS)

Gas chromatography - mass spectrometry was used for identification and semiquantitative analysis of the main compounds present in the pyrolytic oil, allowing to verify the influence of the temperature in its composition. It was used an Agilent GC-7820A chromatographer and Agilent

MS-5975 mass spectrometer detector, from the Unisinos Toxicology and Molecular Biology Laboratory.

The oil samples diluted in dichloromethane presented a large quantity of suspended solids. Thus, they were subjected to centrifugation, in an Eppendorf centrifuge, model 5430R, for a 5-minute interval at 700rpm. The fluid phase separated by centrifugation was collected and filtered through a syringe filter, with PVDF membrane, 15mm in diameter, and 0.22μm of pore. Finally, the fluid phase was analyzed by GC-MS.

A 1μL sample of the fluid phase of the pyrolytic oil, prepared as described in the previous paragraph, was introduced into the injection port, with flow division (split) of 1:10, using helium as carrier gas. An Agilent HP-5MS non-polar capillary column was used, with a stationary phase formed by 95% dimethylpolysiloxane and 5% phenyl groups, 30m in length, 0.32mm in diameter, and 0.50 μm of film thickness. The programming of the oven for the separation of the components of the oil was carried out according to the methodology proposed by Onwudili et al. (2009) in the study of the composition of the oil obtained in the pyrolysis of virgin polyethylene and polystyrene. Thus, the programming respected the following sequence: constant temperature at 40°C for 5 minutes, ramp of 5°C/min until temperature of 100°C, ramp of 4°C/min until temperature of 280°C, and 30 minutes at 280°C. The data was acquired in the scanning mode, with a detector in the electronic impact mode and 70eV electron beam energy. The attempt of identification of the compounds present in the oil was carried out automatically by comparing with the spectra obtained experimentally with the NIST spectra library, considering a minimum similarity of 70% between the spectra. To perform a semi-quantitative analysis, a simplified approach was adopted, the area normalization technique, in which the composition of the mixture is determined through the expression of the area of each peak as a percentage of the total area of the chromatogram, that is, the sum of the area of all the peaks. The sensitivity of the detector is also considered to be the same for all the compounds of the mixture.

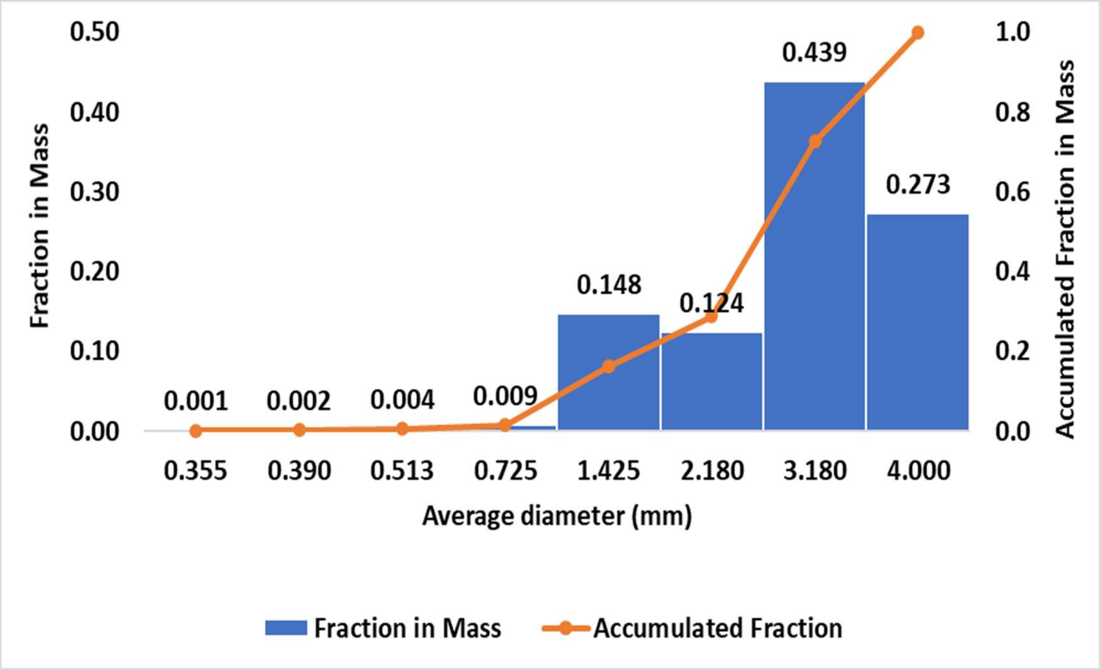
3 Results and Discussion

In this item, the results of the characterization of the LDPE and LLDPE waste are discussed. Also, an analysis of the influence of the pyrolysis temperature in the chemical composition of the pyrolytic oil obtained in the process is carried out.

