Utilization of liquid product through pyrolysis of LDPE and C/LDPE as commercial wax

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Research Article

Keywords: C/LDPE, LDPE, pyrolysis, waste, wax

Posted Date: February 24th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-231058/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on April 22nd, 2021. See the published version at <https://doi.org/10.1007/s11356-021-13999-z>.

Abstract

Background

In this study, pyrolysis of low-density polyethylene (LDPE) and LDPE with aluminum (C/LDPE) wastes was carried out with different heating rates (5-10-20°C/min) at different temperatures (400-600-800°C). The effect of temperature and heating rate on liquid product yield was investigated. Product yields of LDPE and C/LDPE wastes were compared, and optimum liquid products were analyzed to utilize as commercial waxes for future use.

Methods

To determine the parameters of pyrolysis wastes was investigated with proximate, elemental analysis, and TGA. The as-produced liquid from pyrolysis of wastes was characterized by different characteristic tools, such as elemental analyses, GC-MS analyzes, ¹H-NMR tests, FT-IR spectra, the density, melting point, and carbon residue to compare commercial waxes. The characterization process was continued for the parameters with the optimum liquid products.

Results

As a result of pyrolysis, the highest liquid product yield was achieved at 800°C with 5°C/min heating rate (85.87 %), and at 600°C with 5°C/min heating rate (71.3 %) for LDPE and C/LDPE, respectively. The results indicated that the derived liquid products are similar to commercial heavy wax.

Introduction

Plastics are used in various industrial and domestic applications as they are lightweight, hard, durable, and low-cost materials (Pramanik and Gaurh 2019). In recent years, economic and population growth have increased the demand for plastic products and raw materials used in their production, as well as increasing plastic applications in many sectors such as packaging, construction, healthcare, electronics, and automotive (Al-Salem et al. 2017). It has been observed that the demand for plastics has grown faster in the last two decades. Global plastic production was 348 million tons in 2017 (Plastics Europe 2018) and a 75 % increase has been reported since 2000 (Das and Tiwari 2018). The plastic wastes are bulkier than the organic residues and a large part of these wastes do not degrade. High continuous demand for plastics, causes plastic wastes to accumulate in landfills, take up a lot of space, and also environmental hazards (Dwivedi et al. 2019). Mass consumption of plastic threatens the lives of not only marine animals but also humans. Waste plastics must be reused or recycled to protect the ecosystem (Park et al. 2019). Post-use waste plastic is appropriate for recycling (Schneider et al. 2017) and they can be grouped in different kinds of waste plastics such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyamide (PA), polyvinyl-chloride (PVC) (Dwivedi et al. 2019).

Polyolefinic plastics are important components of composite materials. Different types of plastics are combined in the production of composite materials and new products have superior properties. C/LDPE packages which are studied in this paper classified as plastic/aluminum since plastic content is more than aluminum content, the code of the package is abbreviated as LDPE. These materials are used particularly packaging of food products like soups, coffee, dried fruits, etc. However, when these materials become waste, they are also difficult to recycle due to the different ingredient contents. Thermal degradation is a good alternative for these types of waste.

The thermal decomposition method is generally used in the recycling of waste plastics into products with potential application areas as a result of pyrolysis under different operating conditions (Gaurh and Pramanik 2018). Several researchers published articles regarding the pyrolysis process of polyethylene for liquid production. Yang et al. (2016) was investigated the fast co-pyrolysis of LDPE and three kinds of biomass by comparing the product yield and properties of liquid products. They obtained the maximum liquid product at 600 °C of biomass or LDPE pyrolyzed alone. The peak positions of liquid product from the co-pyrolysis were very similar to that from LDPE pyrolysis alone. However, the inorganic elements in biomass improved the decomposition of LDPE. The synergistic effect in the fast co-pyrolysis improved the hydrocarbon content, resulting in the upgrading of oil quality. Jixing et al. (2003) studied the converting process of plastic PE wastes to PE wax. They investigate the pyrolysis process conditions including pyrolysis temperature, retention time, additive materials effect on product yield. Researchers achieved the yield of PE wax is over 90 % and also PE waxes quality such as melting point, penetration degree is obtained. Sharuddin et al. (2018) reviewed the pyrolysis of plastic waste for liquid fuel production as a prospective energy resource. The end product was investigated to optimize yield and properties. Shah et al. (2010) pyrolyzed LDPE in a batch reactor under atmospheric pressure using different catalysts like ZnO, MgO, CaC₂, SiO₂, Al₂O₃, and a mixture of SiO₂ and Al₂O₃. LDPE wastes were converted to liquid product, at 400 °C with 12.0 ± 0.2 % maximum yield. They observed that below the optimum catalyst weight conversion into liquid oil was minimum, while the higher weight of catalyst leads to higher gaseous product. Williams (2006) made a comprehensive comparison of the yield and composition of gas and oil/wax products from different waste plastic types. He reported waxes have high purity and valuable to produce high-grade liquid fuels, and also depending on polymer type, the oils may contain precious feedstock chemicals for use in the petrochemical industry.

