

Plastic waste, as a source of alternative fuel

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Abstract

The environmental issues of plastic waste generation and accumulation present an increasingly serious global problem. While the demand for plastic products is growing, from the 29.5 Mt of collected waste in Europe only 35% was recycled, while 42% represents energy recovery and 23% was landfilled in 2020 [1]. Plastic pyrolysis provides a promising alternative method to utilize plastic waste as secondary raw material [2]. An advantage over traditional waste processing methods is the possibility to obtain valuable products with pyrolysis. The products obtained from thermal decomposition are the pyrolysis coke, gas and oil. GC-MS analysis showed that the composition of the plastic waste gasoline (PWG) derived from low- and high-density polyethylene, polypropylene and polystyrene show similarity to commercially available gasoline. It is possible to operate IC engines using PWG, however, certain parameters such as the olefin concentration do not meet the EN-228 European gasoline standard, therefore further refinement, such as hydrotreatment is needed to achieve standard quality. Another advantage of this method is the utilization of the gaseous pyrolysis product. The pyrolysis gas consists of high concentrations of combustible hydrocarbons with C1-C4 carbon numbers. In part the gas could be used to provide the energy requirements of the process.

Introduction

Plastic usage is on the rise globally. The reason behind this is the low production costs paired with versatile utilisation. However, the popularity of plastic products and packaging materials presents serious environmental and health hazards with the accumulation of plastic waste [3,4]. Between 1950 and 2015 approximately 7.5 billion tonnes of plastic were produced. Recycling and various other utilisations take up ~ 25% of this amount, which means more than 5 billion tonnes of plastic waste was landfilled, or otherwise discarded [5]. Of course, great improvements were made regarding plastic waste management. A 2020 report on the EU waste processing shows that of the collected waste 35% was recycled. While this is promising only 42% was utilized for energy recovery and 23% was still landfilled. These fractions could be processed through pyrolysis. Using plastic waste as raw material, pyrolysis can produce valuable hydrocarbon oils which can be recirculated into the chemical industry or even be eligible as transportation fuel, like gasoline.

The utilisation of high- and low-density polyethylene (HDPE, LDPE), polypropylene (PP) and polystyrene (PS) is beneficial to produce gasoline-like hydrocarbon oils. The pyrolytic oil from HDPE, LDPE and PP contains various hydrocarbons with diverse molecular mass distribution, while the thermal degradation of PS results almost entirely in aromatic compounds [6]. The pyrolytic oils from these plastics or their mixtures show promise as alternative fuels; however, the olefin concentration is usually between

30-55 Vol% or higher [7,8]. This amount is much higher than the 18 Vol% maximum permitted by the EN-228 European gasoline standard [9]. On one hand, the olefin content can improve the reactivity of the fuel and the octane number, but it can also decrease the engine lifespan and increase the emission of air pollutants like 1,3-butadiene which enhances photochemical smog formation [10]. Utilizing PS in the pyrolysis mixture can decrease the olefin concentration, but to achieve standard quality gasoline other methods must be applied, like hydrotreatment. This method employs hydrogen and catalysts to saturate the molecules with carbon double bonds. The hydrotreatment can be used at mild temperatures where the saturation of molecules can be achieved without significantly changing the boiling temperature of the components in oil. As only minor additional cracking can take place, it can be a beneficial method of the pyrolytic oil treatment.

This paper investigates the properties of plastic waste pyrolytic oils with boiling points in the 20-210 °C range obtained by atmospheric distillation from the pyrolysis of HDPE, LDPE, PP and PS materials and their mixtures. Hydrotreatment was also performed to investigate the possibilities of lowering the olefin concentration in oils. The composition of the pyrolysis gas obtainable from the various plastic types and the energy it could potentially provide was also investigated.

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Materials and Methods

The pyrolysis runs were performed in a laboratory-scale batch reactor (Fig. 1). An air-cooled primary heat exchanger or reflux is connected to the reactor. The primary role of the reflux is to adjust the pyrolysis gas temperature. Heavy hydrocarbons with a high boiling point are condensed to re-enter the reactor for further cracking, increasing the gasoline range hydrocarbon yield in the liquid product. Next, a water-cooled secondary heat exchanger is connected to the reflux, where the pyrolysis gas components with boiling points higher than the ambient temperature are condensed. The condensed oils and the light hydrocarbon gases are collected separately.