3.1 Granulometric Analysis of the Agglutinated Waste

The agglutinated material used as load for the pyrolysis reactor had a particle size ranging from 0.001mm to 4mm. The highest percentage of the material retained shows an average particle diameter of 3.18mm (43.9%) and 4mm (27.3%), as seen in the graph of Figure 3.

Figure 3 – Graph of the granulometric analysis of the agglutinated waste



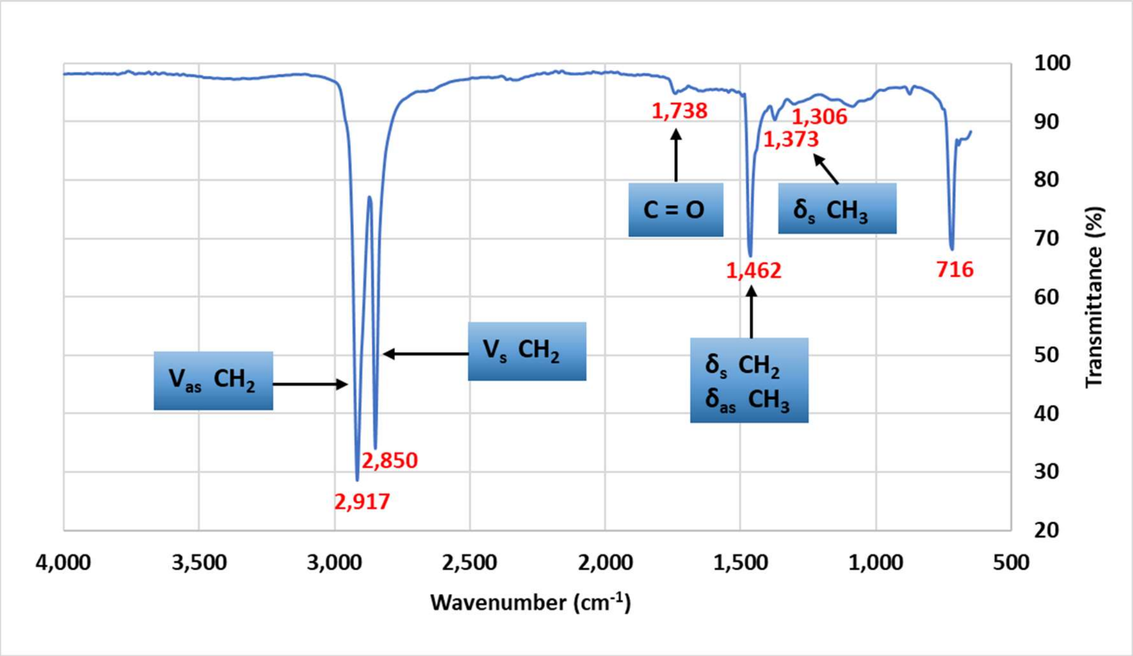
Source: Authors (2019)

According to Luo et al. (2010), the variation in particle size has a greater influence over the materials whose composition shows a higher rate of fixed carbon and ashes. Therefore, the effect of the particle size is less expressive for plastics, as they generally have a higher percentage of volatile matter.

3.2 ATR-FTIR of the raw material

The comparison of the spectrum in Figure 4 with the data from the literature allowed to verify the presence of characteristic bands of polyethylene, generally related to axial (stretching) and angular deformations that involve the C – H, C – C, and C = C bonds.

Figure 4 – Graph of the ATR-FTIR analysis of the raw material



Source: Authors (2019)

Table 1 presents the qualitative analysis of the spectrum in Figure 4, with the characteristic bands and their respective attributions.

It is evident that the asymmetric vibration of CH^3, attributed to the 1,426cm^{-1} band in Table 1, generally overlaps the symmetric angular deformation in the plane of the methylene group (CH2) (SILVERTEIN; WEBSTER; KIEMLE, 2005). The weak intensity band in 1,730cm^{-1} corresponds to the carbonyl group (C = O), which may be due to the presence of amide, an additive used as a flow aid to reduce the friction coefficient in the fabrication of films (SANTOS, 2007; SILVERTEIN; WEBSTER; KIEMLE, 2006). It is also verified that no contamination of the material with polypropylene occurred, another polymer often used in the fabrication of films for packaging. This is evidenced by the absence in 2,722cm^{-1} that is attributed in the literature as a characteristic of polypropylene (SANTOS, 2007).

