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ANALYSIS OF PRODUCTS FROM THE PYROLYSIS OF PLASTICS WASTE FROM A PRINTING PLANT: A PILOT SCALE STUDY

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ABSTRACT. As plastic production increases, new waste management methods are required. Chemical recycling, such as pyrolysis, has the potential to raise recycling rates taking into account that it can use more waste plastics than standard mechanical recycling. Four types of bits of plastic: polyethylene (PE), polypropylene (PP), polystyrene (PS), and biaxial-oriented polypropylene (BOPP) fractions from the printing plant were collected; the possibility of recycling them by batch pyrolysis was investigated. Characterization of the obtained pyrolysis oils was carried out by gas chromatography-mass spectrometry (GC-MS), the analysis showed a mixture of aliphatic (saturated and unsaturated) compounds, in the case of PE and PP, while in the case of PS, aromatics and low quantities of other hydrocarbons were detected. In the case of BOPP the distribution of the pyrolysis products is not as uniform as in the case of PE, PP, or PS plastic samples. The FT-IR results showed clear peaks of aliphatic compounds in two liquid oil samples of PE, and PP that further confirmed the GC-MS results. More than 60% monomer (styrene) can be recovered from the PS pyrolysis, besides other aromatic compounds in low concentration. The pyrolysis oils have a reasonable heating value (calorific value) in the range of 36–45 KJ/g, close to conventional diesel. Therefore, the pyrolysis oils has the potential to be used as an alternative source of energy as fuel, after blending with conventional fuel, or heating combustion products. The research results will contribute to the development of waste valorization via plastic upcycling from a printing press, without using an expensive catalyst or reactor system.

Keywords: *thermochemical process, plastic upcycling, pyrolysis oil, GC/MS analysis, hydrocarbons.*

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INTRODUCTION

Plastic waste are one of the most widespread in nature, their production and consumption are increasing at an alarming rate, due to, both population and economic growth, and lifestyle changes which have the greatest impact. The resulted global plastic waste doubled between 2000 and 2019, reaching 353 million tons. Only 15 % is collected for recycling, just 9 % is successfully recycled, another 19 % is incinerated, and 50 % is landfilled. At this rate the estimated plastic waste generation will be almost triple by 2060 [1, 2]. According to a new report of the Organization for Economic Cooperation and Development, in the European countries, the amount of plastic waste generated annually per person is around 114 kg [3]. During last years pyrolysis has received a lot of attention both in the industrial and scientific communities as a promising, versatile procedure in order to convert plastic waste into valuable resources [4]. Chemical recycling such as pyrolysis, can significantly increase the recycling rates due to the fact that this procedure can convert a wide range of waste plastics in contrast to the traditional mechanical recycling procedure [5]. Pyrolysis is a common technique used for thermal degradation of waste plastics at different temperatures, to convert them into energy, in the production of solid, liquid, or gaseous fuels. In comparison to incineration and gasification, pyrolysis occurs in the absence of oxygen, resulting lower CO_2 emissions and lower amount of toxic impurities [6, 7, 8]. A variety of catalysts [4, 11], reactor types [9], and temperature intervals [10] are described in the literature, but fine-tuning an efficient and selective pyrolysis process to narrow the product distribution for commercial production remains difficult. During pyrolysis, long-chain organic molecules are broken into smaller hydrocarbons, the produced pyrolysis oil can be used as fuel for turbines, boilers, furnaces, etc. Depending on the chemical structure, different plastics have different degradation temperatures. The thermal degradation temperature for common plastics starts at 350 ºC, but in the case of PVC the degradation temperature starts at 220 ºC; furthermore, obtaining the appropriate product (oil, gas or char) is heavily influenced by the operating temperature. In the case of PE and PP, without using any catalyst and applying a higher pyrolysis temperature, at 500 - 600 ºC, the resulting products are mainly C20+ hydrocarbons, as solid wax at room temperature. In the thermal cracking procedure of PE, the resulting product mixture is mainly C_1-C_4 (gases) and C_5-C_{10} non-aromatic hydrocarbons and waxes respectively [13]. A few research works have been reported on the pyrolysis of BOPP, however, mixed plastic waste of different multilayer plastics with a variety of catalysts, such as ZSM-5 zeolite, Ni/Al_2O_3, ZnO, etc., can be found in the literature [20, 21].

A lower temperature range is recommended, 300-500 °C if the desired product is liquid/ pyrolysis oil, and this condition is applicable for all plastics waste types [12]. Pyrolysis involving a feedstock, without any catalyst, can be considered the baseline of the pyrolysis processes, popularly referred to as thermal pyrolysis [22]. In non-catalytic pyrolysis, long-chain polymers are broken into smaller fractions, carbon-carbon linkage can be broken randomly, no rearrangement of the fragments occurs, resulting a wide distribution of products.

J. Lee and coworkers studied the low-density polyethylene (LDPE) waste pyrolysis conditions, both using H-ZSM-11 catalyst and without catalyst. The temperature range applied in the pyrolysis test was between 500 - 900 °C. Using the H-ZSM-11 catalyst, was observed increased pyrolytic gas and propylene yield, which was attributed to propane dehydrogenation promoted by the catalyst via monomolecular and protolytic pathways. In the case of non-catalytic pyrolysis, it was found that the distribution of the fuel-range hydrocarbons in the pyrolytic liquid was dominated by motor oil-range hydrocarbons, over 50% of the obtained product quantities [15]. The use of acidic H-ZSM-11 catalyst dramatically increased the yield of pyrolytic gas [14]. The quantities of pyrolytic gas in non-catalytic experiments did not exceed 30% even at high temperatures (900 °C) [15].

