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Performance and emission characterization of a common-rail compression-ignition engine fuelled with ternary mixtures of rapeseed oil, pyrolytic oil and diesel

Author(s): Mikulski, Maciej; Ambrosewicz-Walacik, Marta; Duda, Kamil; Hunicz, Jacek

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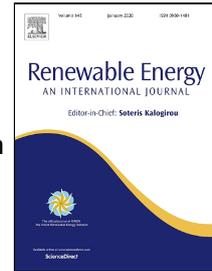
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Performance and emission characterization of a common-rail compression-ignition engine fuelled with ternary mixtures of rapeseed oil, pyrolytic oil and diesel

Maciej Mikulski^{1,a}, Marta Ambrosewicz-Walacik², Kamil Duda², Jacek Hunicz³

¹ School of Technology and Innovation, Energy Technology, University of Vaasa, Wolffintie 34, FI-65200 Vaasa, Finland

² Faculty of Technical Sciences, University of Warmia and Mazury in Olsztyn, Słoneczna 46A, 10-710 Olsztyn, Poland

³ Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, 20-618 Lublin, Poland

^a Corresponding author, e-mail: maciej.mikulski@uwasa.fi

Abstract

Biofuels are one of the short-term alternatives for reducing the well-to-wheel greenhouse gas footprint of transport. In the framework of compression-ignition engine fuels. This study investigates the feasibility of using cold-pressed rapeseed oil as a biocomponent, admixed with distilled tyre pyrolytic oil, as an energy-efficient alternative to commonly considered methyl ester-based mixtures in diesel fuel. Selected ternary and binary fuel blends are subjected to engine tests. Their scope covers 80% of the engine map and aims at identifying tradeoffs between fuel composition, engine performance and emissions. The results show that fuel mixtures containing a large fraction of rapeseed oil (up to 55% by volume) can be effectively combusted when pyrolytic oil distillate is introduced as the additive. The deterioration in brake efficiency for such fuel does not exceed 1.2% with respect to diesel baseline. At the same time, the results are superior in terms of both efficiency and emissions when compared to FAME-based biodiesel. Finally, with indicated efficiencies on a similar level as the diesel baseline, suggesting improved burning rate with pyrolytic oil addition, the study identifies parasitic losses in fuel injection equipment as a significant contributor to the overall efficiency penalty for the examined ternary mixtures.

Keywords: diesel engine; rapeseed oil; pyrolytic oil; waste tyres; efficiency analysis, exhaust emissions.

Nomenclature

1	Nomenclature	
2		
3	Bio ₂₀ -DF ₈₀	binary blend of rapeseed methyl ester and diesel fuel (20:80, v/v)
4	BMEP	brake mean effective pressure [bar]
5	BTE	brake thermal efficiency [%]
6	CA	crank angle [deg]
7	CI	compression ignition
8	CO	carbon monoxide
9	CO ₂	carbon dioxide
10	COV _{IMEP}	coefficient of variation in IMEP [%]
11	DF	diesel fuel
12	DMFTPO	distilled medium fraction of pyrolytic oil
13	DR	binary blend of diesel fuel and rapeseed oil
14	EGO	exhaust gas opacity [%]
15	EGR	exhaust gas recirculation
16	FAME	fatty acid methyl esters
17	G _{air}	air aspired to the engine [kg/h]
18	G _{fuel}	fuel consumption [kg/h]
19	HRR	heat release rate [J/CA]
20	IMEP	indicated mean effective pressure [bar]

21	JME	Jatropha methyl esters
22	LHV	lower heating value [MJ]
23	N	engine rotational speed [rpm]
24	NO _x	total nitrogen oxides
25	PAH	polycyclic aromatic hydrocarbons
26	PM	particulate matter
27	pp	percentage point
28	RME	rapeseed methyl ester
29	RO	rapeseed oil
30	rpm	revolutions per minute
31	SOA	start of actuation [CA]
32	TDC	top dead center
33	Te	engine torque [Nm]
34	THC	total hydrocarbons
35	TPO	pyrolytic oil from waste car tyres
36	TPO1-TPO5	ternary blends of diesel fuel, rapeseed oil and medium fraction of pyrolytic oil