Wax is produced as the main product by pyrolyzing polyolefin plastics such as LDPE at average temperatures such as 600 °C and different heating rates (Arabiourrutia et al. 2012). Waxes derived by thermal degradation of polyolefins can be used as an additive and modifier with high calorific value such as fuel produced from waste materials such as wood and biomass, and as fuel in candles and lights. The molecular weight of waxes with high chemical resistance and low viscosity below the melting point ranges from a few hundred to several thousand g/mol (Urbaniak et al. 2007).

Lately, synthetic hard paraffin and polyethylene waxes have gotten importance. Synthetic hard paraffin is a wax obtained from carbon, oxygen, and hydrogen. Polyethylene waxes are hydrocarbon compounds acquired by controlled thermal decomposition of polyolefins in the presence of neutral gases. The molecular mass of such waxes that do not decompose during the thermal decomposition is lower than the molecular

mass of the raw material and is a mixture of high paraffin hydrocarbons and input material. (Urbaniak et al. 2007). Waxes are long-chain hydrocarbons heavier than C_{20} , and those have between 20 and 36 carbon atoms are considered as light waxes (the boiling point between 300 °C and 500 °C) and those with more than 36 carbon atoms are heavy waxes (Lasek 2018). Several authors reported the oil and wax mixture existed jointly because waxes usually contain liquid hydrocarbons dissolved or vice versa the liquid hydrocarbons contain waxes (Lopez et al. 2017).

There are many studies on pyrolysis of low-density polyethylene wastes in the literature, however, according to the authors' best knowledge, there has been no study in the literature related to pyrolysis of composite LDPEs (C/LDPE). Based on C/LDPE waste while the properties of the pyrolysis liquid product obtained from LDPE waste are compared with commercial waxes, the changes in the pyrolysis of LDPE, which are frequently used in composite packaging with the addition of aluminum, are also examined.

Experimental Methodology

2.1 Characterization of waste materials

In the present study waste LDPE and C/LDPE was supplied to a local coffee shop which was used as food packaging. Before experiments, analytical samples with a size of 10 x 10 mm were prepared from the waste sample for smooth feeding. The characteristics of waste LDPE and C/LDPE have been determined via proximate, elemental, and TGA analysis.

As a part of the proximate analysis of waste LDPE and C/LDPE, when determining moisture, ash, volatile matter, and fixed carbon contents were used ASTM D-3173-85, ASTM D-3174-82, ASTM D-3172-73, and ASTM D-3175-82, respectively. The moisture content was determined by the weight loss that a sample undergoes after it has been heated at a temperature of 110 °C for 1 h. The determination of the volatile matter is an empirical test in which the loss in weight experiences by 1 g of sample is estimated in the crucible at 950 °C temperature for 7 min is estimated. Ash content is the residue that remains after the sample from the moisture analysis were placed in the cold ash oven and heated gradually until 700-750 °C within 4 hours.

The elemental analysis which is performed to determine the relative ratios of the five elements (C, H, O, N and S) that make up the organic structure of the waste was performed using a LECO TruSpec CHN and S. Thermogravimetric analysis of the waste LDPE and C/LDPE were carried out with a SETARAM, Labys TG-DTA/DSC instrument. 25 mg of waste LDPE was heated up to 1000 °C at a constant heating rate of 10 °C/min with Ar.

