Characterization of liquid products from waste tires pyrolysis

Bogumiła WRZESIŃSKA*, Roman KRZYWDA, Tomasz WĄSOWSKI, Leon GRADOŃ – Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland

Please cite as: CHEMIK 2016, **70**, 10, 611–615

Introduction

It is estimated that about 1.5 billion tires are produced worldwide each year. After use they pass to the stream of waste, representing a significant part of them [1]. So far, the main method of tires thermal recycling was burning, mainly as a fuel in cement plants. An alternative way of car tires reprocessing is pyrolysis, which is a thermal, anaerobic decomposition of organic material contained in the tyres at elevated temperature (from 300°C to 900°C). Pyrolytic oil is one of the key products of pyrolysis. The oil is a dark brown or black coloured liquid of medium viscosity with a characteristic sulphurous smell. It is mainly a mixture of paraffin, olefin and aromatic hydrocarbons and their derivatives. Properties of pyrolytic oil are similar to heating or diesel fuel, which indicates the possibility of its application in the fuel and heat industry [2].

Experimental methodology

Pyrolytic oil was tested for its similarity to the standardized properties of petroleum derived products. Therefore, the test methods for crude oil and its products were used:

- Chemical composition qualitatively and quantitatively (selected hydrocarbons) – gas chromatography GC-MS, GC-FID, infrared spectroscopy FT-IR, elemental analysis,
- Fractional composition – distillation,
- Viscosity – Ubbelohde capillary viscosimetry,
- Density – buoyancy effect,
- Flash point – Pensky-Martens closed-cup test,
- The calorific value – calorimetric bomb,
- Sulphur content – ultraviolet fluorescence and the X-ray fluorescence spectrometry,
- Water content – coulometric titration (Karl Fischer),
- Solid impurities content – filtering test.

The oil samples from the local plant of periodic pyrolysis of waste tires were analysed. In the production process the pyrolytic gases after leaving the reactor are condensed in a series of condensers. Sequentially obtained fractions are: very heavy (tarry), heavy, light and non-condensable gases. In this study two main fractions – heavy and light and the so-called averaged oil, which is the composition of these fractions in the ratio corresponding to the production technology, were tested.

Results

Pyrolytic oil contains more than 100 chemical compounds (Fig. 1). Components present in the highest concentration are: aromatic hydrocarbons (such as: benzene, toluene, xylenes, styrene, ethylbenzene, cymene), polyaromatic hydrocarbons (naphthalene), aliphatic hydrocarbons (dodecane, tridecane) and monoterpenes (limonene). The heteroatom (oxygen, nitrogen, sulphur) derivatives of the hydrocarbons are also found in the oil. The elemental analysis shows that the main elements forming the oil are: carbon (79÷84 wt.%, depending on the oil sample), hydrogen (8.5÷9.5 wt.%), nitrogen (approx. 0.8 wt.%), sulphur (approx. 1% wt.).

The aromatic nature of pyrolytic oil is a serious drawback in its application as a fuel. Due to the low hydrogen/carbon ratio, aromatic hydrocarbons tend to incomplete combustion.