Compared to other solid waste, plastics have some unfavorable pyrolytic properties, such as low thermal conductivity, stickiness, low softening and melting temperatures; to achieve the most favorable product composition and minimize secondary reaction possibilities it is very important to use the appropriate pyrolysis reactor. Several reactor configurations have been proposed and developed to minimize heat transfer limitations and avoid common processing issues in the waste plastics pyrolysis [16, 17, 18].

The batch reactor producing pyrolysis oil available on the market is produced by a Japanese company; in this equipment PS, PP, and PE can be pyrolyzed at a relatively low temperature, producing high yields of pyrolysis oil [19].

The most widely used equipment for pyrolysis oil characterization is GC-FID/MS, an analytical method that can provide precise chemical compositions, and quantitative content as well. Fourier Transform Infrared Spectroscopy (FT-IR) is also used to analyze the pyrolysis oils and the wax/ char product. The C-H stretching vibrations of the -CH_3, -CH_2, and -CH groups appeared at 2800–3000 cm^{-1}; the presence of olefins can be identified due to the presence of C=C stretching vibration bands, which can be observed at approximately 1640–1650 cm^{-1}.

The factors that influence the oil conversion rate are: the type of plastic (PE, PP, PS, BOPP), the quality and quantity of additives and the proper temperature range of the pyrolysis process. The main objective of this study was to evaluate the pyrolysis process and the obtained products, using a commercially available pyrolysis batch reactor in a non-catalytic process for the valorization of plastic waste to fuel-range chemicals.

Characterization of plastic waste and pyrolysis product

Product Analysis

The obtained pyrolysis oil was characterized using different techniques such as GC-MS and FT-IR; the physicochemical and thermal characteristics of pyrolysis oil were analyzed using ASTM methods. The caloric values of pyrolysis oil from different types of plastic waste were measured following the standard ASTM D240 [30] method with a Bomb Calorimeter (Parr 6200 Calorimeter) instrument. The flashpoint was determined using a Cole-Parmer Koehler K16000 Pensky-Martens automatic analyzer. The density was measured using a DMA 4500 densimeter. Three replicates measurements were performed. Aniline point or "aniline point temperature," is the lowest temperature (°F or °C) at which equal volumes of aniline ($C_6H_5NH_2$) and the resulting oil form a single phase. The relative aromatic content of the oil is indicated by its aniline point, determined with an aniline point apparatus.

The results of these measurements for each pyrolysis oil are summarized in Table 1. The density of obtained pyrolysis oil from PE and PP ranged from 0.72-0.76 g/cm^3, which is lower than diesel density (0.7999g/cm^3), but a higher density value was obtained in the case of PS, which was 0.92 g/cm^3. The flash point of a liquid fuel is defined as the lowest temperature at which the vapors above the liquid ignite when an external flame is applied. It is considered an important parameter in fuel handling to prevent fire hazards during storage. The flash points of the liquid fractions start at 21 °C for PE and 37 °C for BOPP, respectively which are comparable with light petroleum distillate fuels. The flashpoint values for the obtained pyrolysis oils are much smaller than in the case of diesel, which corresponds to the data found in the literature [23].

The aniline point measurement is useful in order to determine the presence of aromatic compounds in fuel samples. The aniline point temperature in highly aromatic samples is low, 21.7 °C for the pyrolysis oil obtained from PS; however, in other liquid products this value is much higher, indicating low concentration in aromatic compound fractions.

The calorific value is one of the most important characteristics used to evaluate the quality of fuel for future applications. Calorific values of pyrolysis oil obtained from various plastic waste vary from 36.67 KJ/g-45.10 KJ/g, the lowest value was obtained in the case of BOPP; these values are found to be similar to those reported in the literature [20].

Table 1. Physicochemical and thermal properties of the obtained pyrolysis oil.

S. No	Param.	Unit	PE white	SD*	PE with ink	SD*	PS	SD*	PP transp.	SD*	BOPP with ink	SD*
1	Density (at 20°C)	g/ cm^3	0.7596	0.031	0.7648	0.027	0.9252	0.045	0.7631	0.052	0.7251	0.058
2	Flash point	°C	22	0.520	21	0.630	30	0.487	22	0.358	37	0.421
3	Gross Caloric Value	KJ/g	44.78	1.342	42.48	1.536	41.81	0.943	45.10	1.502	36.67	1.605
4	Aniline point	°C	72.2	2.557	67.8	1.867	21.7	1.056	67.6	1.842	57.7	2.067
5	I.D. (diesel index)		86.83	-	80.65	-	47.57	-	81.09	-	84.65	-

*SD was calculated from triplicate analysis results

Chemical fingerprinting of pyrolysis oil

The chemical composition of pyrolysis oil was performed through GC-MS (Shimadzu equipped with an AOC-20i+s injector, and a ZB-Wax MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness, Phenomenex). The temperature of the injector was set to 285 °C and the MS transfer line was set to 220 °C. The oven temperature was held at 40 °C, for 15 min, then programmed to rise from 40 °C to 320 °C, at 5 °C/min, and held at this temperature for 15 min. The carrier gas was helium (99.99990% from Linde), at a constant flow rate of 0.80 mL/min. The injection volume was 1 μL, made in split mode (50:1). The detector was set to electron impact mode (EI, 70 eV) with an acquisition range (m/z) from 35 to 800 in scan mode. NIST (NIST 27, 147 libraries) mass spectral database was used to compare the mass spectra of the unknown organic compounds and the peak percentages were assessed for their total ion chromatogram (TIC) peak area.

The functional groups in pyrolysis oil were confirmed by FT-IR measurements, Bruker Vector 22 instrument. The analysis was performed using 20 scans with an average of 4 cm^{-1} IR signals, within the wavenumber range 500-4000 cm^{-1}.

