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THE POTENTIAL OF WASTE PLASTIC DERIVED OILS FOR USAGE IN COMPRESSION IGNITION ENGINE

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ABSTRACT

The usage of plastic polymer materials is increasing approximately 5% per year. In last decades a lot of different materials like wood and metals have been replaced by plastics material. The production costs of plastics are lower and the production times shorter. Some types of plastics materials are also very convenient for every day usage in food industry where they are mostly used as a single use plastic which preserves the freshness of our food. The problem with most plastic arises at the end of their life cycle when it gets thrown away. A lot of waste plastic get recycled and reused but still a significant part of it finish at landfills, forests, rivers or in oceans. Some of the waste plastic gets further processed in waste-to-energy plants where it gets burned combined with other waste.

One of the promising potential ways to reuse waste plastic is its thermochemical degradation to its primary components, which are in most cases petrochemicals derivative. This can be achieved during a pyrolysis process. Pyrolysis is the process which causes decomposition (degradation) of materials at elevated temperature and in absence of oxygen. During the pyrolysis process long chain polymers of plastic are decomposed into smaller, less complex molecules. Pyrolysis gas, oil and solid products are three main products obtained during the pyrolysis process.

In scope of the presented work the liquid product of waste plastic obtained during the pyrolysis process in single batch reactor were analysed for their possible usage in internal combustion engine. The obtained results of analysed liquid products calorific values and IR spectra indicate that pyrolysis oils of waste plastic have a potential to be used in internal combustion engines as an additive to conventional fuels or as their substitute.

Keywords: Waste plastics, Pyrolysis, Synthetic fuels, Calorific value, IR spectra

INTRODUCTION

Transport sector is one of the main contributors to environmental pollution. In European Union it accounts for one-fifth of total Carbon Oxide emissions realised and consumes around one third of total primary energy. The majority of transport sector is still powered by fossil fuels. [1, 2] In recent decade up to 10 percent of fossil fuels were replaced by biofuel which are very convenient way to reduce harmful emissions in transport. The usage of biofuels is also highly promoted by European Union. Most of the today's biofuels used are first generation biofuels produced from raw materials which are involved in our food chain [3]. Since the production of second and third generation of biofuels is not capable to contribute to emission reduction in large scale more and more research is focused on synthetic fuels. The usage of synthetic fuels in IC engines can also have positive impact on exhaust gas emissions [4].

Polymer plastic materials have significant role in our everyday life. In last decades plastic materials replaced a lot of different materials in several applications. Increased World population, constant need for economic growth, low production costs and shorter production times are just few reasons for rapid increase in use of plastic materials [5]. European Union is heavily promoting circular economy which helps to collect, sort and recycle or reuse more and more waste. Despite all effort a lot of waste plastic still ends on landfills and forest or it get exported to third world countries where plastic get recycled under milder ecological standards. A lot of times it ends in rivers or in oceans or it get illegally burned in nature. In European Union more and more waste, including plastic, are used in waste-to-energy plants. One of the promising way to reuse waste plastic is its thermochemical degradation in a pyrolysis process. The liquid oils obtained in pyrolysis process can be further used as additive to conventional fossil fuels or as their substitute [5, 6]. The usage of obtained pyrolytic oils in internal combustion engines can have several positive effects. It can help to lower overall emitted emissions by recycling and reusing waste materials (plastic). Using waste plastic for production for pyrolytic oils will lower their landfills and forest deposition and also their export to third world countries. Using pyrolytic oil in transport sector can also help to reduce EU or they member countries dependency from oil import.

