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GASOLINE LIKE FUEL FROM PLASTIC WASTE PYSROLYSIS AND HYDROTREATMENT

Balázs Hegedüs, Zsolt Dobó

Institute of Energy and Quality, University of Miskolc, Miskolc, Hungary
hege.balazs94@gmail.com

ABSTRACT

Recycling of plastic waste is desirable to lower environmental pollution and fulfil the requirements of circular economy. Energetic utilization is another possibility, however, municipal solid waste containing plastics is usually combusted to generate heat and electricity. An attractive way of dealing with plastic waste is pyrolysis, which has the potential of producing liquid hydrocarbons suitable as a transportation fuel. The pyrolysis results of three plastics produced in the largest amount globally, namely polyethylene, polypropylene and polystyrene as well as their mixtures are presented. The experiments were performed in a laboratory scale batch reactor. The pyrolysis oils were further processed by distillation to provide gasoline and diesel like (distillation cuts at 210 and 350 °C) hydrocarbons. The gasoline fractions were analysed by GC-MS and the composition was compared with the EU gasoline standard. It was found that the oils from PE, PP and PS contain compounds present in standard gasoline. Mixing PS with PE and PP before the pyrolysis, or the oils afterward produces much closer results to standard requirements as PS pyrolysis generates mostly aromatic content. As standard maximizes the olefin content of gasoline to 18 Vol%, hydrogenation was also performed using Pd based catalyst. The hydrogenation process significantly reduced the number of double bonds resulting in low olefin content. Results show that the pyrolysis of plastic waste mixtures containing PE, PP and PS is a viable method to produce pyrolysis oil suitable for gasoline-like fuel extraction and further hydrogenation of the product can provide gasoline fuels with low olefin content.

Keywords: plastic waste, pyrolysis, hydrotreatment, gasoline

1. INTRODUCTION

According to global statistics, since the beginning of industrial plastic production in 1950, approximately 7,5 billion tonnes of plastic have been produced until 2015, and the amount produced grows each year [1]. From the vast amount of plastic generated so far, only ~10% was recycled, and ~15% was utilized by incineration, which means that more than 5 billion tonnes are discarded or landfilled [2]. Considering these facts, new technologies are being developed and applied for the efficient and economical treatment of plastic waste including pyrolysis. This method not only offers a way to dispose of used plastic products, but it can also produce value-added raw materials or even transportation fuels in the form of pyrolytic oil.

From literature and statistics, it is determined that three plastics produced in the largest amount globally, namely high- and low-density polyethylene (HDPE, LDPE), polypropylene (PP) and polystyrene (PS). PE and PP mainly degrade into various hydrocarbons with diverse molecular mass, while the product from PS is usually made of aromatic compounds [3]. However, for these oils to be applied as fuel, more precisely as gasoline, they must meet various parameters stated in regulations [4]. Usually, the biggest difference is the concentration of olefins in the oils, which is maximized at 18 Vol% in the EN 228 standard. The olefins are hydrocarbon molecules containing at least one carbon double bond. Basically, olefins can improve the performance of internal combustion engines; however, it also causes deposition inside the engine shortening its lifespan. Adding PS into the solid waste blend can also lessen the olefin ratio, however, it is not enough to produce standard quality gasoline.

Hydrotreatment is a possible method to decrease the concentration of olefins. This technology is widely used in the petrochemical industry. During the hydrogenation process catalyst and hydrogen are used to saturate the molecules. There are two types of this method. One of them is hydrotreatment at mild temperatures when the saturation of molecules can be achieved without significantly changing the boiling temperature of the components in oil, as no cracking occurs. The other type is destructive hydrotreatment

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or hydrocracking. This process combines the cracking and the saturation into one step. It is mainly used in crude oil refinement.

This paper investigates the fuel properties of plastic waste gasoline obtained from the distillation of various pyrolysis oils, utilizing LDPE, HDPE, PP and PS waste materials. Additionally, catalytic hydrogenation was performed in case of one fuel to investigate the possibility of lowering the olefin content.