37 1 Introduction

38 The use of fossil resources has led to increased greenhouse gas emissions, adversely affecting the Earth's
 39 atmosphere. Over the past five decades, greenhouse gas emissions, mainly CO₂, CH₄ and N₂O, more than doubled, from
 40 24.5 GtCO₂eq/year in 1970 to 50.9 GtCO₂eq/year in 2017 [1]. The presence of these gases in the atmosphere is one of
 41 the major causes of global warming and other climate changes. World Energy Resources Reports prepared by the World
 42 Energy Council since 1988 show that significant changes have occurred in global consumption of energy resources in
 43 the last 15 years. Intensive growth of energy production from renewable sources has led to new investments for the
 44 energy economy, as well as the development of technologies for obtaining and processing alternative materials [2].
 45 Despite the recent rapid decline in the reputation of diesel engines, they will be in service for many years to come,
 46 particularly in the case of heavy-duty and industrial vehicles. When coupled with environmental and health concerns
 47 relating to climate change and air quality, it follows that it is necessary to shift towards balanced fuel sources including
 48 biofuels and waste fuels.

49 Alcohols are intensively investigated as potential candidates for feasible fuels that can reduce carbon footprint.
 50 Ethanol has already reached substantial market share as a gasoline admixture. Methanol, being low-carbon on a tank to
 51 wheel basis, with its wide-spread infrastructure, and scalability potential, is regaining attention as transport fuel [3, 4]. It
 52 can be inexpensively produced from fossil fuels, but also from, waste, biomaterials, or renewable electricity with
 53 recaptured atmospheric CO₂. As far as the wide utilization of methanol in different combustion concepts goes, it is not
 54 directly applicable as a drop-in fuel in CI engines. However, small admixtures of methanol to diesel (up to 5-7 %) can
 55 be used without hardware or control modifications, as soon as emulsion stabilization is concerned [3]. For actual and
 56 comprehensive review of methanol in internal combustion engine applications the reader is referred to the recent work
 57 by Verhelst et al. [4].

58 It is commonly known that use of oilseed-derived biofuels substantially reduces well-to-wheels greenhouse gas
 59 emissions. The most commonly considered drop-in alternative fuel for CI engines is biodiesel based on FAME. The
 60 effects of biodiesel on CI engine combustion and exhaust emissions are well understood. Combustion characteristics
 61 such as auto-ignition delay and combustion duration are quite similar. In terms of emissions, biodiesel fuels show
 62 reduced soot production but increased NO_x emissions compared with DF [5]. Emissions from biodiesel fuels are widely
 63 investigated for the production of regulated toxic compounds: there are some drawbacks in terms of emissions of some
 64 unregulated species. For example, Koszalka et al. [6] performed a detailed exhaust gas analysis and demonstrated that
 65 combustion of biodiesel fuel causes increased emissions of aldehydes in comparison with mineral diesel fuel.

66 The overall environmental benefit of using biodiesel fuels depends greatly on their energy consumption, extraction
 67 and refining processes, so the ability to use raw organic materials directly in compression-ignition engines would seem
 68 to offer an intrinsic environmental advantage. Recently published studies emphasize the advantages of using crude
 69 vegetable oils but suggest using biodiesel as a fuel for compression-ignition engines has an adverse effect [7, 8, 9].
 70 Studies by Estaban et al. [7] using methods known as life cycle impact assessment and energy return on investment,

71 found that raw oils generate significantly lower well-to-wheel emissions than biodiesel, despite the fact that biodiesel's
72 engine-specific emissions are similar or favorable. Similar conclusions were reached by Hossain and Davies [8].
73 Furthermore, the produced-to-consumed energy ratio turned out to be higher for raw oils. Ortner et al. [9] used life
74 cycle assessment modelling to compare greenhouse gas emissions of pure and waste vegetable oil and the biodiesel
75 produced from them. They concluded that processed vegetable oils generate the highest amounts of CO₂ over the whole
76 life cycle.

77 Summarizing the above considerations, it can be stated that unprocessed oils are renewable, biodegradable and
78 characterized by low environmental impact. However, their physical properties, especially the high viscosity and cold
79 filter plugging point of raw oils, prevent their use as standalone fuels. So the thesis underpinning this study is that the
80 properties of raw vegetable oils and their mixtures with diesel fuel could be greatly improved by a meagre addition of
81 distilled pyrolytic oils, forming a viable ternary blend. Such a fuel could combine environmental benefits with
82 acceptable efficiency and operational characteristics.