The presence of aliphatic/ aromatic compounds in pyrolysis oil was also confirmed by NMR (^1H, ^{13}C) measurements in deuterated chloroform used as the standard for the chemical shift δ= 7.27 ppm for ^1H and δ=77.0 ppm for ^{13}C, on Bruker Avance 600 MHz spectrometer.

RESULTS AND DISCUSSION

Pyrolysis product yield (oil, wax, and gas) was estimated based on the weight obtained for the wax and oil at the end of the pyrolysis process, which is given in Figure 1.

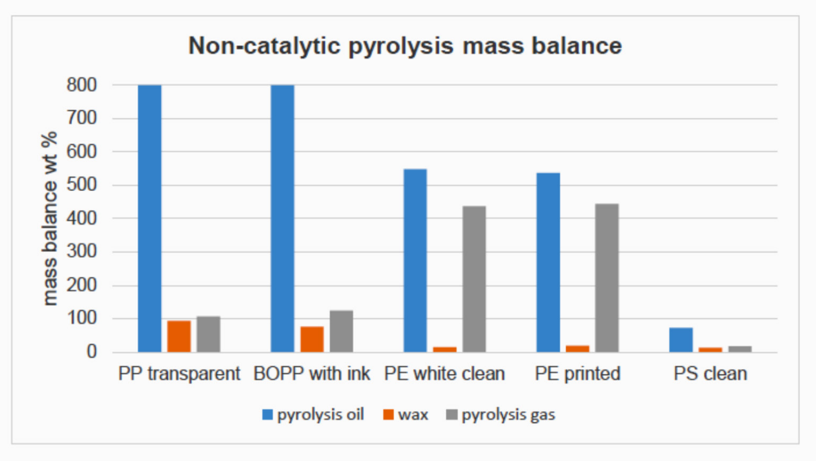


Figure 1. Pyrolysis product yield, using plastic waste in pyrolysis experiments.

In the case of thermal pyrolysis (without catalyst) the ratio of the obtained products is influenced by the initial plastic waste, and the used ink on plastic has little influence on the pyrolysis product amount. The input quality of waste plastics determines the quality and quantity of desirable products. The yield of the liquid fraction obtained from PP waste PP (~80%) is similar to the value described in the literature [24].

The obtained char from the waste plastics pyrolysis varied in the range of 5-45%, depending upon the type of plastic used. The percentage of char formation seems to be higher in the case of PE white and printed. The amount of char in the case of PP and BOPP is almost identical. The yield distribution of three product types (oil, char, and gas) in the case of PS pyrolysis is 72.2%, 14.8%, and 13%, respectively, which are comparable with data reported in the literature obtained using catalysts [26]; the liquid product is the main pyrolysis product in both cases.

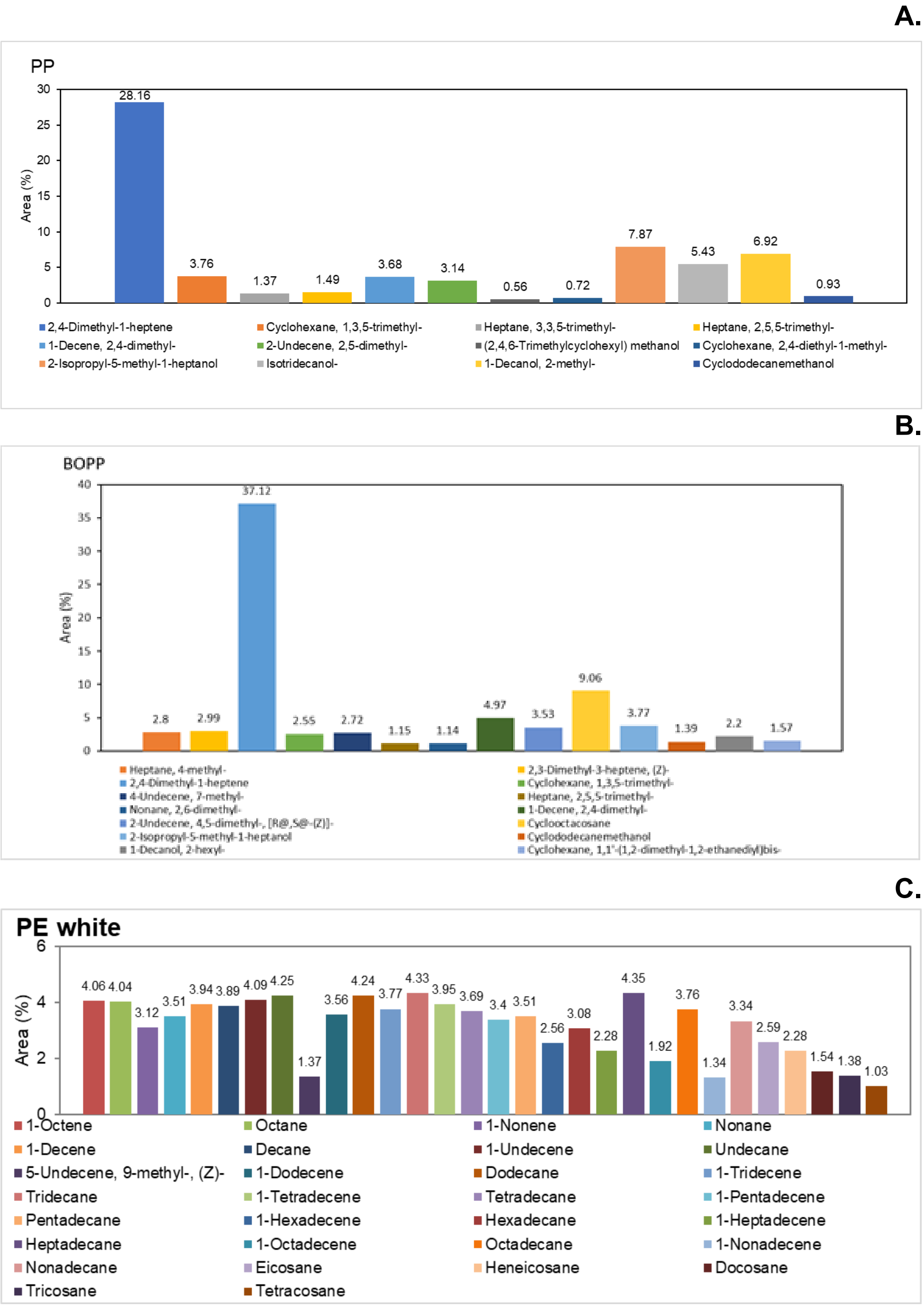
The obtained wax from PE pyrolysis is brownish with high viscosity at room temperature, the char from PP pyrolysis is blackish with a non-compact structure, and are predominantly composed of alkanes and alkenes hydrocarbons, which is also confirmed by FT-IR analysis.