Table 1 – Main bands attributed to LDPE and LLDPE waste

Band (cm^{-1})	Atributtion	Intensity
2,917	Asymmetric axial deformation of CH_2	Strong
2,850	Symmetric axial deformation of CH_2	Strong
1,462	Symmetric angular deformation in the CH_2 plane and asymmetric angular deformation of CH_3	Medium
1,373	Symmetric angular deformation of CH_3	Weak
1,306	Asymmetric angular deformation outside of the CH_2 plane	Weak
716	Asymmetric angular deformation in the CH_2 plane	Medium

Source: Authors (2019)

3. 3 X-Ray Fluorescence (XRF)

The X-ray fluorescence experiment allowed to determine the qualitative chemical composition of the inorganic elements present in the waste, as shown in Table 2. These elements are derived from inorganic fractions that are present in polymers, probably associated with the additives, fillers, and pigments added during processing of the polyethylene in the second generation of the petrochemical chain, and mainly in the industry of processed plastics. The presence of such elements was also observed by Sogancioglu et al. (2017) in the analysis of LDPE and LLDPE post-consumer packaging.

The LDPE and LLDPE waste used in this research are predominantly from food and animal feed packaging, which may be colored. Thus, according to Mateus (1999), they tend to present higher concentrations of the elements in comparison to colorless plastics. This also justifies the higher ash content shown by the waste in the immediate analysis, when compared to virgin or second-generation polymers, which influences the yield of the pyrolysis products. Ti, which appears as major element in Table 2, and Fe are probably due to the addition of pigments of white, yellow, green or red Ti, and yellow FeO. Ca and Si come mainly from the addition of anti-blocking agents (carbonate and natural or synthetic silica), which in general consist of mineral fillers, added in order to reduce the adhesion of the surface of plastic films (MATEUS, 1999).

Table 2 – XRF Analysis of LDPE and LLDPE waste

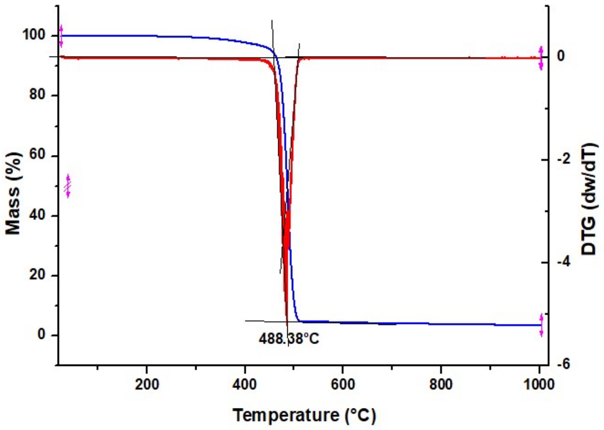
Major elements (>50%)	**Smaller Quantity (5% < x < 50%)**	**Trace Elements (< 5%)**
Ti	Ca, Fe	Si, Cu, Al, Zn, K, P, S

Source: Authors (2019)

3. 4 Thermogravimetry (TGA)

Figure 5 shows the mass loss curve and the mass loss rate (dw/dT) in relation to temperature, for the microscale pyrolysis of the mixture of LDPE and LLDPE waste, in the shape of pellets, at a heating rate of 10°C/min. According to Figure 5, the material has a single stage thermogravimetric reaction curve, that is, only one devolatilization step. In this case, thermal degradation initiates at around 410°C and extends to about 530°C. The temperature of maximum thermal degradation rate was around 488°C.

Figure 5 – Graph of thermogravimetry (TGA) and differential thermogravimetry (DTG) of the LDPE and LLDPE waste



Source: Authors (2019)

Alvarenga et al. (2016), in a study of the activation energy of the pyrolysis of carton packaging, and its pure components, through thermogravimetry, obtained a similar degradation profile por pure polyethylene, with initial temperature at around 403°C and final temperature of 553°C. According to Vidal (2017), who carried out the study of thermal degradation kinetics of the LDPE and Al composite, thermal degradation of polyethylene starts at around 400°C and extends to approximately 550°C.

Das and Tiwari (2017) analyzed the thermal degradation of LLDPE, with a rate of 10°C/min. According to the authors, thermal degradation started at 433°C and extended to 495°C, with maximum reaction rate at around 476°C.

