



Recovery, separation and production of fuel, plastic and aluminum from the Tetra PAK waste to hydrothermal and pyrolysis processes

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ARTICLE INFO

Keywords:

Tetra Pak waste
Hydrothermal treatment
Spent olive oil
Pyrolysis
Recycling

ABSTRACT

The establishment of a method of separation of materials from Tetra Pak waste to obtain products for use as raw material, fuel or other purposes was investigated in this study. First, the feasibility of hydrothermal treatment for the production of a solid fuel (hydrochar) and solid fraction formed by polyethylene and aluminum, called composite was analyzed. The results indicated that hydrothermal treatment performed at 240 °C yield the formation of hydrochar with good properties for its use as fuel and a composite of polyethylene and aluminum. The best conversion and separation of the cardboard and polyethylene/aluminum were obtained using 120 min as operating time. Then, the recovery of the aluminum fraction from the composite by using spent olive oil waste was studied. A partial separation of the composite layers (polyethylene and aluminum) was accomplished with improved aluminum purity for higher operating temperatures. Finally, the operating conditions of the pyrolysis process for the production of a solid (char) and high purity composite (aluminum) were optimized. The characterization results indicated that both char and aluminum resulting from the pyrolysis of the Tetra Pak at 400 °C still have a significant amount of polyethylene while higher purity levels of aluminum can be obtained at temperatures equal of higher than 500 °C.

1. Introduction

The multi-layer poly-coated cardboards are commonly used to produce aseptic packages for a wide range of liquid food including milk, soy beverages, juice, and nectars (Korkmaz et al., 2009). It has become one of the most popular beverage storage systems based on several logistical advantages such as the possibility of a safe and efficient distributing of the products without the need to refrigeration for prolonged periods (Lokahita et al., 2017a; Haydary et al., 2013; Haydary and Susa, 2013; Karaboyaci et al., 2017; Korkmaz et al., 2009; Ma, 2018; Siddiqui et al., 2020; Zawadiak, 2017). Tetra Pak® is one of the most relevant alternatives, with more than 190 billion packages sold and net sales of 11.5 € billion in 2019 (Tetra Pak, 2020). Consequently, large amounts of this kind of package are continuously generating as local solid wastes, which has caused the search for efficient recovery processes to become in an open and very active research line (Haydary et al., 2013; Haydary and Susa, 2013; Karaboyaci et al., 2017; Korkmaz et al., 2009; Lokahita et al., 2017a; Ma, 2018; Martínez-Barrera et al., 2017; Siddiqui et al., 2020; Wang et al., 2019; Zawadiak, 2017; Zhang et al., 2015).

The degradation or modification of the Tetra Pak® packages structure during its useful life is essentially non-existent, with a typical composition of around 70% of cardboard as the major component, 25% of polyethylene, and 5% of aluminum (Haydary et al., 2013). Such components have a wide range of applications; however, the multilayer rugged design makes difficult the separation of each counterpart for recycling. The reference process for its recycling is called hydro-pulping. In this well-established scheme, polyethylene and aluminum layers are separated from the fibers of cellulose using a hydro-pulper (Branco and Saron, 2020). The process is similar to waste paper recycling with some modifications during pulp separation from rejected aluminum and polyethylene composite layers. The extracted cellulose can be later used as raw material for the production of different products such as tissue, napkins, paper bags, etc. (Korkmaz et al., 2009). In fact, according to figures published by Tetra Pak® in its sustainable reports, (Tetra Pak sustainability report 2020) 50 billion of the cartons were recycled in 2019 in more than 170 plants worldwide. Separation of cellulose to the aluminum-polyethylene composite has also been attempted via hydrothermal treatments (Lokahita et al., 2017a; Lokahita et al., 2017b). The

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<https://doi.org/10.1016/j.wasman.2021.11.007>

Received 31 December 2020; Received in revised form 5 October 2021; Accepted 7 November 2021

Available online 15 November 2021

0956-053X/© 2021 The Author(s).

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process is relatively simple and non-expensive, with environmental benefits in comparison to solvent-assisted protocols of delamination. However, hydrothermal-based protocols need also a later stage of liquid–solid separation and the consideration of extra steps for the separation of aluminum and polyethylene layers individually. Less optimized is the separation step of the polyethylene and aluminum layers (usually called composite), which can be considered the main bottleneck of full recycling of tetra pak aseptic packages using hydro-pulping-based schemes. As an alternative for the separation of polyethylene and aluminum, plasma technology can be mentioned. This process produces paraffin from polyethylene components and high purity aluminum (Korkmaz et al., 2009; Rodríguez-Gómez et al., 2015). As the hydro-pulping technology is well-developed, some authors have focused on the separation of the polymer-aluminum composite layers, although similar strategies can be considered using the whole Tetra Pak® packages. Separating aluminum and polyethylene can be carried out using wet and dry processes. Acid-based delamination protocols have been widely essayed, showing, under proper conditions, full-layer separation after relative short contact times (Diop et al., 2017; Yan et al., 2015). Using a solution of methanoic acid at 60–80 °C and a liquid–solid ratio of 30 L/kg the separation can be carried out in less than 30 min (Yan et al., 2015). The utilization of solvents (benzene–ethyl alcohol–water) as delamination agents has shown good results as well. The solubility of utilized solvents in comparison with the polyethylene resulted to be the main parameter for efficient separation of the aluminum–polyethylene layers (Zhang et al., 2014). The temperature, the concentration of the separation agents, mixing parameters as well as the contact time can be considered as main factors to optimize. Waste vegetable oil has been also used as a solvent (non-polar) for the aluminum–polyethylene layers separation (Masegosa et al., 1986; Rodríguez-Gómez et al., 2015). For example, residual canola vegetable oil has previously been successfully used as a non-polar solvent to separate the polyethylene layers of tetra Pak aluminum (Rodríguez-Gómez et al., 2015). According to the results obtained by Masegosa et al. (1986) and Rodríguez-Gómez et al., (2015), the oil penetrates through the polyethylene molecules causing inflammation and forming a kind of gel. In this way, the macromolecules of the polymer chains of polyethylene begin to separate and solubilize in the oil. All aforementioned separation protocols need an extra step in which the separation of the solid and liquid phases are carried out must be optimized. At dry conditions, the polymer-aluminum composite layers recycling has been mainly focused on energy recovery taking into account the relatively high heating value of the aluminum–polyethylene composite (ca. 40 MJ/kg) (Platnieks et al., 2020) although some groups have used aluminum and polyethylene to produce rigid board manufacturing using a hot press. Indeed, one most promising applications of the waste Tetra Pak® is the production of thermoplastic composites (Martínez-Barrera et al., 2017). The composite material can be directly incinerated or mixed with other components to improve the efficiency of the process. The advantages of pyrolysis have been extensively described in the literature and could be considered a very important alternative route for waste aseptic packages recycling. The most common form of tetra Pak waste recycling is the hydrothermal treatment (Dunais, 2009). It is considered as a sustainable method with a low cost of operation. However, the moisture and impurities of cellulose fibers and composite of polyethylene-aluminum greatly affect the quality of these products (Dunais, 2009; Lokahita et al., 2017a). In addition, non-effective process for the separation of aluminum and polyethylene from composite was industrially applied. A potential alternative for recycling tetra Pak into added-value products is pyrolysis. Pyrolysis has been widely applied to organic wastes, such as agricultural wastes and plastic wastes, but has not been widely explored to date for tetra Pak waste. The main advantages of pyrolysis are its simplicity, versatility and low capital investment (Haydary et al., 2013). In addition, the products of pyrolysis are gas, oil and carbonaceous residue. The gas can be used as fuel, frequently for heating the pyrolysis reactor and the oil can either be used as fuel or as raw material for different

