Comparative analysis of heat release in a reciprocating engine powered by a regular fuel with pyrolysis oil addition

The article presents a comparative analysis of heat release rate in a spark-ignition engine powered by various fuels as follows: butanol, gasoline, a mixture of butan with tire pyrolysis oil (TPO), and mixtures of butanol with oil from biomass pyrolysis (BPO). Selected combustion phases were analyzed. Additionally, ignition delay calculations were performed in the ANSYS Chemkin Pro program for the surrogates of the tested fuels. Popular surrogates quoted in numerous publications were used as substitute fuels. The paper presents an original surrogate of oil from tire pyrolysis.

Key words: pyrolysis oil, butanol, ignition delay, surrogate, Ansys Chemkin-Pro

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1. Introduction

Pyrolysis is a thermochemical process in a reactor in an oxygen-free atmosphere at a temperature of 300°C to 2000°C. As a result of the temperature, the input material is decomposed into simpler chemical compounds. The pyrolysis process can be divided into three stages. The first is drying, the temperature of the material does not exceed 100°C. The second step is to separate the volatile matter from the material. The last phase is the breakdown of long chains of hydrocarbon compounds into shorter ones. Secondary reactions between the pyrolysis products take place in this stage [1, 3].

Pyrolysis can be a process that converts waste into a high-calorific liquid, in addition to producing gas and a carbon-containing solid. The oil produced has many uses, one of which is to power a reciprocating internal combustion engine. All kinds of materials of organic origin can be used as input materials for the pyrolysis process: biomass waste, municipal waste, polymer waste, etc [7, 9].

Depending on the raw material used for the pyrolysis process, an oil with different physical-chemical properties and compositions is obtained. Other factors which influence the compositions of the obtained oil are as follows: type of pyrolysis reactor, process conditions, additional catalytic compounds [1, 9, 19].

In recent years, extensive research has been carried out on the pyrolysis process. The number of publications on this topic is gradually growing from year to year. In the SCOPUS database, 9,737 articles were published in 2021, compared to 2015, when the number of articles with this keyword was 5,560. In addition, pyrolysis is used on an industrial scale to process waste. The largest global companies research the use of pyrolysis products, by name ChemCycling™ project, including BASF, New Energy, Quantafuel, Remondis [10].

The main novelty in the article is a comparative analysis of the thermodynamic cycle, taking into account the course of heat release in a reciprocating internal combustion engine powered by a mixture of pyrolysis oil with butanol and selected reference fuels.

2. Materials

At the first stage of the research, it was necessary to find a solvent that can mix and make blends with the two oils taken for analysis. The first one was the tire pyrolysis oil (TPO) and the second one: the biomass pyrolysis oil (BPO). Gasoline was not taken as the reference fuel due to solubility problems [3, 4]. BPO was not miscible with gasoline, as shown in Fig. 1b. To achieve a stable mixture, n-butyl alcohol was used as the reference fuel and solvent. Both pyrolysis oils formed a stable and premixed blend as shown in Fig. 1a.

![Fig. 1. On the left, a mixture of tire pyrolysis oil with butanol, on the right, a mixture of biomass pyrolysis oil and gasoline](image)

Table 1 compares the properties of a typical tire pyrolysis oil and unleaded Eurosuper 95 gasoline. What distinguishes TPO compared to gasoline is its high oil density, high kinematic viscosity, and high flash point. The calorific value and elemental composition are similar to that of gasoline [2, 6].

<table>
<thead>
<tr>
<th>Property</th>
<th>Tire pyrolysis oil</th>
<th>Gasoline Eurosuper 95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm³]</td>
<td>0.943–0.935</td>
<td>0.742</td>
</tr>
<tr>
<td>Kinematic viscosity [cSt]</td>
<td>4.62–5.68</td>
<td>0.5–0.75</td>
</tr>
<tr>
<td>Flash point [°C]</td>
<td>&lt; 30–53</td>
<td>–40</td>
</tr>
<tr>
<td>LHV [MJ/kg]</td>
<td>41.6–43.5</td>
<td>42.8</td>
</tr>
<tr>
<td>Composition (% wt)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>87.57–81.0</td>
<td>86</td>
</tr>
<tr>
<td>H</td>
<td>10.35–6.6</td>
<td>14</td>
</tr>
<tr>
<td>N</td>
<td>&lt; 1–0.6</td>
<td>0</td>
</tr>
</tbody>
</table>
Tire pyrolysis oil is a mixture that contains a large number of compounds. As reviewed from the literature one can find results of the GC-MS analyzes that showed over 100 chemical compounds in a typical pyrolysis oil. An exemplary analysis is presented in Table 2, in which the substances of their highest content are depicted [1, 20].