Through the data obtained in the thermogravimetric analysis conducted at a rate of 10°C/min, and based on the methodology of the ASTM E1131-08 standard, it was determined the immediate analysis of the LDPE and LLDPE waste, presented in Table 3. According to Table 3, the values obtained for the immediate analysis of the waste are in agreement with the data present in the literature. The material showed a high content of volatile matter and a low content of fixed carbon. The ash content was close to the typical range for plastics in general, which goes from 0.2% to 4% (JAMRADLOEDLUK; LERTSATITHANAKORN, 2014).

According to Abnisa and Daud (2014), when it comes to the composition of the material, the content of volatile matter and ashes are the two main factors that influence the product obtained by the pyrolysis process. Thus, the higher the volatile matter content, the higher the yield of the liquid fraction of pyrolysis; on the other hand, a higher ash content favors the formation of gases and char. Therefore, due to its high volatile matter content, the LDPE and LLDPE waste present great potential for the production of pyrolytic oil.

Table 3 – Results of the immediate analysis of LDPE and LLDPE waste

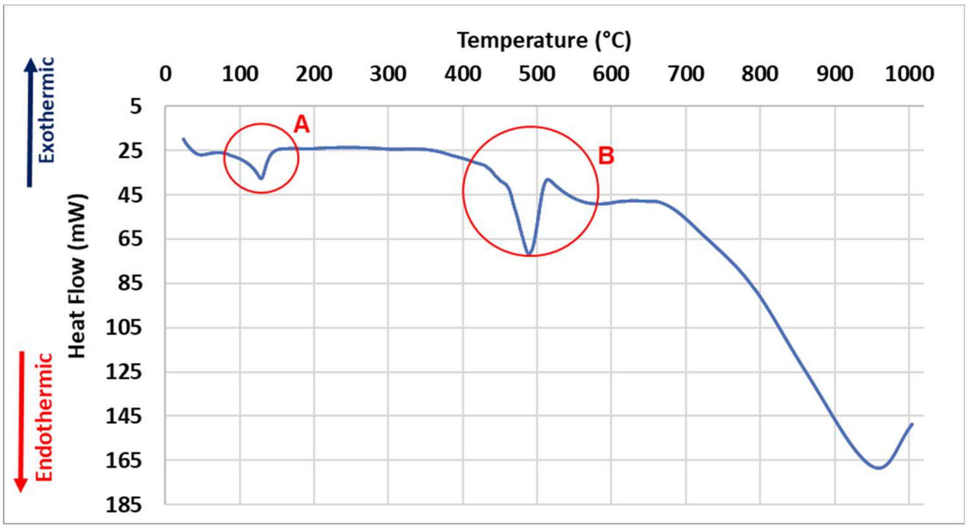
Material	**Humidity (%)**	**Fixed Carbon (%)**	**Volatile Matter (%)**	**Ashes (%)**	**Reference**
Raw material of this study	0.00	0.52	95.54	4.07	
LDPE	0.00	0.00	99.60	0.40	Sharuddin et al. (2017)
HDPE	0.00	0.03	98.57	1.40	
PP	0.15	1.22	95.08	3.55	

Source: Authors (2019)

3. 5 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry of the mixture of LDPE and LLDPE waste, in the shape of pellets, was carried out in order to complement the thermal analysis by thermogravimetry. Figure 6 shows the calorimetric curve of the raw material, observing the occurrence of two endothermic regions, to be discussed separately below.

Figure 6 – Results of the DSC analysis of the LDPE and LLDPE waste used as raw material in this study



Source: Authors (2019)

The endothermic peak of region A, between 90°C and 150°C, represents the melting of the material. According to Gulmine (1999), each type of polyethylene presents a typical melting temperature, which is given by the minimum point of the endothermic region. Thus, it was found that the mixture of LDPE and LLDPE waste showed melting temperature (129.13°C) closer to LLDPE (127.9°C), demonstrating its bigger influence over the thermal behavior of the mixture. On the other hand, the melting temperature of the material distanced itself from the characteristic temperature of PP (169.4°C) and HDPE (138.4°C), indicating that there was no contamination with such polymers during the sampling process (GULMINE, 1999).

The endothermic peak of region B, located between 400°C and 520°C, represents the thermal degradation of the material, which is accompanied by a great loss of mass, as seen in the thermogravimetric curve of Figure 5.

3. 6 Characterization Experiments of the Pyrolytic Oil

The oil obtained in the pyrolysis of the LDPE and LLDPE waste appeared in solid state at room temperature, with an aspect similar to that of a paraffinic wax, as shown in Figure 7. When heating the oil to a temperature of approximately 50°C, a reduction of its viscosity was observed.