83 The European Union is tending to lean towards a gradual phase-out of first generation biofuels, preferring instead
84 advanced biodiesel from algae or cellulose and use of pyrolytic oils from waste products like plastics and rubbers [10,
85 11]. Each year around the world 1.5 billion of tyres are produced, corresponding to approximately 17 Mt [12]. Waste
86 tyres are very problematic for the environment, but can also provide some opportunities for resource conservation
87 because they can be sources of valuable fuels, e.g. pyrolytic oils [13]. However, use of unprocessed pyrolytic oils, as
88 with raw vegetable oils, is limited generally by their high viscosity, density and impurity content. The viscosity issue in
89 particular concerns countries with a colder climate [6, 14, 15]. Other issues associated with the application of pyrolytic
90 oils include their low flash point, which affects safety, and high sulphur content of oils that are produced from waste
91 rubber, e.g. TPO [16, 18].

92 To make raw vegetable oils or pyrolytic oils feasible fuels for CI engines, some engine fueling system modifications
93 or fuel treatment methods have been proposed. Ikura et al. [18] stated that oils produced by pyrolysis and intended for
94 use as fuels in CI engines should be preheated or subjected to higher injection pressure. They also highlighted pyrolytic
95 oils' inferior auto-ignition properties compared with DF. These shortcomings can be minimized when pyrolytic oils are
96 used as additive to DF, but that in turn creates another difficulty associated with these liquids' poor miscibility.
97 Bridgwater et al. [19] added alcohols such as ethanol and propanol to improve miscibility. Ikura et al. [18] suggested
98 subjecting the mixture to emulsification. Such emulsions are, however, unstable and require the use of on-board
99 ultrasound hemispheres or need to be chemically stabilised. Mulimani and Navindgi [20] examined emulsions of
100 pyrolytic oil from de-oiled seed cake of the mahua (share from 10 to 40%, v/v) with DF (share of 50 to 80%, v/v), and
101 additions of surfactant (Polysorbate 20, 8%, v/v) and diethyl ether (2% v/v). Such a mixture enabled the creation of a
102 stable emulsion.

103 Pyrolytic oil's applicability as a fuel component for a CI engine can further be constrained by combustion
104 characteristics and the environmental impact of the exhaust gases. Mulimani and Navindgi [16] examined emission
105 characteristics of a CI engine fueled with emulsions mentioned in the previous paragraph. The smoke emissions of
106 emulsified fuel blends were lower in comparison with DF. The authors emphasized that the examined fuel mixtures
107 were characterized by higher oxygen content compared to DF, which reduced soot formation. It was also observed that
108 increasing the amount of emulsified TPO also elongated combustion duration, which in turn led to lower NO_x.

109 Murugan et al. [21] investigated combustion of fuel blends containing high fractions (from 10% to 50% v/v) of TPO
110 and DF. The research was performed on a single-cylinder CI engine with a mechanical fuel injection system. The HRR
111 analysis showed that an increase in the TPO fraction delayed the high temperature reaction phase. This was attributed to
112 higher viscosity and lower volatility of TPO. Consequently, the fuel fraction burned during the premixed combustion
113 phase was higher. This ultimately gave a clear increase in peak pressure when increasing the TPO fraction. However,
114 the large-scale additions of TPO to DF produced increased emissions of all exhaust gas toxic compounds and higher
115 opacity. For a lower TPO content, the trends in emissions were less clear and dependent on engine load.

116 Frigo et al. [22] also investigated the effect of using fuel blends with high fractions (20 and 40%, v/v) of TPO in
117 mixtures with DF on a single-cylinder CI engine. The authors found that an increase in TPO content reduced THC
118 emissions, but increased emissions of CO at high engine-loads. This trade-off resulted from elongated ignition delay,
119 which ultimately was considered a limiting phenomenon for fuels with very high TPO contents. Hürdoğan et al. [23]
120 investigated blends of DF with additions of 10%, 20% and 50% of TPO. The authors noted that the sample with the
121 highest pyrolytic oil content was too viscous to allow attainment of the engine's rated performance. For the two other
122 fuel blends, there were no meaningful changes in exhaust emissions with respect to pure DF. One exception was NO_x
123 emissions under high engine-load conditions, which decreased as the TPO fraction increased. Nevertheless, the authors

124 concluded that a 10% addition of TPO in DF is an optimal composition in terms of efficiency and environmental
125 impact.