The second tested oil, obtained from biomass pyrolysis, has different properties than TPO. Table 3 shows its typical properties. Compared to BPO to gasoline Eurosuper 95, BPO has a lower calorific value, higher water content, higher density, and higher kinematic viscosity. The elemental composition of BPO is characterized by a small proportion of carbon which is replaced by a large proportion of oxygen [11].

The following simplifications were used in the analysis: heat release to the cylinder walls is ignored, therefore the determined heat is net heat, and the gap losses are also ignored. The quotient $\gamma = c_p/c_v$ can be calculated as the polytropic index of compression before ignition. The final form of the equation for the heat release rate is defined with equation 2 [5]:

$$\frac{dQ_{net}}{d\varphi} \approx \left(1 - \frac{1}{\gamma - 1}\right)p \frac{dv}{d\varphi} + \left(\frac{\gamma}{\gamma - 1}\right)v \frac{dp}{d\varphi}$$

where: $\gamma$ – the ratio of the specific heats ($c_p/c_v$) at constant pressure and constant volume, respectively, $p$ – in-cylinder combustion pressure, $V$ – in-cylinder volume, $\varphi$ – crank angle (CA) deg, $Q_{net}$ – net heat release during combustion.

The quotient $c_p/c_v$ was determined as depicted in Fig. 2 by equation (3). Where $p_0$ and $v_0$ are the pressure and volume of the combustion chamber just before the spark timing, and $p_1$ and $v_1$ are the pressure and volume of the combustion chamber 5 CA deg ahead of point 0 (Fig. 2) [5].

$$\gamma = \frac{\log \frac{p_0}{p_1}}{\frac{v_1}{v_0}}$$

To calculate the total heat release, equation (2) should be integrated. Additionally, the heat release charts were recalculated to the normalized range of 0–1. An exemplary course of cumulative heat release consistent with equation (4) is shown in Fig. 3.
The presented curve of net heat release can be divided into 3 combustion phases [5]:

- Phase I can be managed as the preliminary combustion—this is the time that elapses from the spark discharge to the release of 10% of the cumulative heat release.
- Phase II is a developed course of combustion—it defines the time in which the production of 80% of heat takes place, i.e., combustion duration.
- Phase III is the burning of fuel residues in the cylinder surrounded by a large amount of exhaust gases.

The exact determination of the end of combustion (100% NCHR) is difficult, therefore the first two phases of combustion are of interest in further analysis.

4. Experimental conditions

During the experimental tests, the test stand with the UIT-85 engine was used, presented in Fig. 4. The test stand consists of a spark-ignition engine, which is equipped with an encoder built on the camshaft, an air flow meter is installed in the intake manifold to measure the intake air flow rate. The sensor for indicating the engine was built into the spark plug. The engine load was realized with the aid of an electric asynchronous motor powered by a frequency converter and connected to the electric grid. Fuel injection was into the engine’s intake manifold. Table 3 shows the technical parameters of the engine.

![Fig. 3. The course of heat release as a result of butanol combustion in the UIT-85 engine](image)

![Fig. 4. View of the test stand with the UIT-85 engine](image)

![Fig. 5. In-cylinder pressure vs. crank angle](image)

During the experiment, the engine was running at 600 rpm. The compression ratio, CR, was set to 10. The amount of fuel injection was determined based on the excess air ratio. The engine was fed with a stoichiometric mixture.

The ignition timings that generated the highest value of IMEP were selected for the analysis of heat release curves. The list of spark timings for the tested fuels is presented in Table 3.

![Table 3. Technical data of the engine UIT-85](image)

![Table 3. Spark discharge angle for tested fuels](image)

The most delay spark timing was set for gasoline, which was 8 CA before TDC. Spark angle of 10 CA before TDC was set for pure butanol. 12 CA spark timing was set for butanol mixtures with the addition of tire pyrolysis oil. Figure 5 shows the pressure curves for the tested fuels vs. crankshaft angle.
Based on the recorded in-cylinder pressure curves, the heat release rate was calculated by equation (2).

5. Experimental results

The calculated heat release rate for all tested fuels is shown in Fig. 6. For easy comparison of the curves, it was assumed that the spark timing was 0 CA for all these tests. In Figure 6, it can be seen that butanol burns the fastest. However, the maximum NHRR value is the lowest. The rate of heat release has the highest value for gasoline. Butanol + 50% TPO burns the longest. After integrating the waveforms from Fig. 6, a cumulative heat release profile for the tested fuels was obtained and is presented in Fig. 7.