2. MATERIALS AND METHODS

The experiments were carried out in a laboratory-scale batch reactor (Fig. 1). An air-cooled reflux is connected to the reactor, and after that a water-cooled heat-exchanger. The primary role of the reflux is regulating the pyrolysis gas temperature, therefore changing the molecular weight distribution of the liquid product, while the heat-exchanger ensures the condensation of hydrocarbon vapours. The non-condensable gases in the case of experiments without continuous hydrogen flow were separately collected and analysed. During the experiment where hydrogen stream was applied, the gases were flared. A hydrogen pre-heater unit was also used in the case of continuous hydrogen flow to avoid cold gas inlet into the reactor. Typically, the hydrogen temperature was set to 300 °C, while the flow rate to 15 l/h (standard conditions).

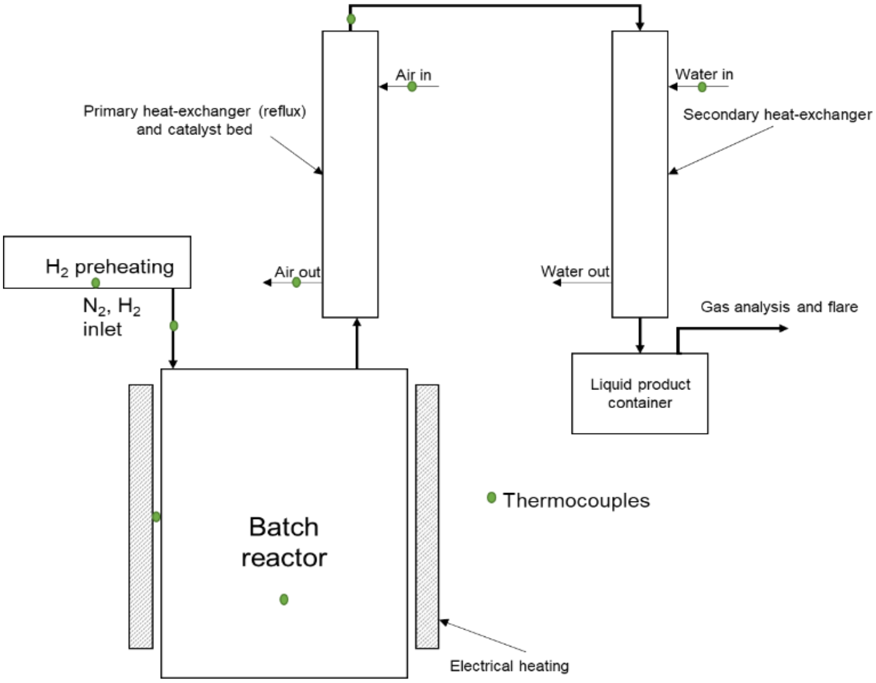

Figure 1. Schematic illustration of the experimental setup.

HDPE, LDPE, PP and PS plastic wastes were used with ratios summarized in Table 1. Seven experiments were performed with various feed compositions. Samples I-IV. were the individual plastic materials, while sample V. and sample VI. were mixtures, with and without PS, respectively. The composition of the mixtures was determined by plastic production statistics [5]. Another pyrolysis run was performed to reduce the ratio of olefins in the liquid product (sample VII.), where 15 g Pd-based catalyst was applied, placed into the reflux.

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In each case, 150 g of plastic waste materials were prepared. The endpoint of the pyrolysis experiments was indicated by the inner temperature of the reactor reaching 530 °C, as all the plastic materials used are degraded by reaching that temperature [6].

