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Combustion comparative analysis of pyrolysis oil and diesel fuel under constant-volume conditions

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The article discusses the research results on the combustion of pyrolysis oil derived from the pyrolysis of HDPE plastics after its distillation. The tests were carried out in a constant-volume combustion chamber in conditions similar to those in a compression-ignition engine with a compression ratio of 17.5:1. The phases of premixed and diffusion combustion and the ignition lag were determined. Then, diesel fuel combustion tests were performed under similar pressure-temperature conditions. Comparative analysis was used to draw conclusions as follows: the percentage fraction of heat released from the premixed combustion phase to total heat for pyrolysis oil was nearly 22%, whereas this parameter is 15% for diesel fuel, the maximum combustion rate for the premixed combustion phase for pyrolysis oil was approximately 27% higher than the premixed combustion rate for diesel fuel, the ignition lag for pyrolysis oil was slightly longer compared to that for diesel fuel. The presented parameters have a significant impact on both the development of combustion and the thermal efficiency of the internal combustion engine. Summing up, one can conclude, that pyrolysis oil can be applied as a substitute for diesel fuel both as a single fuel or blend component with it.

Key words: *pyrolysis oil, diesel fuel, combustion, heat release rate, IC engine*

1. Introduction

In the search for renewable fuels, more and more attention is paid to by-products generated during the thermal processing (torrefaction, pyrolysis, gasification) of organic substances. Such by-products include post-process liquid commonly referred to as pyrolysis oil. Pyrolysis oil is a condensate from liquid vapors generated during pyrolysis. Typically, biomass and organic waste (plastics, tires) are organic substances that are used as feedstock for a pyrolysis reactor. Due to the relatively well-developed technologies of torrefaction, pyrolysis, and gasification of plant biomass, attempts are made to use these technologies for the thermal processing of organic matter other than biomass, mainly car tires and plastics without the possibility of recycling them. Based on these technologies, solutions for the thermal decomposition of sewage sludge, plastics, and rubber from used tires have been successfully implemented. As discussed in the available literature [2, 10], plastic waste and used car tires, due to their high carbon and hydrogen content, are considered attractive materials for the production of liquid and gaseous substances with a satisfactory good calorific value. Hence, in the short-term future, these products may have a significant share in the fuel sector, provided that a number of changes in the waste laws are introduced in order to convert waste into a full-value material.

Currently, research is being carried out on the combustion of raw pyrolysis oil and mixtures with other fuels to enrich its combustible properties [3]. Mixing crude pyrolysis oil with another fuel substance can also be caused by reducing the content of unfavorable components, e.g. sulfur present in crude pyrolysis oil obtained from the pyrolysis of used car tires. On the basis of the studies carried out so far, there is a number of reasons to clearly confirm that pyrolysis oil should be tested in terms of its use as fuel for both automotive engines and engines in cogeneration units. Crude pyrolysis oil is a black, opaque substance with a strong characteristic odor. This oil mainly contains hydrocarbon compounds, alcohols, water, and organic acids [1]. On the other hand, due to its relatively high calorific value, pyrolysis oil is considered a potential fuel for reciprocating, piston engines and gas turbines [7, 14, 15]. Umeki [15] found that a mixture of pyrolysis oil and diesel fuel has physical and chemical properties that aspire to be directly used in a diesel engine. In addition, his research showed that the pyrolysis oil was characterized by a research octane number close to 90, i.e. such as typical gasoline for internal combustion engines of vehicles. Tudu [14] investigated and proposed a blend consisting of 50% diesel, 40% light pyrolysis oil, and 10% dimethyl carbonate. Hurdogan, after adding 10% of pyrolysis oil to diesel fuel, obtained a fuel that did not deteriorate engine performance in terms of torque and output power [7]. Furthermore, the implementation of a fuel that is a mixture of butanol (renewable fuel) and pyrolysis oil (as a product of the use of biomass/plastic waste) can be considered an innovative action [11]. The research described in this manuscript focused on the application of this fuel to a stationary engine, but the results indicate that it can also be used for automotive SI engines. Based on the literature review, a growing interest in plastic pyrolysis oil and its use as a potential primary or additional fuel for an internal combustion engine can be observed [4, 5, 8, 9, 13, 16].