2.2 Pyrolysis

The pyrolysis setup used in this experiment is shown in Fig 2. According to the earlier literature studies, pyrolysis studies were carried out at different temperatures (400-600-800 °C) and three different heating rates (5, 10, and 20 °C/min). 10 g of waste LDPE and C/LDPE prepared as an analytical sample was filled in a fixed bed stainless steel 240 cm³ reactor for each pyrolysis. At the atmospheric pressure, the nitrogen gas

was introduced into the reactor at the rate of 300 mL/min to ensure there is no oxygen in the reactor. The products of pyrolysis were next separated. Liquid phase was collected in a cold trap placed in an ice bath maintained at about 0 °C. The liquid product accumulated in the cold trap was taken by washing with dichloromethane (DCM) solvent and the remaining amount was determined by removing the solvent with a temperature of 40 °C and 40 rpm in the IKA rotary evaporator. The amount of solid product was determined by weighing the residue remaining in the reactor chamber. The collected liquid products were calculated by weighing. Gas yield results were calculated by mass difference using at least three test averages. Yield results are given on a dry ash-free basis.

2.3 Characterization of liquid products and commercial waxes

The liquid products derived from LDPE and C/LDPE were characterized for composition. In addition to FT-IR, ¹H-NMR, and GC-MS, liquid properties determined included density, melting point, carbon residue, and viscosity. The same analyzes were carried out for "heavy wax" and "bright wax" obtained from a commercial production plant, and all results were compared with the products.

The compositional functional group analysis of the samples was carried out by using a Shimadzu IR Tracer 100 FT-IR which has data processing and spectral library search facilities. The ¹H-NMR of the samples was obtained at a Bruker 500 MHz Ultra Shield. The sample was dissolved in chloroform-d. The chemical composition of the wax/oil products was characterized by GC-MS. The samples were fractionated with hexane and DCM in silica gel column, and GC-MS analyzes of prepared fractions were performed in Shimadzu brand GCMS-QP2010 Plus System. The device has a feature that TRB 5-MS with a thickness of 0.25 µm, a capillary column of 30 m x 0.25 mm, and helium as the carrier gas at a flow rate of 1.2 mL per minute. For sample analysis, calibration was made using certified alkane and PAH standards (Dr. Ehrenstorfer, Alkanes Mix 10, lot no. 90703TO; Dr. Ehrenstorfer, PAH Mix 16, lot no. G127042AL) The samples were analyzed by methods created for alkane and PAH standards, and the quantifications of the compounds present in the samples were done according to the calibration graphs.

The density, melting point, and carbon residue were determined according to ASTM D4052, ASTM D127, and ASTM D4530, respectively. In density determination after weighing a vessel with known volume, it was filled with the samples and weighed again. In the calculation of melting point, the sample was placed on a watch glass and the sample was slowly melted until the temperature reached at least 10 °C above the expected drop melting point.

For the determination of carbon residue, the sample of 1 g was fed into crucibles. The sample was kept in the ash oven at 100 °C for 30 minutes, and the temperature of the ash oven was increased to 350 °C after 30 minutes. The sample was kept at 350 °C for 45 minutes were taken from the ash oven.

For the viscosity, the sample, which was melted in a chamber in rheology measurement (Anton-Paar MCR 102), was placed in the test cavity containing a double conical disc under continuous high temperature and positive pressure. Force was applied to the sample with the help of a piston and the capillary with a certain length and diameter was passed through the mold at different constant sliding speeds (0,1- 100 s⁻¹). Flow

curves of the material (change of apparent viscosity with shear rate) were determined as a result of these measurements.

Results And Discussion

The proximate analysis of samples was performed to determine the parameters of the pyrolysis process as moisture, volatile matter, ash content, and fixed carbon. The results of proximate analysis and elemental analysis results of waste LDPE and waste C/LDPE are shown in Table 1. The samples have high carbon and hydrogen content as expected due to their polymeric structure. It is noteworthy that C/LDPE has a lower carbon and volatile matter content and higher ash content than LDPE due to its aluminum content. According to the result of the literature review about LDPE elemental analysis results, a fixed carbon ratio is not expected or is observed in very low amounts (Sharuddin et al. 2016). Nevertheless, contrary to what is expected a fixed carbon may be in wastes LDPE (Das and Tiwari 2018). The oxygen in the wastes sample may be due to the ingredients that are added to the resin in the manufacturing of LDPE.

Table 1 The proximate and elemental analysis results of waste LDPE and waste C/LDPE.

Sample	Waste LDPE	Waste C/LDPE
Moisture (%)	0.05	<0.001
Ash (%)	1.05	18.37
Volatile matter (%)	98.62	80.71
Fixed carbon (%)	0.28	0.92
Element (%)		
C	75.69	65.68
H	11.25	10.23
O ^a	11.06	5.22
N	<0.001	0.56
S	<0.001	<0.001

^a calculated from the difference.