The pyrolytic oils were separated by atmospheric distillation into three fractions, "gasoline" fraction at the 210 °C cut, "diesel" fraction at the 350 °C cut, and the residue containing heavy hydrocarbons with higher boiling temperatures. The gasoline fractions were analyzed by GC-MS to investigate the molecular distribution of such distillates. It is worth noting that during the distillation process, there was a certain amount of material loss in each case. This loss is attributed to the light hydrocarbons with low boiling temperatures, which were not able to condense. The "gasoline" fraction of sample VI. was hydrogenated separately using the same type of Pd catalyst as it was during the pyrolysis experiment. The process was performed in a hydrogenation reactor at 300 °C and with 15 g catalyst.

Table 1. Composition of the batches prepared for pyrolysis.

Sample ID	HDPE wt%	LDPE wt%	PP wt%	PS wt%	Note
I.	100	0	0	0	-
II.	0	100	0	0	-
III.	0	0	100	0	-
IV.	0	0	0	100	-
V.	14	20,5	45,5	20	-
VI.	17.5	25.62	56.88	0	-
VII.	17.5	25.62	56.88	0	Hydrogen + Pd catalyst

3. RESULTS

The summary of the oil yields from the pyrolysis experiments and the distillation is summarized in Table 2. PS pyrolysis provided the highest oil yield of 84,6 wt%, while LDPE pyrolysis resulted in the lowest oil yield of 62,07 wt%. A decrease can be observed in the oil yield in the case of sample VII. and also there is a significant change in different distillation cuts, compared to sample VI. This can be explained by the additional hydrogen stream, which physically "pushed" the pyrolysis gas through the reflux, therefore it could not efficiently regulate the molecular weight distribution. It is also shown in the table, that the material loss during the distillation is non-negligible. This loss can mainly affect the distillation step parameters of the EN 228 standard.

Table 2. Pyrolysis oil and the different distillation cut yields.

Sample	Oil yield, wt%	20-210 °C		210-350 °C		Above 350°C		Loss	
		wt%	g/kg$_{plastic}$	wt%	g/kg$_{plastic}$	wt%	g/kg$_{plastic}$	wt%	g/kg$_{plastic}$
I.	70.47	50.4	355.1	37.56	264.67	8.08	56.95	3.96	41.88
II.	62.07	53.01	311.68	37.78	222.16	4.51	26.53	4.70	41.5
III.	79.60	63.73	507.30	31.17	248.12	3.71	29.52	1.39	16.6
IV.	84.60	90.36	764.42	1.92	12.83	6.72	56.83	1.41	17.87
V.	76.00	63.58	483.22	37.63	250.86	3.05	23.14	0.37	4.17
VI.	75.20	58.59	440.58	38.48	256.56	4.12	30.96	3.18	35.83
VII.	66.00	36.61	241.61	32.5	328.00	16.7	196.82	1.07	10.61

The 20-210 °C fractions were compared to EN 228 European gasoline standard, the results are summarized in Table 3. The properties in grey coloured cells were not measured, green indicates the value meets the parameters stated in the standard, while red means that the parameter is out of range. As expected, the samples from normal thermal degradation have high olefin content excluding the oil from polystyrene which is made of aromatic compounds entirely. Regarding density, all the 20-210 °C distillates originating from the mixtures meets the standard parameters, while from the individual plastic pyrolysis, sample III. and IV. are out of range. In the case of sample VII. the olefin content, while still higher than 18 Vol%, was significantly decreased. The best outcome, respective to the olefin content, was achieved with sample VI.H, the separately hydrogenated distillate of sample VI. In this case, the olefin content almost entirely disappeared, however during the hydrogenation process the same material loss was observed as during the distillation, therefore the 100 °C distillation step is not met.

Table 3. Comparison of the EN 228 standard and the pyrolysis oil distillates.

