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THE PYROLYSIS OIL AS AN ALTERNATIVE MARINE FUEL

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Abstract

The paper analyses physicochemical properties of oil obtained as a result of waste tyre pyrolysis and assesses their usefulness as alternative marine fuel for diesel engines. The results of the analysis of oil parameters and marine distillate fuel were compared with ISO 8217 requirements. The analysed fuels were, moreover, subjected to the examination of number, size, and shape of solid particles which was conducted in the Fuel Research, Hydraulic Fluids and Environmental Protection Centre of the Maritime University of Szczecin. Based on the tests it has been found out that the oil obtained by pyrolysis of waste vehicle tyres has not met some of the requirements in the standards for marine distillate fuel and must not be used as independent fuel. However, the pyrolysis oil may be applied as an additive to conventional fuels or in fuels mixture for marine vessels propelling.

Key words: *alternative marine fuel, pyrolysis oil, marine distillate fuel, morphology, physical and chemical properties.*

INTRODUCTION

With dwindling oil resources and their restricted accessibility as well as a rising environmental awareness, the need for alternative fuel research has increased. The MARPOL convention has imposed on ship owners a duty of sulphur reduction (since 2015) from 1% to 0,1% in fuels used within the Emission Control Area (ECA).

One of the ways to do that would be to use alternative fuels for marine vessels propelling. Such fuels may be obtained from a variety of sources and by means of technology which is under constant development. The alternative fuels can be used independently or as components in conventional fuels mixtures. The alternative fuels currently in use include methanol, ethanol, biodiesel (FAME), Dimethyl ether (DME), also known as methoxymethane as liquid fuels or LNG, LPG and hydrogen as gas fuels (Deniz, Zincir, 2016). Attempts have also been made to apply recycled fuels for diesel engines. Recycled fuels comprise oils from polyethylene and polypropylene waste (Mani at el. 2011) and oils recycled from used lubricant oils (Gabina at el.2016)

As another alternative fuel a liquid fraction obtained from pyrolysis of waste vehicle tyres is also used. The oil resulting from a high temperature pyrolysis (300-900 ^{0}C) is a mixture of over 100 different organic compounds (aliphatic, aromatic compounds and their derivatives) (Williams, 2013).

The physicochemical properties of the oil obtained from waste tyre recycling show some similarity to the diesel oil properties , which makes it possible to use it as fuel (Quek, Balasubramanian, 2013). The article aims at examining the properties of the oil obtained from the waste vehicle tyres pyrolysis as well as marine distillate fuel and comparing the with the standards and requirements of ISO 8217.

MATERIALS AND METHODS

The testing material were samples of marine distillate fuel and waste tyres pyrolysis oil. The samples were analysed in the context of viscosity, density, sulphur content, flash point, acid number, carbon residue and lubricity. The presence of vanadium, aluminium and silicon was tested by means of a rotating disc electrode.

Moreover, the oil samples were filtered through membrane filterand morphologically singled out. With the aid of Morphologi G3 (Malvern) shape and size particle analyser, the number of solid particles was stated and they were classified according to their diameter.

All the research was carried out in the Fuel Research, Hydraulic Fluids and Environmental Protection Centre of the Maritime University of Szczecin.

RESULTS AND DISCUSSION

Table 1 shows the results of the physicochemical properties of the analysed fuels.

Tab. 1 Main properties of Pyrolysis Oil, Marine Distillate Fuel, and requirements according to the standard ISO 8217

Property	Unit	Pyrolysis Oil	MDF	Limits by ISO 8217
Viscosity at. 40°C	mm^2/s	4,17	3,69	2,00 – 6,00
Density at. 15°C	kg/m^3	906	882	max. 890
Cetane index	–	40,5	45,8	min. 40
Sulphur	mass %	1,09	0,1	max.1,5
Flash point	°C	50	90	min. 60
Acid number	mg KOH/g	0,3	0,1	max. 0,5
Carbon residue (10%V/V distillation bottoms)	mass %	0,74	0,11	max. 0,3
Vanadium	mg/kg	0	0	–
Aluminum i Silicon	mg/kg	26	2,5	–
Lubricity, corrected wear trace diameter wsd 1,4 at 60 ° C	µm	458	319	max. 520

Based on the examination it was shown that the viscosity of pyrolysis oil (4,17 mm^2/s) is bigger than of the distillate fuel (3,69mm^2/s). But in both cases the results are still within the norms of ISO 8217. The density for pyrolysis oil was 906 kg/m^3 and went above the allowed norm for this parameter. The obtained results of the cetane index referring to the flash point quality of the compressed fuels mixture in both tested fuels were in accordance with the required norms.