Thermogravimetric analysis was used to observe the relationship between temperature and mass change of the waste and allowed the understanding of the mechanism of thermal decomposition and reaction during pyrolysis. TG curves show the mass loss of the sample depending on temperature during thermal degradation and DTG curves show the corresponding mass-loss rates of the TG curves. The TGA results are represented in Fig. 3. When TGA curves are examined, LDPE and C/LDPE have almost the same tendency, which is proof that they have the same pyrolysis behavior due to similar chemical bonds in their molecular structures. The weight losses show that the degradation of plastics occurs almost totally in a one-step

process. The TG and DTG curves showed simple results that the degradation in wastes begins at 400 °C and continues up to 520 °C, and when the DTG curve is looked at, the greatest mass loss occurs between 450-500 °C. Since chemical bonds break more easily at higher temperatures, as the temperature rises, a large amount of volatile matter evaporates and an equal mass loss of about 97 % occurs for LDPE (Fig 3a). It was found that LDPE formed a very small amount of solid residue and almost degraded completely (the solid residues were approximately 1 %). The decomposition range was narrow, and the decomposition domain was much more intense. The thermal degradation of C/LDPE took place between 375 and 500 °C, and, when the temperature reached 480 °C, the degree of thermal degradation reached the maximum. The apparent peak seen in the TG curve of C/LDPE (400-450 °C) is thought to be due to PET in the waste content. In addition, some mass losses are seen in the DTG curve of LDPE before the temperature of 400 °C, which indicates the presence of some additives in the waste LDPE. The amount of solid residue (20 %) of C/LDPE waste is higher than that of LDPE. This difference is thought to be due to the aluminum content of C/LDPE remaining undegraded. Further 20 % of C/LDPE wastes are non-volatile fractions, 80 % are volatile fractions (Fig 3b). The volatile matter for all plastics is very high. These characteristics indicate that waste package plastics (LDPE and C/LDPE) have a high potential to produce large amounts of waxes/oils using a pyrolysis process.

3.2 Product yield of the pyrolysis

Product yield graphs obtained from pyrolysis of waste LDPE and C/LDPE are given in Fig. 4-5. The highest liquid product of 85.87 % was obtained at the temperature of 800 °C and a heating rate of 5 °C/min result of the pyrolysis of LDPE. The high temperature does not allow the lower molecular weight hydrocarbon to remain in the reactor for a longer time. Thus, they collected as a liquid product. Considering the yield results, similar yields were obtained in the 600 °C temperature band for both waste LDPE and C/LDPE, but after 600 °C, aluminum contained in C/LDPE caused an increase in degradation of the sample, served as a catalyst, and yield of liquid decreased obviously, while that of gas increased reduced as in similar studies (Liu 2013). The highest liquid product yield for C/LDPE (71.3 %) at 600 °C temperature and with a 5 °C/min heating rate is obtained. For LDPE, the maximum liquid yield is achieved at 800 °C with 5 °C/min. LDPE and C/LDPE liquid product properties were determined in the pyrolysis conditions, where the highest liquid product yield was obtained, to compare with the next stage of the study, commercial waxes.

3.3 Analysis of the liquid product

The elemental analyses of liquid products of wastes and commercial waxes are shown in Table 2. Elemental analysis results indicate mainly the presence of carbon and hydrogen for all, N and S percentages are quite small. Also, according to the elemental analysis results, the oxygen contents of wastes are seen both in the initial analysis (Table 1), and in the product obtained after pyrolysis. When the liquid products obtained after pyrolysis were compared on LDPE and C/LDPE basis, it was observed that the carbon content of C/LDPE was slightly higher than LDPE since the aluminum content in C/LDPE acts as a catalyst and enhances the degradation. There was no significant difference in the chemical composition of the liquid products which obtained from pyrolyzed wastes, depending on the heating rate and temperature, and they are similar in themselves. However, it is different from commercial waxes.

Table 2 Elemental composition of liquid products for wastes and commercial waxes.