126 Recently Uyumaz et al. [24] performed a detailed combustion analysis from single in-cylinder pressure
127 measurements. The focus was on one particular fuel blend: 10% TPO and 90% DF. Significant reduction in combustion
128 duration with TPO addition was correlated with a substantial increase in pressure rise rates. The calculated ringing
129 index for the fuel blend was doubled when compared with DF. Additionally, the combustion of fuel with TPO was less
130 stable in terms of cycle-to-cycle variability in IMEP.

131 It should be noted that the above-mentioned studies were performed on CI engines with mechanical fuel injection
132 systems offering single fuel injection. Martínez et al. [25] performed tests on a modern engine with an electronically
133 controlled, common-rail injection system. The engine was fueled with DF with 5% TPO addition, and the experiments
134 were conducted at a limited number of operating points, mainly partial load. The combustion of fuel containing TPO
135 produced more smoke than DF under all tested operating conditions. The increased smoke was attributed to TPO's
136 higher content of aromatic compounds, which were considered to be precursors for soot generation. The study's authors
137 also cited the greater opacity was associated with a higher boiling point of the TPO sample and the presence of
138 distillation residues in the fuel sample. Additionally, a detailed analysis of PM size distribution showed that TPO
139 extensively promotes creation of small-size particles.

140 Recently Shahir et al. [26] investigated the performance and emission characteristics of a four-cylinder, common-
141 rail direct injection CI engine operating with blends of TPO ranging from 10% to 50% with DF. The engine tests
142 showed that the 30% TPO mixture provided the best BTE. Emissions of NO_x and unburned hydrocarbons increased
143 with increasing the TPO fraction. In contradiction, Bodisco et al. [27] demonstrated on a modern diesel engine that
144 under real driving conditions the effect of TPO on NO_x emissions is low and far below the inaccuracies resulting from
145 repeatability of the operating conditions.

146 All the above studies indicated different optimal TPO/DF compositions for CI engine fuelling. Furthermore,
147 inconsistent emission trends were reported in different studies. These discrepancies may result from different TPO
148 properties, stemming from differences in pyrolysis processes and refining. It is sufficient to mention that kinematic
149 viscosity at 40 °C of tested raw TPO components varied from 2.4 mm²/s to 9 mm²/s.

150 Murugan et al. [28] proposed subjecting TPO to distillation to reduce the soot content and viscosity of the additive.
151 Distillation enabled the authors to fuel the engine with a mixture containing up to 90% of distilled TPO. Observed
152 ignition delays were proportional to the content of TPO for all operating conditions. The delayed combustion reduced
153 NO_x emissions, whereas smoke emissions increased.

154 Doğan et al. [29] fuelled an engine with refined (pure) TPO. However, combustion of pure TPO caused a
155 deterioration of thermal efficiency. In general, the results showed that higher TPO content gave lower exhaust gas
156 opacity. Changes in NO_x emissions were moderate, but with pure TPO there was a substantial increase for all tested
157 conditions. Note that these results are opposite to those achieved by Murugan et al. [28]. It should be underlined,
158 however, that properties of the various TPO-derived fuel were different, affecting mixture formation during injection
159 and, subsequently, combustion itself.

160 Sharma and Murugan [30] investigated the combustion of binary blends of JME and TPO at various compositions.
161 The studies showed that the start of combustion at full engine load for the blends with TPO content of 10% and 20%
162 was 1 ° of CA earlier than for DF. The study's authors explained that this earlier auto ignition stems from the fact that
163 JME has a higher oxygen content and cetane number than DF. Conversely, a higher TPO content delayed auto-ignition
164 due to the decrease in the cetane number. The authors stated that a 20% addition of TPO is an optimal fuel composition.
165 In another work, Sharma and Murugan [31] demonstrated improvement in the oxidative stability of Jatropha-originated
166 biofuel by 20% addition of TPO. Engine tests with this fuel blend showed reduction of smoke emissions when
167 compared to DF.