The sulphur content in the marine distilled fuel was 0,1% and met the norms of both ISO and ECA. However, while the sulphur content in the pyrolysis oil was 1,09 % and was still within the ISO norm, it definitely did not meet the MARPOL directive. What imposes limitations on pyrolysis oil as fuel for marine vessels is – first - the flash point temperature – the parameter essential for fire safety during the fuel application, which is highly combustible. The pyrolysis oil sample was ignited at 50°C and did not fulfill the requirements, while the distilled fuel at 90°C, which met the norms.

The second parameter restricting the use of pyrolysis oil as independent fuel is the high carbon residue (0,74%) over twice as much as the allowed amount. Such a high value is due to the chemical composition of pyrolysis oil which contains unsaturated hydrocarbons, organic acids and sulphur compounds (Williams, 2013) facilitating the fuel to create residue in the combustion chamber, on valves, piston rings, and injection elements.

The acid number of pyrolysis oil was 0,3mg KOH/g, while the distillate fuel 0,1 mg KOH/g. Both values were below the allowed level. The content of vanadium, aluminium, and silicon was defined by means of a rotating disc electrode spectrometer. In both samples there was no trace of vanadium responsible for high temperature corrosion (Chaala, Roy, 1996). The acceptable amount of aluminium and silicon equals 25ppm. If it exceeds the norm, both metals may contribute to an excessive wear of the fuel feed system. In the case of pyrolysis oil the altogether content of the metals was just slightly above the norm – 26ppm.

Next, the lubricity of the sampled fuels was examined, i.e. the wear scar diameter corrected to the value of the normal water vapour pressure conditions of 1.4 kPa. The results showed that both samples met the required norms. Yet, the wear scar diameter in pyrolysis oil was significantly greater than in the distilled fuel.

In order to determine differences in the structure of petroleum product samples, a morphological analysis was conducted to identify solid contaminants, using a microscopic image analysis by a G3 particle MALVERN size and shape analyzer. Example images of contaminant particles contained in the samples of Pyrolysis Oil and Marine Distillate Fuel (MDF) are depicted in Fig. 1.