Parameter	Units	Limits		Properties of the „gasoline” fractions									
		Min.	Max.	I.	II.	III.	IV.	V.	VI.	VII.	VI.H	VI.He	VI.Htb
Research octane number		95	-	-	-	-	-	-	-	-	-	-	-
Motor octane number		85	-	-	-	-	-	-	-	-	-	-	-
Vapour pressure, summer period	kPa	45	60	-	-	-	-	-	-	-	-	-	-
Density (15°C)	mg/cm^3	720	775	724	721	716	887	765	721	736	723	731	729
Distillation													
Percentage evaporated at 70 °C	% (V/V)	20	48	50.77	52.04	35.03	0.00	27.28	41.00	24.75	24.42	21.98	23.27
Percentage evaporated at 100 °C	% (V/V)	46	71	63.61	62.34	37.7	0.00	30.38	45.56	31.75	33.92	41.38	44.1
Percentage evaporated at 150 °C	% (V/V)	75	-	91.88	91.31	99.01	100	95.38	96.14	96.35	80.18	82.16	83.15
Residue above 210 °C	% (V/V)	-	2	0.38	0.54	0.24	0	0.24	0.7	0.34	0.57	0.51	0.49
Hydrocarbon analysis													
Olefins	% (V/V)	-	18	70.51	70.65	75.28	0	46.06	63.85	48.6	0.62	0.59	0.53
Aromatics	% (V/V)	-	35	1.13	1.5	0.29	100	31.21	0.73	0.97	3.67	0,87	0.82
Benzene	% (V/V)	-	1	0.15	0.17	0.06	0	0.18	0.08	0.18	0.17	0,14	0.14
Oxygen content	% (m/m)	-	3.7	-	-	-	-	-	-	-	-	3.33	3.23
Oxygenates:													
Methanol	% (V/V)	-	3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
Ethanol	% (V/V)	-	10	<10	<10	<10	<10	<10	<10	<10	<10	10	<10
Iso-propyl-alcohol	% (V/V)	-	12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12
Tert-butyl-alcohol	% (V/V)	-	15	<15	<15	<15	<15	<15	<15	<15	<15	<15	15
Iso-butyl-alcohol	% (V/V)	-	15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15
Ethers containing five or more carbon atoms per molecule	% (V/V)	-	22	<22	<22	<22	<22	<22	<22	<22	<22	<22	<22
Other oxygenates	% (V/V)	-	15	<15	<15	<15	<15	<15	<15	<15	<15	<15	<15
Sulphur content	mg/kg	-	10	-	-	-	-	-	-	-	-	-	-
Lead content	g/l	-	0.005	-	-	-	-	-	-	-	-	-	-

The difference between the distillation curves of sample VI. and VI.H can be seen in Fig. 2. Additional distillation scenarios are also depicted as adding various alcohols to the gasoline in limited concentrations is enabled by the EN228 standard. For this reason, ethanol and tert-Butyl alcohol addition were investigated regarding the distillation properties of plastic waste fuel. Usually, these oxygenates are added to gasoline to increase the octane rating, but the oxygen content in the fuel provides more complete combustion as well, improving the emission properties of the engine [7].

In this case, adding alcohol to plastic fuel also helps to achieve the distillation requirements. As seen in Table 3, by adding ethanol to VI.H sample the percentage of evaporation till 100 °C increased to 41.4 Vol%, while the same in case of adding tert-Butyl alcohol is 44.1 Vol%. It is worth noting, that although these numbers do not fulfil the distillation properties, they are close enough to presumably reach the requirement by fine-tuning the operational parameters of pyrolysis and distillation steps.