The pyrolysis of HDPE plastic usually yields high percentage of pyrolytic oils. The amount of produced oils usually excide 80 % of total raw material used [7, 8, 9]. Even higher pyrolytic oil yield, up to 95 %, were obtained when using temperatures between 500 and 550 °C and LDPE plastics in [8, 10]. Uddin et al. in [11] perform pyrolysis on LDPE plastic at lower temperature and obtained slightly lower oil yield of 76 %. Negative impact of high temperatures on pyrolysis oils yields was found in study of Sogancioglu et al. [12]. They concluded that, HDPE, LDPE and PP plastic oil yield decreases when increasing the temperature during pyrolysis process. Reverse trends were obtained with use of PS plastic, which yield slightly more oil at higher pyrolysis temperature. The highest yields, comparable with results in [7, 8, 9] were obtained with use of HDPE plastics. PS plastic produce the smallest yields which were in range of 55 – 65 percent. In work of Liu et al. [13] and in work of Demirbas et al. [14], higher yields of PS plastics, up to 97 % and 90 %, were obtained. Some of the papers, like the work of Kamisky et al. [15] also focus on pyrolysis of mixed plastics, where oil yield heavily depend on mixed plastic structure.

Singh et al. [16] produced pyrolytic oil from waste plastic mixture and use it to power single cylinder diesel engine. The obtained pyrolytic oil consisted mainly from alkanes and alkenes with high amount of aromatics, had slightly lower calorific value and contained some amount of oxygenated compounds. Lower calorific value influenced on slight increase in engine fuel

consumption while oxygenated compounds cause elevated exhaust temperature and slight increase in emissions production. Mangesh et al. [17] performed catalytic pyrolysis using PP, HDPE and LDPE plastics and determine the obtained pyrolytic oils properties. The obtained pyrolytic oils have similar calorific value as diesel fuel but have distinctive higher kinematic viscosity. According to this, only pyrolytic oil produced from PP plastic, was mixed with diesel fuel in smaller ratios and use to power 4 cylinder diesel engine. Again, the use of pyrolytic oils increased engine fuel consumption, exhaust gas temperature and emissions. Similar conclusion were also presented by Das et al. [18] where pyrolytic oils, produced from medical plastics wastes, were mixed with conventional diesel fuel in different ratios. The increase of exhaust gas emissions and slightly decrease of tested CI engine break power was obtained when they increased the ratio of pyrolytic oil in fuel mixture.

As can be seen from brief literature review, most of the studies focus on pyrolysis of single, un-mixed plastic. The results of studies are not always consistent, especially when mixed plastic is being used. The obtained pyrolytic oil composition and quality heavily depend from type of plastic, pyrolytic process operating parameters, catalyst used, etc. All this parameters must be studied in order to define optimal values for further usage.

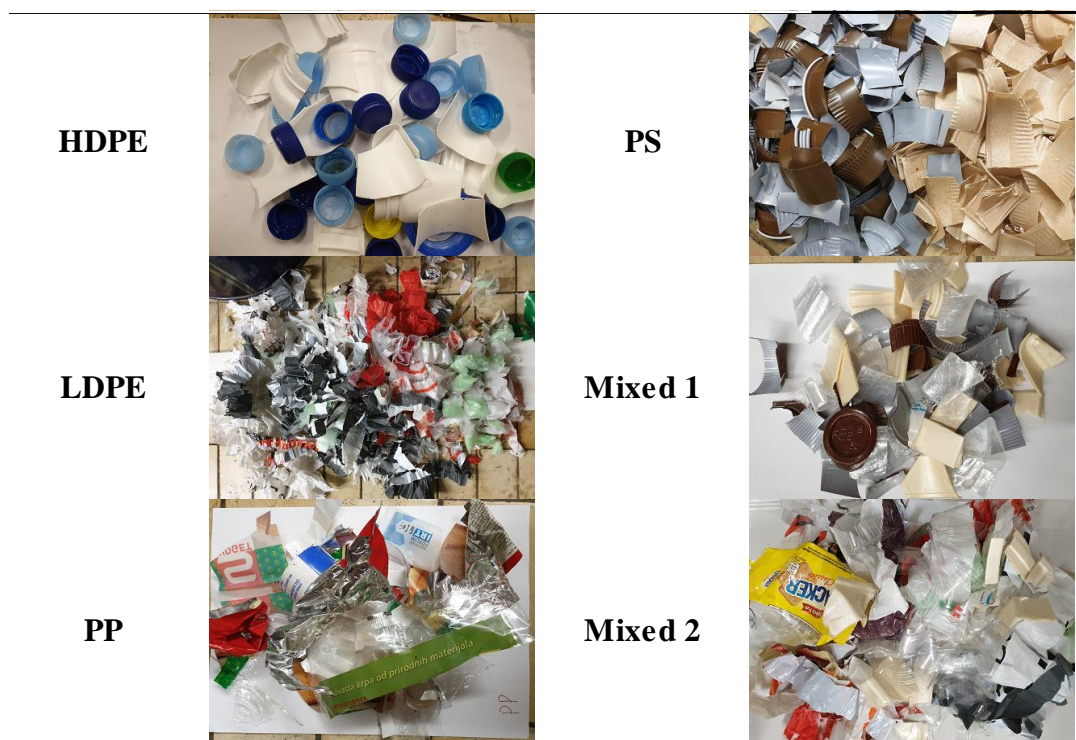
Before pyrolytic oily can be used as an additive to conventional fuels or as their substitute several studies of obtained fuel properties and their influence on engine operating condition, emission formation, injection system operations, etc. must be made. In the presented work for different types of waste plastics (HDPE, LDPE, PP and PS) and two mixtures of waste plastics where used in pyrolysis process performed in single batch reactor for production of synthetic, pyrolysis oils. The obtained liquid oils where further analysed. The results of obtained oils calorific values and IR spectres where further compared to results of diesel fuel. From the comparison we can conclude that obtained pyrolysis oils of used waste plastic have a potential to be used in internal combustion engines as an additive to conventional fuels or as their substitute. Additional studies are needed in order to answer on more raised issues regarding pyrolytic oils usage in IC engines.