Analysis of pyrolysis oil through GC–MS showed significant production of a large fraction of unsaturated hydrocarbons including linear alkenes (dienes, trienes). Mid-chain b-scission reactions of midchain secondary alkyl radicals are generally responsible for the formation of linear alkenes.

From the pyrolysis of PP, a complex mixture of liquid oil containing saturated hydrocarbons and olefins can be obtained. Aromatic compounds are obtained when the pyrolysis took place in presence of a catalyst; in our case, without using a catalyst, in the GC/MS analysis no aromatic compounds were detected. Supriyanto et al. [26] proposed a mechanism in which they explained the PP pyrolysis products formation, including the formation of 2,4-dimethyl-1-heptene (~28%), the main compound found in PP oil (Fig. 2. A). The presence of 2,4-dimethylhept-1-ene in high yield can confirm that, during the thermal decomposition of polyolefines, the isomerization reaction is widely preferred. Taking account that the raw material for BOPP is polypropylene (PP), the resulting pyrolysis oil in the same condition, yielded the same product, but in higher yield of 2,4-dimethyl-1-heptene 37% (Fig. 2. B). The main components of pyrolysis oil from BOPP are largely the same as those of PP oil.

The liquid fuel can be classified into light ($C_7 – C_{11}$), middle ($C_{12} – C_{20}$), and heavy ($C_{21} – C_{36}$) fractions [27]. In the composition of pyrolysis oil obtained from PE (white, and with ink) no aromatic compounds could be identified. The components of the liquid fuel were mainly 1-alkenes and n-alkanes ranging from C_8 to C_{24}. In the sample obtained from PE white (Fig. 2. C), the most abundant alkanes are C_8, C_{11}, C_{13}, and C_{17}; these compounds are present in large quantities (<4%). However, the specific component proportions of the liquid fuels were different. The most abundant saturated hydrocarbon contained in the sample obtained from PE with ink (Fig. 2. D) is C_{15} (<5%), and the middle fraction is in a larger quantity (<50%). Based on GC/MS analysis no saturated branched hydrocarbons could be detected in any of the PE pyrolysis oil as described by E. Hajekova and coworkers, which explained the formation of linear hydrocarbons using the free-radical mechanism of thermal degradation [28].

The PS pyrolysis oil (Fig. 2. E) contains a major compound, in these conditions, more than 68% is the monomer, styrene, and the other resulting compounds are also aromatic compounds; toluene and ethyl benzene also appear in lower concentrations - between 5-10%.


A.
PP
Area (%)
30
25
20
15
10
5
0
28.16
3.76
1.37
1.49
3.68
3.14
0.56
0.72
7.87
5.43
6.92
0.93
2,4-Dimethyl-1-heptene
Cyclohexane, 1,3,5-trimethyl-
Heptane, 3,3,5-trimethyl-
Heptane, 2,5,5-trimethyl-
1-Decene, 2,4-dimethyl-
2-Undecene, 2,5-dimethyl-
(2,4,6-Trimethylcyclohexyl) methanol
Cyclohexane, 2,4-diethyl-1-methyl-
2-Isopropyl-5-methyl-1-heptanol
Isotridecanol-
1-Decanol, 2-methyl-
Cyclododecanemethanol
B.
BOPP
Area (%)
40
35
30
25
20
15
10
5
0
2.8
2.99
37.12
2.55
2.72
1.15
1.14
4.97
3.53
9.06
3.77
1.39
2.2
1.57
Heptane, 4-methyl-
2,3-Dimethyl-3-heptene, (Z)-
2,4-Dimethyl-1-heptene
Cyclohexane, 1,3,5-trimethyl-
4-Undecene, 7-methyl-
Heptane, 2,5,5-trimethyl-
Nonane, 2,6-dimethyl-
1-Decene, 2,4-dimethyl-
2-Undecene, 4,5-dimethyl-, [R@,S@-(Z)]-
Cyclooctacosane
2-Isopropyl-5-methyl-1-heptanol
Cyclododecanemethanol
1-Decanol, 2-hexyl-
Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-
C.
PE white
Area (%)
6
4
2
0
4.06
4.04
3.12
3.51
3.94
3.89
4.09
4.25
1.37
3.56
4.24
3.77
4.33
3.95
3.69
3.4
3.51
2.56
3.08
2.28
4.35
1.92
3.76
1.34
3.34
2.59
2.28
1.54
1.38
1.03
1-Octene
Octane
1-Nonene
Nonane
1-Decene
Decane
1-Undecene
Undecane
5-Undecene, 9-methyl-, (Z)-
1-Dodecene
Dodecane
1-Tridecene
Tridecane
1-Tetradecene
Tetradecane
1-Pentadecene
Pentadecane
1-Hexadecene
Hexadecane
1-Heptadecene
Heptadecane
1-Octadecene
Octadecane
1-Nonadecene
Nonadecane
Eicosane
Heneicosane
Docosane
Tricosane
Tetracosane