chemicals production. The carbonaceous residue can be burnt as fuel or used for the production of activated carbon. Both thermal and catalytic pyrolysis have been essayed with tetra pak waste to obtain products with potential valuable applications (Haydary et al., 2013; Haydary and Susa, 2013; Huo et al., 2021; Korkmaz et al., 2009; Rutkowski, 2013; Siddiqui et al., 2020; Tekin et al., 2019; Wu and Chang, 2001; Zúñiga-Muro et al., 2021). For example, Korkmaz et al., (2009) investigated pyrolysis of tetra pak waste in a batch reactor at temperatures in the range of 400 and 600 °C and analyzed the distribution of products in function of temperature. They indicated that the organic parts of tetra pak have a high calorific value. Haydary et al., (2013) studied the pyrolysis of tetra pak waste at temperatures ranging from 650 °C to 850 °C to maximize the amount of the gas product that was analyzed including its tar content. The authors also characterized by proximate and elemental analysis and calorimetric measurements the char produced. Rutkowski, (2013) studied montmorillonites as acidic catalysts used to produce bio-oil from tetra pak waste pyrolysis. This researcher found that the type of montmorillonite used as catalyst strongly influences the degree of decomposition of the sample reaching a yield of bio-oil of 65 wt% for pyrolysis performed at 450 °C. Siddiqui et al., (2020) found that the use of catalyst HZSM-5 in the pyrolysis of tetra pak waste promoted the generation of aromatic compounds. Co-pyrolysis of tetra pak waste with motor oil with different blend ratios was investigated at 500 °C by Tekin et al., (2019). The results suggested that tetra pak waste could be co-pyrolyzed with motor oil to produce liquid, solid, and gaseous fuels. More recently, pyrolysis of tetra pak waste was studied to obtain novel adsorbents, by different methods, and used them in the adsorption of different contaminants. Huo et al., (2021) investigated porous carbons obtained from tetra pak waste pyrolysis in the adsorption of methylene blue. These authors got carbons with a high surface area (741 m²/g) and good adsorption capacities (140 mg/g). Also, Zúñiga-Muro et al., (2021) prepared new adsorbents for mercury removal from tetra pak waste pyrolysis. The produced carbons also showed high adsorption capacities (up to 215.7 mg/g). Regarding, thermogravimetric studies of Tetra Pak® pyrolysis, previous works have shown twowell-defined stages during its thermal decomposition which corresponds with the degradation of cellulose and polyethylene, respectively (Haydary and Susa, 2013; Reyes et al., 2001). Besides, information about the pyrolysis of each component of Tetra Pak® has been also extensively reported. As well-known, the polyolefinic polymers are thermally decomposed through a mechanism of random-chain scission. The degradation of these components produces several hydrocarbon products, being able to detect the production of light paraffins and olefins at temperatures above 700 °C (Buekens and Huang, 1998). On the other hand, pyrolysis of cellulose can be performed at temperatures from 510 to 850 K producing char, gas and tars (Haydary et al., 2013; Korkmaz et al., 2009).

Although a wide range of contributions to Tetra Pak® recycling can be found in the specialized literature, only the hydro-pulping scheme to recover the cellulose fraction is usually considered as a mature technology, the identification and optimization of a protocol for the recycling of this kind of waste are not resolved. The main objective of this work is to establish a method of separation of materials from Tetra Pak waste to obtain products for use as raw material, fuel, or other purposes. The specific objectives are: (i) analyze the feasibility of hydrothermal treatment for the production of a solid fuel (hydrochar) and a solid fraction formed by polyethylene and aluminum, called composite, (ii) analyze a new separation process of the composite components obtained from the previous method by using spent olive oil which can also be considered as a sustainable and low-cost process and (iii) optimize the operating conditions of the pyrolysis process for the production of a solid (char) and high purity aluminum.

2. Materials and methods

2.1. Tetra Pak waste

Tetra pak containers from milk bottles of different brands have been used to analyze both recycling protocols. The containers were cut in fragments of 1x1 cm, washed with soap and water, and dried at 40 °C for 24 h. The washing step provides a starting material free of the product-related substances stored such as fats and proteins which could provide disruption to recycling results. [Figure S1](#) shows the different steps performed to Tetra Pak waste and the terminology used in this work.

2.2. Characterization of Tetra Pak waste

The cut, washed, and dried material was characterized using the following techniques:

Moisture content: It was determined according to the standard UNE-EN ISO 18134:2016.

Ash content: Determined according to UNE-EN ISO 18122:2016. 2 g of the starting material were prepared and spread on the surface of a plate. The dish was then placed in an oven and the temperature raised to 250 °C for 30 to 50 min, by heating rates of 4.5 to 7.5 °C/min and subsequently kept at a temperature of 250 °C for 60 min to eliminate the volatiles before ignition. The furnace temperature was then raised to 550 °C for 30 min, with a heating rate of 10 °C/min, and remained for at least 120 min.

Volatile matter (VM) content: Determined according to the procedure indicated in standard UNE-EN ISO 18123:2016. For this test, 2 g of sample was weighed in a crucible. First, the oven was preheated to 900 °C and the temperature was allowed to stabilize; then the sample was introduced and left for 7 min. The crucible was then allowed to cool to room temperature in a desiccator.

Fixed carbon (FC) content: Fixed carbon content was calculated by difference from the other components (moisture, ash, and volatile contents).

FTIR analysis: Infrared analysis was performed with a Fourier Transformed Infrared Spectrophotometer (FTIR), Perkin-Elmer, Spectrum-65 model, in the range of 4000–400 cm⁻¹.

TGA analysis: Dynamic thermogravimetric and calorimetric studies of the material were performed using a TGA-DSC Perkin-Elmer STA6000 thermobalance. For this study, 15 mg sample, a temperature range of 30 to 900 °C and a total gas flow of 20 mL/min were used and decomposition was fractionated in 2 stages: i) Nitrogen atmosphere up to 900 °C; ii) oxygen atmosphere once 900 °C has been reached for 20 min (step only used for the determination of the aluminum content).

All characterization tests were performed by duplicate and mean values were reported in Figures and Tables.

2.3. Hydrothermal treatment of Tetra Pak waste

The Tetra Pak residue was hydrothermally treated using an ILSHIN laboratory agitated reactor, with a total capacity of 2 L and manufactured to operate under maximum temperature and pressure conditions of 350 °C and 100 bar, respectively.

Experiments were conducted using 30 g solid sample (1x1 cm fragments) and 1500 mL of distilled water. The sample was introduced into the reactor vessel along with the water and the temperature and operating time at which the sample was maintained was programmed once the setpoint temperature has been reached for each test. Three temperatures levels (160, 200 and 240 °C) and three residence times (40, 80 and 120 min) were tested.

Once the hydrothermal treatment trials were completed, the two products were separated. The solid phase was separated from the liquid phase by atmospheric pressure filtration and allowed to dry for 24 h on a stove at 40 °C. Once dried, the hydrochar and the composite were manually separated. The composite fraction was washed several times to

remove the traces of bonded hydrochar. On the other hand, the liquid phase was vacuum filtered to recover the hydrochar suspended in the liquid fraction to optimize the separation and obtain the maximum amount of product. This small amount of recovered hydrochar was mixed with the major amount obtained by filtration and dried to produce the final subproduct. Finally, the two solids were stored in a sealed bag to avoid contamination before subsequent characterization analyses.