MATERIALS

The plastics materials used in the presented were taken from municipal waste. The high density polyethylene (HDPE) plastic used consists of plastic bottle caps and hard plastic food containers. Plastic shopping bags find in normal grocery stores present our low density polyethylene (LDPE) raw material. The polypropylene (PP) plastic used in this study was taken from food storage bags while polystyrene (PS) plastic used was from plastic cafe mugs used on wending machines. The first sample of mixed plastic (Mixed 1) consist of 50% LDPE of and 50% of PS. The second mixture of plastic waste (Mixed 2) consist of 20% PP, 20% PS, 20% PET and 40% LDPE. The raw materials used for pyrolysis process are presented in Table 1.

Table 1: Raw material of plastic types used for pyrolysis process

Plastic type	Material	Plastic type	Material
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EXPERIMENTAL SET-UP

Before the beginning of pyrolysis process the plastic was cut to smaller pieces proximate size of 2x2 cm and weighed. Total amount of plastic for each experiment was 100 g. In the next step we put plastic in to the reactor, place a seal and screw the bolts on reactor top. The reactor was further placed in a chimney pipe. At the bottom of the pipe the gas burner was placed as a heat source. The gas used for burning was a mixture of propane and butane gas, typical for camp burners. The reactor was connected to the condenser which was cooled using tap water. The experiment set-up is schematically presented at.