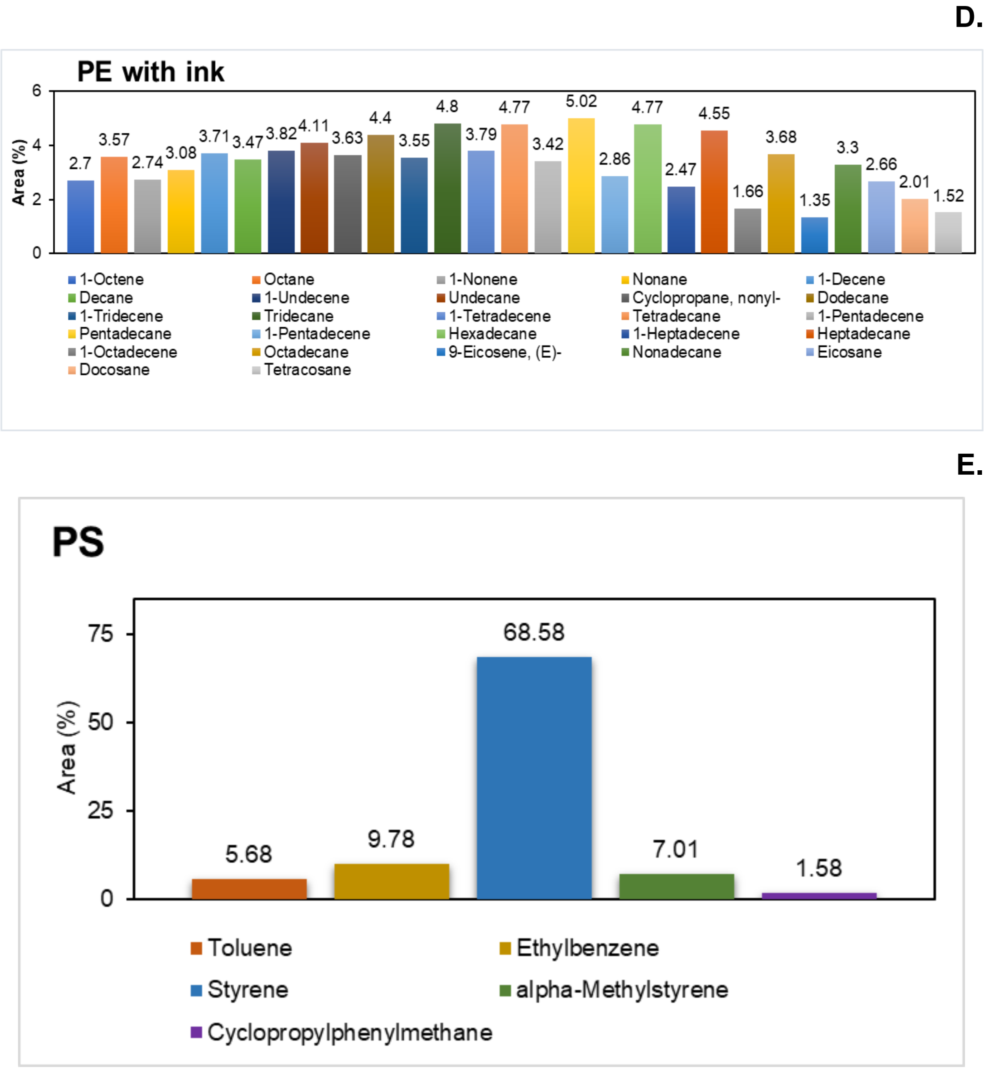


Figure 2 A-E. Distribution of compounds in pyrolysis oil based on GC/MS analysis

According to GC/MS analysis, pyrolysis of PE-type plastic waste led to more than 50% saturated hydrocarbons; the presence of printing inks has little effect on the quality of the compounds in the oil. In the case of PP and BOPP pyrolysis oil, the major components were unsaturated hydrocarbons, while most of the PS pyrolysis oil consists in aromatic compounds, with a high percent of styrene (Fig. 3).

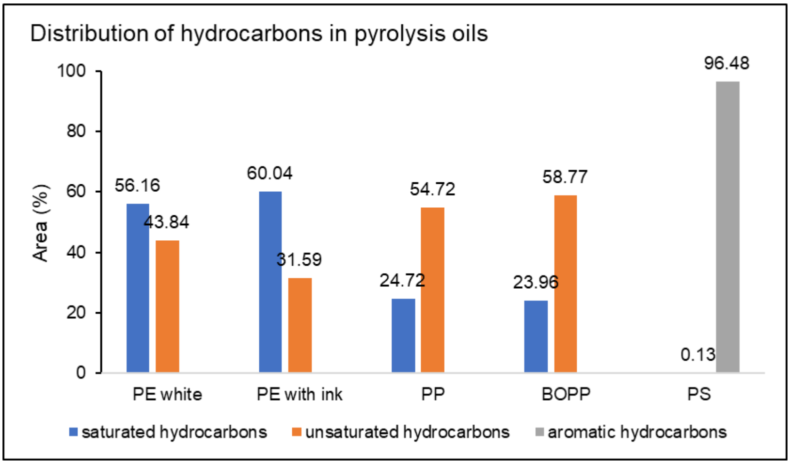


Figure 3. Distribution of hydrocarbon types in pyrolysis oil based on GC/MS analysis

The chemical composition of pyrolysis oil, by different functional groups, was studied using FT-IR. The obtained data corroborated with GC-MS measurements revealed the presence of aliphatic functional groups in the PE, PP and BOPP pyrolysis oil, and aromatics in PS oil respectively (Fig. 4).

