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THE PYROLYSIS OF PLASTIC WASTES CONTAINING OXYGEN

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ABSTRACT

This paper investigates the pyrolysis of five different oxygen-containing plastic wastes and evaluates the possibility of utilizing such plastics in transportation fuel production. Pyrolysis runs were performed in a batch reactor and the plastic waste types include polyethylene terephthalate (PET), polyoxymethylene (POM), polycarbonate (PC), polyvinyl butyral (PVB), and polyphenyl ether (PPE). Liquid products from PC, PVB, and PPE were further processed by atmospheric distillation to extract the 20-200 °C fractions. These fractions were analyzed by GC-MS to identify major compounds. PET and POM did not result in liquid products. Instead, solid deposits formed in the system, causing potential operational instability. Based on the results, three oxygen-containing plastic types were identified as promising candidates in liquid fuel production.

Keywords: pyrolysis, plastic waste, fuel

1. INTRODUCTION

Between 1950 and 2015, approximately 7,500 Mt of plastic was produced globally, of which 5,800 Mt is still present in the environment, mainly in landfills [1]. According to statistics, in 2010, 24.7 Mt of plastic waste was generated in the EU, with only 24.3% being recycled. By 2020, the amount of plastic waste had increased to 29.5 Mt, and while the recycling rate of 34.6% presents a slightly more favorable picture, the remaining waste was either landfilled or used for energy recovery (incineration) [2]. Untreated plastic waste can cause significant environmental damage, and therefore, alternative treatment methods are gaining interest in the three main pathways today (recycling, energy recovery – incineration, and landfilling). The thermochemical decomposition of various plastic wastes is one such alternative, allowing the production of synthetic fuels. Although the oils produced through this process have been examined from various perspectives, available publications highlight several barriers to the widespread adoption of fuel derived from plastic waste. One such barrier is the lack of reaching standard fuel requirements, which likely stems from the fact that different types of plastic yield fundamentally different oils. Additionally, the composition of the oil is highly dependent on operational conditions. Dai et al [3] published a review paper and concluded that there is a lack of publications regarding plastic-derived gasoline that reaches the same quality as fossil-based gasoline. Achieving this is likely to be a milestone in the widespread adoption of the technology.

Our previous studies showed that the refining of oils gathered from the pyrolysis PE (polyethylene), PP (polypropylene), and PS (polystyrene) waste blends is a promising pathway for standard fuel production [4], [5], [6]. However, there is a lack of information about other possible plastic types that could be potentially suitable for transportation fuel sources through pyrolysis and refinery, either in neat or blend form. However, previous investigations showed that reaching standard requirements such as EN 228 cannot be fulfilled by a single plastic type; therefore, blending of various plastics is crucial to reach standards. Additionally, the identification of plastic types that can be present as contaminants in solid plastic waste mixtures in cases of transportation fuel production is a primary objective. From this perspective, the investigation of oxygen-containing plastic waste types is a group of materials that can be utilized in such scenarios. In this study, the pyrolysis results of five plastic waste types, including polyethylene terephthalate (PET), polyoxymethylene (POM), polycarbonate (PC), polyvinyl butyral (PVB), and polyphenyl ether (PPE), are presented. PET is a frequently studied feedstock in terms of

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pyrolysis; among oxygen-containing plastics, most of the literature is available for PET. Compared to the pyrolysis of PP and PE, fewer paraffinic structures are formed, and the formation of aromatic hydrocarbons is more characteristic for PET. In addition, it results in a significantly higher amount of residual pyrolysis coke compared to the other two materials [7]. The pyrolysis of POM is often aimed at the recovery of formaldehyde monomer. Berkowicz et al. [8] investigated the pyrolysis and combustion of POM under various conditions. In a fluidized bed reactor, a monomer yield of up to 90 wt% was achieved at 400 °C. Higher temperatures favored gas formation. Among fluidizing agents, nitrogen proved most favorable for monomer recovery. Siddiqui et al. [9] investigated the thermal degradation mechanism and kinetics of PC. It was concluded that higher temperatures are more suitable for PC pyrolysis since the liquid and gaseous fractions are increased. The degradation of PVB using thermogravimetric analysis under a nitrogen atmosphere was investigated by Liau et al. [10], with the evolved gases identified via FT-IR spectroscopy. The major degradation products were butyraldehyde, 2-butenal, butanoic acid, acetic acid, 2,5-dihydrofuran, and butanol. PVB plastics are commonly used in composites containing glass particles or fibers. PPE is often referenced in the literature as a plastic alloyed with PS. Stack et al. [11] investigated the thermal degradation of PPE blended with three different molecular weights of syndiotactic PS. Using IR spectroscopy, it was shown that PPE undergoes chain rearrangement prior to weight loss, whereas the PS chains exhibit no significant changes. PS decomposition occurs at higher temperatures, and PPE degradation is accelerated compared to the pure polymer.