A crucial environmental challenge is the analysis of exhaust gas toxicity from an engine fueled with pyrolysis oil. Due to its diverse origin, this oil may be a mixture of polycyclic aromatic hydrocarbons and may also contain chlorine which is a precursor for dioxins formation. Examination of the exhaust gas toxicity may result in supplementing the exhaust gas purity standards with compounds that may be formed from the combustion of pyrolysis oil and are not present during the combustion of conventional fuels.

2. Methodology and test stand description

The studies presented in the article are based on experiments. These studies were conducted with the aid of comparative analysis. The results of the combustion of two liquids in a constant-volume combustion chamber were used for the analysis. One of the liquids was the tested pyrolysis oil. The reference liquid was light diesel fuel.

The constant-volume combustion chamber is a test stand where the pressure course was recorded in the time interval including injection, ignition, and flame development until its extinction for pyrolysis oil and reference fuels in conditions similar to those in a real diesel engine prevailing at the time of fuel injection into the combustion chamber and the cylinder. Techniques of testing various liquids as potential engine fuels in a constant-volume chamber assisted with high-speed video cameras is a relatively new measurement methodology, which usability was confirmed among others in work by Grab-Rogalinski [6]. Tests of injection in an oxygen-free atmosphere were also carried out to eliminate ignition and to determine the fuel flow rate from the injector nozzle and the maximum range of the injected fuel stream.

In addition, the presented phenomena were recorded using a high-speed digital camera at a frame speed of up to 20,000 fps. Figure 1 shows the combustion chamber where the injection and combustion experiment was carried out. The combustion chamber has a volume of 1.1 dm^3. Inside, the chamber is oval with a diameter of 101.6 mm.

Fig. 1. The constant volume combustion chamber

The test bench with a combustion chamber is presented in Fig. 2. The placement of both cameras and the monochromatic light source is shown. Camera 1 recorded the image in transmitted light using the Schlieren technique (Fig. 3a). This camera was set transversely to the direction of the outgoing fuel stream. Whereas, Camera 2 was positioned along the longitudinal symmetry axis of the injector and was used to record the image of self-illumination from the flame (Fig. 3b). However, in this case, the camera could also record the reflected light generated by one of the sources. It was particularly useful in the analysis of injection and spraying in an oxygen-free atmosphere, where the lack of self-luminance from the flame made the recorded image practically illegible.

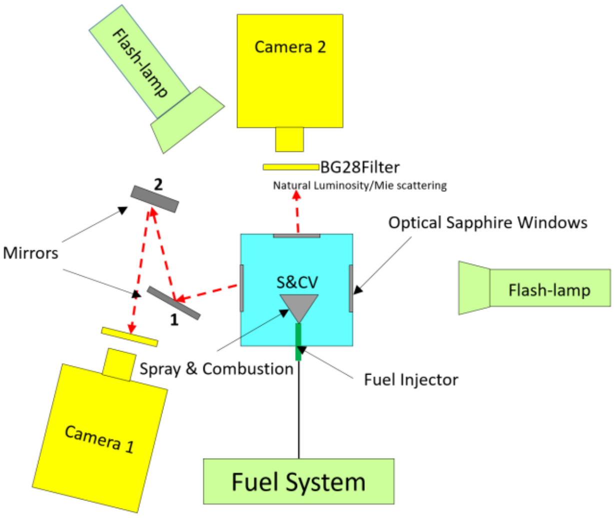

Fig. 2. The diagram of the test set-up with the constant-volume combustion chamber

The test stand consisted of two high-speed digital cameras Photron Fastcam SA1.1 with the following operational parameters:

- lenses: focal length/aperture: 85 mm/1.4 and 60 mm/1.7
- resolution: 512 × 512 pixels, monochrome image, 8-bit gray scale
- image recording speed: 20,000 fps
- shutter speed: 3.26 μs
- protective filter: 550 nm.

The methodology and the course of the experiment of combusting the tested liquid in the combustion chamber were precisely described in the procedure, the most important points of which are presented as follows:

- the combustion chamber is designed for fuel self-ignition tests at elevated temperature and pressure
- the combustion chamber is initially filled with a mixture of H_2-C_2H_2-O_2-N_2 gases in appropriate proportions
- ignition of the gas mixture is initiated from the spark plug
- as the result of the combustion of H_2 and C_2H_2 the following mixture was created: H_2O, CO_2, O_2 and N_2 with the proportions required by the experiment, especially taking part in the study, which in this case was at a concentration of 21% in terms of the total volume filling the chamber
- injection of the tested fuel is performed automatically.