![Fig. 6. The net heat release rate for various fuels](image)

The net cumulative heat release was used to analyze the individual combustion phases. Based on diagram 7, the duration of the preliminary combustion (0–10% NCHR) and the duration of the main combustion phase (10–90% NCHR) were calculated.

![Fig. 7. Net cumulative heat release for various fuels](image)

The shortest preliminary heat combustion was for butanol and amounted to 10.5 CA deg (Fig. 8), and converted into time units, this delay is 2.8 ms (Fig. 9). Gasoline (11.5 CA deg = 3.1 ms) and Butanol + 25% TPO (11.8 CA deg = 3.2 ms) had a slightly longer preliminary combustion. The fuel Butanol + 50% TPO had the longest preliminary combustion, which was 15 CA deg, and converted into time units, this delay is 4 ms.

![Fig. 8. Preliminary combustion for various fuel in [CA deg]](image)

The combustion duration phase was the shortest and almost identical for butanol and Butanol + 25% TPO. It amounts to 13.2 CA deg, which in milliseconds gives the result of 3.55 ms. Gasoline had a longer combustion duration phase by 0.7 CA deg, which in terms of time units gives the result of 3.73 ms. The combustion duration of the mixture Butanol + 50% TPO was the longest. This process lasted 15.1 CA deg what corresponds to the time of 4.06 ms (Fig. 10 and 11).

![Fig. 9. Preliminary combustion for various fuel in [ms]](image)

![Fig. 10. Combustion duration for various fuels in [CA]](image)
Based on the analysis of the two combustion phases, the following conclusions can be drawn. Pure butanol burns up the fastest. Gasoline and Butanol + 25% TPO have very similar heat release patterns. Butanol + 50% TPO has the longest preliminary combustion and the longest duration of the main combustion phase.

In the second phase of the experiment, the analysis included butanol as the reference fuel and the mixture designated as Butanol + 20% BPO, which consists of butanol of 80% and 20% oil from biomass pyrolysis by volume. For the comparative analysis, it was established that the spark timing will be constant for both fuels and will be 15 CA before TDC. For such ignition timing, the highest mean indicated engine pressure was calculated. The IMEP chart for the tested fuels is shown in Fig. 12.

The p-V diagram shows a lower pressure peak for Butanol + 20% BPO. The maximum pressure recorded during the indication for this fuel was 3.35 MPa. For pure butanol, the maximum pressure was 4.45 MPa. The maximum value for butanol occurred noticeably earlier, which indicates faster ignition of the fuel, and confirms the NHRR course presented in Fig. 15.

Fig. 11. Combustions duration for various fuels in [ms]

Fig. 12. IMEP for butanol and Butanol + 20% BPO

Fig. 13. In-cylinder pressure vs. crank angle

Fig. 14. In-cylinder pressure vs. volume

Fig. 15. The net heat release rate for butanol and Butanol + 20% BPO
The curve of NHRR after integration gives the result in the form of cumulative net heat release, which is presented in Fig. 16.

![Net cumulative heat release](image)

**Fig. 16. Net cumulative heat release**

The selected combustion phases are marked in the NCHR diagram (Fig. 16). The preliminary combustion for butanol was 2.2 ms. Adding 20% BPO to the reference fuel increased the preliminary combustion by 1.6 ms. The duration of the main combustion phase was also longer for the Butanol + 20% BPO mixture. It was 4 ms. Butanol burned shorter by 0.8 ms. Additionally, the combustion duration phase is divided in half. It has been checked which half lasts longer. For both tested fuels, it was registered that the combustion of the second part of the combustion duration takes place faster than the first one. The individual values are presented in Fig. 17.

![Combustion phases](image)

**Fig. 17. Combustion phases**

### 7. Combustion modeling in ANSYS Chemkin-Pro

In the next part of the research, simulations were carried out in the ANSYS Chemkin-Pro program to calculate the ignition delay of the tested fuel surrogates [18]. The simulations were carried out in the Closed Homogenous Reactor in which conditions similar to those prevailing in a spark-ignition engine were assumed. In the program, the ignition was autoignition but in the experiment, the ignition was forced by a spark. A stoichiometric mixture was burned in the reactor. The combustion kinematics mechanism developed by scientists from the CRECK Modeling group at the Milan University of Technology was used for the calculations. The kinetic combustion mechanism consisted of 402 chemicals and 16118 reactions [16]. The ignition delay in the performed simulations was defined as the time from the start of the simulation to the moment of the maximum VHPR value. An exemplary course of heat release from the simulation is shown in Fig. 18.