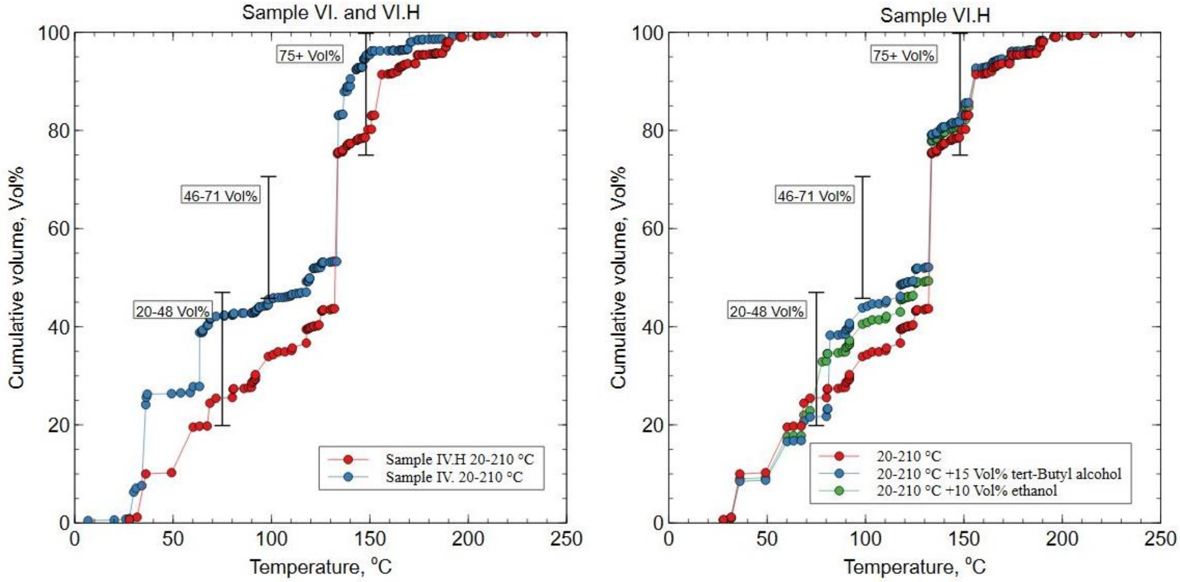

Figure 2. Distillation curves of sample VI., VI.H, and VI.H with ethanol and tert-Butyl alcohol additives.

4. CONCLUSIONS

The thermal degradation of high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and their mixtures resulted in oils with high olefin content. In the case of pure polystyrene (PS) being pyrolyzed, the GC-MS analysis showed only aromatic compounds. Adding 20 wt% PS into the mixture, significant decrease could be observed in the olefin content. The experiments performed with Pd-based catalyst placed into the reflux and continuous hydrogen flow also showed a decrease in the olefin content, however in this case the oil yield, and especially the gasoline range hydrocarbon yield decreased as well. 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. Adding oxygenates, such as ethanol or tert-Butyl alcohol to gasoline fraction obtained from pyrolysis oils further improves the quality of plastic gasoline. These results suggest, that hydrotreatment and mixing alcohol to the gasoline is a potential pathway to improve the quality of gasoline fractions.

REFERENCES

[1] E. Beckman, „THE CONVERSATION,” 03 12 2020. [Online]. Available: https://theconversation.com/the-world-of-plastics-in-numbers-100291.

[2] H. Ritchie, „Our World in Data,” 02 09 2018. [Online]. Available: https://ourworldindata.org/faq-on-plastics#what-are-the-environmental-impacts-of-landfills. [07 12 2020].

[3] R. Miandad, M. Barakat, M. Rehan, A. Aburiazaiza, I. Ismail és A. Nizami, „Plastic waste to liquid oil

through catalytic pyrolysis using natural and synthetic zeolite catalysts," *Waste Management,* 2017 . https://doi.org/10.1016/j.wasman.2017.08.032

[4] „European Parliament Directive 2009/30/EC," 2009.

[5] „Manufacturers, PlasticsEurope - Association of Plastics," 2019. [Online]. Available: https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf. [03 12 2020].

[6] Z. Dobó, Z. Jakab, G. Nagy, T. Koós, K. Szemmelveisz és G. Muránszky, „Transportation fuel from plastic wastes: Production, purification and SI engine tests," *Energy,* 2019. https://doi.org/10.1016/j.energy.2019.116353

[7] F. Nadim, P. Zack, G. E. Hoag és S. Liu, „United States experience with gasoline additives," *Energy Policy,* 29(1) 2001, 1-5. https://doi.org/10.1016/S0301-4215(00)00099-9