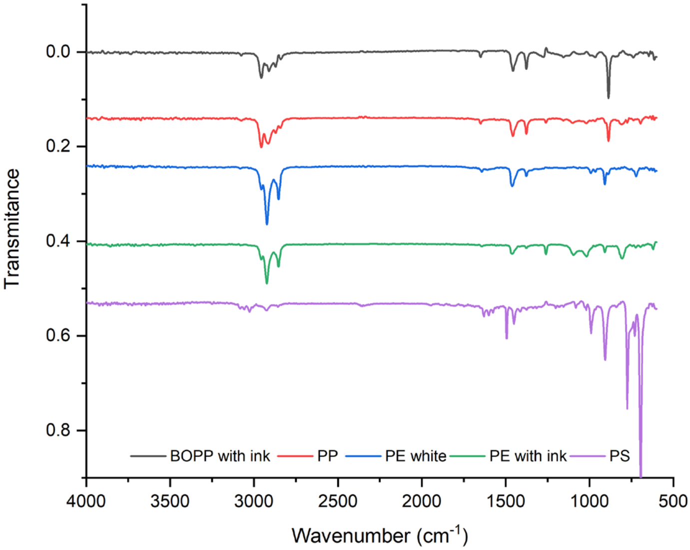


Figure 4. Comparison of FT-IR spectra of pyrolysis oil obtained from different raw materials

The observed peaks at 2853, 2923, and 2956 cm^{-1} confirmed the presence of the CH stretch of alkanes, and 1465 cm-1 CH scissoring from saturated hydrocarbons, which was identified in all of the pyrolysis oils from PE (Table 2). The aromatic hydrocarbon's presence was confirmed by the observed peak at 3026 cm^{-1} corresponding to the =C-H stretch, 1493 cm^{-1} C=C stretch, 1456 cm^{-1} C-C stretch from the aromatic ring, and 695 cm^{-1} for C-H also from aromatic compounds (Table 2).

Table 2. FT-IR data of liquid oil obtained from non-catalytic pyrolysis.

Peaks (cm^{-1})	PE white	PE with ink	PP	PS	BOPP with ink	Bond	Functional group
695	X	X	✓	✓	✓	C-H “oop”	Aromatics
965	✓	✓	✓	X	✓	C=C bending	Alkenes (disubstituted, trans)
1377	✓	✓	✓	✓	X	=C-H bend	Alkenes
1456	X	X	✓	✓	✓	C-C stretch	Aromatic (ring)
1465	✓	✓	X	X	X	C-H scissoring	Saturated CH
1493	X	X	X	✓	X	ring C=C stretch	Aromatics
1640	✓	✓	✓	✓	✓	C=C stretch	Alkenes
2853	✓	✓	✓	X	✓	C-H stretch	Alkanes
2923	✓	✓	✓	X	✓	C-H stretch	Alkanes
2956	✓	✓	✓	X	✓	C-H stretch	Alkanes
3026	X	X	X	✓	X	C-H stretch	Unsaturated

The obtained residues (wax) were also analyzed by FT-IR measurements, and the identified peaks from 2965, 2921, and 2854 cm^{-1} C-H stretch, 1470, and 1465 cm^{-1} C-H scissoring were attributed to alkanes. Peaks from 1381 cm^{-1} are associated with =C-H bend from unsaturated hydrocarbons (Fig. 5). The resulted degradation products were influenced by the structure of the original polyolefin. The PP-derived wax is more branched as compared with PE-derived wax [28].

The ^{1}H NMR spectra of PP and BOPP pyrolysis oil showed no difference, indicating that their chemical composition is quite similar (Fig. 6. b and d spectra). Pyrolysis oil from PP (Fig. 6. b) presents chemical shifts ranging from 0.82 to 4.70 ppm for all protons. In the aromatic region of the spectra no signals were observed, that could be associated with aromatic protons. The doublets from 4.70 ppm are known as the terminal double-bonded protons of the methylidene group.

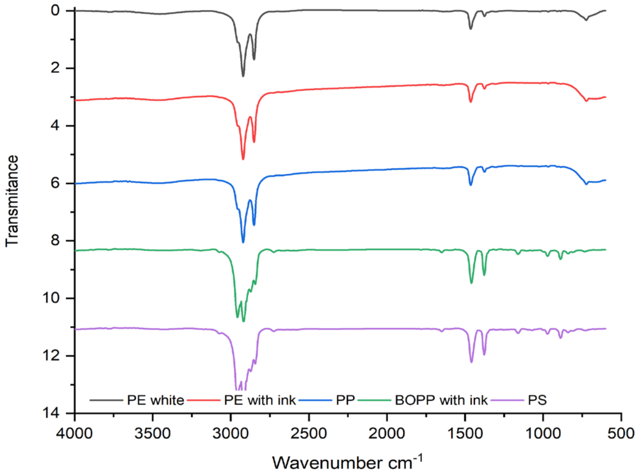


Figure 5. Comparison of FT-IR spectra of pyrolysis residue obtained from different raw materials