			Composition						
Sample	Heating rate (°C/min)	Temperature (°C)	C (%)	H (%)	O (%)	N (%)	S (%)	Atomic H/C ratio	Atomic O/C ratio
LDPE	5	400	77.36	12.32	10.32	<0.001	<0.001	1.911	0.100
		600	70.02	11.59	18.39	<0.001	<0.001	1.986	0.197
		800	69.91	11.82	18.27	<0.001	<0.001	2.029	0.196
	10	400	79.96	12.48	7.56	<0.001	<0.001	1.873	0.071
		600	77.87	12.41	9.72	<0.001	<0.001	1.912	0.094
		800	77.30	12.80	9.90	<0.001	<0.001	1.987	0.096
	20	400	77.01	12.20	10.79	<0.001	<0.001	1.901	0.105
		600	80.77	12.85	6.38	<0.001	<0.001	1.909	0.059
		800	76.54	12.35	11.11	<0.001	<0.001	1.936	0.109
C/LDPE	5	400	81.07	12.12	6.81	<0.001	<0.001	1.794	0.063
		600	82.94	12.26	4.80	<0.001	<0.001	1.774	0.043
		800	82.98	12.35	4.67	<0.001	<0.001	1.786	0.042
	10	400	81.71	12.62	5.67	<0.001	<0.001	1.853	0.052
		600	82.70	12.60	4.70	<0.001	<0.001	1.828	0.043
		800	83.04	12.38	4.58	<0.001	<0.001	1.789	0.041
	20	400	81.91	12.47	5.62	<0.001	<0.001	1.827	0.051
		600	81.45	12.46	6.09	<0.001	<0.001	1.836	0.056
		800	80.82	12.37	6.81	<0.001	<0.001	1.837	0.063
Commercial heavy wax			81.68	17.92	0.40	<0.001	0,40	2.633	0.004
Commercial bright wax			83.42	16.39	0.19	<0.001	0,19	2.358	0.002

Fractions of the samples of the highest liquid product yields (5 °C/min heating rate and 800 °C for LDPE; 5 °C/min heating rate and 600 °C for LDPE), commercial heavy wax and bright wax were confirmed by GC-MS. The gas chromatogram shows triplets aliphatic hydrocarbons containing alkenes, alkanes, and alkadienes with the same carbon number (see Figure S1-S2). The pink peaks show that the liquid product they obtained from the pyrolysis of LDPE is mostly composed of alkanes and the other peaks indicate the presence of alkenes and alkadienes with the same carbon number (Williams and Williams 1999). Nevertheless, since the largest peaks are alkanes, they were quantified. Aliphatic fractions with n-hexane and aromatic fractions

with DCM of hydrocarbons with different carbon chain lengths of the liquid product derived from pyrolysis of LDPE and C/LDPE were determined. Results compiled in Tables 3-4. Table 3 shows that the liquid products were enriched in hydrocarbons predominately C₂₀ to C₃₅ ranging from 35.67 to 38.48 %, while the bright wax and heavy wax were 45.14-83.98 %. In similar studies in the literature, it has been observed that the liquid products of LDPE were found to be consist of mainly C₈ – C₃₀ hydrocarbons. For example, Williams and Williams (1999) obtained a liquid product consisting of a high proportion of aliphatics as a result of the pyrolysis of LDPE. Ahmad et al. (2015) reported that the pyrolysis liquid of polyethylene consists of 59 % alkanes. Cit et al. (2010) observed that the liquid product they obtained from the pyrolysis of LDPE at 700 °C was mostly composed of alkanes. All hydrocarbon compounds in the liquid products obtained are heavy hydrocarbons and derivatives (Cit et al. 2010; Sarker et al. 2012). According to the GC-MS results, liquid products show more similar properties to heavy wax. Polyaromatic compound analysis results in Table 4 shows that heavy wax is mainly composed of naphthalene, fluorene, and phenanthrene. When it comes to pyrolysis products, heavier aromatics also becomes more significant.

Table 3 Alkane fractions (%) in liquid products and commercial waxes.