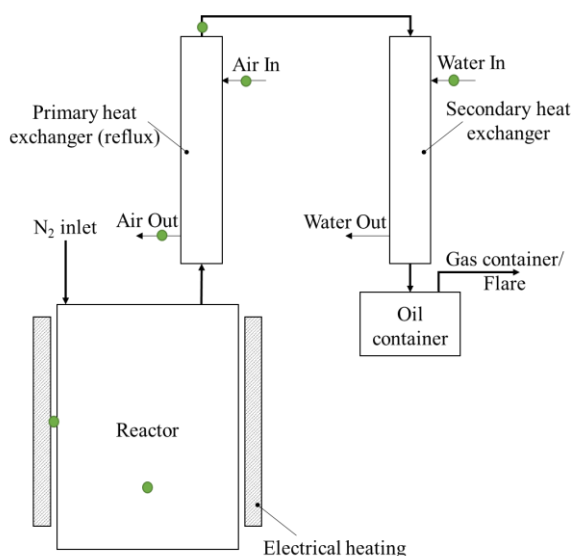


Figure 1. Schematic illustration of the experimental setup.

HDPE, LDPE, PP and PS plastic wastes were used with ratios summarised in Table 1. Six pyrolysis experiments were performed with various feed compositions. Samples I-IV were the individual plastic materials, while sample V and VI were mixtures, with and without PS content, respectively. The composition of the mixtures was determined by plastic production statistics to represent an average distribution of plastic waste generated in Europe [1].

The experiments were performed with 150 g of plastic waste material in each case. Starting from room temperature, the reactor was continuously

Table 1. Composition of the batches prepared for pyrolysis.

ID	HDPE wt%	LDPE wt%	PP wt%	PS wt%
I	100.00	-	-	-
II	-	100.00	-	-
III	-	-	100.00	-
IV	-	-	-	100.00
V	14.00	20.50	45.50	20.00
VI	17.50	25.62	56.88	-

heated to an endpoint of 530 °C, as all the plastic materials used were degraded by reaching that temperature [11].

The pyrolytic oils were separated into three fractions using atmospheric distillation. The yields were categorized by boiling temperatures into plastic waste gasoline (PWG) at the 210 °C cut, plastic waste diesel (PWD) at the 350 °C cut, and the residue containing heavy hydrocarbons with boiling temperatures above 350 °C.

The PWG of sample VI was hydrogenated separately (sample VI.H). The hydrotreatment was carried out at 350 °C reactor temperature, using 15 g of a catalyst with 3 g/kg Pd content on alumina support.

During the process, the feed rate of the oil sample was 30 ml/h with a 15 l/h continuous hydrogen stream. The composition of a reference gasoline sample (sample R.S.), purchased from a gas station (95 RON with 10 Vol% ethanol), the PWG obtained from the pyrolysis experiments and the separately hydrogenated sample were investigated by GC-MS.

Results and Discussion

The yield of the pyrolysis experiments and the atmospheric distillations are summarised in Table 2. The two highest oil yields are from the experiments with polystyrene and polypropylene, while the pyrolysis of the low- and high-density polyethylenes yielded a more significant gas fraction. The PS produced the most char and the least amount of gas. The reason for the product distribution is the molecular structure of PS and its behaviour during thermal degradation. The PS mainly produces styrene and toluene, with boiling points of 145.2 and 110.6 °C, respectively. The aromatic hydrocarbons are also prone to coking, which explains the higher amount of residual char.

The pyrolysis of HDPE yielded more oil and less gas than the LDPE, however, the distillation results show more similarity concerning the yield of PWG and PWD fractions. As these plastics have straight-chain molecule structures, the cracking process produces more diverse hydrocarbons, both light and heavy, as evidenced by the gas and distillation yields. The oil yields of the two mixtures are similar; however, the distillation of sample V resulted in more gasoline-range hydrocarbons, which may be attributed to the toluene and styrene content from the polystyrene.

Table 2. Pyrolysis and distillation yields.

