

Analysis of the pollutants, including polycyclic aromatic hydrocarbons emitted by the internal combustion engine powered by pyrolytic oil

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Abstract. Possibility of powering the compressed combustion engine, 1.9 TDI produced by Volkswagen concern by pyrolytic oil was presented. Three blends with different pyrolytic oil and diesel content were prepared. To compare additionally diesel oil was tested. In researches measurements of concentrations pollutants emitted from the engine such as soot, NO_x, CO, CO₂ and PAHs were carried out. Also fuel consumption for each fuel was measured. Tests were conducted in chosen engines operation points: two values of rotation speed (1500 and 3000 rpm) and 6 values of torque from minimum value to 150 Nm every 30 Nm. In researches different methods and devices were used such as chromatography method, exhaust analyser and smoke meter. Studies have shown that it was possible to supply the engine by mixture of pyrolytic oil and diesel, but it was justified only in under certain conditions related to the composition of the mixture.

1. Introduction

The worldwide economic development has always included a dynamic growth and spreading different kinds of mode of transport. The discovery and usage of combustion engine in vehicles was a great technological revolution in a transportation major itself. Firstly power units with compression ignition were powered by alcohol and vegetable oil. On the cusp of the 19th and the 20th centuries, the German engineer Rudolf Diesel was using arachnid oil as a fuel to his compression-ignition engine, well known as the diesel engine. Nevertheless an increasing availability of cheap oil resources led to a successful blockade of biofuels' sector development. Petroleum and carbon have become an essential energy source for the world, which has been developed not only industrially, but also demographically. During the II World War, a limited access to conventional diesel oil supply caused a temporary return to research on alternative oil in a vehicle propulsion. After fuel crisis in 70's and 80's [1], the world paid attention afresh to alternative fuels. Despite the lapse of years, an unconventional fuel has never displaced the petroleum-derived fuel from use.

Nowadays, the growth of agricultural production, environment pollution and limited resources of petroleum has led to increase the attention paid to vegetable origin oil as a fuel to diesel engine. According to the top-down directives, member countries of the European Union are obliged to rise a usage of bio-fuels in a transportation, which share in the total mass of fuels shall increase up to 20% in



2020 [2]. A sustainable development requires an appliance of biomass as a renewable energy source. Taking into consideration ecological aspects, we shall remember that the demographic growth is inseparably attached to higher quantity of waste. Constantly piling up humps of trashes on garbage dumps are being also generated due to the activity of automotive industry. The increase in number of vehicles has caused an enhancement of operating elements, which are essential to a safe and correct functioning of means of transport, one of which are tires. A possibility of processing rubber elements has always been quite problematic. Furthermore, the growing amount of tires stored on garbage dumps constitute a fire hazard due to self-igniting, which can lead to serious ground water, soil and air pollution. It has been estimated that the stock of tires is equal to 21 million tons, moreover, less than 25% of which have found its application [3]. The rest of this amount is not recycled on account of lack of profitable methods. According to the 217th resolution of the Council of Ministers dated 24 December 2010 in Poland it is prohibited to abandon in random places or store on a landfill used tyres. In spite of this, it is quite a frequent activity.

The main methods of processing rubber waste are: recycling; regeneration process and co-firing in a cement plant. The alternative to those conventional processes could be a transformation of used tires into pyrolytic oil as well as the application of it as a supplement to diesel oil. The pyrolysis itself is a smouldering process in a high temperature. Tires headed to this operation shall be shredded to 5-15 cm pieces in advance. This featured process is accompanied by a formation of pyrolytic gas, pyrolytic oil and biocarbon [4]. Products obtained as a result of pyrolysis depend on chemical composition of tires, the way of its fragmentation as well as on parameters of the process. Pyrolytic gas can be used for energetic purposes of the process itself, while biocarbon can be applied for a plastics production or as a fuel in a cement plant. Nonetheless, the most desired pyrolysis product is oil, which treated further might be used as a liquid fuel [5]. Taking into consideration the fact that both engine oil and car fuel have high heating value, it is possible to mix them with pyrolytic oil (heating value about 43.5 MJ/kg). Thanks to this we may achieve a potentially alternative fuel. In the article [4] there is shown a process of pyrolysis of used tires and a comparison of selected physico-chemical properties of diesel oil bought on Polish gas station in 2014 with pyrolytic oil with three kerosene fractions separated from it. Crude pyrolytic oil is a mixture of saturated and unsaturated hydrocarbons (linear and cyclic) and aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons (PAHs) also known as polycyclic organic matter (POM) are a side product of reactions taking place during incomplete combustion of organic matter and constitute a very diverse group of pollutions. They contain from two to a few aromatic rings in a particle and form a huge group to which rank several hundred of compounds. National Institute of Standards and Technology administered over 660 formulas of PAHs in 2013 [6]. Given their toxicity and influence on a human being, the most denoted 17 are: acenaphten, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, phenanthrene, pyrene and indeno (1,2,3-cd) pyrene. They hold various structural forms characterized by different mutual placement of benzene rings in a molecule. It shall be pointed out that those compounds are always existing in a mixture. A numerous research has confirmed that the presence of at least one compound of PAH group in environmental test drags on the presence of other compounds from this group. The best examined aromatic hydrocarbon is benzo(a)pyrene, which due to prevalence and strength of carcinogenesis has been found as an indicator of the entire group of aromatic hydrocarbons.