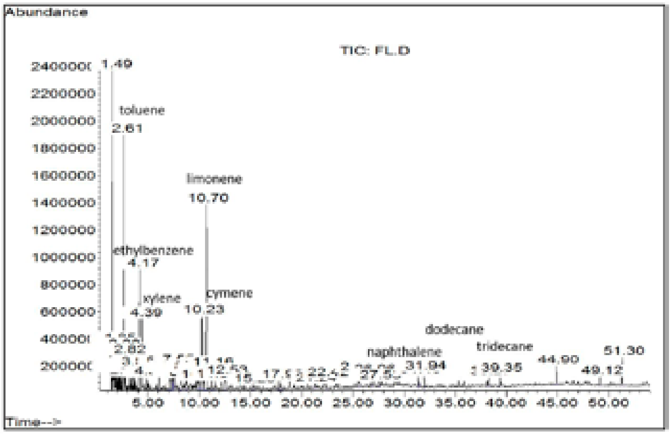

Fig. 1. GC-MS chromatogram of the light fraction of pyrolytic oil

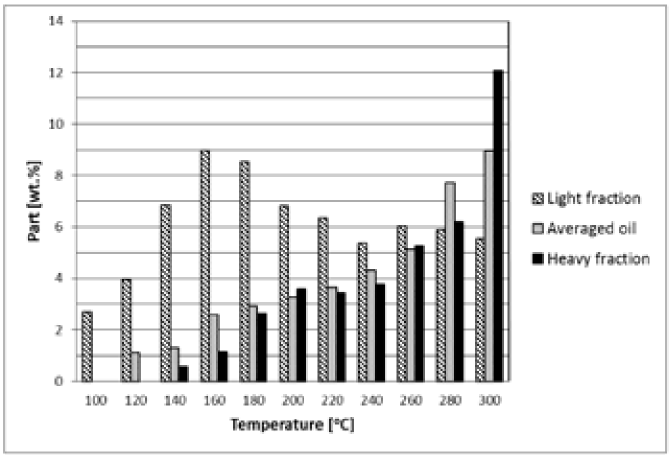

Fig. 2. Fractional composition of pyrolytic oil

Fractional composition of fuel (distillation range) is a parameter used to assess the engine starting ability, tendency to self-ignition, combustion uniformity and a tendency to create deposits. Oil containing too much of the very heavy fraction is undesirable because it is not completely combusted, and during combustion forms excessive amounts of carbon deposits and tars. Too little light fraction adversely affects the ignition properties of fuel. Fractional composition of the tested oil was determined by simple distillation. Figure 2 shows typical results, as the mass ratio of the oil fraction depending on the final boiling point.

*Corresponding author:
Bogumiła WRZESIŃSKA – Ph.D., (Eng.), e-mail: b.wrzesinska@ichip.pw.edu.pl

The examined pyrolytic oil differs from the commercial motor fuels or heating oils. Its properties are most similar to petroleum derived, heavy heating oil. Table 1 summarized the main parameters of the tested oil, compared to the heavy heating oil standards, according to PN-C-96024: 2011.

Table 1

Comparison of the pyrolytic and heavy heating oil standards

Parameter		Heavy heating oil	Pyrolytic oil		
	Unit	Value	Light fraction	Heavy fraction	Averaged oil
Density, 15°C, max.	kg/m^3	–[1]	904	963	949
Calorific value, min.	MJ/kg	39.7	42.8[2]	41.5[2]	42.7[2]
Flash point, min.	°C	62	<10	54	26
Kinematic viscosity 100°C, max.	mm^2/s	55	<1.2	2.85	2.05
Pour point, max.	°C	40	<40	<40	<40
Sulphur content, max.	%(m/m)	1.0	0.89	1.03	0.91
Solid impurities content, max.	%(m/m)	0.5	0.0019	0.0080	0.0061
Water content, max.	%(V/V)	1.0	0.0667	0.0895	0.0750

[1] Not standardized. Value to be given in the test report
[2] Higher heating value

The raw pyrolytic oil, either as a whole (averaged oil) and as the selected fractions collected directly from the pyrolysis plant (light and heavy), cannot be used as heating fuel primarily because of the much lower than the required flash point. The flash point is important because of fire hazards associated with transport, storage and use of fuel.

The second parameter limiting oil application is the content of sulphur, which for the tested oil is near the upper limit, but in case of the heavy fraction slightly exceeds it. The sulphur affects the emissions and the quality of exhaust gas, the corrosivity of the fuel and the performance and efficiency of any catalytic converter. Sulphur is found in the form of organic compounds, mostly thiophenes and thiols (mercaptans) with a strong, unpleasant odour.

The tested pyrolytic oil has low viscosity and good properties in low temperature. Figure 3 shows the relationship between the kinematic viscosity of the oil fractions and the temperature.

The high calorific value of the oil has beneficial effects on the economics of fuel combustion. Many literature sources report also the very low concentration of vanadium which is corrosive.

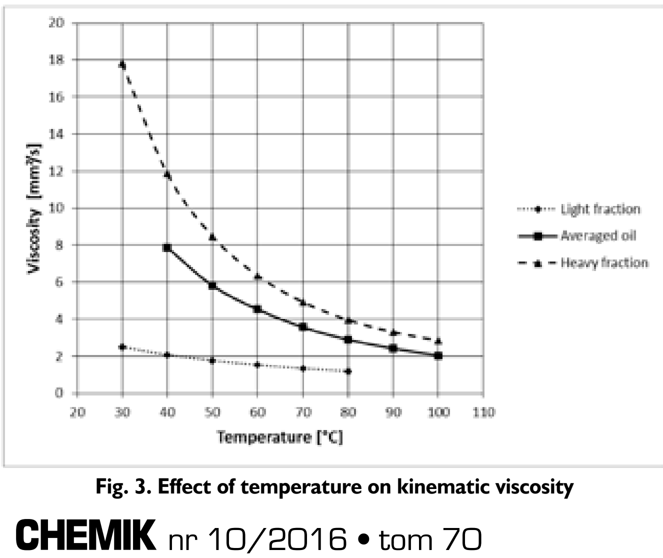

Fig. 3. Effect of temperature on kinematic viscosity

Summary

The experimental studies of composition and physicochemical properties of pyrolytic oil such as: density, viscosity, calorific value, flash point, content of sulphur, solid impurities and water were carried out.