168 Koc et al. [32] investigated the effects of biodiesel and TPO additives to DF on a four-cylinder CI engine. Analysis
169 of exhaust emissions from a binary blend (97% DF and 3% biodiesel or 3% TPO) and a tertiary blend (94% DF, 3%
170 TPO and 3% biodiesel) revealed that blends with TPO generated lower NO_x emissions than binary blends of biodiesel
171 and DF. Moreover, combustion of the ternary fuel blend (TPO, FAME and DF) produced lower CO emissions than the
172 binary blend of TPO and DF. One of the most important conclusions drawn by Koc et al. [32] was that adding TPO to
173 conventional diesel fuel or biofuel could be an effective way to reduce NO_x emissions. In a follow-up work by Koc and
174 Abdullah [33] the same engine was fuelled with a ternary mixture of TPO, biodiesel and DF (10%, 10% and 80%,
175 respectively). As well as lowering NO_x emissions, the addition of TPO was found to reduce the exhaust gas CO
176 concentration.

177 The above review of published studies of ternary mixtures in combustion engines shows that testing has been solely
178 with methyl esters of jatropha [30] or rapeseed [21, 28, 34]. There are no available research results for mixtures that
179 include raw bio-oil components. Furthermore, the cited studies were performed mainly on relatively simple single-
180 cylinder engines. Data on the impact of ternary mixtures on the performance of modern multi-cylinder production
181 engines is limited.

182 This study addresses these knowledge gaps by testing ternary mixtures of directly pressed rapeseed oil, diesel and
183 distilled TPO, mixed at different proportions, in a multi-cylinder, common-rail direct injection engine with factory
184 calibration. An attainable map of steady-state operating points was assessed in the study. The paper discusses the
185 production and physicochemical properties of tested samples and examines emission characteristics, engine operating
186 parameters and engine efficiency.

187 The full scope of these experiments is further narrowed down to the selected best (in terms of well-to-wheels CO₂
188 footprint and emission trade-off) ternary fuel blend. This is subjected to a detailed in-cylinder measurement-based
189 combustion analysis aimed at providing insight into the prospects of further combustion process optimization. Due to
190 the broad scope of the study, these results are discussed in a separate paper by the authors [35], being Part 2 of the
191 present work.

192 2 Materials and methods

193 2.1 Preparation of samples

194 2.1.1 Tire pyrolytic oil

195 The industrial sample of TPO was obtained by anaerobic pyrolysis of scrapped, used car tyres (pieces approximately
196 6cm by 6 cm), conducted in a discontinuous operation reactor at 450-500 °C for approximately eight hours. The
197 remaining products of the thermal decomposition of tyres were: pyrolytic gas (used for sustaining the pyrolysis
198 process), carbon black and steel wire (component of tyres). The density at 20°C, viscosity at 40 °C, acid value, sulphur
199 content, flash point and oxidative stability of supplied TPO samples were determined according to the methodology
200 described in Subsection 2.2. The values of the analyzed physicochemical parameters indicated that pure TPO should not
201 be used directly as a fuel component.
202
203



204

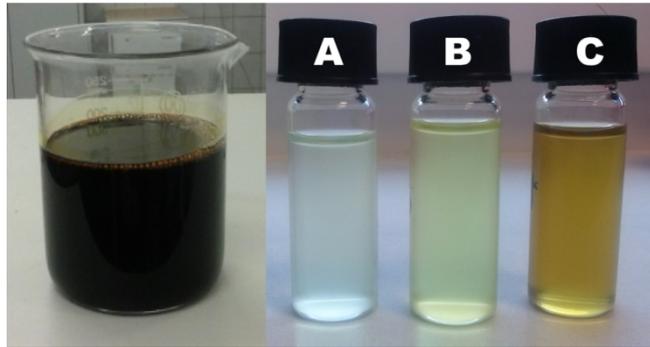
205 **Fig. 1.** The laboratory setup used for TPO distillation.
206

207 After a basic physicochemical analysis, TPO was distilled in order to remove highly volatile components and soot
208 particles present in the initial sample. Fig. 1 shows the laboratory setup used for TPO distillation, consisting of a heater,
209 a three-neck flask fitted with a mercury thermometer and a thermocouple, a spherical condenser and a collection vessel.