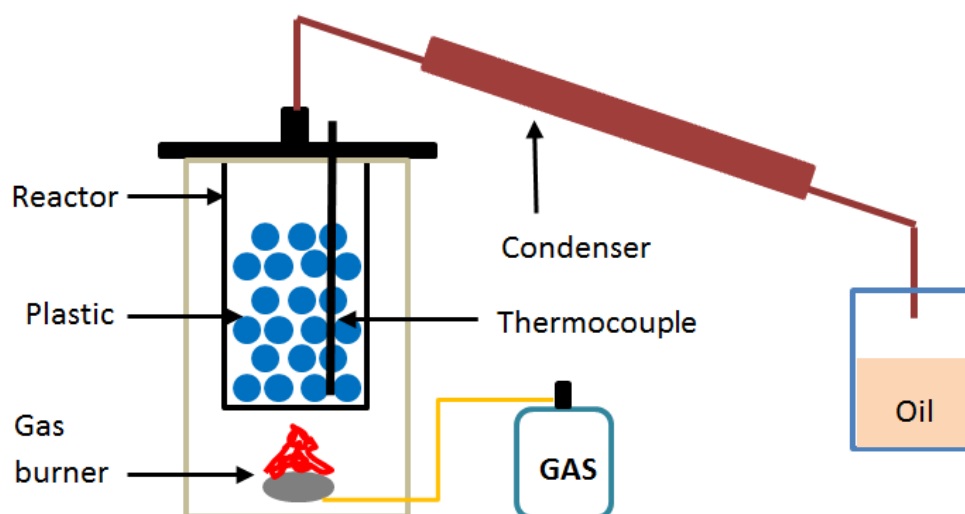


Figure 1: Schematic presentation of experimental set-up

During the pyrolysis process we monitored temperature inside the reactor, temperature of exhaust gases and water temperature in the condenser. The application for monitoring

pyrolysis process was made in LabVIEW program. National Instruments DAQmx WLS-9163 and NI-9219 module were used for temperature data acquisition. The pyrolysis process was stopped (heat source turned down) when the interval between oil droplets increased above 10s in three consecutive droplets.

RESULTS

In the presented paper different types of plastic or its mixtures were used in pyrolysis process in order to obtain liquid oil, gas and solid products. The results of pyrolytic process are presented in Table 2.

Table 2: Results of pyrolytic process and obtained calorific values

	Oil [%]	Solid [%]	Gas [%]	Calorific values [MJ/kg]	EROI
HDPE	75.09	11.00	13.91	42.8	1.2
LDPE	53.24	26.32	20.44	40.3	0.76
PP	74.52	11.26	14.22	41.6	1.3
PS	58.59	22.56	18.85	38.3	0.7
Mixed 1	45.34	8.50	46.16	39.6	0.72
Mixed 2	52.44	8.50	39.06	40.8	0.76
D2	42.8				

It can be seen from the results in Table 2 that different types of plastic produced different amount of pyrolytic oils. The highest amount of oil was obtained when using high density polyethylene (HDPE) plastic, while the first sample of mixed plastic (Mixed 1) produced the lowest amount of pyrolytic oil and the highest amount of pyrolytic gas.

The calorific values of obtained pyrolytic oils are also presented in Table 2. As can be seen from the results obtained oil of HDPE plastic have the highest calorific value. Its value is the same as CV of conventional diesel fuel (D2). All other oils have slightly lower calorific value than diesel fuel but the difference was in range of 10 % which is similar to calorific value of rapeseed oil biodiesel commonly used as biofuel in EU countries. The calorific value was measured using IKA C 4000 calorimeter. The Energy Returned On Investment (EROI) are presented in last column in Table 2. As can be seen from the presented results EROI are in most cases smaller than one (1) which means that we have invested more energy than we obtained with pyrolytic oil fraction. EROI will increase if we also consider calorific value of pyrolytic gas.

The yield of different pyrolytic fraction heavily depends from temperature inside the reactor and from temperature gradients. The measured values of temperature inside the reactor during the pyrolytic process are presented at Figure 2.