ID	Product yields, wt%			Distillation yield, wt%		
	Char	Oil	Gas	PWG	PWD	Residue
I	0.87	70.47	28.67	50.40	37.56	8.08
II	2.73	62.07	35.20	53.01	37.78	4.51
III	2.93	79.60	17.47	63.73	31.17	3.71
IV	4.53	84.60	10.87	90.36	1.52	6.72
V	1.93	76.00	22.07	63.58	33.01	3.05
VI	2.07	75.20	22.73	58.59	34.12	4.12

The compositions of PWGs and the separately hydrogenated sample were compared to the reference gasoline sample. The ratio of different hydrocarbon types (expressed in Vol%) is shown in Table 3. On average, the pyrolysis oil fractions contain significantly more hydrocarbons with carbon double bonds than the reference sample, except for the distillate of the PS oil, which is almost entirely made of aromatic compounds. The 20-210 °C fraction of sample VI was further processed with hydrotreatment resulting in a PWG with reduced olefin concentration as can be seen in Table 3. Another difference in composition is the distribution of hydrocarbons respective to molecular mass, which also correlates with the boiling points.

Table 3. Hydrocarbon types of the various PWG and the R.S. samples.

ID	Olefin, Vol%	Paraffin, Vol%	Aromatics, Vol%
R.S.	10.06	63.47	26.47
I	70.51	28.32	1.13
II	70.65	27.84	1.50
III	75.28	24.43	0.29
IV	n.d.	n.d.	~100
V	46.06	22.72	31.21
VI	63.84	35.42	0.73
VI.H	0.62	95.70	3.68

The reference gasoline contains n-pentane and other C5 hydrocarbons in the highest amount (~40 wt%). The rest of the sample is nearly equally distributed into C6-C9 hydrocarbon groups, approximately 12 wt% each. The most similarity in the molecular mass distribution of gasoline fractions can be found in cases of samples I and II, however, the amount of C5 molecules (mainly 1-pentene in the gasoline fractions) is roughly halved, while the C6 hydrocarbons are doubled compared with the reference sample. The olefin content shows greater difference, as in samples

I and II are 70.51 and 70.65 Vol% was found, compared to the 10.06 Vol% in the gasoline sample. Additionally, a non-negligible, 1.13 and 1.50 Vol% aromatic content could also be found in samples I and II respectively. It may be beneficial, but in the case of mixed material pyrolysis it should be taken into account, not to exceed the 35 Vol% aromatic limitation of the EN-228 standard.

In the case of polypropylene, the difference is more pronounced. While PP pyrolysis resulted in more oil, and the distillation produced higher a 20-210 °C yield than the polyethylene samples, the resulting fraction might be unfavourable, especially with the higher (~75 Vol%) olefin content. The main component of the polypropylene gasoline fraction is 2,4-dimethyl-1-heptene, which regarding the European gasoline standard, may be detrimental in the case of the distillation requirements. Sample IV almost entirely consist of aromatic compounds, which is not applicable as fuel, however, the EN-228 standard permits 35 Vol% aromatic content, which can be provided by polystyrene in the pyrolysis feed as evidenced by the results of sample V. The 20 wt% PS resulted in 31 Vol% aromatic content which is within the allowed range of the EN-228 standard. The PWGs of the two mixtures (sample V and VI) show the qualities of the samples from the individual plastic pyrolysis experiments, indicating that feed composition heavily influences the molecular mass distribution and, therefore, the quality of the product.

The result from the separately hydrogenated gasoline fraction of sample VI showed that most of the hydrocarbons with carbon double bonds were saturated, as the olefin concentration was reduced to 0.62 Vol%.

The fuel quality may be further improved with the addition of different oxygenates permitted by the European gasoline standard. For example, adding tert-butyl alcohol in 15 Vol%, or ethanol in 10 Vol% can reduce the olefin concentration, therefore improving