![Ignition delay](image)

**Fig. 18. Ignition delay determined in ANSYS Chemkin-Pro**

To perform the simulation in the reactor, the reactants had to be declared. From the literature data, the used fuel surrogates for modeling the combustion of real fuels were taken. The list of selected surrogates and their composition is presented in Table 4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>[wt. %]</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-Butanol</td>
<td>C4H8O</td>
<td>1</td>
<td>Reference fuel</td>
</tr>
<tr>
<td>PRF</td>
<td>C8H17</td>
<td>0.95</td>
<td>A gasoline surrogate with an octane number of 95 corresponding to the Eurosuper 95 lead-free gasoline used in the experiment.</td>
</tr>
<tr>
<td>TRF-E</td>
<td>C7H16</td>
<td>0.05</td>
<td>Unleaded gasoline surrogate containing an alcohol additive in the form of 5% by weight. Ethanol is a bio component of the popular Eurosuper 95 gasoline.</td>
</tr>
<tr>
<td>BPO</td>
<td>C10H16</td>
<td>0.30</td>
<td>Surrogate of pyrolysis oil obtained from biomass (biomass pyrolysis oil-BPO). The composition took from the research report of the Residue2heat project. Surrogate mixed with butanol in various proportions [15].</td>
</tr>
<tr>
<td>TPO</td>
<td>C10H16</td>
<td>0.15</td>
<td>The proposed composition of tire pyrolysis oil surrogate.</td>
</tr>
</tbody>
</table>

Butanol was the reference fuel in both the simulation and the tests. Butanol is one compound from the IC4H8O database. In the case of gasoline, two alternative surrogate fuels were selected that reflected the properties of the real gasoline. The first, designated PRF, is a mixture of isoctane and n-heptane. The second, more complex, surrogate is...
a 4-component mixture containing ethanol, toluene, isooctane, and n-heptane, designated as TRF-E. A surrogate developed by the research team as part of the Residue2Heat research was used to model the combustion of oil from biomass pyrolysis. The last modeled fuel was a tire pyrolysis oil surrogate. No surrogate for oil from tire pyrolysis has been found in the literature, therefore an attempt was made to compose an own surrogate that would reflect the properties consistent with those of the tire pyrolysis oil.

The proposed tire pyrolysis oil surrogate consisted of four substances: Limonene, Ethylbenzene, Toluene, Xylene. These are compounds selected from the analyzed GC-MS reports of tire pyrolysis oils. The compounds that had the largest share in the composition were selected. The properties of the individual components of the TPO surrogate are presented in Table 5.

Table 5. Properties of compound of tire pyrolysis oil [13, 17]

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Limonen</th>
<th>Etylene</th>
<th>Toluene</th>
<th>Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fraction</td>
<td>[%]</td>
<td>15</td>
<td>45</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Formula</td>
<td></td>
<td>C_{10}H_{16}</td>
<td>C_{6}H_{5}</td>
<td>C_{7}H_{8}</td>
<td>C_{6}H_{5}</td>
</tr>
<tr>
<td>Carbon content</td>
<td>[wt %]</td>
<td>0.88</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>[wt %]</td>
<td>0.12</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Density</td>
<td>[kg/m³]</td>
<td>841</td>
<td>866</td>
<td>867</td>
<td>874</td>
</tr>
<tr>
<td>Viscosity</td>
<td>[mPas]</td>
<td>–</td>
<td>678</td>
<td>587</td>
<td></td>
</tr>
<tr>
<td>LHV</td>
<td>[MJ/kg]</td>
<td>–</td>
<td>40.9</td>
<td>40.24</td>
<td>40.9</td>
</tr>
<tr>
<td>Pour point</td>
<td>[°C]</td>
<td>–74.35</td>
<td>–94.9</td>
<td>–95</td>
<td>–48</td>
</tr>
<tr>
<td>Boiling point</td>
<td>[°C]</td>
<td>176</td>
<td>136.2</td>
<td>110.6</td>
<td>139</td>
</tr>
<tr>
<td>Flash point</td>
<td>[°C]</td>
<td>51</td>
<td>15</td>
<td>4</td>
<td>28</td>
</tr>
<tr>
<td>Autoignition temperature</td>
<td>[°C]</td>
<td>245</td>
<td>432</td>
<td>480</td>
<td>525</td>
</tr>
<tr>
<td>Cetane number</td>
<td>–</td>
<td>19</td>
<td>4/6</td>
<td>30/–5</td>
<td>8</td>
</tr>
<tr>
<td>Octane number</td>
<td>–</td>
<td>73</td>
<td>98</td>
<td>112</td>
<td>124</td>
</tr>
</tbody>
</table>

Ignition delay was calculated for all fuel surrogates for 3 temperatures: 900 K, 1000 K, 1100 K and 1200 K. Additionally, simulations were carried out for various pressures: 10 bar, 15 bar and 20 bar. Figure 19 shows the ignition delay for PRF and TRF-E.