Both solids, the hydrochar and the composite were characterized following the methods described in subsection 2.2. including the determination of the elemental analysis for the hydrochar obtained (carbon, according to UNE EN ISO 16948:2015; hydrogen, according to UNE EN ISO 16948:2015; nitrogen, according to UNE EN ISO 16948:2015; sulfur, according to UNE EN ISO 16994:2015).

2.4. Treatment with spent olive oil to recover aluminum from solid composite fraction

A solvent-assisted protocol using spent olive oil was tested to recover the aluminum fraction. The experiments were conducted using a 250 mL stainless steel beaker, 80 g of spent olive oil and 2 g of the composite obtained from hydrothermal treatment. The treatment was carried out at 140 °C for 60 min (heating rate: 5 °C/min) under magnetic stirring. The treatment produced a viscous liquid fraction based on olive oil and dissolved polyethylene (PE) and precipitated layers with the aluminum component which were easily manually separated. The obtained aluminum was washed with water and ethanol to remove the residual olive oil. Aluminum materials were then analyzed by TGA and FTIR techniques following the methods described in subsection 2.2. Also, a differential scanning calorimetry (DSC) analysis was performed using a TGA-DSC Perkin-Elmer STA6000 thermobalance maintaining the experimental conditions set in the TGA analysis.

2.5. Pyrolysis of Tetra Pak waste

Pyrolysis tests were performed on a R50/250/12 Nabertherm reactor. To recover the liquid product, the equipment incorporated a series of standard laboratory glass bottles (250 mL) located in a salt/ice/external water bath to drastically decrease the temperature and be able to condense some of the gas.

Three experiments (in duplicate) were conducted at 400, 500 and 600 °C, using 30 g of the tetra pak starting material, in an oxygen-free atmosphere, with a nitrogen flow of 120 L/h. In addition, it worked with a heating rate of 15 °C/min and a residence time of 40 min.

The yield to solid/liquid/gas was determined and the two solids, char and aluminum were manually separated and analyzed using TGA and FTIR. The char was further analyzed following the standard procedures mentioned above (immediate analysis and elementary analysis) and its higher heating value was determined according to UNE-EN 14918.

3. Results and discussion

3.1. Characterization of Tetra Pak waste

Immediate or proximate analysis of Tetra Pak samples is presented in [Table 1](#). The approximate analysis showed a moisture content of 7.92%, a VM content of 79.64%, a FC content of 5.90% and an ash content of 6.53%. These results are similar to those found by other researchers. For example, [Haydary et al., \(2013\)](#) found a FC content between 6.25% and 8.18%, VM content between 76.62 and 79.64% and an ash percentage between 5.05 and 5.96% for different Tetra Paks samples that had been used as milk containers, apple juice and blackberry juice. In the contribution of [Wu and Chang \(2001\)](#), moisture content of 4.73% was found, an ash content of 12.75% and a VM content of 82.52%. In this case, the ash and FC content were measured as a whole. Meanwhile, in

Table 1

Elemental and proximate analyses of the Tetra Pak waste and hydrochars obtained by hydrothermal treatment of it.

| Analysis | | | Material | | | | | |
|-----------|-------------|-----------|----------|-------|-------|-------|-------|-------|
| | | | TPW | HT-1 | HT-2 | HT-3 | HT-4 | HT-5 |
| Proximate | Moisture, % | Wet basis | 7.92 | 7.21 | 6.54 | 3.51 | 3.47 | 4.24 |
| | | VM, % | 79.64 | 78.36 | 77.45 | 77.00 | 75.64 | 73.07 |
| | FC, % | Dry basis | 86.49 | 84.45 | 82.87 | 79.80 | 78.36 | 76.31 |
| | | Wet basis | 5.90 | 11.93 | 13.48 | 16.90 | 18.78 | 20.66 |
| | | Dry basis | 6.41 | 12.86 | 14.42 | 17.51 | 19.46 | 21.57 |
| | Ashes, % | Wet basis | 6.53 | 2.50 | 2.53 | 2.59 | 2.11 | 2.03 |
| Dry basis | | 7.09 | 2.69 | 2.71 | 2.68 | 2.19 | 2.12 | |
| Elemental | C, % | Dry basis | – | – | – | 46.06 | 48.09 | 50.83 |
| | H, % | Dry basis | – | – | – | 8.11 | 7.91 | 7.68 |
| | S, % | Dry basis | – | – | – | 0.00 | 0.00 | 0.00 |
| | N, % | Dry basis | – | – | – | 0.09 | 0.19 | 0.07 |
| | O, % | Dry basis | – | – | – | 43.69 | 41.69 | 39.23 |
| | O/C | – | – | – | 0.949 | 0.867 | 0.772 | |
| | H/C | – | – | – | 0.176 | 0.164 | 0.151 | |

Tests' code:

TPW: Original Tetra Pak waste;

HT-1: Hydrochar obtained by hydrothermal treatment of Tetra Pak waste at 160 °C during 40 min; HT-2: Hydrochar obtained by hydrothermal treatment of Tetra Pak waste at 200 °C during 40 min; HT-3: Hydrochar obtained by hydrothermal treatment of Tetra Pak waste at 240 °C during 40 min; HT-4: Hydrochar obtained by hydrothermal treatment of Tetra Pak waste at 240 °C during 80 min; HT-5: Hydrochar obtained by hydrothermal treatment of Tetra Pak waste at 240 °C during 120 min.

Ružičková et al. (2013), a humidity of 4.92% is obtained, a FC content of 5.35% and a VM content of 89.73%. The main source of VM and FC comes from cardboard and PE, while the ash source is mainly aluminum.

The thermogravimetric analysis (TGA) is shown in Figure S2 (including TG and DTG curves) and in Fig. 1 (including only TG curve). The thermal degradation of the container can be observed as the temperature increases in the form of weight loss. The results show the presence of 3 well-defined peaks. The peaks are associated with the loss of moisture of the material, the degradation of the cardboard and the degradation of PE, respectively. Finally, weight loss remains constant as aluminum does not suffer volatilization mechanisms reflected as a mass loss to operating temperatures. The results were in accordance with those previously reported. Cellulose is known to begin to volatilize at temperatures between 280 and 400 °C (Shen and Gu, 2009; Stefanidis et al., 2014), which corresponds to the second region of degradation, while the volatilization of PE begins at temperatures above 400 °C, usually between 450 and 480 °C (Contat-Rodrigo et al., 2002; Majewsky et al., 2016; Beyler and Hirschler, 2002), which corresponds to the third region of degradation.

3.2. Hydrothermal treatment

3.2.1. Elemental and proximate analyses of hydrochar

Table 1 also summarizes the results of the elemental and proximate analysis of the hydrochars obtained from the hydrothermal treatment of Tetra Pak samples under the experimental conditions studied. The VM content of native untreated Tetra Pak samples was high (approximately 80% by weight), while its FC content was low (approximately 6%), however, after the hydrothermal process, the FC content increased, mainly for hydrochars obtained at 240 °C, while the VM content decreased. In Table 1, the data from the immediate analysis have also been presented in dry-based base to normalize the values and avoid the effect of different moisture content of the samples. It is observed that, at temperatures of 160 °C and 200 °C, the VM content (dry base) remains essentially constant. However, for more severe operating conditions of the hydrothermal treatment, lower VM and higher FC content were obtained. This general VM decrease and FC increase with increasing operation temperature and residence time are results of dehydration and decomposition reactions that took place during the hydrothermal treatment. Similar observations were reported earlier by researchers as Chen et al., (2018), Funke and Ziegler (2010), Kim et al., (2014), Uzun et al., (2010), or Yao et al., (2016) between others. It should be pointed

out that the FC was especially high for hydrochars obtained at 240 °C and VM decreased significantly between 200 °C and 240 °C, which may result from the reason that cellulose began to decompose at 220 °C and that a higher temperature the aromatization and polymerization reactions to generate the hydrochars are enhanced (Kim et al., 2016, Lin et al., 2016). In this way, both temperature and operating time are key parameters to achieve optimal degradation. The results indicate that the highest FC content, produced by the thermal degradation of the cardboard, is achieved at 240 °C and 120 min (21.57 % on dry base). Meanwhile, the VM content decreases, reaching the minimum for the aforementioned experimental conditions with 76.31%, on a dry basis. The ash fraction decreased slightly to 2.12% at 240 °C and 120 min.