The injection of the tested fuel took place after reaching the pressure in the combustion chamber at the level of, for example, 41 bar or at a temperature set-point of e.g. 1000 K, which corresponded to conditions similar to those prevailing at the end of the compression stroke in the engine with a compression ratio of 17.5:1.

The tests were carried out for pyrolysis oil and light diesel fuel according to the data shown in Table 1 and Table 2.

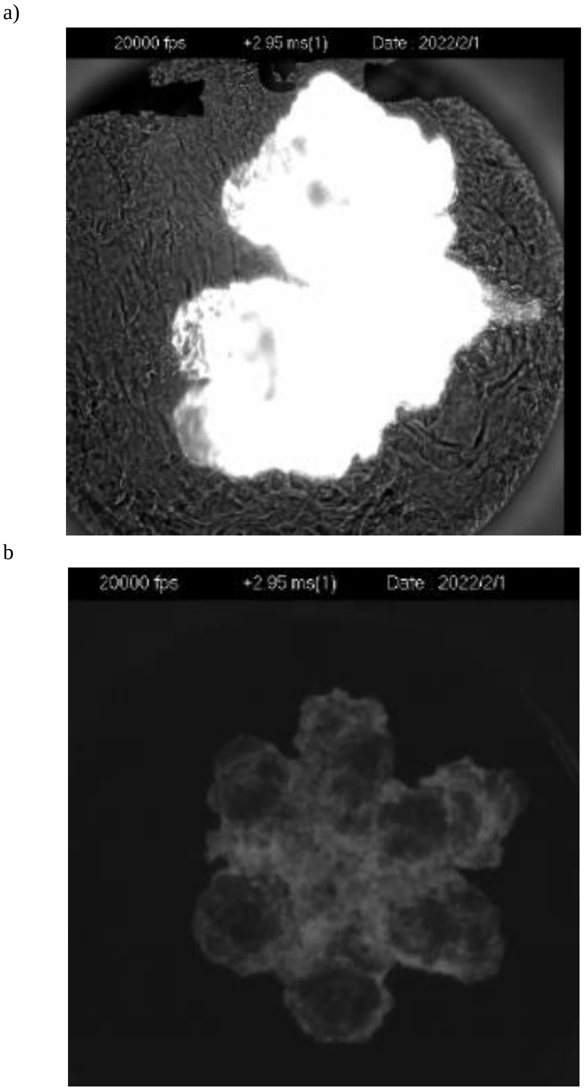

Fig. 3. Exemplary images: image from Camera 1 (a), image from Camera 2 (b)

Table 1. Selected fuel properties

		Fuel	
		Pyrolysis oil	Diesel fuel
Density	kg/dm^3	738	852
Surface tension	mN/m	22.9	27.6
Dynamic viscosity at 40°C	mPa·s	0.48	3.77
Cetane number	–	10–40	50

Table 2. Experimental matrix

		Fuel	
		Pyrolysis oil	Diesel fuel
Number of tests of combustion in the atmosphere 21% O_2		2	5 (41 bar)
Number of tests when the chamber was filled with nitrogen, without oxygen		2	2
Initial temperature	K	453	453
Injection temperature	K	1000	1000
Pressure inside the chamber during injection	bar	41	41
Injection pressure	bar	400	400

For the initial pressure of 41 bar, five tests were carried out to check the repeatability of the results and evaluate the measurement accuracy.

In the thermodynamic analysis, calculations of the heat release rate (HRR, dQ/dt) were performed. In order to calculate the heat release rate during the combustion of the tested fuel in a constant-volume chamber, a number of simplifications were adopted as follows:

- the constant-volume combustion chamber is an insulated chamber, which means that there is no heat transfer from the chamber to the environment
- gases filling the chamber are treated as an ideal gas
- the increase in mass and number of moles resulting from the injection of the tested fuel into the chamber is considered marginal and does not cause a significant change in the calculations
- the change in the chemical composition of the gases before and after the combustion of the tested fuel is irrelevant for the accuracy of the calculations, it is assumed that the mixture does not change.