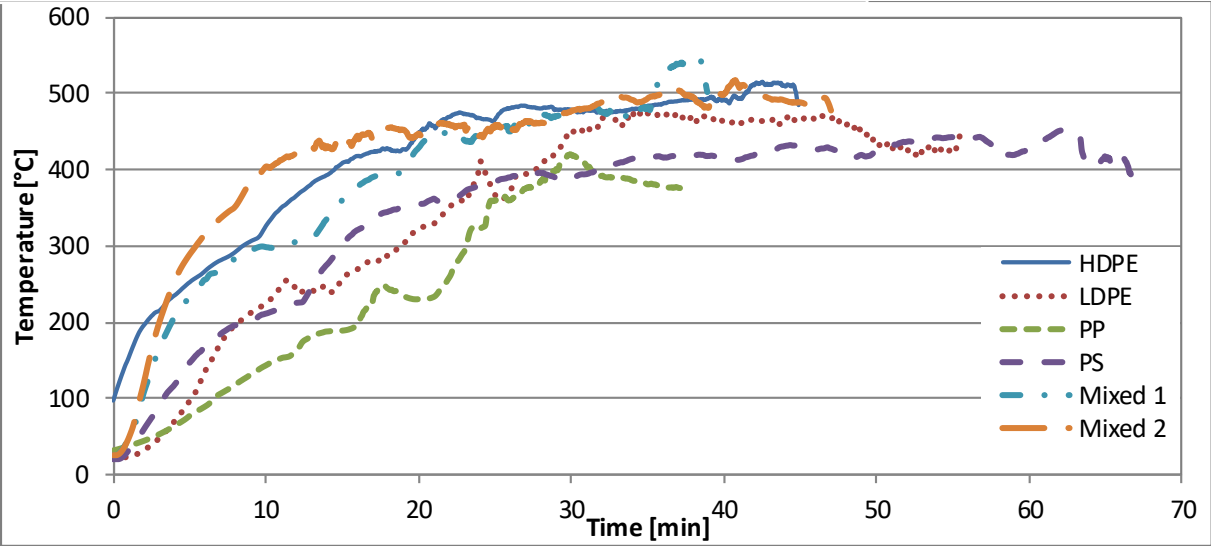


Figure 2: Temperature inside the reactor during the pyrolytic process

From the measured values of temperature inside the pyrolytic reactor, Figure 2, maximal values and temperature gradients can be seen. Since our experimental set-up does not allow setting temperature gradients since we need to increase gas flow (amount of heat applied to reactor) manually. The amount of heat was also regulated based on the intensity of oil flow. As long the flow of pyrolytic oil was consistent, the heat applied to the reactor was kept constant. When the flow was slowed down, more heat (gas) was applied until the process was stopped.

Plastic type	Products	Plastic type	Products
HDPE		PS	
LDPE		Mixed 1	

PP



Mixed 2



Figure 3: Products of pyrolysis process

Obtained pyrolytic oils have been analysed with ATR FT-IR spectroscopy. FT-IR spectra of pyrolytic oils were compared with FT-IR spectra of conventional diesel fuel (D2). From the recorded spectra functional group composition have been predict. ATR FT-IR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer. The ATR accessory (supplied by Specac Ltd.,UK) contained a diamond crystal. A total of 16 scans were taken for each sample with a resolution of 4 cm^{-1} . All spectra were recorded at ambient temperature over at wavelength interval between 4000 and 650 cm^{-1} .

The obtained pyrolytic oils of HDPE plastic and conventional diesel fuel (D2) were given almost the same FT-IR spectra (Figure 4). Spectra presented the typical signals of alkanes: signals in the range from 2900 - 2850 cm^{-1} correspond to the C-H stretching vibration, and the signals at around 1450 and 1380 cm^{-1} represent C-H bending vibration. Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the C=C bond stretching vibration at about 1600 - 1700 cm^{-1} and some alkenes might also show a band for the =C-H bond stretch, appearing around 3080 cm^{-1} . C=C signal at 1650 cm^{-1} is present in the FT-IR spectra of PP pyrolytic oils, Mixed 1 and Mixed 2 pyrolytic oils.

The =C-H stretch in aromatics is observed at 3100 - 3000 cm^{-1} and is at slightly higher frequency than is the -C-H stretch in alkanes. Aromatic hydrocarbons show signals in the regions 1600 - 1585 cm^{-1} and 1500 - 1400 cm^{-1} due to carbon-carbon stretching vibrations in the aromatic ring. These signals have been detected in pyrolytic oils of PS FT-IR spectrum (brown spectrum, Figure 4).