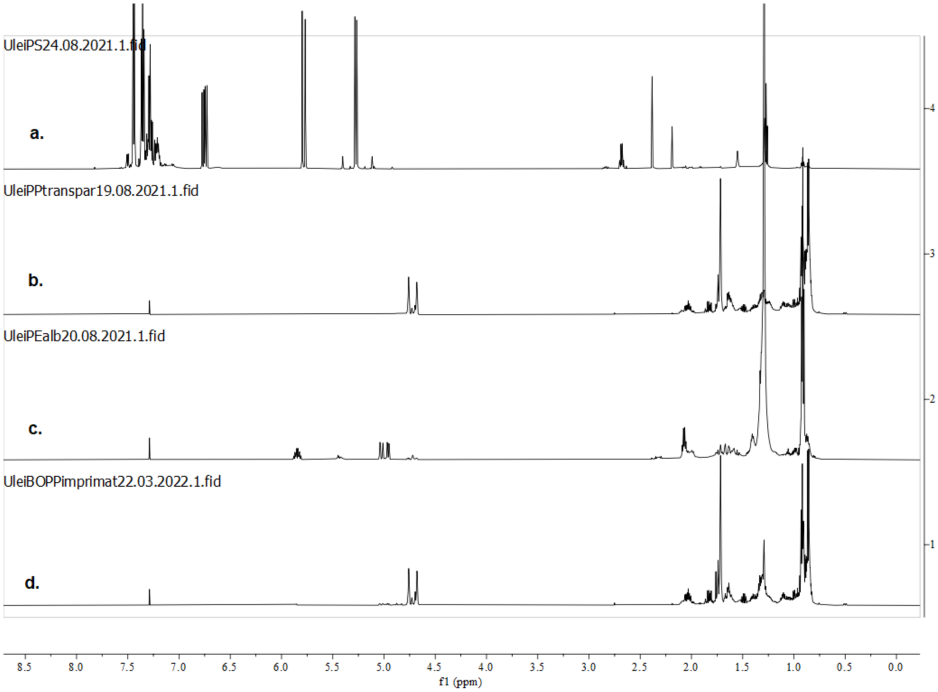


Figure 6. a-d Comparison of ^{1}H NMR (*CDCl*$_3$, 600MHz) spectra of pyrolysis oil obtained from different raw materials: a - PS oil; b - transparent PP oil; c - white PE oil; d - BOPP with ink oil

The multiplet signals at 4.92–5.01 ppm and 5.78–5.85 ppm observable in oil samples from PE (Fig. 6. c.) were assigned to protons of the vinyl end group. In this region of spectra, other signals from vinylidene and vinylene, cannot be observed.

The 1H NMR spectra sown in Fig. 6. a., displayed typical peaks for a monosubstituted aromatic ring (7.44-7.26 ppm) and the vinyl moieties (5.78 ppm and 5.27 ppm two doublets, and 6.74 ppm doublet of doublets).

In the ^{13}C NMR spectra (Figure 7) we have observed signals between 100 and 120 ppm, which corresponds to the alkene sp2 hybridized carbon atoms. Signals corresponding to chemical shifts of 109, 111.3, 111.4, and 145.1 ppm could be assigned to the sp^2 hybridization carbon atoms. Also, we have concluded that the carbon atoms of the pyrolysis oils with chemical shifts from 14.4 to 46.0 ppm could be assigned to paraffinic carbon atoms, these signals are present in the PE, PP, and BOPP pyrolysis oils (Fig. 7. b, c, d).

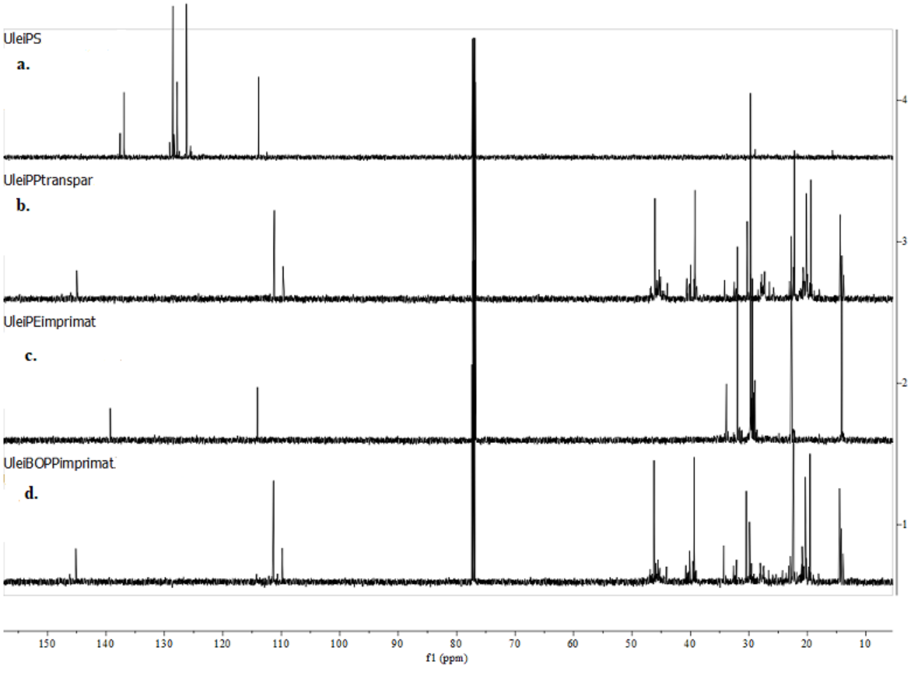


Figure 7. a-d Comparison of 13C NMR (CDCl3, 150MHz) spectra of pyrolysis oil obtained from different raw materials: a - PS oil; b - transparent PP oil; c - white PE oil; d - BOPP with ink oil

The aliphatic carbon signals are absent in the PS sample, which is supported by previous analyses. In the case of the PS sample, the aromatic region of the spectra contains specific signals corresponding to styrene, ranging from 125 to 137 ppm and an alkene signal at 113 ppm for the sp^2 hybridized carbon atom (Fig. 7. a). The spectral data obtained show that the pyrolysis products contains unsaturated compounds. According to the literature [29], the signals between 100–150 ppm can be assigned to α-alkenes in the case of paraffinic samples.