Other authors such as Lokahita et al., (2017b) studied the hydrothermal treatment of Tetra Pak residues. The VM was gradually reduced with an increase in operating temperature while the FC content increased. Thus, these authors published that, for the hydrothermally treated sample for half an hour, the VM content ranged from 94.7% to 57.6% for a temperature of 200 °C to 240 °C, respectively. However, the FC content increased from 1.8% to 39.5%. In this sense, some differences are observed if the results presented in this study are compared with those found in the work of Lokahita et al., (2017b). Such differences may be related to the starting material, since different tetra pak residues may have differences in their ash content, FC and VM as published by Haydary et al., (2013). Besides, it also highly depends on the type of reactor and the effectiveness of the separation process, which was carried out manually in this contribution.

Regarding elemental analysis, as can be seen in Table 1, the elemental analysis of the by-product obtained at 160 and 200 °C is missing. The separation under these operating conditions resulted to be inefficient and the results can not be considered significant. The product was composed of a heterogeneous mixture of non-degraded cardboard and the PE-aluminum composite (PE-Al composite). Other hydrochar samples showed high oxygen and carbon contents, 50.83% and 43.69%, respectively. The elemental composition of the hydrochar samples was also different for the operating conditions tested. However, the variations in carbon and oxygen detected in the samples as a function of the operating conditions were small in comparison to similar reports (Lokahita et al., 2017b). In the aforementioned work, the authors reported 65.72% and 27.48% of carbon and oxygen, respectively while, under the same experimental conditions, our experiments yield lower carbon (50.83%) and higher oxygen contents (39.23%). These decreases in hydrogen and oxygen contents it consistent with the removal of O and

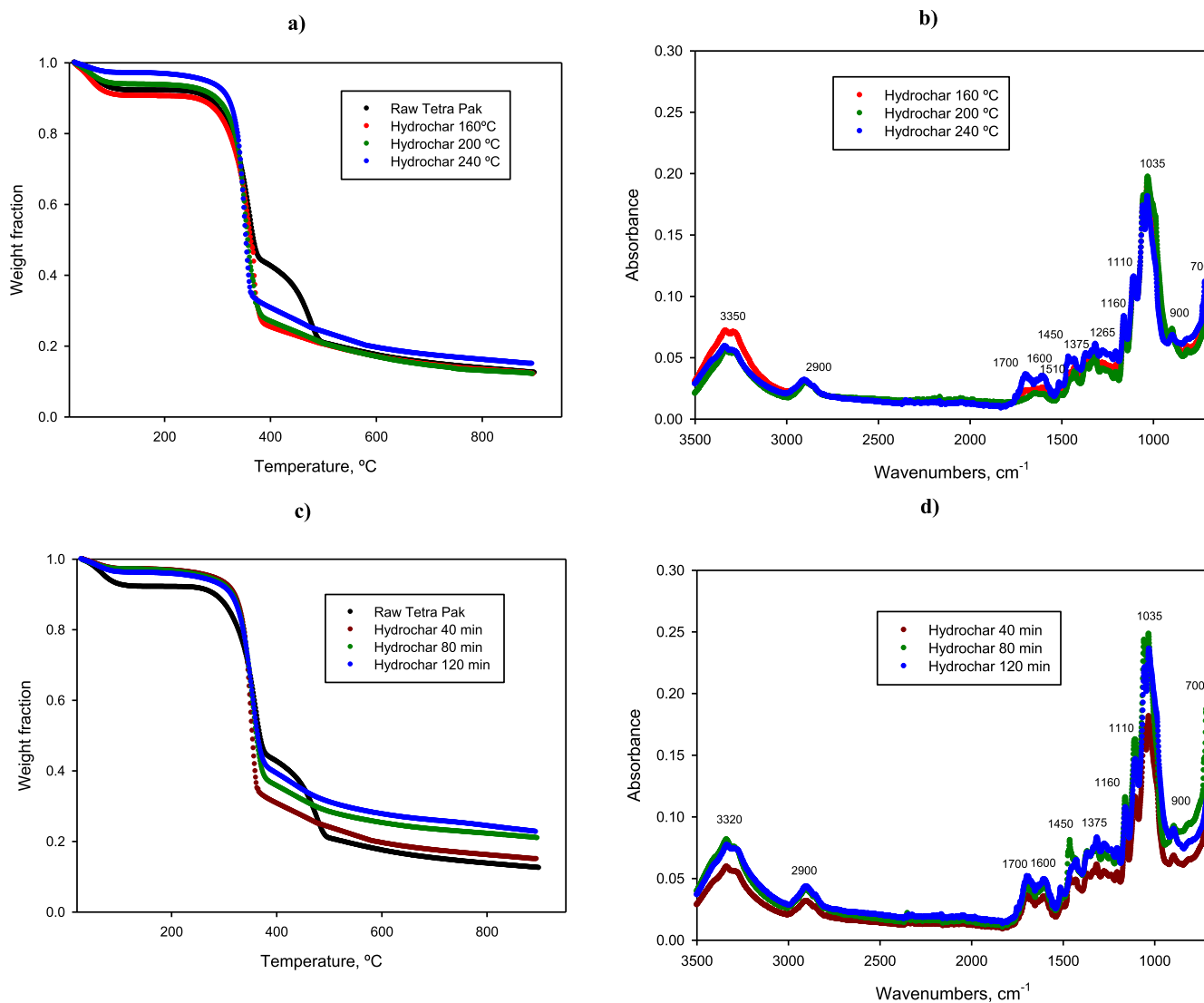


Fig. 1. Thermogravimetric curves and FTIR spectra of Tetra Pak waste and the hydrochar obtained by hydrothermal treatment of Tetra Pak waste. a) and b) Treatment performed at 160 °C, 200 °C and 240 °C during a residence time of 40 min.; c) and d) Treatment performed at 240 °C during a residence time of 40, 80 and 120 min.

H during the hydrothermal treatment due to demethanation, dehydration and decarboxylation reactions (Fuentes et al., 2010). In particular, the lower O/C and H/C ratios were obtained for samples obtained at 240 °C for 120 min. The increase of residence time could explain the intensification of the dehydration and decomposition reactions, especially modifying the carbon, hydrogen and oxygen contents due to the release of H₂, CH₄, CO and CO₂ as gas products (Chen et al., 2018, Funke and Ziegler, 2010).

3.2.2. Thermogravimetric and FTIR analysis of hydrochar

Fig. 1 shows thermogravimetric curves (mass fraction as a function of the temperature) for the starting tetra pak material and hydrochar obtained after the hydrothermal treatment. The data correspond to different temperatures levels and operating time of 40 min (Fig. 1a), and different operating times and temperature of 240 °C (Fig. 1c).