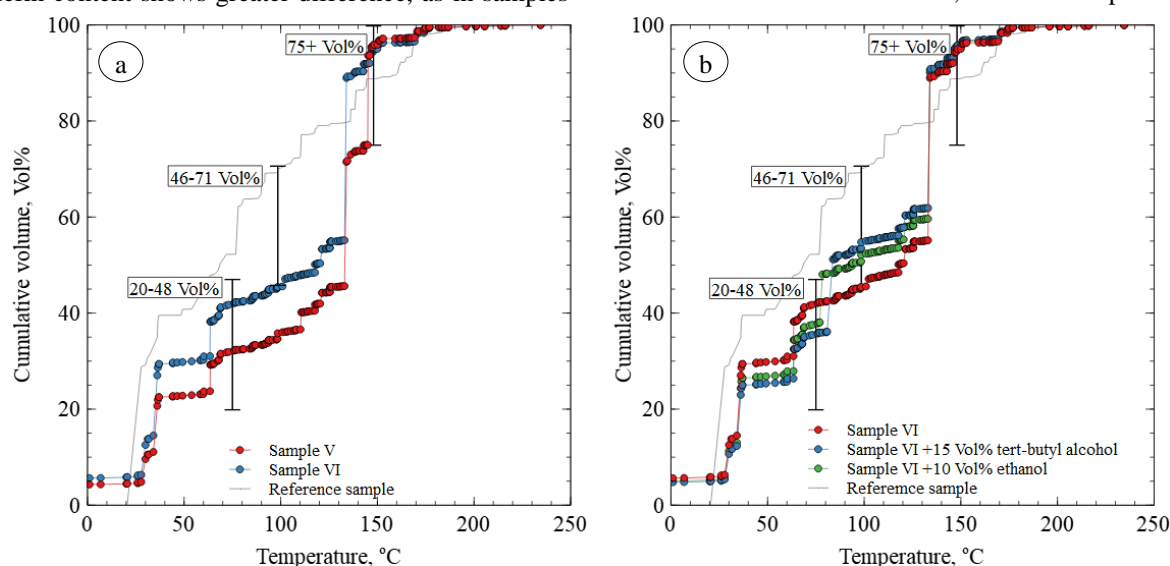


Figure 2. Distillation curves of sample V and VI PWG (a) and the effect of additives in the case of sample VI (b).

the fuel not only regarding the olefin concentration but the distillation requirements as well. The distillation curves are also heavily influenced by the feed composition of the pyrolysis.

The difference between the PWG distillation curves (calculated from the results of the GC-MS analysis) of sample V and VI and the effect of the oxygenates are shown in Fig. 2.

As it can be seen from the results of sample V and VI, neither could achieve the 100 °C distillation step, albeit sample VI came close with 45.56 Vol%, while in the case of sample V the volume decrease is only 36% at that temperature. The difference between the R.S. and the PWGs are evident. On one hand, the high concentration of 2,4-dimethyl-1-heptene, originating from the PP, and in the case of sample V the 31.21 Vol% aromatic content, which is mainly the product of polystyrene, shifts the intensity of the volume decrease to the 100-150 °C range. The addition of oxygenates however, could reinforce the low boiling point fraction of PWG, as both ethanol and tert-butyl alcohol has lower boiling point, 78.37 and 82 °C respectively. As the EN-228 permits the addition of tert-butyl alcohol in 15 Vol%, it could be especially effective in improving the fuel quality.

The gaseous products of the experiments were also investigated. The composition of gases from sample V and VI are shown in Table 4.

Table 4. Composition of the gaseous products in the case of sample V and VI.

Components	Limit of detection (LOD), ppm	Concentration, Vol% Sample V	Concentration, Vol% Sample VI
CO	920	0.75	0.59
CO ₂	440	0.77	1.03
H ₂ S	1070	n.d.	n.d.
H ₂	5000	n.d.	n.d.
CH ₄	240	22.00	24.12
C ₂ H ₆	2	18.73	18.86
C ₂ H ₄	2	17.31	18.16
C ₃ H ₈	1	8.64	7.30
C ₃ H ₆	1	22.12	21.51
C ₄ H ₁₀	1	1.44	1.11
C ₄ H ₈	1	5.72	4.63
Other		2.53	2.68
HHV	MJ/m ³	72.45	70.42

The gas produced by the two mixtures contain high concentration of C2-C4 molecules, with ~36% ethane, ethylene, ~30% propane, propene being the main components, and a not insignificant amount of other, C5-C6 hydrocarbons which further enhances the heating value of the pyrolysis gas. Additionally, as no H₂S could be found in the samples, it can be said that no sulphur was present in gas phase which is also beneficial from the point of standard quality fuel production. According to the calculated HHV,

significantly more energy could be obtained by the combustion of these gases than from the typical natural gas. The results suggest that the gas yield of the process may be able to provide at least part of the energy requirement of the pyrolysis process.