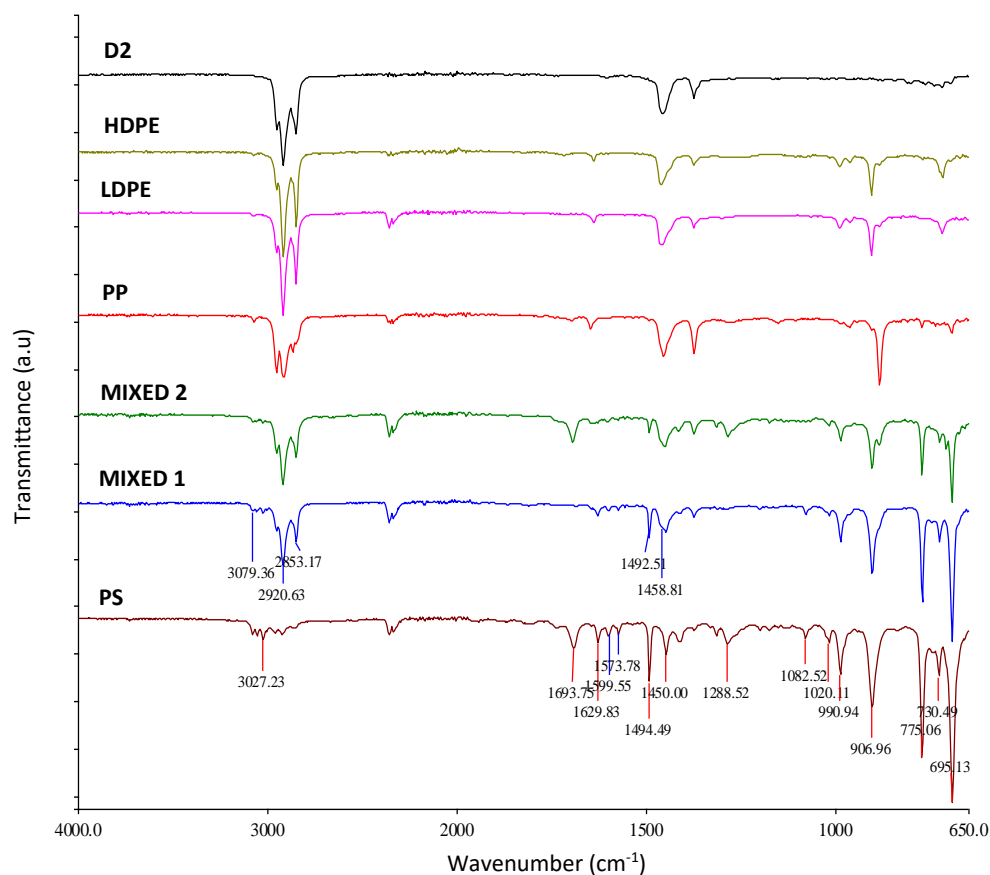


Figure 4: ATR FT-IR spectra pyrolytic oils of different plastics and conventional diesel fuel

CONCLUSIONS

In scope of the presented work pyrolytic oils were obtained from different types of waste plastics. The pyrolytic process was performed in semi batch pyrolytic reactor. At the end of each pyrolysis process the yields of oil, gas and solid material were determined and the ATR FT-IR spectra of pyrolytic oils were recorded. According to the results obtained with ATR FT-IR spectroscopy we can conclude that pyrolysis oil consists mainly of alkanes, alkenes and aromatic rings. The calorific values of all obtained pyrolytic oil indicate that they have enough chemical energy to mix with conventional diesel fuel or to be used as their substitute. The EROI results indicate that our system is not economical and that it needs further improvement in order to increase efficiency. This problem was not addresses in scope of presented work since the optimization of pyrolytic reactor present different field of research.

PLANS FOR FUTURE WORK

This conference paper only covers a start of our work in field of waste plastic pyrolysis and usage of obtained pyrolytic oils in internal combustion engines. In order to increase pyrolytic oil yield, USY Zeloit, with specific properties, produces by SILKEM d.o.o. will be mixed with plastic. According to our knowledge, no such study using USY zeolite with these specific properties exists.

In order to test suitability of obtained pyrolytic oils more properties, like density, viscosity, surface tension, etc. will be determined. This will allowed us to do more detailed comparison

about the ability to use obtained pyrolytic oils in internal combustion engines. It will also give us the information in which amount this oil can be blended with diesel fuel so that its properties stay in range of EN 590 standard.

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