The main difference found between the starting residue and the hydrochars obtained is the disappearance of the decomposition of the PE, because it is no longer present in the hydrochar. On the other hand, it is observed that the degradation curve of cellulose is still present in the same way as in the starting material, indicating that much of the hydrochar is still composed of cellulose fibers in its original state. Thus,

hydrothermal treatment is observed to effectively separate the sheets of cardboard/paper (hydrochar) from PE and aluminum (composite).

Concerning the operating temperature effect, the obtained hydrochar materials at 160 and 200 °C showed similar thermogravimetric curves. However, the experiment at 240 °C presented a similar profile to, but with a higher solid residue content (FC plus ash), which is consistent with the values described in Table 1. Finally, In Fig. 1c a noticeable effect of operating time is detected. The aforementioned effect was mainly detected for the amount of solid residue present between the experiments performed at 40 and 80 min, although the maximum value was measured at 120 min of operation time.

The characterization of the hydrochar materials was completed by Infrared Spectroscopy. Fig. 1b and 1d show the infrared spectra for the hydrochar samples using different levels of temperatures and operating times. Table 2 summarizes the position and functional group identified. The small absorption band at 2950–2850 cm⁻¹ is attributed to the aliphatic C–H group. The peak at 1700 cm⁻¹ is attributed to the C=O groups present in the generated organic matrix. Peaks at 1600 cm⁻¹ and 1510 cm⁻¹ are assigned to polyaromatic systems and benzene rings. In general, peaks at 1450–1440 cm⁻¹ and 1380–1375 cm⁻¹ correspond to aliphatic bending modes, and the peak at 1265–1250 cm⁻¹ at the

Table 2

Bands and peaks of FTIR spectra of hydrochars obtained from Tetra Pak by hydrothermal treatment and LDPE and cellulose.

| Material | Position, cm^{-1} | Functional group |
|------------|----------------------------|--|
| Hydrochars | 3500–3200 | O–H stretching |
| | 2950–2850 | C–H stretching (aliphatic) |
| | 1710–1700 | C=O stretching (conjugated) |
| | 1600–1590 | C–H (aromatic) |
| | 1510 | C–C stretching (aromatic) |
| | 1450–1440 | C–H bending (aliphatic) |
| | 1380–1375 | –CH ₂ – bending |
| | 1265–1250 | C=O stretching |
| | 1160 | C–O stretching of ethers and carboxylic groups |
| | 1100 | |
| | 1060–1035 | |
| | 900–700 | H–C–C rocking (aromatic) |
| | LDPE | 2915–2910 |
| 2850 | | CH ₂ symmetric stretch |
| 1475–1470 | | CH ₂ scissors |
| 1377 | | CH ₃ umbrella |
| 720–715 | | CH ₂ rock |
| 3350 | | OH stretch |
| Cellulose | 2915–2910 | CH ₂ asymmetric stretch |
| | 1750–1740 | C=O stretch nonionic carboxylate |
| | 1640 | C=O stretch ester/carboxylic acid |
| | 1373 | CH ₃ umbrella |
| | 1162 | C–OH stretch/bend |
| | 1070 | C–OH bend |

stretching of C–O, probably due to the predominant presence of ethers and etheric oxygen. Absorption peaks/bands at 1110, 1060–1035 cm^{-1} could correspond to the inorganic matter (ash) of the hydrochar. Finally, the bands between 900 and 700 cm^{-1} correspond to aromatic bending modes and are mainly due to aromatic oscillating vibrations of H–C–C (hydrogen-carbon-carbon) in aromatic ring systems and aromatic condensates.

Fig. 1b shows FTIR spectra of hydrochar at different temperatures. If spectra are compared, with an operating temperature increase, the peaks at 1700 cm^{-1} (C=O stretching), 1600 cm^{-1} (C–H aromatic) and 1510 cm^{-1} (C–C stretching, aromatic) become wider and stronger. These changes suggest that the aromatic compounds are formed and/or recombined at higher temperature (Jaruwat et al., 2018). However, the broad absorption band corresponding to O–H vibrations at 3200–3500 cm^{-1} decreased with the increase of temperature of the treatment, confirming that the dehydration reaction occurs. Regarding the operating time effect at a constant temperature of treatment of 240 °C, more marked peaks were observed at 1100, 1035 and 700 cm^{-1} , mainly to the increase in stretching of ether and carboxylic groups and H–C–C rocking vibrations (aromatic compounds). Also, increases in 1700 and 1600 cm^{-1} peaks were observed. This confirms the formation of complex carboxylates and aromatics obtained by crosslinking induced by the thermal treatment (Kang et al., 2012; Kruse and Zevaco, 2018).

3.2.3. Thermogravimetric and FTIR analysis of the PE-Al composite

During the hydrothermal treatment, a robust and rich in aluminum and PE composite material was also obtained, which has previously been referred to as PE-Al composite or composite. Fig. 2 shows thermogravimetric curves (mass fraction versus temperature) for the original residue and composites obtained from the hydrothermal treatment at different temperatures and a residence time of 40 min (Fig. 2a) and at different operating times and a temperature of 240 °C (Fig. 2c). As can be seen in this figure, when the residue is treated at 160 °C for 40 min, the composite showed a similar curve to the starting Tetra Pak residue. Besides, the enhancement of the temperature to 200 °C led to a decrease of the paper/cardboard component in the sample (see how cellulose decomposition appears less marked and with less weight loss) while at 240 °C only the PE decomposition was appreciated. Concerning the operating times, no differences in the thermogravimetric curves of the composite were observed using operating time of 40, 80 and 120 min

and 240 °C. It can be seen as the curves of the three composites obtained at 240 °C and different operating times appear practically overlapping. This result indicates that the obtained composition in the composite materials at different times was essentially the same which corresponds to an aluminum content between 20.8% and 23.6%.

Also, Fig. 2b and 2d show the infrared spectra of the composite materials and Table 2 also reports the characteristic peaks of cellulose and low-density PE (LDPE). According to the results, the presence of cellulose residues from Tetra Pak paper/cardboard in composite materials can be observed, mainly on those obtained at lower operating temperatures. This is an expected result taking into account that, after several cleaning steps with soap and water, traces of the hydrochar in contact with the composite were still easily observed. As aforementioned, at 160 °C a large number of paper/cardboard fibers are observed that are still present in the composite, while the graph shows important removal of characteristics peaks of cellulose at 240 °C. For example, the board band appearing at 3350 cm^{-1} associated with OH vibration in the hydroxyl group or the peaks between 1200 and 1000 cm^{-1} deeply reduced its intensity. In Fig. 2d, very similar spectra were obtained for the three analyzed samples and, also, they revealed characteristics peaks of LDPE. In addition, the results confirmed that, for a temperature of 240 °C, operating time was not especially influenced the composition of obtained PE-Al composite.

The percentage of aluminum in this fraction is summarized as follows: HT-1, 8.9%; HT-2, 16.2%; HT-3, 23.6%; HT-4, 20.8%; HT-5, 22.0% (see tests' code on Table 1). A clear enhancement of the aluminum component was detected when the temperature was increased from 160 °C and 240 °C while the effect of operating time was not remarkable. It should also be noted that the cleaning of the hydrochar residues deposited on the composite surface after the hydrothermal process was manually carried out, so this factor could influence the final fraction of PE, aluminum and hydrochar residues present in the composite. The results were similar to those presented by Lokahita et al., (2017b) in which a fraction of the aluminum between 21 and 25% was detected in the composite for different operating conditions. In addition, they also did not find a positive trend between the treatment time and the aluminum content, since the maximum was obtained at 220 °C and 30 min.