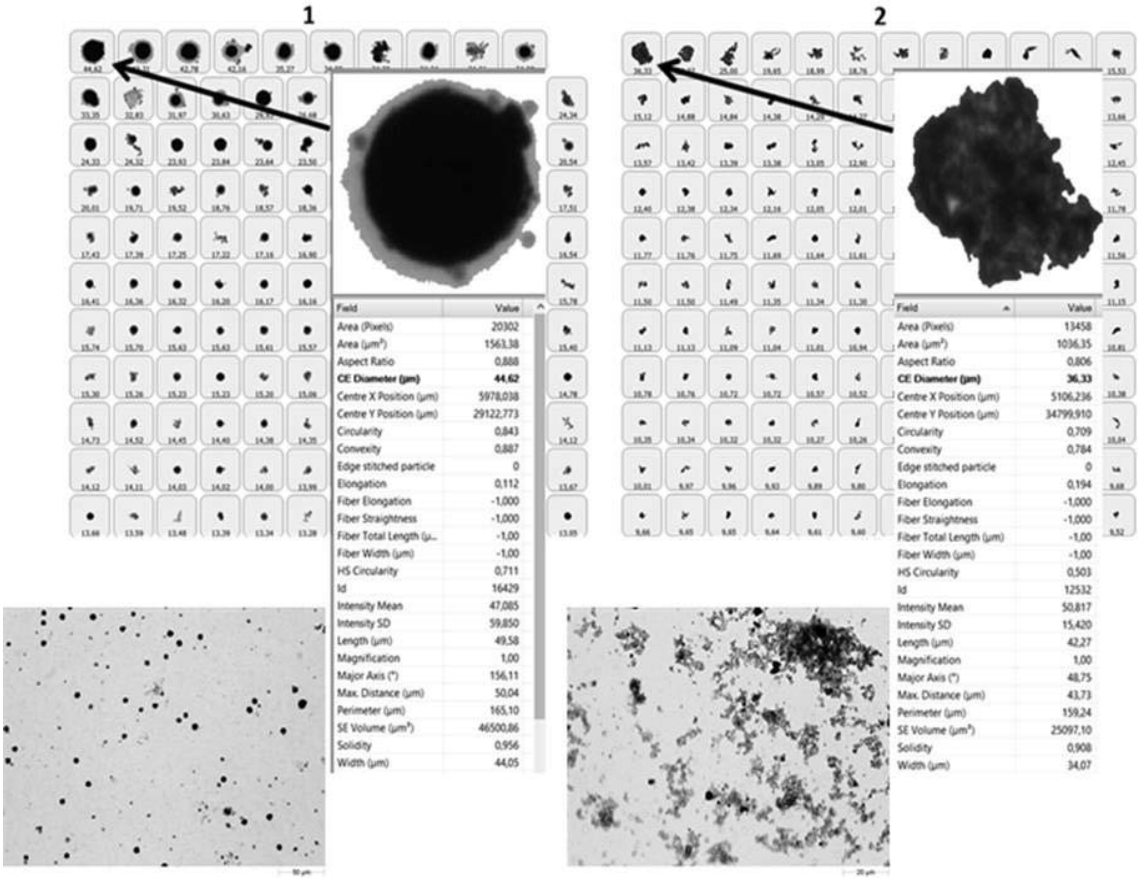

Fig.1 Examples of Particle window and detailed information on single particles
1- Pyrolysis Oil, 2 - Marine Distillate Fuel

Having analyzed the morphology of the samples, it has been found out that the contaminants in pyrolysis oil and marine distilled fuel differ in size and shape. One of the most important morphological parameters of the shape is the circularity. Circularity is the ratio of the circumference of a circle equal to the object's projected area to the perimeter of the object. Figure 2 displays the HS (HS for High Sensitivity) Circularity distribution of particles for Pyrolysis Oil and Marine Distillate Fuel. HS Circularity has a squared term in the numerator and denominator to sensitise the parameter to very subtle variations in the area and perimeter relationship (Malvern Instruments Ltd., 2008).

Circularity has values in the range 0 - 1. A perfect circle has a circularity of 1, irregular or spiked particles has a circularity value closer to 0. For Pyrolysis Oil HS Circularity maximum of particles is 1,00, minimum equals 0,092, HS Circularity D [n, 0.5] is 0,952, D [n, 0.1] is 0,763, D [n, 0.9] is 0,989 and HS Circularity Mean: 0,9114. D [n, 0.5], D [n, 0.1] and D [n, 0.9] are standard percentile readings from the analysis when :D [n, 0.5] is the size at which 50% of the sample is smaller and 50% is larger. This value is also known as the Mass Median Diameter (MMD) or the median of the volume distribution. D[n, 0.1] is the size of particle below which 10% of the sample lies. D [n, 0.9] is the size of particle below which 90% of the sample lies (Malvern Instruments Ltd., 2008).