2. Material and methods

The test bench was consisted of the following elements: the engine, exhaust gases analyser and the sampling kit (for samples taken to chromatographic analysis). The tested engine was a diesel unit with classification: 1.9 R4 TDI PD AWW, produced by Volkswagen concern. The engine was coupled to eddy current brake AVL.

To analyse exhausts the portable gas analyser AVL PG-350E brand Horiba was used. With using that device it was able to measure up to five different gas components at the same time, such as: nitrogen oxides, sulphur dioxide, carbon oxide, carbon dioxide and oxygen according to norm PN-EN 15267-3:2008 and procedure concerning quality assurance PN-EN 14181:2015-02 for automatic measurement systems.

The main element of research was to take exhaust gases from working engine in order to analyse its composition with a view to notify volatile organic compounds and polycyclic aromatic hydrocarbons. In order to make it possible, there were made particular bags to accumulate the fumes. The research was carried out for three mixtures prepared beforehand and for pure diesel oil. The measurement of diesel oil was taken as a control sample for comparison of tested alternative fuels. It was established to take 6 measurements for each fuel mixtures for values of engine's loads from the minimum allowed by the apparatus (about 15,5 Nm) to 150 Nm. The work conditions were tested for two rotation speeds: 1500 and 3000 rpm. The samples for chromatography analysis were taken only at the lowest rotation speed. At both of engine speeds the fuel consumption, the pressure inside the cylinder and the soot content and concentration of NO_x and CO was measured. To analyse the composition of PAHs in exhausts it was needed to take more than 30 dm³ of gases at each load due to very low concentration values of these pollutants in the exhausts.

The analysis of concentration of PAHs in exhaust gases were conducted on the stationary gas chromatograph brand Agilent Technologies, model 7890B (GC) coupled with mass spectrometer 5977A (MSD). Before the analysis it was needed to carried the fumes collected inside the bags carried through glass tubes with active carbon (SKC with classification 226-01) from a coconut husk and are intended for taking samples of organic compounds. The dual-channel portable aspirator ASP-3 II was used in this regard. It has two independent measurement's channels and is designed for a collection of gases from different kinds of technological process emitters. The device contains an efficient pump with high vacuum and built-up flow stabilizer, so that the flow doesn't change during measurement despite of changes of resistance on filters. The flow is being regulated smoothly and measured by electronic flowmeter with high accuracy. The current value of the flow is being displayed on LCD screen. A quantity of gas which shall be carried through an sorbent is established before measuring. For the analysis purpose there was used a volume regulation. Analysis of PAHs were conducted in following parameters of chromatograph:

- Capillary column: DB-EUPAH 20 m x 180 µm x 0.14 µm,
- Temperature program of oven: 45°C (hold 0.8 min) - 200°C (45 °C/min) - 225°C (2.5°C/min) - 266°C (3°C/min) - 300°C (5°C/min – hold 5.289 min),
- Analysis time duration: 40 minutes.

Measurement of soot content was conducted directly in exhausts flow using smoke meter AVL 415. That device enables the measurement of content of soot by the phenomenon of the change in the amount of electromagnetic waves absorbed by various shades of colour on a scale from 0 (perfectly white, which means no smoke) to 10 (black, the highest degree of smokiness). It is possible to obtain the results in scale called FSN (filter smoke number) or in mg/m³. Each test was started with the flushing of device by clean air. The pressure in the system is higher, what prevents it from entering and retaining solid particles contained in the exhaust. During the measurement, precisely defined volume sample is passed through a paper filter. The soot particles are stopped on it, which causes it to darken depending on number of soot particles. In the next step, from the filter containing the sample of exhaust gases electromagnetic wave is reflected and goes to the photoelectric detector. The ratio of the amount of absorbed and reflected electromagnetic radiation is directly proportional to the opacity of the filter, so also to the amount of soot particles in the exhaust.