3.2.4. Use of spent olive oil for separation of aluminum and PE of composite obtained from the hydrothermal treatment of Tetra Pak samples

The recovery of the aluminum fraction was tested using a solvent-assisted method based on the utilization of spent olive oil. Fig. 3a shows the mass loss (TGA curve) and Fig. 3b the heat flow for each of the samples as a function of temperature (DSC curve). To better understand the thermal decomposition process and assign mass loss to oil and residual PE, the TGA curves of spent olive oil and virgin LDPE have been added. No mass loss was observed in TGA curves, at approximately 300 °C, which indicates that the samples did not contain traces of cardboard fibers. However, a pronounced weight loss from 300 °C to 485 °C, which can be associated with the presence of oil and residual PE in the samples. This indicates that the separation of PE and aluminum only occurs partially. Besides, it is observed that the weight loss is significantly smaller for longer operating times with a minimum detected at 120 min. As can be seen in the figure, the PE and/or oil content for the sample obtained using 40 min of operating time during the hydrothermal process is approximately 40–45%, while this value decreases to 15–20%, for the sample to 120 min.

On the other hand, DSC curves for different samples (Fig. 3b) have similar profiles, with endothermic and exothermic transitions. The samples did not show significantly the marked peak of the endothermic process corresponding to the fusion of LDPE (105–118 °C), which indicates that it is in low proportion.

The first peak at 370 °C showed an exothermic transition probably due to the polymerization of components of olive oil fatty acids (Gouveia de Souza et al., 2004). The following peaks, between 400 °C and 500 °C,

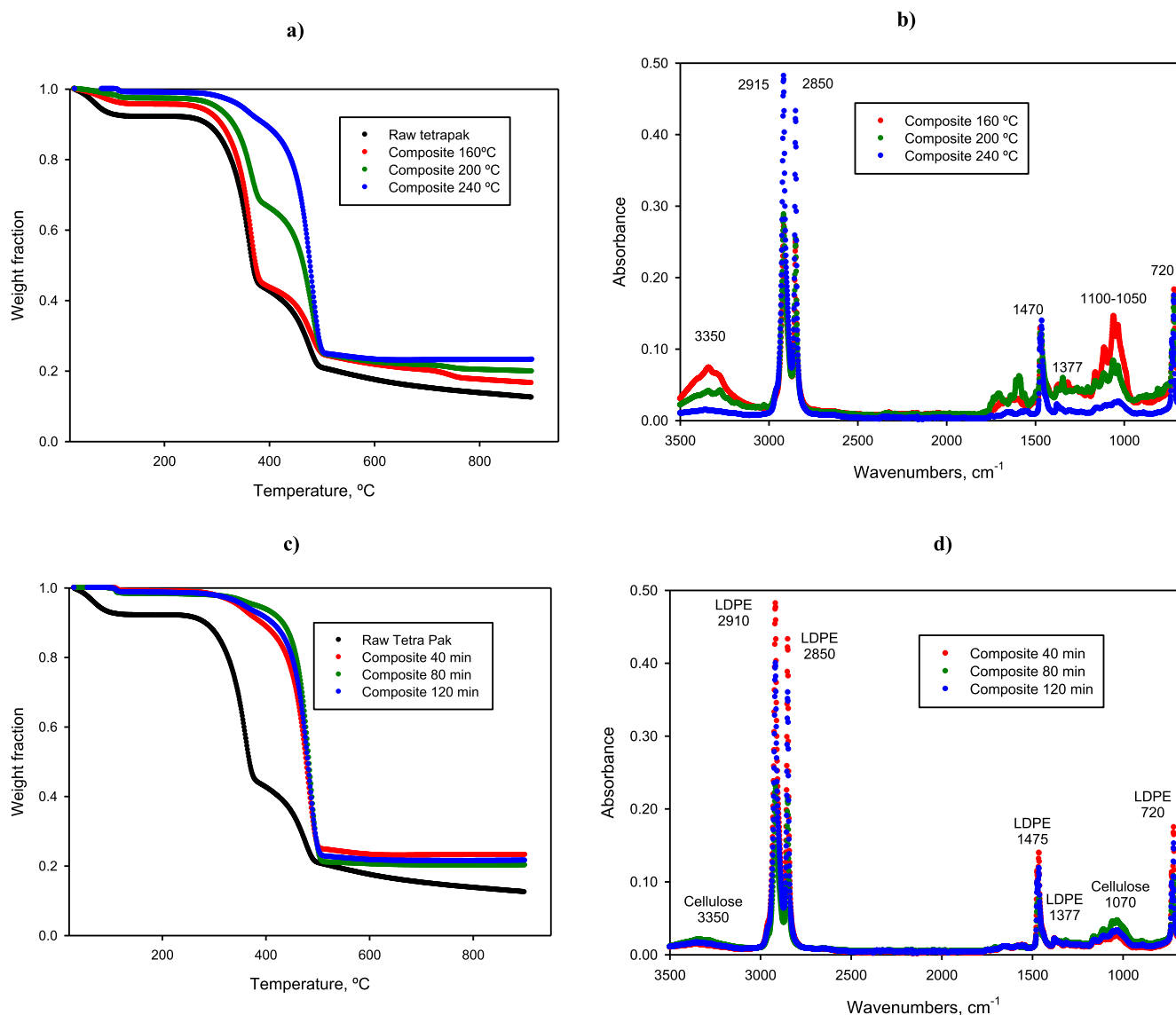


Fig. 2. Thermogravimetric curves and FTIR spectra of Tetra Pak waste and the composites obtained by hydrothermal treatment of Tetra Pak waste. a and b) Treatment performed at 160 °C, 200 °C and 240 °C during a residence time of 40 min.; c and d) Treatment performed at 240 °C during a residence time of 40, 80 and 120 min.

can be assigned to the decomposition of PE (Rodríguez-Gómez et al., 2015). These are very subtle peaks due to the small amount of PE present in the samples, mainly for the solid obtained after the oil treatment using the composite obtained from the hydrothermal treatment at 240 °C and 120 min. Finally, the last peak of endothermic character around 650 °C is related to the aluminum fusion process. In this case, it is a well-defined peak since aluminum is the major component of this fraction.

Finally, the sample obtained after treatment with oil was subjected to FTIR analysis (Fig. 3c) to detect the possible presence of functional groups of PE and oil, including C–H stretch (2915 cm⁻¹, CH₂ asymmetric and 2850 cm⁻¹, CH₂ symmetric), C=O stretch (1720 and 1640 cm⁻¹), CH₃ umbrella mode (1377 cm⁻¹), C–O stretch (1240 and 1150 cm⁻¹) or CH₂ rocking (720 cm⁻¹), between others. The results also confirm the presence of PE after the oil treatment on the aluminum film. The magnitude of the peaks associated with PE decrease with the enhancement of temperature, although remain present in all final samples, which can significantly affect the quality of the resulting aluminum, decreasing its market value.