		LDPE	C/LDPE	Commercial	Commercial
		5 °C/min 800 °C	5 °C/min 600 °C	Heavy wax	Bright wax
Alkane	Compound Formula	%	%	%	%
n-Decane	C ₁₀ H ₂₂	0.59	0.44	-	3.06
n-Undecane	C ₁₁ H ₂₄	1.74	0.99	-	2.97
n-Dodecane	C ₁₂ H ₂₆	2.18	1.33	0.04	2.92
n-Tridecane	C ₁₃ H ₂₈	2.34	1.46	0.04	2.76
n-Tetradecane	C ₁₄ H ₃₀	0.18	0.20	0.04	-
n-Pentadecane	C ₁₅ H ₃₂	0.23	0.24	0.04	2.76
n-Hexadecane	C ₁₆ H ₃₄	0.21	0.24	0.05	2.97
n-Heptadecane	C ₁₇ H ₃₆	0.19	0.23	0.05	2.92
n-Octadecane	C ₁₈ H ₃₈	0.20	0.25	0.05	2.90
n-Nonadecane	C ₁₉ H ₄₀	0.23	0.26	0.08	3.05
n-Eicosane	C ₂₀ H ₄₂	0.24	0.32	0.18	-
n-Heneicosane	C ₂₁ H ₄₄	0.23	0.27	0.45	-
n-Docosane	C ₂₂ H ₄₆	0.31	0.37	0.84	3.69
n-Tricosane	C ₂₃ H ₄₈	0.32	0.38	1.25	3.85
n-Tetracosane	C ₂₄ H ₅₀	0.30	0.35	1.80	3.91
n-Pentacosane	C ₂₅ H ₅₂	3.46	3.86	2.16	4.06
n-Hexacosane	C ₂₆ H ₅₄	0.11	0.22	2.82	4.40
n-Heptacosane	C ₂₇ H ₅₆	0.32	0.23	3.73	3.36
n-Octacosane	C ₂₈ H ₅₈	3.22	0.25	4.79	4.85
n-Nonacosane	C ₂₉ H ₆₀	0.09	0.22	6.20	5.28
n-Triacontane	C ₃₀ H ₆₂	4.65	6.00	8.24	5.61
n-Hentriacontane	C ₃₁ H ₆₄	3.19	6.84	11.20	-

n-Dotriacontane	$C_{32}H_{66}$	4.65	6.42	10.99	-
n-Tritriacontane	$C_{33}H_{68}$	5.48	6.45	10.77	-
n-Tetratriacontane	$C_{34}H_{70}$	4.85	6.09	10.16	-
n-Pentatriacontane	$C_{35}H_{72}$	4.25	0.19	8.39	6.13
Total hexane fraction		43.76	44.12	84.37	71.47

Table 4 PAH fractions (%) in liquid products and commercial waxes.

		LDPE	C/LDPE	Commercial	Commercial
		5 °C/min 800 °C	5 °C/min 600 °C	Heavy wax	Bright wax
PAH	Compound Formula	%	%	%	%
Naphthalene	C ₁₀ H ₈	-	0.39	0.16	0.41
Acenaphthylene	C ₁₂ H ₈	0.10	0.12	-	-
Acenaphthene	C ₁₄ H ₈	-	-	-	-
Fluorene	C ₁₃ H ₁₀	0.20	0.42	0.16	-
Phenanthrene	C ₁₄ H ₁₀	0.37	0.31	0.18	-
Anthracene	C ₁₄ H ₁₀	-	0.13	-	0.46
Fluoranthene	C ₁₆ H ₁₀	0.19	0.16	-	-
Benz(a)anthracene	C ₁₈ H ₁₂	0.19	0.18	-	-
Pyrene	C ₁₆ H ₁₀	0.16	0.16	-	-
Chrysene	C ₁₆ H ₁₀	0.24	0.18	-	-
Benzo(b)fluoranthene	C ₂₀ H ₁₂	0.20	-	-	-
Benzo(k)fluoranthene	C ₂₀ H ₁₂	0.20	-	-	-
Benzo(a)pyrene	C ₂₀ H ₁₂	0.16	0.14	-	-
Dibenz(a,h)anthracene	C ₂₂ H ₁₂	0.14	0.14	-	-
Benzo(g,h,i)perylene	C ₂₂ H ₁₄	0.15	-	-	-
Indeno(1.2.3c.d)pyrene	C ₂₂ H ₁₂	0.12	0.13	-	-
Total DCM fraction		2.42	2.47	0.50	0.87

¹H-NMR tests were conducted on the liquid samples to characterize their properties. The ¹H-NMR spectrum and hydrogen distributions of the commercial waxes and liquid product obtained from pyrolysis of LDPE and C/LDPE in the highest liquid product yield conditions (see Figure S3-S4). ¹H-NMR results of the pyrolytic oils are given in Table 5. According to the H-NMR results, 72.72 and 71.16 % of the liquid products of LDPE and C/LDPE consist of aliphatics respectively. Approximately 28 % are phenolic, olefinic, and aromatic. It was observed that all (100 %) of commercial waxes consisted of aliphatics. From these results, impurities (especially olefins) contained in the liquid product can be seen.