The heat release rate was calculated based on the following relationships:

- equation of state for an ideal gas (1)
- relation for the universal gas constant R_u and the specific heats c_p and c_v (2)
- caloric equation for internal energy (3)
- first law of thermodynamics (4).

$$p \cdot V = n \cdot R_u \cdot T \tag{1}$$

$$\frac{c_V}{R_u} = \frac{c_V}{c_P - c_V} = \frac{1}{\kappa - 1} \tag{2}$$

$$U_i(T_i) = n_i \cdot c_{V,i} \cdot T_i \tag{3}$$

$$Q = U_2(T_2) - U_1(T_1) \tag{4}$$

After rearranging the equations (1-4) it yields

$$dQ = \frac{1}{\kappa - 1} \cdot V \cdot dp \tag{5}$$

Hence, the elementary dQ as a time-dependent variable will be proportional to the heat release rate dQ/dt, which is related to the time of 1 second.

An exemplary dQ/dt course is shown in Fig. 4. As seen from equation (5), the pressure change dp is in strict proportion to change in the heat released dQ, so does to dQ/dt. The index κ of specific heats c_p/c_v was calculated for a given pressure and temperature based on c_p and c_v for the mixture of gases filling the combustion chamber before the start of injection of the tested fuel.

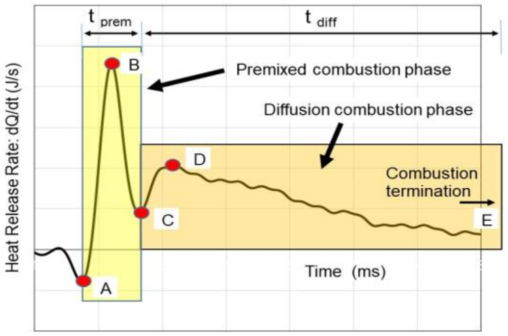

Fig. 4. Exemplary plot of heat release rate with highlighting premixed and diffusion combustion

In the initial range, a decrease in the HRR can be observed. This drop is located in the time interval when the injector opens (point A in Fig. 4) and fuel flows into the chamber. The most likely explanation for this heat loss is the evaporation of the injected fuel. In addition, it can be also assumed that the negative HRR is also influenced by chemical reactions that initiate ignition, which are usually endothermic reactions.

From the heat release rate HRR, one can read the range typical for premixed and the diffusion combustion. It is obvious that both types of combustion occur one by one in time, but it is difficult to identify when one ends and the other begins. Hence, a simplification was introduced, according to which the premixed combustion starts from point A and it goes until achieving a local minimum (point C). Diffusion combustion, on the other hand, was assumed to last from point C to the end of combustion, i.e. until dQ/dt reaches 0 at point E, the location of which is not indicated in Fig. 4.

Additionally, knowledge of the heat release rate dQ/dt will lead to determining combustion phases based on the accumulated heat Q(t) with Eq. 6.

$$\mathrm{Q(t)} = \frac{1}{\kappa-1}\cdot \mathrm{V}\cdot \int_{\mathrm{t_0}}^{\mathrm{t}} \mathrm{dp} \qquad (6)$$

where: t_0 – start of injection.

The total heat Q released from combustion can be calculated as a maximum heat defined by Eq. 6.

On the basis of Q(t) recalculated to normalized percentage scale, the combustion phases can be introduced as follows:

- t_{0-2} – initial combustion phase measured from the start of injection to the release of 2% of heat released. This phase is usually considered a reliable parameter representing the ignition delay of the air-fuel combustible mixture
- t_{0-10} – the initial combustion phase managed as another reliable parameter to assess the ignition delay
- t_{10-90} – the main combustion phase
- t_{0-90} – the initial and main combustion phases.

Characteristics of pyrolysis oil used for tests

As a result of distillation at 280°C, the pyrolysis oil was practically free of hydrocarbons with the number of carbon atoms above 15 (Fig. 5).