Due to the difficulty of mixing diesel oil with pyrolytic oil there was also used butanol in order to create a homogeneous mixture. Three mixtures were composed in proportions shown in table 1.

Table 1. Content of specified composites

<i>Number of mixture</i>	Content [%]		
	Diesel oil	Pyrolytic oil	Butanol
<i>I</i>	50	25	25
<i>II</i>	33,3	33,3	33,3
<i>III</i>	25	50	25

3. Results

In table 2 all results, except PAHs concentrations, obtained during the test were presented. Unfortunately, due to unsterilized work of engine in case of the III mixture, it was impossible to continue the measurements.

Table 2. Concentrations of measured pollutants emitted from the engine powered by tested fuels

No.	rpm	Diesel						Mixture I				
		M, Nm	Soot, mg/m ³	NO _x , ppm	CO, ppm	CO ₂ , %	Fuel cons., dm ³ /h	Soot, mg/m ³	NO _x , ppm	CO, ppm	CO ₂ , %	Fuel cons., dm ³ /h
1	1500	15,5	4,88	30,69	740	3,3	0,93	6,46	21,78	2013	2,22	1,24
2		30	18,07	59,02	475	3,91	1,51	6,02	53,86	2022	3,39	1,76
3		60	34,09	111,8	402	5,84	2,58	5,85	77,87	2336	5,28	2,86
4		90	11,76	348,18	301	6,62	3,12	17,6	279,37	1309	6,56	3,78
5		120	23,43	592,3	230	8,57	4,78	15,9	425,06	190	6,35	5,08
6		150	79,32	749,73	676	9,73	5,94	20,58	872,37	216	9,35	5,71
1	3000	15,5	6,48	84,36	448	2,83	2,33	4,18	40,03	2294	3,11	2,97
2		30	13,23	90,9	419	3,82	3,15	6,97	85,21	1387	3,96	3,64
3		60	24,02	167,08	490	6,07	5,04	20,4	166,65	743	5,79	5,64
4		90	32,96	281,98	288	7,52	7,43	24,06	302,96	310	6,48	8,17
5		120	11,37	579,13	277	8,29	10,13	39,25	436,4	261	8,67	11,44
6		150	91,36	722,54	623	9,8	11,6	33,59	321,39	133	4,55	12,19

No.	rpm	Mixture II						Mixture III				
		M, Nm	Soot, mg/m³	NO _x , ppm	CO, ppm	CO ₂ , %	Fuel cons., dm³/h	Soot, mg/m³	NO _x , ppm	CO, ppm	CO ₂ , %	Fuel cons., dm³/h
1	1500	15,5	9,43	3,02	34	0,03	1,37	36,47	36,63	1827	3,13	1,56
2		30	13,4	45,96	1954	3,8	1,85	46,72	44,61	1003	1,78	2,94
3		60	11,62	75,4	1641	4,67	2,9					
4		90	29,15	283,87	551	5,33	3,86					
5		120	30,24	548,79	623	8,26	5,01					
6		150	30,56	775,68	285	8,54	6,34					
1	3000	15,5	4,25	486,23	1789	7,19	2,87					
2		30	6,23	97,91	2084	3,8	4,02					
3		60	21,05	231,55	1214	5,67	5,33					
4		90	28,97	331,58	751	7,48	7,86					
5		120	41,47	334,58	152	4,18	10,61					
6		150	30,73	332,94	93	3,32	12,69					

As can be seen from the table, it was hard to indicate the best fuel in terms of all pollutants and fuel consumption in all range of set parameters of engine. Generally, in both rpm values, content of soot in exhausts was the lowest for mixture I. Similar situation was for NO_x concentrations. Only for a few points of engine's work (in lower loads at 1500 rpm) for mixture I concentration of NO_x was higher than for mixture II. In turn, CO concentration values were the lowest for diesel, both at 1500 and 3000 rpm. Only at torque above 100 Nm, concentrations of CO were lower during powering the engine with mixtures. In figures 1 and 2, the relationship between the CO₂ concentrations and fuel consumption at 1500 rpm (fig. 1) and at 3000 rpm (fig. 2) have been presented.