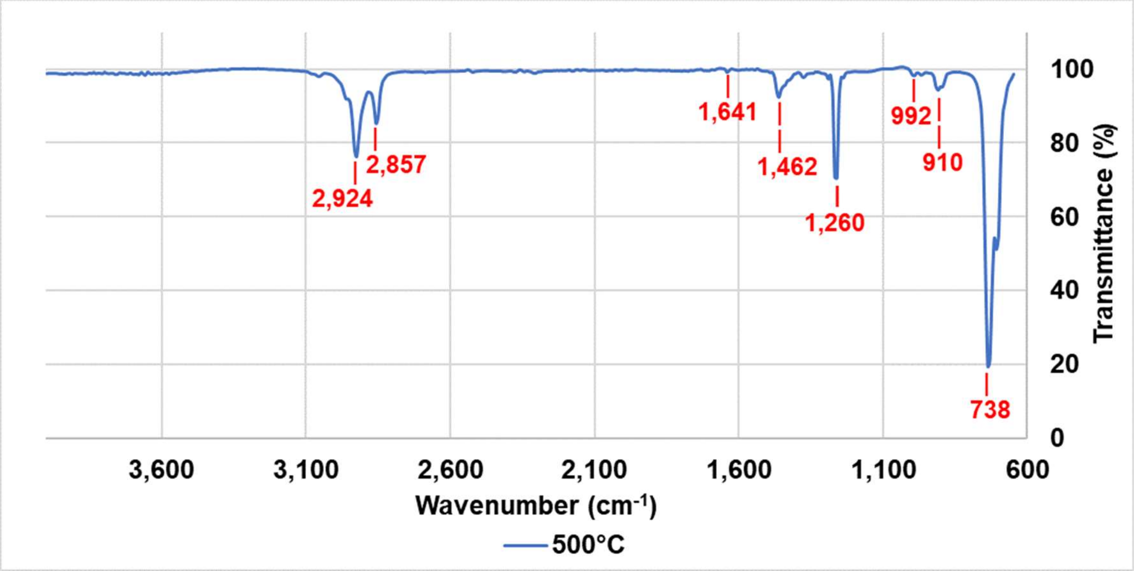
Figure 7 – Photography of the Pyrolytic Oil obtained in this study

Source: Authors (2019

Quesada et al. (2019), in the study of pyrolysis of polyethylene plastic film from municipal solid waste, varied the pyrolysis temperature from 450°C to 550°C, producing oil with aspect and behavior similar to the one of this study. The oil obtained by the authors also presented itself in solid state (wax) at room temperature. By increasing the temperature, the authors found that the viscosity of the oil decreased, and it gradually became liquid. The oil viscosity for the temperatures of 50°C and 60°C, whose values obtained by the authors were, respectively, of 115.4cSt and 67.5cSt, are much higher than those of commercial fuels, such as diesel (3,162cSt) and gasoline (0.31-0.44cSt), in the same temperature, having a greater proximity to the viscosity of crude oil (80.4cSt). Both the oil obtained in this study, as well as the one produced by Quesada et al. (2019) were not subjected to a fractionation process, therefore presenting in their composition both light and heavy compounds, which explains the high viscosity that was observed.

Figures 8 and 9 show the infrared spectra of the oil samples obtained at 500°C and 700°C respectively. The spectra are representative, once most samples analyzed did not present expressive differences. When comparing the spectra and their respective bands, it is verified that the oils produced at 500°C and 700°C present, in general, similarities in relation to the functional groups present. It also becomes evident the effect of the temperature in the chemical composition, since its variation promotes not only changes in the intensity, as well as the appearance of new bands. When analyzing the spectra of the oils, the predominant presence of functional groups characteristic of paraffins, olefins, and aromatic compounds was found, reflecting the nature of the LDPE and LLDPE waste of which they originated from, previously analyzed through the specter of Figure 4.