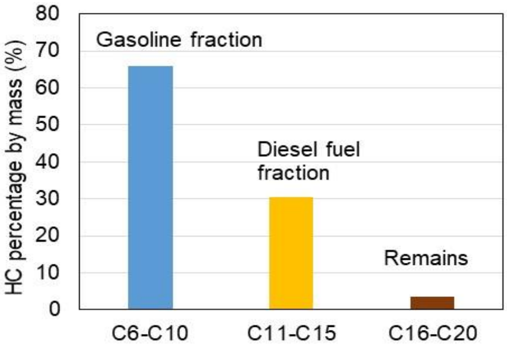

Fig. 5. Percentage hydrocarbons fractions by mass for the pyrolysis oil after distillation

Detailed analysis of processing technology of this pyrolysis oil is present in work [12]. As it results from the mass composition (Fig. 5), the fractions present in gasoline (C_6–C_{10}) are dominant. On the other hand, the fractions characteristic of diesel fuel (C_{11}–C_{15}) present in the amount of approximately 30% may adversely affect the octane number of pyrolysis oil due to their lower self-ignition temperature and thus higher tendency to generate knocking combustion.

3. Results and discussion

According to the assumptions, the heat release rate dQ/dt was determined on the basis of combustion pressure trace as depicted in Fig. 6. To avoid high numbers from deriving, the pressure was filtered.

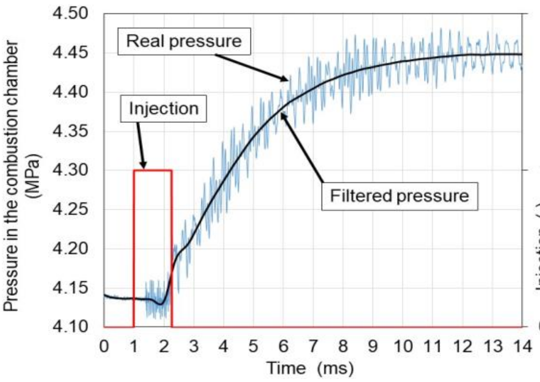

Fig. 6. Real and filtered combustion pressure trace in the combustion chamber at 41 bar initial pressure

Figure 7 shows the heat release rate dQ/dt for both tested fuels. The phases of premixed and diffusion combustion can be identified. As depicted, the premixed combustion for both fuels is faster than diffusion combustion. Additionally, higher dQ/dt is observed for pyrolysis oil, which confirms the conclusion about the higher chemical rate of reactions of substances forming pyrolysis oil.

Selected results from combustion analysis were included in Table 3.

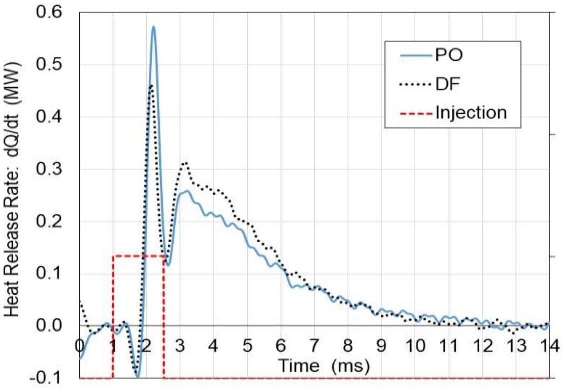

Fig. 7. Heat release rate history for pyrolysis oil and diesel fuel at initial pressure of 41 bar

Table 3. Selected combustion parameters for pyrolysis oil and diesel fuel combusted in the constant-volume combustion chamber

		Pyrolysis oil	Diesel fuel
Initial pressure	bar	41	41
t_{0-2}	ms	1.03	0.99
t_{0-10}	ms	1.22	1.21
t_{prem}	ms	0.91	0.89
t_{diff}	ms	5.06	4.55
t_{prem}/t_{diff}	%	18	20
Q_{prem}	J	202	181
Q_{diff}	J	907	997
Q_{total}	J	1109	1178
Q_{prem}	%	18.2	15.3
Q_{diff}	%	81.8	84.7
Q_{prem}/Q_{diff}	%	22.2	18.1
$dQ_{prem, max}$	MJ/s	0.57	0.46
$dQ_{diff, max}$	MJ/s	0.26	0.31

Figure 8 presents the combustion phases for pyrolysis oil and diesel fuel as follows: t_{0-2}, t_{0-10}, t_{10-90}, and t_{0-90} for an initial pressure of 41 bar at the start of injection. As can be seen, the time intervals t_{0-2} or t_{0-10} that represent the ignition delay do not differ significantly from each other. Although, the time t_{0-10} is the time in which combusted fuel was 5 times larger of compared to the time t_{0-2} as concluded from heat released. This can be explained by rapid acceleration of combustion in the initial combustion phase, caused by premixed combustion. As investigated, the main combustion phase denoted as t_{10-90} is longer for pyrolysis oil. Even though, the change can be managed as insignificant, but it can affect higher soot and unburnt hydrocarbons in exhaust emissions if this pyrolysis oil would be implemented as a fuel to automotive compression ignition engines.