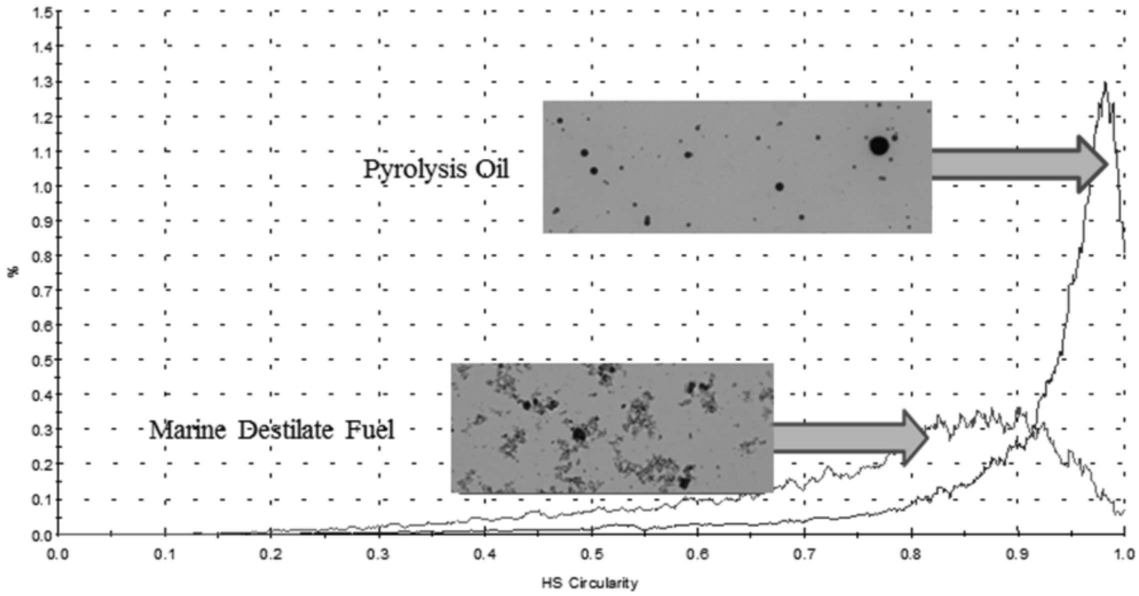

Fig.2. HS Circularity number distribution for Pyrolysis Oil and Marine Distillate Fuel

For Marine Distillate Fuel HS Circularity maximum of particles is also 1,00 minimum equals 0,071, HS Circularity but D [n, 0.5] is 0,807, D [n, 0.1] is 0,503, D [n, 0.9] is 0,935 and HS Circularity Mean equals 0,764.

The particles in pyrolysis oil are characterized by a greater circularity than in MDF, thus the MDF contaminants have a higher tendency to accumulate asphaltene-resinous conglomerates than pyrolysis oil.

In each sample the particles were counted and subsequently grouped by the following particle diameter size: 1 – 5 µm, 5-10 µm, 10-15 µm, 15-25 µm, 25-50 µm, and above 50 µm.

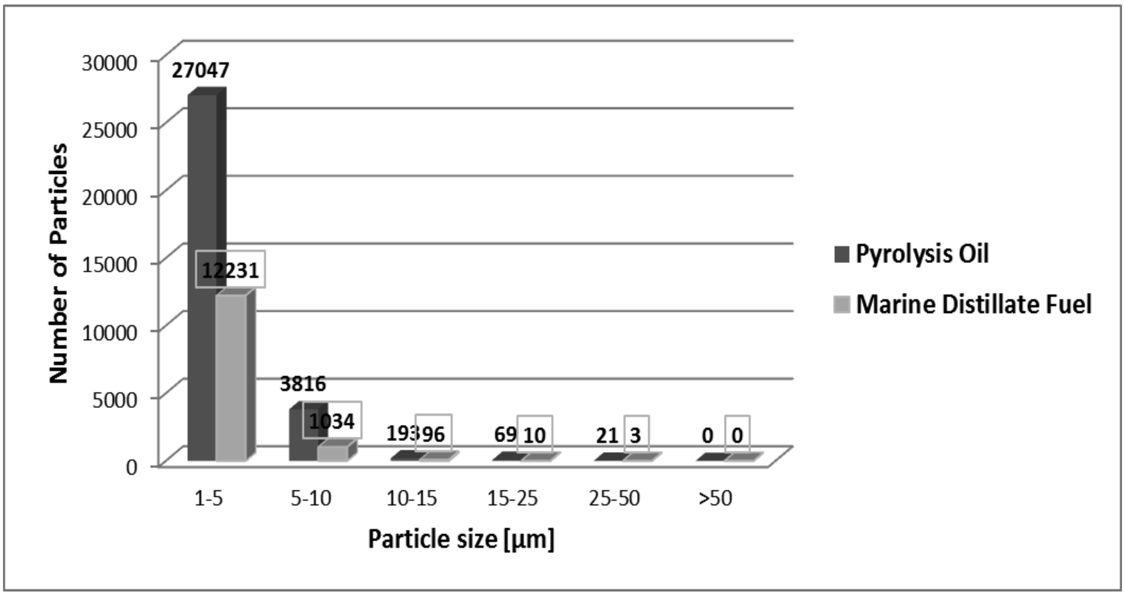

Fig.3. Number of particles in the tested liquids

The morphological analysis of the tested samples (Fig. 3) shows that within the size range of 1- 50 μm Pyrolysis Oil contains the biggest number of particles insoluble in Pentane. Above 50 μm for all samples there were no particles visible for the selected sample preparation method for analysis.