2. MATERIALS AND METHODS

A batch reactor (Fig. 1) equipped with a 1 kW electric heater was utilized for pyrolysis runs. The pyrolysis vapors were condensed in a water cooled heat exchanger while the gases were flared. The liquid pyrolysis oil (WPO – Waste Plastic Oil) was further processed by atmospheric distillation to separate the 20-200 °C fraction considered as gasoline range hydrocarbons. Each measurement started with flushing the reactor with nitrogen at environmental conditions (WPG – Waste Plastic Gasoline). The reactor was heated up to 500 °C, typically enough to complete the pyrolysis of plastic. A total of five different plastic types containing oxygen in their molecular structure were selected for pyrolysis runs, namely polyethylene terephthalate (PET), polyoxymethylene (POM), polycarbonate (PC), polyvinyl butyral (PVB), and polyphenyl ether (PPE). The ultimate and HHV analyses of these plastic waste types are summarized in Table 1. The source materials were collected from real-world waste plastic streams and crushed into 5-15 mm particle size before the pyrolysis runs. The molecular structure of the five feedstocks is shown in Fig. 2. Each material was utilized in neat form, i.e., without blending.

Samples were taken from the collected pyrolysis gases and analyzed with gas chromatography (model: Dani Master; TCD detector with three columns: Restek RT-Q-Bond 30 m 0.32 mm × 10 μm, Restek RT-Q-Bond 15 m 0.53 mm × 20 μm, and Restek RT-Msieve 5 A 30 m 0.53 mm × 50 μm; FID detector with 1 column: Rt-Alumina BOND/Na2SO4 30 m 0.53 mm × 10 μm). The hydrocarbons condensed in the water-cooled heat exchanger were stored in airtight containers at ~10 °C. Preliminary analyses of WPGs were performed utilizing GC-MS to qualitatively analyze the liquid composition (Agilent 7890 A GC; detector: Agilent 5975C MSD; column: Restek Rtx-DHA-150, 150 m × 0.25 mm ID x 1.0 μm df).

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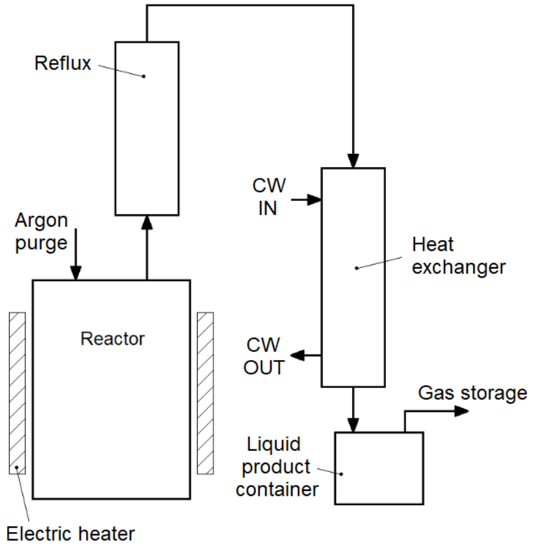

Figure 1. Schematic illustration of the pyrolysis system.

Table 1. Ultimate and HHV analysis of plastic wastes utilized in this research.

		Concentration, m/m%			
	HHV, MJ/kg	C	H	N	S
PET	22.7	63.48	4.65	0.05	<0.01
POM	17.4	40.09	6.82	-	<0.01
PC	26.8	75.26	5.68	-	<0.01
PVB	27.9	61.60	9.64	-	<0.01
PPE-PS	22.4	79.94	7.18	-	0.02

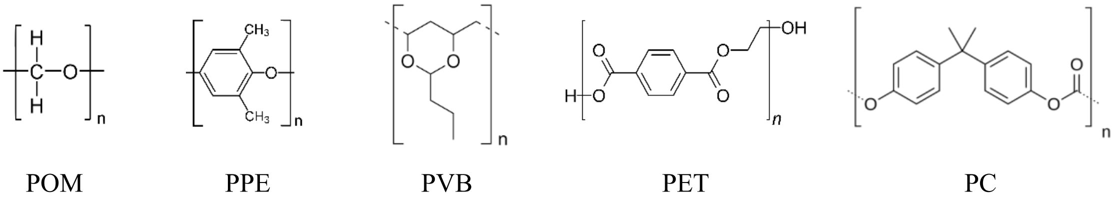

Figure 2. Molecular structure of plastic wastes utilized in this study.