3.3. Pyrolysis

3.3.1. Products yields at different operational temperatures

The pyrolysis experiments were conducted at three temperatures levels (400, 500 and 600 °C). The yields to solid, liquid and gas obtained in each test are presented in Table 3. Since Tetra Pak's main components are cardboard/paper, PE and aluminum, the solid residue of pyrolysis consisted of char (cardboard/paper is primarily responsible for char formation during Tetra Pak pyrolysis) and aluminum. According to the results, the yield to liquid and gas increased and the amount of char decreased with the increase of the temperature from 400 °C to 600 °C. Such results can be understood considering that for higher the operating temperature, the greater the degradation of the cardboard forming a pyrolytic gas composed of condensable substances (liquid fraction) and non-condensable (gases). These findings are similar to those provided in contributions of Korkmaz et al., (2009) and Haydari et al., (2013) although these authors also measured other compounds such as wax and tar in the liquid fraction. As a main difference from the aforementioned works, in this case, the gas fraction and aqueous phase remained almost constant, with 23.9% and 29.6–32.6% (400–600 °C). In addition to the

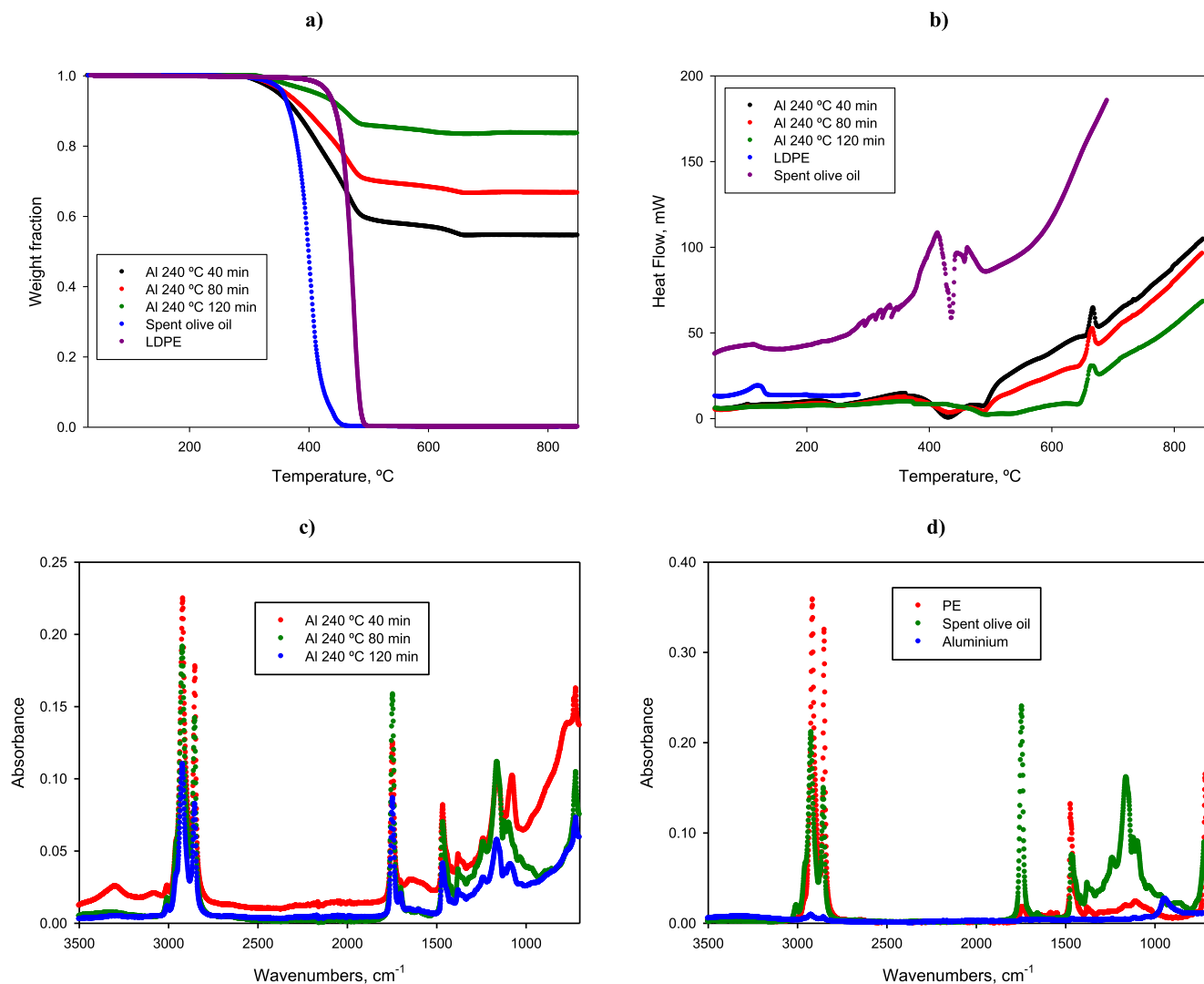


Fig. 3. a) Thermogravimetric curves; b) heat flow supplied and c) and d) FTIR spectra of aluminum materials recovered after treatment with spent olive oil of composites obtained from hydrothermal treatment and separated materials.

Table 3
Yields to solid, liquid and gas obtained in each pyrolysis test.

| Component | Operating temperature | | |
|-----------|-----------------------|--------|--------|
| | 400 °C | 500 °C | 600 °C |
| Solid | 45.84 | 25.28 | 20.52 |
| Char | 39.14 | 18.68 | 14.02 |
| Aluminum | 6.70 | 6.60 | 6.50 |
| Liquid | 26.65 | 37.69 | 38.17 |
| Gas | 27.51 | 37.04 | 41.31 |

possible differences of the tetra pak starting materials, may be also associated with differences in the condensation system (system for condensing part of pyrolytic gas) and the measurement of other substances (ceramic and tarred compounds). The amount obtained from char and aluminum (solid residues) is more closely similar to that obtained by the authors with values of 18.4% and 7.0%, respectively, at 600 °C.

3.3.2. Elemental and proximate analysis of char

Table 4 summarizes the results of the elemental and proximate analyses of the different carbon residues (chars) obtained from the pyrolytic treatment of Tetra Pak samples. As the temperature of pyrolysis

Table 4
Elemental and proximate analyses of the chars obtained by pyrolytic treatment of Tetra Pak waste

| Analysis | | Operating temperature | | |
|-----------|-------------|-----------------------|--------|--------|
| | | 400 °C | 500 °C | 600 °C |
| Proximate | Moisture, % | 1.50 | 2.54 | 1.68 |
| | VM, % | 59.60 | 22.88 | 12.67 |
| | FC, % | 32.84 | 64.63 | 77.21 |
| | Ashes, % | 6.06 | 9.95 | 8.44 |
| Elemental | C, % | 71.44 | 70.12 | 59.37 |
| | H, % | 10.22 | 8.06 | 4.69 |
| | S, % | 0.00 | 0.00 | 2.73 |
| | N, % | 0.07 | 0.06 | 0.04 |
| | O, % | 12.21 | 11.81 | 24.73 |
| | O/C | 0.171 | 0.168 | 0.417 |
| | H/C | 0.143 | 0.115 | 0.079 |

increased, the content of carbon in the solid product decreased from 71% at 400 °C to 59.37% at 600 °C. In addition, an increase in sulfur content in char was observed. Similar results have been also reported by Haydary et al., (2013) in their study on Tetra Pak pyrolysis at temperatures between 650 and 850 °C and Raclavská et al (2018), where the composition of the char obtained at different operating temperatures is

observed. In the latter, a char is obtained with 63.78 % and 1.97 % carbon and hydrogen, respectively, for an operating temperature of 600 °C. In addition, for the same conditions, 42.45% VM, 34.63% FC and 22.92% ash, present in the char, are obtained. The latter values differ from those obtained in the experimental test, although this may be due to the type of Tetra Pak (not specified in the article), type of condensation system and analytical technique used.