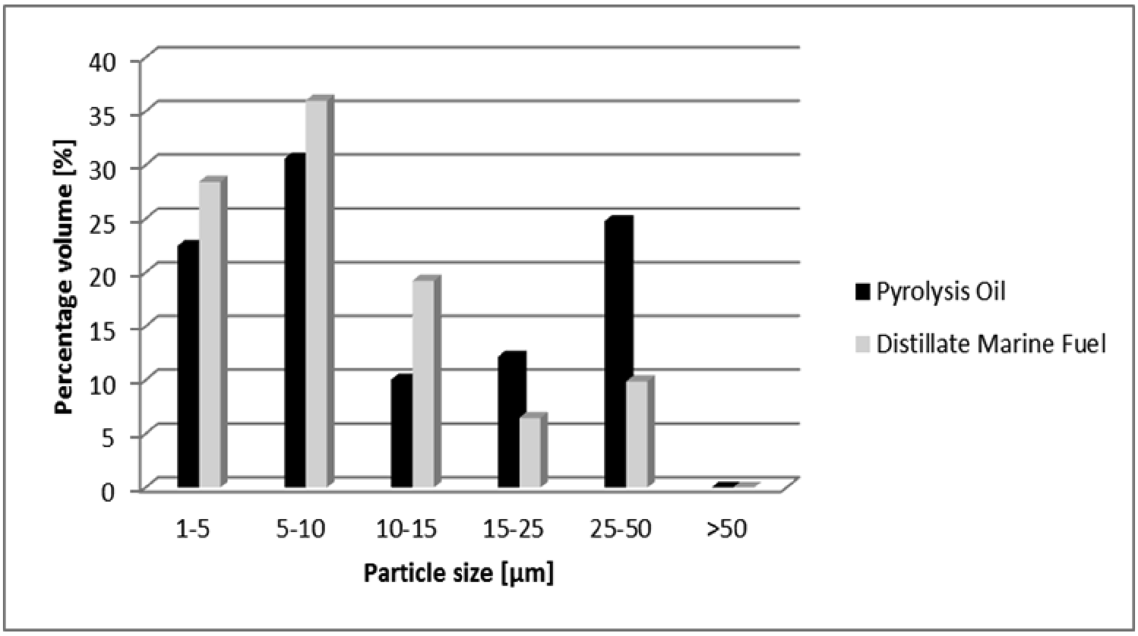

Fig.4. Percentage volume of particle groups distinguished in the tested liquids

Figure 4 shows the percentage volume of particles' groups distinguished in the tested liquids. The carried out analysis proved that for Marine Distillate Fuel the biggest percentage volume is seen in 1-10 μm, 5-10 μm, 10 – 15 μm and equals 28,43%, 35,98% and 19,24% respectively. Pyrolysis Oil can be characterized by a bigger percentage volume within size range of 15 - 25 μm (circa 12,16%) and 25- 50 μm equals 24,75% (above 50 μm for all samples there were no particles visible for the selected sample preparation method for analysis).

Having analysed the samples, it has been proved that Pyrolysis Oil contains the biggest number of insoluble particles, while the biggest percentage volume of particles is seen in Marine Distillate Fuel within the size range of 15 - 25 μm and 25- 50 μm.

The particle contamination analysis proved that in order to use Pyrolysis Oil as engine fuel, the gravitational sedimentation, filtering process and/or the centrifugal separation process are highly inevitable.

CONCLUSIONS

1. The oil obtained by high temperature waste tyres pyrolysis does not fulfill all standard requirements for marine distilled fuel ISO 8217.
2. The tested pyrolysis oil had higher values of density, sulphur content, and carbon residue.
3. The disqualifying factor as an independent fuel was the too low flash point.
4. The morphology of the tested fractions requires the processes of their gravitational sedimentation, filtration and separation due to heavy contamination (big number of particles present) within the wide diameter range.
5. Due to the positive results of the remaining physicochemical indicators meeting the norms of Marine Distillate Fuel MDF, pyrolysis oil may be used as one of the components of fuel mixtures for marine diesel engines

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