Table 5 ^1H -NMR analysis results of liquid products obtained from pyrolysis of LDPE and C/LDPE wastes.

Type of hydrogen	Chemical shift, ppm	%			
		LDPE	C/LDPE	Commercial	Commercial
		5 °C/min	5 °C/min 600 °C	Heavy wax	Bright wax
		800 °C			
Aromatic	9 – 6.3	6.78	9.66	-	-
Phenolic (OH) or olefinic proton	6.3 - 4	20.50	19.18	-	-
Aliphatic adjacent to aromatic/alkane group	3 – 1.8	24.94	25.00	-	-
Other aliphatic (bonded to aliphatic only)	1.8 – 0.4	47.78	46.16	100.00	100.00

The FT-IR spectra of liquid products derived from LDPE and C/LDPE under optimum conditions showed similar configurations (Fig.6). The peaks at the 2850–3000, 1470, and 721 cm^{-1} wavelengths represent the chemical functional groups of $-\text{CH}_2-$ stretching, $-\text{CH}$ bending, and $-\text{CH}_2-$ rocking vibration of the aliphatic hydrocarbon, respectively. The presence of these peaks confirmed the presence of alkanes in the liquid products and commercial waxes. The presence C=C stretching at wavebands 1680–1600 cm^{-1} , confirms the presence of alkenes in the liquid products. Peaks between 1680-1700 cm^{-1} correspond to C = O bonds; represents ketones, aldehydes, or with the existence of the peaks between 1250-1310 cm^{-1} referring to the ester bond (C–O) stretch reveals the existence of carboxylic acids. Peaks between 700-1000 cm^{-1} represent C = C bonds and are indicative of alkenes and aromatics (Lee 1997; Waziri et al. 2019; Jia et al. 2020). As a result, no significant differences were observed in the FT-IR spectra of liquid products obtained as a result of pyrolysis of LDPE and C/LDPE wastes, both of which were largely made up of alkanes. However, supporting the H-NMR results, the presence of olefinic groups, ketones, aldehydes, and esters appear in pyrolysis liquids, unlike commercial waxes. Also, commercial waxes have more stronger peaks at 2900 and 2960 cm^{-1} corresponding to the CH_3 terminal group bonds, which is evidence that the liquid products obtained from this study are less branched chains than commercial waxes (Arabiourrutia 2012).

The density, melting point, and carbon residue for liquid products and commercial waxes are given in Table 6. According to the table, the density of C/LDPE liquid products is closer to the density of commercial waxes than LDPE. The chemical properties of polyolefins, such as their composition and bond structure, significantly affect the melting point. Therefore, in the examined liquid products, the material with the highest density (commercial heavy wax) has the highest melting point, while the lighter material (LDPE) has the lowest melting point (Arabiourrutia 2012). Knowing the melting point is essential for the use of waxes as phase exchange materials. The melting points of the resulting liquid products are in the range of values corresponding to the melting point of commercial paraffin waxes used as phase change material

(Vakhshouri 2019). Also, it was found that carbon residue was negligible in the case of LDPE and C/LDPE derived liquids.

Table 6 Density, melting point, and carbon residue determination results of liquid product

Liquid product	Density (kg/m ³)	Melting point (°C)	Carbon residue (%)
LDPE liquid products obtained at 800 °C with heating rate of 5 °C / min	0.817	60	0.22
C/LDPE liquid products obtained at 600 °C with heating rate of 5 °C / min	0.862	65	0.19
Commercial heavy wax	0.869	70	0.14
Commercial bright wax	0.864	65	0.11

The viscosity shear rate graphics obtained from the analysis results using the rheometer device are given in the Figure 7-9. Due to the physical properties of the bright wax, it could not be analyzed in the rheology measuring device. According to the viscosity results, it is seen that the viscosity values decrease with increasing shear rate and viscosity reaches the old level again with the shear rate decrease. As the sliding speed increases (100 s⁻¹), it is observed that the viscosity value drops below 200 Pa. This behavior shows that wax samples have a non-Newtonian flow property, In these fluids, viscosity decreases with shear rate. As a result, the resistance of this substance decreases as displacement increases. When the graphs are examined, it is observed that there is an increase in shear stresses (between 0 and 500 Pa) with an increase in the shear rate of the wax samples (between 0 and 100 s⁻¹). However, it was observed that the wax samples showed pseudoplastic flow characteristics, with the increase here not occurring linearly. Visible viscosities of fluids with pseudoplastic behavior decrease with increasing sliding speed and increasing shear stress. As a result, as the sliding speed increases, the resistance of the fluid to flow decreases.