CONCLUSIONS

Non-catalytic pyrolysis of various polyolefins (PE white, with ink, PP, PS) and multi-layer plastic (BOPP) waste samples were investigated experimentally, using plastic oil maker equipment, available on market. The quantities of oil, gas and char/ wax obtained from different plastics have been analyzed. Due to the waste plastic's inorganic content and the unconverted plastic left behind from insufficient pyrolysis, a solid yield was obtained. Pyrolysis oils have been physiochemically characterized, the calorific value of oil varies between 36- 45 KJ/g depending on the plastic quality, similar to conventional diesel. As a result, after further treatment and refining, pyrolysis oils have the potential to be used in a variety of energy and transportation applications. The flash point values of the pyrolysis oils are much lower than the diesel flash point, this property can be improved by removing lighter components from the pyrolysis oils. Hydrocarbon fingerprinting of pyrolysis oil has been determined using GC–MS, FT-IR, and ^{1}H ^{13}C NMR respectively, in order to understand the feasibility of using it. The analysis of the composition of the oil fraction originating from PE and PP using gas chromatography/mass spectrometry (GC-MS) confirmed the formation of both linear alkanes and alkenes ranging from C_8 to C_{24}. Styrene can be obtained in a high yield (68%) from the PS pyrolysis, the obtained monomer after treatment can be reused for further polymerization and/ or to obtain other valuable chemicals.

The results of this study will contribute to develop more industrially feasible pyrolysis processes for the treatment of plastic waste.

EXPERIMENTAL SECTION

Materials and methods

Plastic waste, PE white, PE with ink, PP transparent, and BOPP with ink were collected from label printing equipment used at the Rottaprint company, a label printing leader in Romania.

Pyrolysis reactor and experimental setup

Batch pyrolysis experiments were carried out in a plastic oil maker, Be-j, equipment (Fig.1), manufactured in Japan, Nagata Shigyo Co., Ltd. 1 kg of polyolefin plastic waste was fed into the pyrolizer's inner chamber, which is surrounded by a stainless-steel outer compartment. The temperature measurement was performed using a thermocouple in the top and bottom of the pyrolizer inner chamber. The temperature range was maintained at 400-450 °C interval for the thermocatalytic depolymerization of different types of plastics. The equipment's processing ability is approximately 0.7- 1.0 kg/ a time in absence of oxygen. The cracked hydrocarbon vapors from the inner chamber were passed through the gas tube (Fig. 8) and bubbled in water, where the pyrolysis oil was collected. The noncondensable exhaust gases from the thermal oxidizer were passed on a filter and conducted to a fume hood. The pyrolysis experiments were repeated twice; in each case 1 kg of plastic waste was weighed, shredded into pieces of 2−5 cm size and was used without further treatments in the pyrolysis experiment, except polystyrene in which case only a smaller amount was introduced in the reactor due to its large volume. The obtained oil was collected from the oil collector tank (Fig. 8), and further characterization was carried out to reveal its chemical composition and

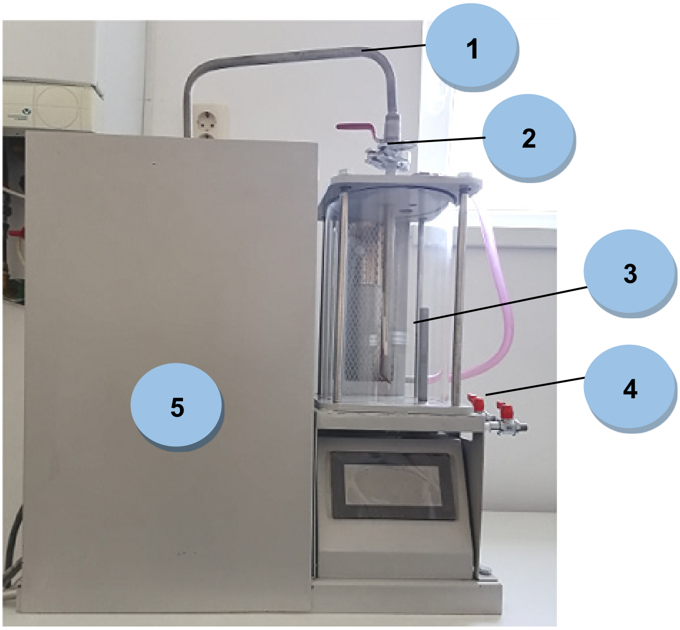


Figure 8. The used plastic oil maker, Be-j, equipment Components:
1. Gas tube; 2. Anti-counter current valve; 3. Water tank; 4. Oil taking valve;
5. Pyrolysis chamber, with stainless steel outer chamber.

characteristics for other potential applications. The obtained yield of each pyrolysis product (oil and wax) in wt % was calculated after the completion of each experiment. The produced liquid oil/ wax characterization was carried out in order to investigate the effect of feedstock composition on the quality of the obtained products.

Fig. 8 illustrates the pyrolysis equipment used in these experiments. The reactor is a 1000 ml bench-scale batch reactor. The waste plastics (non-printed and printed) were collected from the printing plant, 1 kg was used in each experiment, excepting the case of polystyrene, where was used 200 g of raw material. The equipment used does not permit to perform the experiment into an inert atmosphere. The water tank was filled up to the mark with water (2 L). After the raw material was loaded into the reactor, the top of the reactor was sealed using screws. The reactor was heated from room temperature (20 °C) to the target temperature of 450°C in each experiment. Subsequently, the reactor was maintained at the target temperature for 3.5 h, the condensed pyrolysis oil was drained from the tank. The reactor was cooled to 20 °C and the residue was collected and weighed.

The pyrolysis experiments were repeated twice. Following the completion of each experiment, the yield (wt%) of each pyrolysis product was calculated, the collected oil and the wax from each experiment were analyzed as it was described above.

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