Comparing the calculated ignition delay with the experiment, conclude is that all surrogates except BPO have a delay consistent with the results of the experiment. Oil from biomass pyrolysis should have a longer ignition delay than that of butanol and gasoline supplements, but the simulation results did not confirm this. In an attempt to find the cause of this discrepancy, the ignition delay calculations were performed for the individual components of the BPO surrogate. The simulation results are presented in Fig. 21.
The calculated ignition delay of the individual components revealed that the mixture consists of two groups of compounds. The first group of substances had a short ignition delay of less than 3.1 ms, and two compounds with a long ignition delay of more than 9 ms. Compounds with long ignition delay accounted for only 11% by weight.

Figure 22 shows the ignition delay for all tested surrogates, for a pressure of 15 bar and a temperature of 1000 K.

Figure 22 show that with the increase in the share of the proposed oil surrogate from tire pyrolysis, the ignition delay increases. Which is in line with the trend observed during the experiment. The influence of TPO on the ignition delay is shown in Fig. 23.

The proposed tire pyrolysis oil surrogate consists of 4 chemical compounds. To investigate how a given component influences the ignition delay, calculations of the ignition delay were performed separately for all components of the supplement. The obtained results are presented in Fig. 24.

The proposed composition of the TPO surrogate contains two groups of compounds. The first two, limonene, and ethylbenzene, had a shorter ignition delay compared to the value for the mixture, while the other two components, i.e. xylene, and toluene had a longer ignition delay than the obtained value for the surrogate.

8. Summary

Butanol can be considered a universal solvent for biomass pyrolysis oil (BPO) and tire pyrolysis oil (TPO), unlike Eurosuper 95 gasoline with which BPO cannot be mixed. Butanol burns the fastest but has the lowest maximum heat release and the shortest fuel preliminary combustion.

Eurosuper 95 gasoline and Butanol + 25% TPO have similar heat release profiles for each stage of fuel combustion.

A mixture of Butanol + 50% TPO burns the longest and has the longest preliminary combustion.

Oil from biomass pyrolysis (BPO) increases the preliminary combustion phase compared to the reference fuel – butanol and also extends the main combustion phase.

For all tested fuels, the combustion phase of 10–50% lasts longer than the combustion duration 50–90%.

The ANSYS Chemkin Pro software was used to model the combustion of a homogeneous stoichiometric mixture of butanol and for fuel surrogates in a closed and insulated reactor as a reference.

The gasoline was modeled using two surrogates. For the temperature of 900 K, a bigger delay in ignition of the TRF-E surrogate can be observed compared to the PRF. For higher temperatures, latency was almost identical for both surrogates.

The composition of the oil surrogate from biomass pyrolysis proposed in the report on the Residue2Heat project does not correctly reflect the fuel ignition delay for the assumed conditions. 5 out of 7 components of the proposed surrogate have a shorter ignition delay time than the value for the mixture. The surrogate has a much shorter ignition delay than butanol, which is inconsistent with the experiment.

To model the combustion of oil from tire pyrolysis, a four-component surrogate consisting of toluene, ethylbenzene, xylene, and limonene was developed and proposed based on the literature. The influence of the proposed TPO surrogate on the ignition delay is correct with the experiment.

There is a correlation in trends between the experiment and simulations calculated using the Chemkin program for all tested fuels, except for the oil surrogate from biomass pyrolysis (BPO).
Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>BPO</td>
<td>biomass pyrolysis oil</td>
</tr>
<tr>
<td>CA</td>
<td>crank angle</td>
</tr>
<tr>
<td>CR</td>
<td>compression ratio</td>
</tr>
<tr>
<td>GC-MC</td>
<td>gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>HHV</td>
<td>higher heating value</td>
</tr>
<tr>
<td>IMEP</td>
<td>indicated mean effective pressure</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value</td>
</tr>
<tr>
<td>NCHR</td>
<td>net cumulative heat release</td>
</tr>
<tr>
<td>NHRR</td>
<td>net heat release rate</td>
</tr>
<tr>
<td>OHV</td>
<td>overhead valve</td>
</tr>
<tr>
<td>TDC</td>
<td>top dead center</td>
</tr>
<tr>
<td>TPO</td>
<td>tire pyrolysis oil</td>
</tr>
<tr>
<td>VHPR</td>
<td>volumetric heat production rate</td>
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</tbody>
</table>

Bibliography


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