According to the results obtained, the solid (char) obtained from pyrolysis can be considered appropriate material for use as solid fuel due, in particular, to its high percentage in carbon and hydrogen, highlighting that obtained at 500 °C. Although in return it has moderate ash content which could lead to the accumulation of ashes during the combustion process. In this case, the aluminum, which is the main component that forms the ash, is released as liquid residue since it melts at approximately 650 °C. It can produce negative impacts during operation if it adheres to the walls of the boiler which, given the huge amounts involved in the process, can interfere with the normal operation of the installation. In addition to this application, other researchers such as Raclavská et al., (2018), have evaluated the properties of the biochar obtained for the use in the agriculture field as fertilizer.

3.3.3. Thermogravimetric and FTIR analysis of the char and aluminum composite

Fig. 4 shows the curves resulting from thermogravimetric analysis and infrared analysis of char and aluminum composite samples obtained from Tetra Pak pyrolysis, respectively.

First, it is observed as the curve described in the TGA analysis of char at 400 °C presents a loss of mass in a temperature range of 400–450 °C. This corresponds to the degradation of PE, still present in char samples due to a low operating temperature. On the other hand, the TGA curves of the char analyzed at 500 and 600 °C are similar, highlighting a lower VM content for the most severe temperature, as well as a complete absence of PE in both samples.

Fig. 4c shows the resulting aluminum TGA curve, in which PE is still present at the temperature of 400 °C, while, from 500 °C, it does not suffer from thermal degradation or mass loss. This indicates that the composite is almost entirely made up of aluminum.

The main observation of thermograms and infrared spectra is that the char and composite (aluminum) resulting from the pyrolysis of the Tetra Pak at 400 °C still has a significant amount of PE and that from 500 °C the composite samples are composed almost entirely of aluminum. However, small peaks at 2915–2910 cm^{-1} and 2850 cm^{-1} , characteristic

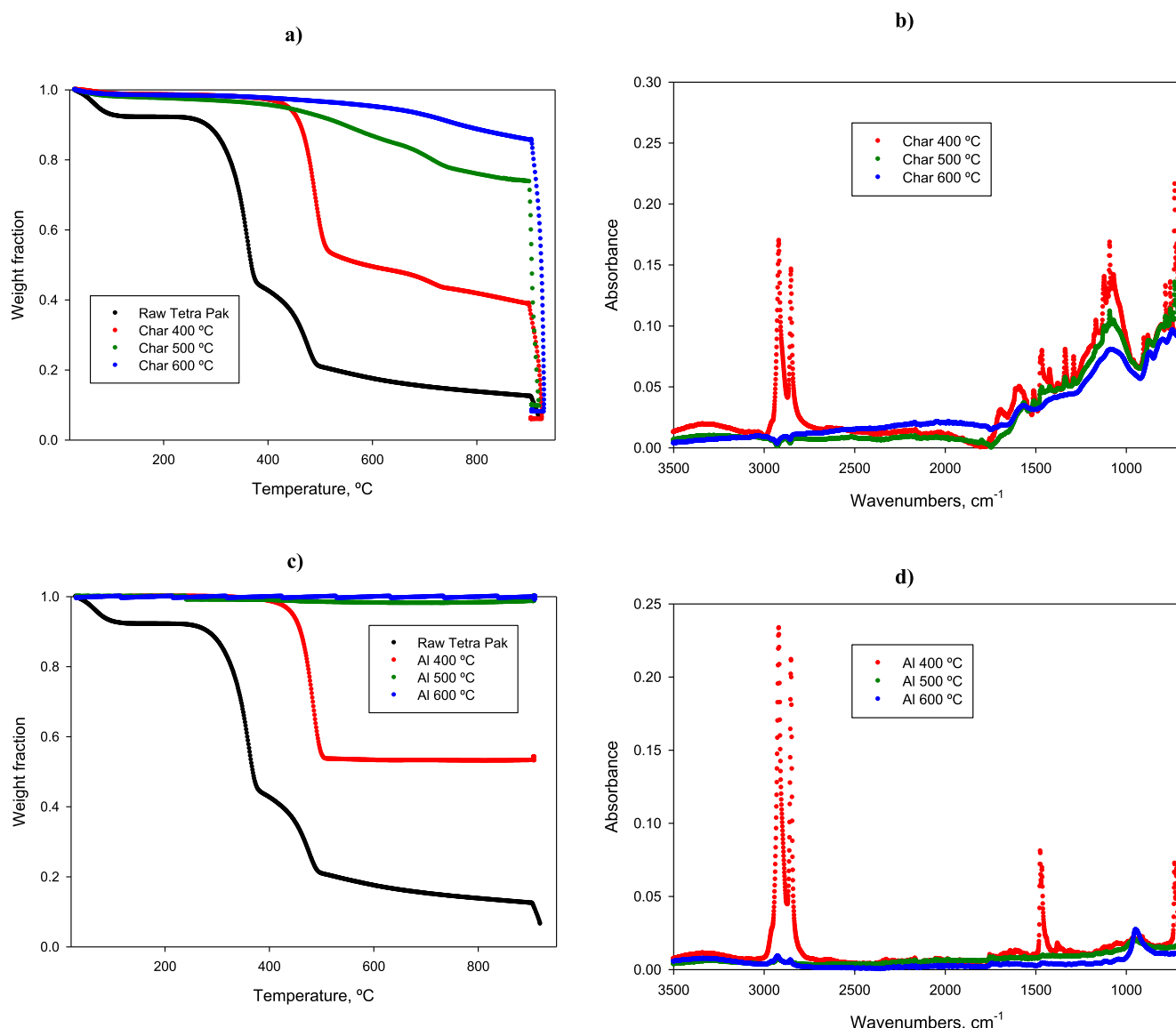


Fig. 4. Thermogravimetric curves and FTIR spectra of char (a and b) and aluminum materials (c and d) obtained by pyrolytic treatment of Tetra Pak waste.

of LDPE, can still be seen in the infrared spectra. However, the presence of PE in these samples should be minimal because the thermogram has not observed the weight loss at 450 °C corresponding to the PE.

4. Conclusions

Hydrothermal and pyrolysis-based protocols have been investigated for the recycling of post-consumer Tetra Pak waste.

- 1) The hydrothermal process resulted strongly dependent on temperature and operation time. An hydrochar with high carbon content and a PE-Al composite were efficiently separated operating at 240 °C during 120 min. In a second step, the PE-Al composite was partially separated using spent olive oil as solvent at 140 °C. The practical application of hydrothermal treatment combined with the olive oil treatment still needs further investigation to get an enhanced PE removal and a purer aluminum fraction. In any case, the process can be considered promising taking into account that products with relatively high value for a long range of applications are recovered and using a scheme that focuses on waste valorization.
- 2) A clear relation of the produced fractions was obtained as a function of the pyrolysis operating temperature. At lower temperatures, the least degradation of cardboard leads to a greater fraction of the solid char obtained. In addition, a pyrolytic gas composed of condensable substances (liquid fraction) and non-condensable (gases) were also produced. Pyrolysis at temperatures equal or higher than 500 °C allows obtaining an aluminum layer with high purity. Also, the obtained char from pyrolysis could find applications as solid fuel. In particular, the fraction obtained at 500 °C presents a high percentage of carbon and hydrogen.

Both alternatives, although must be situated at an initial investigation stage, show Tetra Pak waste as a useful recycling resource to obtain products for use as raw material (i.e., aluminum), fuel (i.e., char), or other purposes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

None.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2021.11.007>.

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