CONCLUSION

The thermal degradation of high-density polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP) resulted in oils with high olefin content. According to the GC-MS analysis, the gasoline fraction from pure polystyrene (PS) pyrolysis resulted mainly in aromatic compounds, other components being negligible. Co-pyrolysis of the plastic materials also resulted in high olefin content, however by adding 20 wt% PS into the mixture, a significant decrease could be observed regarding the ratio of unsaturated hydrocarbons. It should be noted that the aromatic compounds in the gasoline fraction originating from the mixture with PS content may be detrimental to the gasoline standard's distillation parameters. The 20-210 °C fraction from the pyrolysis of polypropylene resulted in a significant amount of high boiling point hydrocarbons, while the thermal degradation of high- and low-density polyethylene produced more light molecules in the C5 and C6 range.

The olefin content disappeared almost entirely in the case of the separately hydrogenated gasoline fraction of sample VI as it was converted to saturated hydrocarbons. Apart from hydrotreatment, the ratio of unsaturated hydrocarbons in the gasoline fractions can be decreased with oxygenates, permitted by the EN-228 standard. Adding tert-butyl alcohol, or the more commonly used ethanol to the distillates can be beneficial concerning the distillation parameters as well. These results suggest that hydrotreatment, mixing alcohol to the PWG and improving the composition of the plastic waste feed has the potential to produce standard quality transportation fuels using 100% plastic waste.

REFERENCES

- [1] 'Plastics - the Facts 2021 • Plastics Europe', *Plastics Europe*, <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/> (accessed May 03, 2022).
- [2] A. K. Panda, R. K. Singh, and D. K. Mishra, 'Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective', *Renew. Sustain. Energy Rev.*, vol. 14, no. 1, pp. 233–248, Jan. 2010, doi: 10.1016/j.rser.2009.07.005.
- [3] A. D. Vethaak and H. A. Leslie, 'Plastic Debris Is a Human Health Issue', *Environ. Sci. Technol.*, vol. 50, no. 13, pp. 6825–6826, Jul. 2016, doi: 10.1021/acs.est.6b02569.
- [4] W. C. Li, H. F. Tse, and L. Fok, 'Plastic waste in the marine environment: A review of sources, occurrence and effects', *Sci. Total Environ.*, vol.

- 566–567, pp. 333–349, Oct. 2016, doi: 10.1016/j.scitotenv.2016.05.084.
- [5] ‘FAQs on Plastics’, *Our World in Data*, <https://ourworldindata.org/faq-on-plastics> (accessed Feb. 21, 2023).
- [6] P. T. Williams, ‘Yield and Composition of Gases and Oils/Waxes from the Feedstock Recycling of Waste Plastic’, in *Feedstock Recycling and Pyrolysis of Waste Plastics*, John Wiley & Sons, Ltd, 2006, pp. 285–313. doi: 10.1002/0470021543.ch11.
- [7] G. Elordi, M. Olazar, G. Lopez, M. Artetxe, and J. Bilbao, ‘Product Yields and Compositions in the Continuous Pyrolysis of High-Density Polyethylene in a Conical Spouted Bed Reactor’, *Ind. Eng. Chem. Res.*, vol. 50, no. 11, pp. 6650–6659, Jun. 2011, doi: 10.1021/ie200186m.
- [8] A. Demirbas, ‘Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons’, *J. Anal. Appl. Pyrolysis*, vol. 72, no. 1, pp. 97–102, Aug. 2004, doi: 10.1016/j.jaap.2004.03.001.
- [9] E. Standards, ‘BS EN 228:2012+A1:2017 Automotive fuels. Unleaded petrol. Requirements and test methods’, <https://www.en-standard.eu>. <https://www.en-standard.eu/bs-en-228-2012-a1-2017-automotive-fuels-unleaded-petrol-requirements-and-test-methods-1/> (accessed May 05, 2022).
- [10] M. Hajbabaie, G. Karavalakis, J. W. Miller, M. Villela, K. H. Xu, and T. D. Durbin, ‘Impact of olefin content on criteria and toxic emissions from modern gasoline vehicles’, *Fuel*, vol. 107, pp. 671–679, May 2013, doi: 10.1016/j.fuel.2012.12.031.
- [11] Z. Dobó, Z. Jakab, G. Nagy, T. Koós, K. Szemmelveisz, and G. Muránszky, ‘Transportation fuel from plastic wastes: Production, purification and SI engine tests’, *Energy*, vol. 189, p. 116353, Dec. 2019, doi: 10.1016/j.energy.2019.116353.