Figure 8 – Result of ATR-FTIR Specter of the pyrolytic oil obtained at 500°C



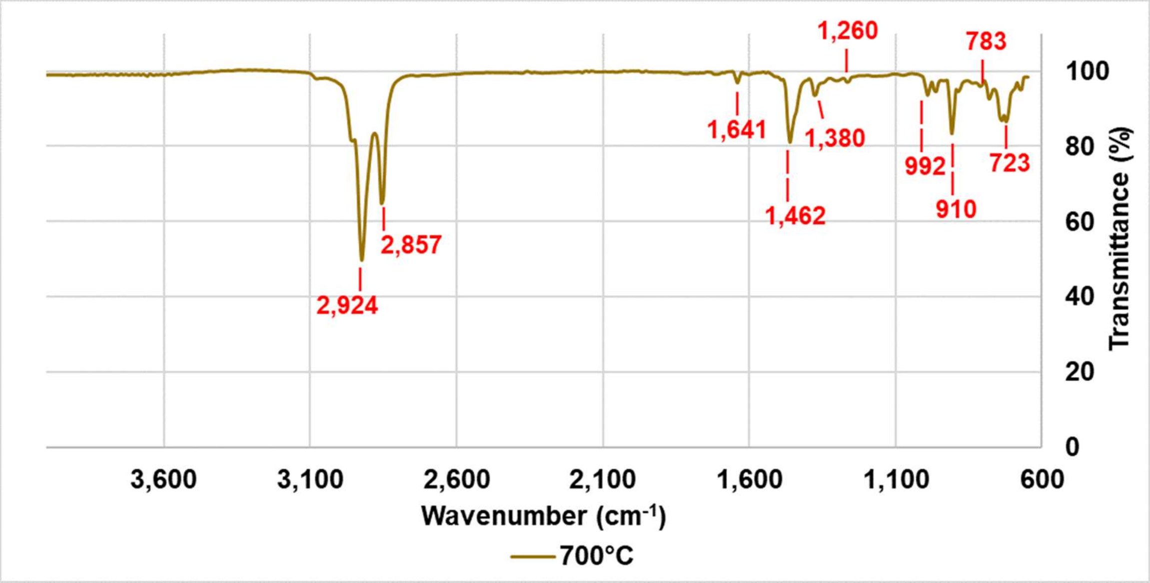
Source: Authors (2019)

The 2,924cm^{-1} and 2,857cm^{-1} bands are characteristic of paraffins, and are respectively related to the asymmetric and symmetric axial deformations of the C – H bonds of the methylene group (CH2). It is observed in the specter of the oil obtained at 500°C that these bands present less intensity and are closer. This can indicate a higher presence of compound with terminal alkene groups, which lead to the widening of the CH3 and CH2 bands (SILVERSTEIN et al., 2005; WILLIAMS; WILLIAMS, 1997; DAS; TIWARI, 2018; QUESADA et al., 2019).

In 1,641cm^{-1} and 1,462cm^{-1} it is verified the axial deformations of the C = C bond of olefins. The region between 1,659cm^{-1} and 1,600cm^{-1} is also characteristic of asymmetric conjugated dienes. In 1,380cm^{-1} symmetric angular deformation occurs in the C – H bonds of the methyl group (CH3). The bands in 992cm^{-1} and 910cm^{-1} represent the angular deformation outside the plane of C – H bonds of monosubstituted olefins (SILVERSTEIN et al., 2005; QUESADA et al., 2019). All the bands previously described presented less intensity in the oil obtained at 500°C. However, the same does not occur with bands in 738cm-1 and 723cm^{-1}, resulting from the asymmetric angular deformation of the C – H bonds of the terminal methylene group in alkenes (QUESADA et al., 2019). It can be verified that the band in 738cm^{-1} of the oil produced at 500°C presents greater intensity, which can indicate a higher quantity of this class of compounds in its composition. The reduction in the intensity of this band for the oil obtained at 700°C appears to originate a new band in 738cm^{-1}, which, although weak, may show the occurrence of axial deformation vibrations of C – H in aromatic compounds (WILLLIAMS; WILLIAMS, 1997). The specter of the oil obtained at 500°C also shows a band of medium intensity in 1,260cm^{-1}, almost inexistent in the specter of the oil at 700°C. This band suggest the presence of an ether functional group (C – O – C) (ÇIT et al., 2009).

Quesada et al. (2019) performed the FTIR analysis of the oil obtained in the pyrolysis of polyethylene plastics films, conducted at a temperature of 450°C to 500°C. Williams and Williams (1997) analyzed the oil derived from the fast pyrolysis of a mixture of plastic waste, with LLDPE and HDPE being predominant in the composition. Das and Tiwari (2017) analyzed the oil collected in the slow pyrolysis of PE packaging. In all these works, the results of the infrared spectra of the pyrolytic oil were similar to the ones obtained in this study. The bands of the specter of the oil obtained at 500°C are similar to both the PE oil produced by Quesada et al. (2019), as well as the characteristic bands of commercial diesel, demonstrating its potential application as fuel.