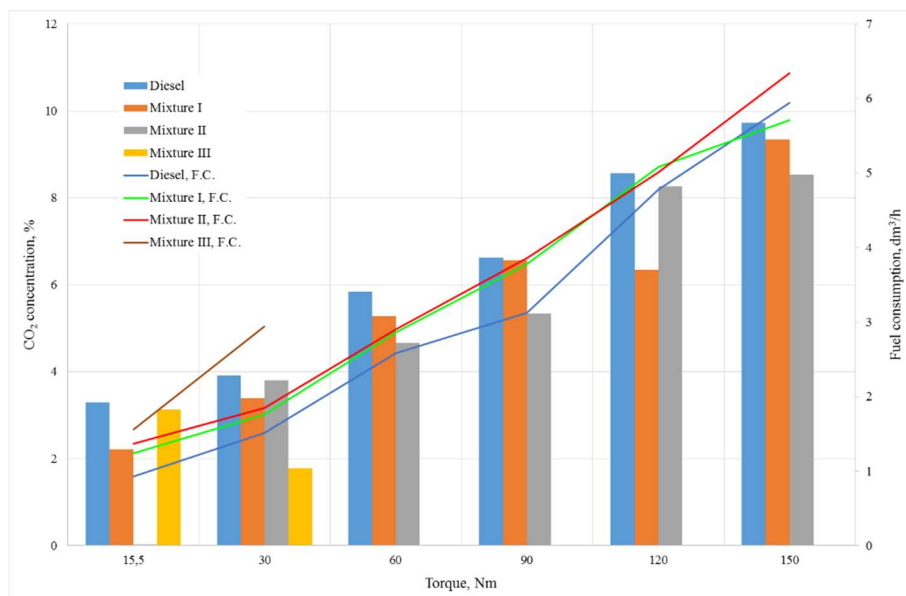


Figure 1. CO₂ concentrations and fuel consumption values measured for tested fuels at 1500 rpm

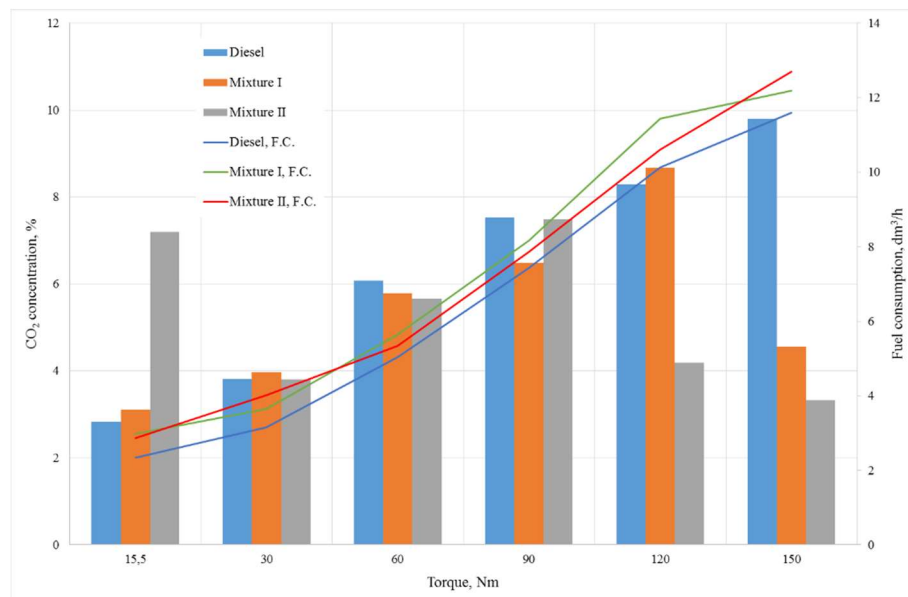


Figure 2. CO₂ concentrations and fuel consumption values measured for tested fuels at 3000 rpm

The figures showed that although the fuel consumption for diesel is the lowest among all tested fuels, concentrations of CO₂ are the highest for the diesel. It could mean that the efficiency of combustion is better for pure diesel in contrast to mixtures with pyrolytic oil. However, concentrations of pollutants are lower for the mixtures, which meant that exhaust had less toxic ingredients when the engine is supplied by mixtures containing pyrolytic oil, except the mixture III (with 50% content of pyrolytic oil).