Properties of liquid products and commercial waxes are summarized in Table 7. It has been observed that pyrolysis liquid products are less viscous than heavy wax due to olefinic and aromatic impurities in their structure. Impurities arising from such olefinic and aromatic components are removed by concentrated sulfuric acid alone or with the addition of silver sulfate and anhydrous phosphor pentaoxide, thus kinds of paraffin can be purified (Kincannon and Manning 1955). Besides, in the purification of waxes, oils trapped between the wax crystals are dissolved by using solvents such as methyl ethyl ketone, toluene, and propane. The mixture is filtered through filters to remove impurities from the wax crystals and the product wax is obtained (Yorulmaz 1983; Butler et al. 2011). Also, filtration processes using nanomaterials are used for decolorization and separation of solid residues (Missau et al. 2020; Missau et al. 2018).

Table 7 Summary of the characterization results for the liquid products and commercial waxes

Parameters	Important findings
Elemental analysis	It is noteworthy that the carbon content in the C/LDPE liquid product is similar to the commercial heavy wax.
Alkanes	Liquid products contain heavy alkanes similar to heavy wax.
H-NMR	The H-NMR results of the liquid products are similar, but they contain impurities.
FT-IR	There are not significant differences between liquid products but the presence of long carbon chain olefinic groups appears unlike commercial waxes.
Density	Density of the C/LDPE liquid product are similar to commercial waxes.
Melting point	The melting points of both liquid products are close to commercial bright wax.
Carbon residue	Carbon residue of the C/LDPE liquid product are similar to commercial heavy waxes.
Viscosity	The viscosities of liquid products are close to each other, but they are less viscous than wax.

Conclusion

In this study, LDPE wastes and composite LDPE wastes were pyrolyzed at different temperatures and heating rates in a fixed bed reactor which is an efficient technology for the recycling of polyolefin waste. The obtained liquid products and commercial waxes were analyzed, and the results were compared.

The highest liquid product yield was found to be 85.87% for LDPE at a heating rate of 5 °C/min at 800 °C. Aluminum in the C/LDPE content is thought to act as a catalyst, causing an increase in degradation. The highest (71.3 %) liquid product yield of the C/LDPE waste is obtained at 600 °C temperature and with a 5 °C/min heating rate. It has been observed that the volatile materials are very high for both types of waste. The main compounds in liquid products for both LDPE and C/LDPE are aliphatics. Impurities such as about 25% olefins were found in liquid products and very little aromatic was found. It is thought that the processes such as filtration can be used to remove these impurities. According to the GC-MS results, liquid products show more similar properties to heavy wax. LDPE, which has a lower density, has a lower melting point. The melting point and density of the liquid product of C/LDPE are like commercial wax and are within the melting point range of paraffin waxes. This can allow the liquid product obtained to be used as phase change material. Liquid products are less viscous than heavy wax due to olefinic and aromatic impurities in their structure. It has been observed that the process of removing impurities is needed before the liquid products obtained are used as a paraffin wax.

As a result, it was determined in this study that liquid products made of C /LDPE can be used instead of commercial waxes. Thus, a solution will be produced with a circular economy approach for such composite wastes, which are difficult to recycle and whose amount is increasing.

Declarations

Acknowledgement

This study was supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) under the grant number 117Y041 and Eskişehir Technical University Scientific Research Projects Commission under the grant number 1703F074. The authors also would like to thank to Anadolu University Medicinal Plants, Drugs and Scientific Research Center (AUBIBAM) and Ceramic Research Center staff for their technical support and Ece Yılmazbilek for experimental contribution.

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Figures

Figure 1

Flow chart of the study.

Figure 2

The schematic diagram of pyrolysis reactor

(a)

(b)

Figure 3

TGA-DTG curve (a) LDPE (b) C/LDPE

Figure 4

Product yields for pyrolysis of waste LDPE

Figure 5

Figure 6

FT-IR spectrums of liquid products and commercial waxes

Figure 7

Viscosity versus shear rate for LDPE liquid products

Figure 8

Viscosity versus shear rate for C/ LDPE liquid products

Figure 9

Viscosity versus shear rate for heavy wax

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