Figure 9 – Result of ATR-FTIR specter of the pyrolytic oil obtained at 700°C



Source: Authors (2019)

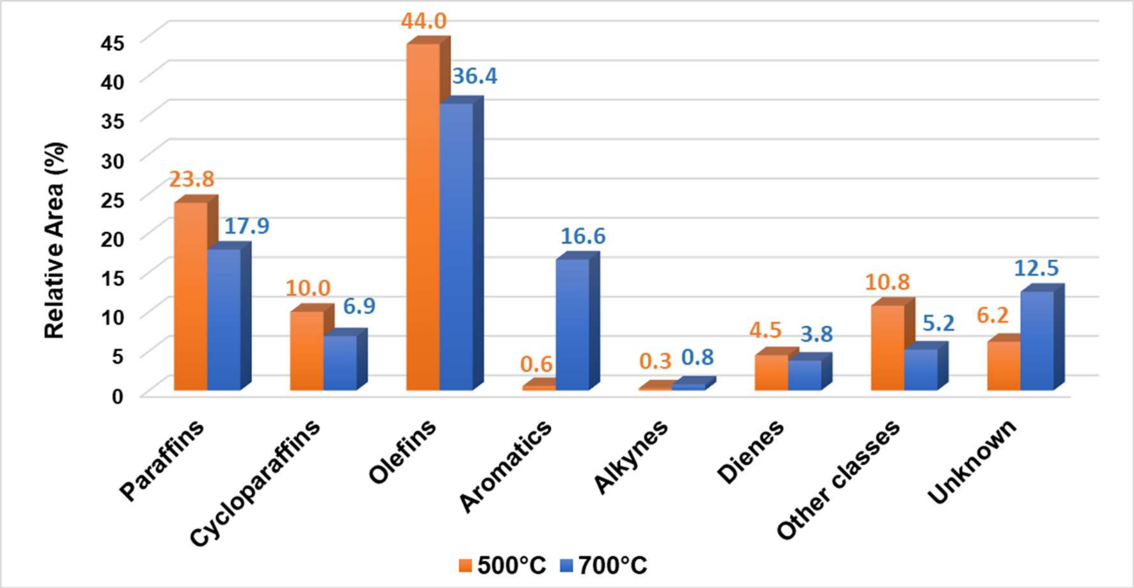
The GC-MS analysis was performed in order to verify the influence of the temperature over the composition of the oil collected in the pyrolysis of LDPE and LLDPE waste, conducted at 500°C and 700°C. It should be noted that the analysis was performed in a semi-quantitative way and, therefore, the percentages of the compounds are given in relation to the total area of the chromatogram and not in percentage of volume or mass. Each mass specter obtained showed about 500 peaks. Thus, similarly to Onwuidili et al. (2009), it was considered only the compounds with a similarity degree equal or superior to 70%. In Figure 10, the identified compounds were grouped in classes. It is observed that the oil collected at 500°C is formed predominantly by olefins, followed by aliphatic and cyclic paraffins, in agreement with the functional groups observed in the previously analyzed infrared specter from Figure 8. The olefins present are situated in the range of 8 to 35 carbon atoms (C8 to C35). However, the highest percentage, 29.4%, is in a closer range, from C8 to C19. Still in the class of olefins, there is a considerable percentage of alpha-olefins, 25.56%, with emphasis for 1-nonadecene ($C_{19}H_{38}$), 1-tricosene ($C_{23}H_{46}$), and 1-octadecene ($C_{18}H_{36}$), with 10.17%, 5.95%, and 2.05%, respectively. The alpha-olefins have a great value for the petrochemical industry, where they are used as raw material to produce polymers and detergents (ONWUDILI et al., 2009).

The paraffins present are in the range of C9 to C32, while cycloparaffins are situated between C6 and C28. The aliphatic compounds situated in the range of C12 to C18, as well as the alpha-olefins, are important for the detergent industry, which uses them, for example, in the production of alkylbenzene sulfonic acid and sodium lauryl ether sulfate (ONWUDILI et al., 2009). The percentage of these compounds is considerable, around 9%. The aromatic compounds appeared only in trace percentage. The percentage by area of compounds from other classes, among which the ether functional group (C – O – C) appears, is 50% higher in relation to the oil collected at 700°C. This fact agrees with the 1,260cm^{-1} band, which presents a higher intensity in the infrared specter of the oil obtained at 500°C (Figure 8).