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3. RESULTS AND DISCUSSION

The initial masses and the yield ratios of the pyrolysis products are summarized in Table 2. No liquid product was produced in the case of POM and PET, and therefore, these materials were not investigated further by distillation. Although a liquid product was not observed, a solid phase formed during the process for the two materials, threatening the operability of the piping system and creating a potential clog. The deposits appeared in the liquid collection vessel, the gas collection bag, the heat exchanger, and the general tubing. Based on the polymer's molecular structure, it is presumed that the snow-like solid material formed in large quantities is a decomposition product of POM, most likely paraformaldehyde, while the formation of benzoic acid is presumed in the case of PET. No signs of clogging were detected in the reactor piping in the cases of PC, PVB, and PPE. The solid residue from PPE and PC was brittle, porous, and hard to fracture. In contrast, the solid residue from PVB contained glass particles, originating from residual fragments in the windshield-derived PVB feedstock. These glass particles became concentrated in the pyrolysis solid residue, significantly lowering the HHV of the material. In addition to the glass, the remaining solid consisted of a black, fused mass, likely characterized by a high carbon content. The HHV values of pyrolysis solid residues for PC, PVB, and PPE were 34.9 MJ/kg, 12.2 MJ/kg, and 30.1 MJ/kg, respectively.

Table 2. Summary of mass balance.

	Unit	PET	POM	PC	PVB	PPE
Sample	g	95.0	91.0	153.8	200.0	200.0
Solid residue	m/m%	23.6	94.9	32.5	17.9	27.3
Pyrolysis oil (WPO)	m/m%	-	-	47.1	55.3	59.0
Pyrolysis gas	m/m%	76.2	5.1	20.4	26.8	13.7
20-200 °C fraction of pyrolysis oil (WPG)	g/kg_{oil}	-	-	274	515	580
	g/kg_{waste}	-	-	129	285	342
200+ °C fraction of pyrolysis oil	g/kg_{waste}	-	-	342	268	248

The pyrolysis of PPE resulted in a high oil yield, and the distillation also produced a significant amount of the 20–200 °C fraction, being 580 g/kg_{oil}. On the other side, WPG produced by PC was only 274 g/kg_{oil} and 129 g/kg_{waste}. The relatively low WPG yield in the case of PC can be elucidated by the fact that the pyrolysis oil contains a significant amount of 200+ °C fraction as well (Table 2). PVB resulted in a moderate amount of WPG being 285 g/kg_{waste}. The WPG products can be considered as an additive in the case of transportation fuel production from plastics, or even the utilization of such liquids in neat form is also possible. Therefore, the produced WPG streams were analyzed by GC-MS to obtain preliminary results about the composition of the liquids (Table 3). The WPG contains mostly oxygenated molecules, which can be originated from the initial plastic structure. The EN 228 standard for gasolines in the EU enables oxygen content to be present in the fuel up to 2.7 wt%. The limited allowed presence of an oxygen atom means that these WPGs can be utilized only as additives in transportation fuel. The amount of such an additive depends on the initial fuel properties. Based on these results it can be stated that the WPGs originated from PC, PVB, and PPE through thermochemical cracking are promising candidates as additives in plastic gasoline production.

Table 3. Major compounds identified in the WPG of PC, PVB, and PPE.

Feedstock	Compounds identified in WPG
PC	Phenol
	4-Methylphenol
	4-Ethylphenol
	Toluene
	Ethylbenzene
PVB	2-Ethyl-2-hexenal
	Butanal
	2-Butenal
	1-Butanol
	Diethylacetic acid
PPE	Ethylbenzene
	Toluene
	Phenol
	2,6-Dimethlyphenol
	2-Methlyphenol

4. CONCLUSIONS

This study investigates the pyrolysis outcomes of PET, POM, PC, PVB, and PPE plastic wastes from a standard transportation fuel point of view. PET and POM resulted only in solid and gaseous products with a potential clogging hazard, and therefore, these plastics are not recommended for such utilization. However, PC, PVB, and PPE resulted in a significant amount of oil being 47.1 wt%, 55.3 wt%, and 59.0 wt%, respectively. The pyrolysis oils were further processed by atmospheric distillation to extract the 20-200 °C fraction. These liquids, considered as gasoline-range hydrocarbons (WPGs), were analyzed by GC-MS to gather preliminary qualitative information about the composition. It was found that these WPGs contain oxygenates, which are strictly regulated by the EN 228 standard. Therefore, the utilization of WPGs originated from PC, PVB, and PPE is proposed to be used as additives.

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