Due to the great complexity of analysis of PAHs, samples for that tests were taken only in two load values: the lowest (15,5 Nm) and the highest (150 Nm) one only at 1500 rpm. In figure 3 results of measured total PAHs' concentrations were presented.

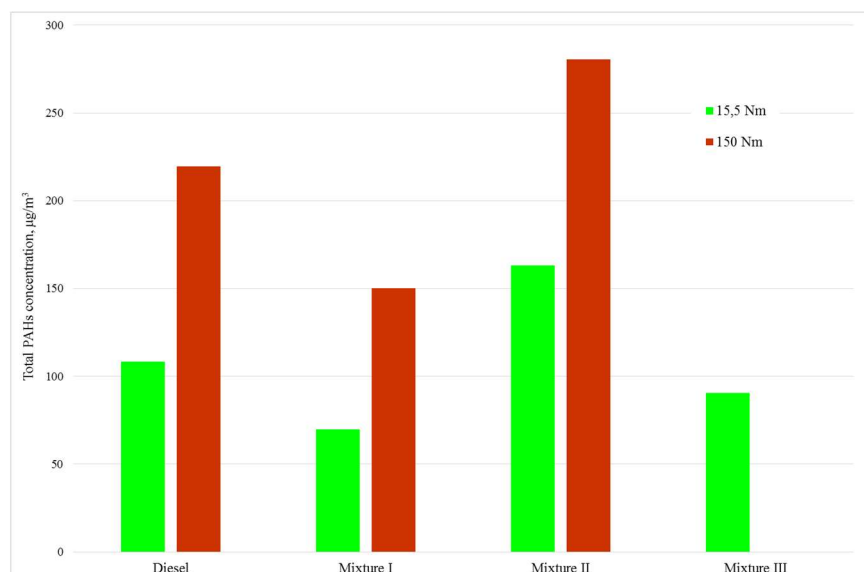


Figure 3. Concentration of total PAHs at 1500 rpm and torque values 0 and 150 Nm

The lowest values of total PAHs concentrations were measured for mixture I at both, 15,5 and 150 Nm. For mixture II there were higher total PAHs concentrations than for pure diesel. Because of the engine's

unstable work it was no possibility to take the sample at 150 Nm torque value for mixture III. It confirmed that mixtures with high content of pyrolytic oil was not suitable for powered diesel engine.

4. Summary and conclusions

In the article a possibility of powering an engine with compression ignition with a mixture of diesel oil and pyrolytic oil was presented. The inclination of using a product of tyres' pyrolytic was closely related to ecological aspects. Used tires pilling up on landfills have become an onerous problem. The conventional method of its utilization is insufficient, hence it is worth looking for different possibilities to reduce a quantity of used tires. Three mixtures of pyrolytic oil, diesel fuel and butanol were used in researches. Each of them had various concentrations of the components.

According to measurements of a temporary fuel consumption for each sample it can be concluded that along with the usage of mixture richer in pyrolytic oil, the fuel consumption increased in 5-10%. It was presumably caused by a lower total calorific value.

During a measurement of grade of opacity of exhaust gases, the opacity increased with a higher engine speed and loading. Together with an increase in braking torque there was observed an increase in the content of nitrogen oxides and carbon dioxide, while the concentration of carbon monoxide decreased.

The content of polycyclic aromatic hydrocarbons in exhaust gases was very low. However, due to its carcinogenic properties, each source of PAH should be eliminated. After conducting the analysis by gas chromatography it turned out that in terms of emissions of PAH the best quality is the mixture I. Perhaps, it's connected to a relatively low content of pyrolytic oil and the replacement of diesel fuel by butanol in a mixture. Therefore it can be concluded that its emission depends on the engine's loading.

The application of pyrolytic oil as a component to compression ignition engine's fuel is possible but with some restrictions concerning on the composition of the mixture. Generally, in many ways the best mixture was mixture I, which contained 25% of pyrolytic oil and 50% of diesel. Exhaust gases for that mixture were characterized by the lowest PAHs, NO_x and soot concentrations and quite low fuel consumption. Mixture II, which contained 33,3% pyrolytic oil and 33,3% diesel also could be used as fuel supplied compression ignition engine, but it was less justified in terms of economy and ecology. Mixtures with 50% and more content of pyrolytic oil were not suitable to power the tested engine due to problems with maintaining stable engine operation.

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