The composition of the oil produced at 500°C is similar to the one obtained by Quesada et al. (2009) in the pyrolysis of PE plastic films, under the same temperature. The authors verified that the oil is formed predominantly by olefins, followed by paraffins, in a range of C7 to C28. Çit et al. (2009) performed the LLDPE pyrolysis in the form of powder and absence of additives and pigments, in a horizontal quartz reactor coupled with a muffle oven, similar to the one in this study, and with the same heating rate, 10°C/min. The authors verified that the composition of the PE oil was predominantly constituted by aliphatic olefins and paraffins, in the range of C8 to C30, with the aromatic compounds present at a trace level. Also, according to the authors, the polyethylene present weaker C – C bonds when compared to other polyolefins. Thus, during the thermal degradation process, these bonds are broken, forming radicals, which stabilize and originate double bonded compounds, which explains the higher percentage of olefins present in the oil.

(Continue...)

Figure 10 – Influence of the temperature in the composition of the oil obtained in the pyrolysis of LDPE and LLDPE waste



Source: Authors (2019)

By raising the temperature from 500°C to 700°C, the oil composition shows a reduction in the percentage in area of olefins, paraffins and cycloparaffins. The reduction in the percentage of olefins is expressive, from 44% for 36.4%. On the other hand, there is an increase from 0.6% for 16.6% in the relative area of aromatic compounds. Williams and Williams (1999) performed the pyrolysis of virgin low-density polyethylene, in the shape of pellets, in a fluidized bed reactor. Then analyzing the composition of the PE oil obtained at 500°C and 550°C, it was verified the inexistence of aromatic compounds. However, when increasing the temperature of the reactor to 600°C, 650°C and 700°C, the rate of mono and polycyclic aromatic compounds already comprised more than 25% of the oil composition. Lopez et al. (2011a) performed the pyrolysis of a mixture of plastics consisting of PE, PP, PS, PVC, and PET in a fixed bed reactor. By varying the temperature from 460°C and 600°C, they analyzed the composition of the oil produced, and also verified a reduction in aliphatic compounds (olefins, paraffins, and cycloparaffins) in percentage of area from 22.3% to 0.4%, accompanied by an increase in the percentage of aromatic compounds from 71.7% to 99.3%. These results demonstrate that olefins are the main precursors of the formed aromatic compounds, which is reported both by Williams and Williams (1997), as well as by Lopez et al. (2011). Still according to the authors, the formation of mono and polycyclic aromatic compounds is associated with secondary reactions of dehydrogenation and unimolecular cyclization, followed by dehydrogenation of the primary compounds of pyrolysis, which is favored by the increase of the temperature. By raising the temperature to 700°C, the paraffins present in the oil of this study remained in the range of number of carbon atoms of C9 to C30, while the cycloparaffins were situated between C8 and C24. Despite the reduction of the percentage in area of olefins, the alpha-olefins maintained an expressive value of 18.18%. Among the aromatic compounds, the ones that presented a higher percentage in area were azulene (2.14%), phenanthrene (1.09%), p-xylene (0.78%), and ethylbenzene (0.71%). The first two are polycyclic aromatic compounds with 10 and 14 carbon atoms, respectively. While the last two present 8 carbons and they are situated in the range of aromatic compounds in gasoline (C5 to C9). Based on what was discussed, it can be claimed the great potential for using pyrolytic oil of LDPE and LLDPE waste as raw material for the petrochemical industry, in substitution to petroleum derivatives. The oil or wax obtained in this study can be subjected to conventional steam cracking or catalytic cracking processes, as described by Williams and Williams (1997). According to this authors, the LDPE oil or wax obtained at 500°C is more favorable to the processes, as they are rich in aliphatic hydrocarbons, and present inexistence or trace level percentages of aromatic compounds, responsible for the increase in coke deposition rates in the processes.

4 Conclusion

The results obtained in this study show that thermal pyrolysis is an attractive alternative for the treatment of LDPE and LLDPE waste, from plastic packaging, reducing its disposal in landfills. The characterization of waste in the shape of pellets revealed, through the immediate analysis, a high rate of 95.54% of volatile matter, which shows its tendency to produce a high percentage of oil when submitted to the pyrolysis process.

The effect of the variation of the temperature was verified in the analysis of the chemical composition of the pyrolytic oil. The oil obtained at 500°C present a high percentage in the area of olefins (44%), paraffins (23.8%), and cycloparaffins (10%). While the percentage of aromatic compounds were presented at trace level. When comparing the infrared specter of the obtained oil with the specter of commercial diesel, a great similarity of functional groups was obtained. By increasing the pyrolysis temperature to 700°C, an increase in the percentage in area of aromatic compounds to 16.7% was obtained. Thus, it was evidenced that both the oils collected have potential application in conventional steam cracking or catalytic cracking processes, in order to obtain raw material for the petrochemical industry.

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