The primary application of pyrolytic oil should be to use it as a heating oil. However, it was found that the raw pyrolytic oil does not meet all of the quality standards for heating oils. Its properties are most similar to those of heavy heating oil.

In order to use the pyrolytic oil for heating purposes two ways are possible: the use of oil or its selected fractions as a component for blends with the standard heating oil or vegetable oils or oil treatment, so it can be used as a stand-alone fuel. Valorisation of pyrolytic oil or its fractions should increase the flash point temperature, lower sulphur concentration and possibly weaken the aromatic nature of the oil.

Literature

1. Williams P. T.: Pyrolysis of waste tyres: A review, Waste Manage., 2013, 33, 1714–1728.
2. Quek A., Balasubramanian R.: Liquefaction of waste tires by pyrolysis for oil and chemicals – A review, J. Anal. Appl. Pyrol., 2013, 101, 1–16.

Acknowledgements

This Project is co-founded by the National Centre for Research and Development and the European Union under the European Regional Development Found according to the agreement UOD-DEM-1–217/001.

INNOWACYJNA GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ ROZWOJU REGIONALNEGO

Bogumiła WRZESIŃSKA – Ph.D., (Eng.), graduated from Warsaw University of Technology, Faculty of Chemical and Process Engineering in 1991. In 1997 she obtained Ph.D. degree in chemical engineering science. She works as a senior lecturer in Department of Integrated Process Engineering, Faculty of Chemical and Process Engineering, Warsaw University of Technology. She is co-author of 1 patent, 5 industrial technologies, 7 scientific papers. Scientific interests: cleaning of exhaust gases from solid and gas impurities, pyrolysis processes of solid wastes, treatment and valorisation of the pyrolysis products, biofuels.

e-mail: b.wrzesinska@ichip.pw.edu.pl, phone: +48 22 234 63 23

Roman KRZYWDA – Ph.D., (Eng.), graduated with honors from Warsaw University of Technology, Chemical Engineering Institute. In 1989 he obtained Ph.D. degree in chemical engineering science. He works as assistant professor at the Faculty of Chemical and Process Engineering, Warsaw University of Technology. He is co-author of 2 patents, author or co-author of 10 science articles as well 7 lectures and posters on conferences. Scientific interests: computer simulation of the processes of the chemical industry and related, flue gas purification, pyrolysis of waste rubber.

e-mail: r.krzywda@ichip.pw.edu.pl, phone: +48 22 234 62 74

Tomasz WĄSOWSKI – Ph.D., (Eng.), graduated from Warsaw University of Technology, Faculty of Chemistry (specialization – chemical engineering). In 1980 he obtained Ph.D. degree with honors in chemical engineering science. In the years 1983-1985 he held an internship researcher at the Technical University in Munich. He works as a senior lecturer in Department of Integrated Process Engineering, Faculty of Chemical and Process Engineering, Warsaw University of Technology. He is author and co-author of 6 patents, 6 licenses, 10 industrial implementations and a number of publications. Scientific interests: process equipment, cleaning of exhaust gases, pyrolysis processes of solid wastes, biofuels.

e-mail: t.wasowski@ichip.pw.edu.pl, phone: +48 22 234 64 92

Professor Leon GRADOŃ – Ph.D., D.Sc., graduated from Warsaw University of Technology, Faculty of Chemistry (specialization – chemical engineering), University of Warsaw, Faculty of Mathematics and Mechanics and post-doctoral studies at the University of Houston. Visiting professor at the universities in US, Japan and Europe. Research and implementation in the field of filtration and particle transport mechanisms in the human respiratory system. Awards of: Polish Academy of Sciences, Prime Minister, Smoluchowski prize, Japan Society for Promotion of Sciences, Minister of Science, Minister of Labour. Author and co-author of 15 books and chapters in monographs, over 230 international papers, over 280 conference proceedings and 65 patents.

e-mail: l.gradon@ichip.pw.edu.pl, phone: +48 22 825 91 80