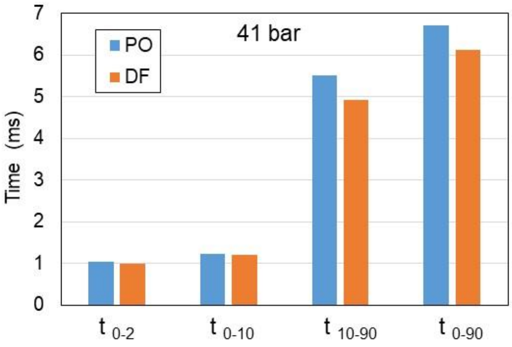

Fig. 8. Time period for combustion phases t_{0-2}, t_{0-10}, t_{10-90} and t_{0-90} for pyrolysis oil and diesel fuel combusted under initial pressure of 41 bar

In regards to Fig. 4, Fig. 9a shows the times of premixed t_{prem} and diffusion t_{diff} combustion phases for both tested fuels. It is obvious that the time t_{prem} is definitely shorter than the time t_{diff} as the flame at the premixed zone consumes fuel several times faster in comparison to the diffusion combustion zone. Hence, the fraction of the premixed combustion phase in relation to the diffusion combustion phase seems to be important. The percentage t_{prem}/t_{diff} quotient is shown in Fig. 10. As found, the premixed combustion is nearly five times shorter in general for both tested fuels.

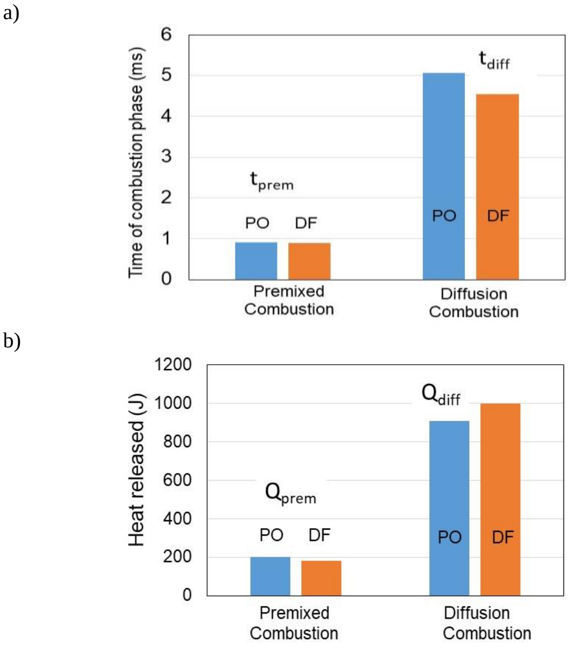

Fig. 9. Time periods for premixed and diffusion combustion phases t_{prem} and t_{diff} (a) and heat released Q_{prem} and Q_{diff} (b) for pyrolysis oil and diesel fuel combusted under initial pressure of 41 bar

In addition to comparing the time t_{prem} vs. t_{diff}, Fig. 9b depicts the amount of heat released in the premixed combustion phase Q_{prem} in relation to the diffusion combustion phase Q_{diff}. As observed, the heat contribution Q_{prem} is much higher than the time contribution t_{prem} relative to the diffusion combustion phase represented by parameters Q_{diff} and t_{diff}, respectively.

The summary of the analysis of the phases of premixed and diffusion combustion is the percentage fraction of the premixed phase referred to the diffusion phase. This comparison was made for time and heat released in these phases. As presented in Fig. 10, the time t_{prem} is nearly 5.5 times shorter than the time t_{diff} for pyrolysis oil, however, the heat released during premixed combustion is only 4.5 times lower, respectively. It means that more heat is released during premixed phase. If anyone compare these relations with diesel fuel tests, would notice opposite trend. Therefore, the maximum heat release rates dQ/dt were determined for the premixed and the diffusion combustion phases as depicted in Fig. 11. One can expect the premixed fuel burns faster if it concerns higher amount of light hydrocarbons, due to their faster evaporation.

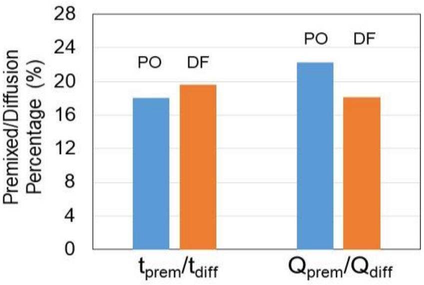

Fig. 10. Premixed to diffusion combustion percentage (t_{prem}/t_{diff} and Q_{prem}/Q_{diff}) for pyrolysis oil and diesel fuel in the combustion chamber under initial pressure of 41 bar

Thus, it is confirmed from the observation of maximum heat release rates for both tested fuels in their premixed and diffusion phases (Fig. 11). Pyrolysis oil in comparison to diesel fuel burns faster when it is premixed with air. On the other hand, pyrolysis oil burns slower in its diffusion phase in reference to diesel fuel.

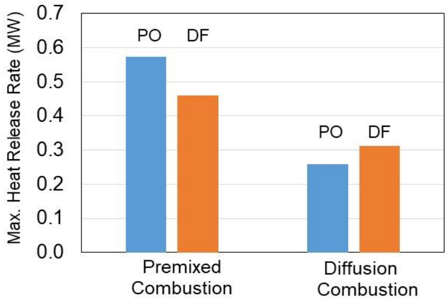

Fig. 11. Maximum heat release rate of premixed and diffusion combustion for pyrolysis oil and diesel fuel in the combustion chamber under initial pressure of 41 bar

6. Conclusions

Combustion tests were carried out on pyrolysis oil made of high density polyethylene (HDPE) as a result of pyrolysis at 575–600°C, which was then subjected to distillation in order to remove hydrocarbons with a C number above 15. The basic research tool was a comparative analysis, to which diesel fuel was used as the reference fuel. On the basis of the conducted research, the following conclusions can be drawn:

- The duration of the premixed combustion phase for pyrolysis oil is approximately 5% shorter than the premixed combustion phase for diesel fuel. Hence, this change can be considered marginal.
- The maximum combustion rate (assumed as heat release rate) for the premixed combustion phase for pyrolysis oil was approximately 27% higher than the premixed combustion rate for diesel fuel. However, the maximum rate of diffusion combustion was lower by 16% with respect to diesel fuel.
- The percentage fraction of heat released from the premixed combustion phase to total heat for pyrolysis oil was nearly 22%, whereas this parameter is 15% for diesel fuel. This is important because a bigger amount of fuel burned at the premixed phase leads to a faster pressure increase in the engine cylinder and improves the indicated efficiency of the thermodynamic cycle, which at the same time will improve the completeness of fuel combustion and reduce the specific fuel consumption.
- The self-ignition delay (t_{0-2}, t_{0-10}) for pyrolysis oil was slightly longer compared to the delay for diesel fuel. This affects the progress in further combustion, including the increase in pressure, however, in this case, it can be assumed that the ignition delay for both fuels has a similar value and in this approach, there is no significant difference between these tested fuels;
- It is proposed to use pyrolysis oil after distillation with the removal of hydrocarbons above C15 to power car engines, while for large stationary engines, attempts to burn raw pyrolysis oil can be made after examining its viscosity and sulfur content.
- It is recommended to test the exhaust gases toxicity of pyrolysis oil in stationary and dynamic load conditions.

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Nomenclature

c_p	specific heat at constant pressure
c_v	specific heat at constant volume
dQ/dt	heat release rate
dp	infinitesimal pressure change
$dQ_{diff,max}$	maximum heat release rate in diffusion combustion phase
$dQ_{prem,max}$	maximum heat release rate in premixed combustion phase
DF	diesel fuel
HDPR	high density polyethylene
HRR	heat release rate
κ	specific heat ratio
n	number of moles
PO	pyrolysis oil
Q	heat
Q_{diff}	heat released from diffusion combustion phase
Q_{prem}	heat released from premixed combustion phase
R_u	universal gas constant
t_0	start of injection
t_{0-2}	initial combustion phase
t_{0-10}	10% initial combustion phase
t_{10-90}	main combustion phase
t_{diff}	time of diffusion combustion phase
t_{prem}	time of premixed combustion phase
T	temperature
U	internal energy
V	volume

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