210 Three fractions differing in terms of boiling temperature were distinguished during distillation:

- 211 - Fraction I – consisting of fractions with boiling temperature > 160 °C - this fraction was distilled in order to
212 remove components characterized by high volatility, significantly influencing the low flash point of the
213 pyrolytic oil;
- 214 - Fraction II – consisting of fractions with boiling temperature from 160 °C to 204 °C - this fraction was used as
215 a fuel component;

- 216 - Fraction III – consisting of fractions with boiling temperature from 205 °C to 350 °C - in the fraction distilled
 217 over 204 °C a soot penetration form pyrolytic oil has occurred; over 350°C only tar-like substance remained in
 218 the distillation flask.
 219



220

221 **Fig. 2.** From the left – obtained raw TPO sample and products of its distillation; A – light naphtha fraction, B – medium naphtha
 222 fraction, C – heavy naphtha fraction.
 223

224

225 Fig. 2 presents fractions obtained by distillation. During distillation it was observed that visible soot amounts
 226 penetrated into the heavy fraction, which was also noted in the previous works by Ambrosewicz-Walacik and
 227 Danielewicz [36], Ambrosewicz-Walacik et al. [35]. Thus, the medium naphtha fraction II, which accounted for 59% of
 228 the total TPO sample mass, was used for further investigations.

229

229 2.1.2 Cold-pressed rapeseed oil

230 The Komet screw oil-exPELLER CA 59 G featuring a cylindrical perforated strainer basket was used to extract
 231 rapeseed oil at a temperature below 40 °C. The seeds were thermally treated at 130 °C for an hour and then cooled
 232 down before extraction. Mechanical impurities were filtered by centrifugation at 12 000 rpm for 10 minutes in a
 233 centrifuge type C 5810 R (Eppendorf, Germany).

234

234 2.1.3 Rapeseed methyl esters

235 The sample of crude pressed RO was subjected to transesterification to obtain RME which were used as fuel
 236 components. In the first step of RME preparation, the acid number of crude RO was determined to select the right
 237 method for transesterification. Due to a low value of this parameter (2.0 mg KOH/g), a single-base transesterification
 238 method was chosen. The reaction was carried out in 500 ml glass flasks placed in electric heaters. Weighed portions of
 239 300 g of oil were heated to 60±1°C. Next, a solution of potassium methoxide (3.75 g KOH mixed with 125 ml of
 240 methanol) was added to the preheated oil. The reaction was carried out at 60±1°C for 1 hour with stirring at a rate of
 241 250 rpm. The reacted mixture was then distilled in a vacuum evaporator from Heidolph (Germany) to remove any
 242 residue. Afterwards, the mixture was subjected to separation for 24 hours. When the sedimentation phases were
 243 separated, an approximate yield of the process based on the percentage of ester (94.2%) and glycerine phases (5.8%)
 244 was determined.
 245

246

246 2.1.4 Diesel fuel

247 The sample of diesel fuel was supplied from a commercial fuel station in Olsztyn, Poland. The fuel's specification
 248 complied with EN590 standard and it already contained a 7% biocomponent.

249

249 2.2 Properties of fuels

250 The crude TPO, distilled TPO fractions of naphtha, RME, crude rapeseed oil and diesel fuel were analyzed to
 251 determine viscosity at 40 °C (pycnometric method), density at 15 °C (EN ISO 3104), acid number (EN 14104), sulphur
 252 content (ISO 20884), flash point (ISO 3679), cold filter plug point (EN 116), oxidative stability (EN 14112) and
 253 calorific value (D4809). The properties of the tested fuels and their components are listed in Table 1. The distilled
 254 medium fraction naphtha of TPO (DMF_{TPO}) was selected for the composition of ternary fuel blends. Interestingly,
 255 DMF_{TPO} has a very low viscosity, so can be used as a viscosity enhancer for biocomponents. Also note that the flash

256 point of DMF_{TPO} is very low, which eventually will have a significant effect on both flammability and handling safety
 257 of fuel mixtures with TPO additives.

258
 259

Table 1. Properties of fuel components used in this study.

Samples	TPO	Distilled fraction of naphtha from TPO			RO	DF
		light	medium	heavy		
viscosity at 40 °C [mm ² /s]	5.59	0.814	0.842	0.897	39	2.73
density at 15 °C [kg/m ³]	949	779	1008	1361	920	827
acid value [mg KOH/g]	4.63	2.37	3.12	3.88	2.00	0.07
sulphur content [wt%]	0.42	0.34	0.54	0.79	0.007	0.006
flash point [°C]	53	< 3.5	13	23	> 200	57
cold filter plug point [°C]	n.d.	> - 30	> - 30	> - 30	n.d.	-1
oxidative stability [h]	> 27	0.5	> 27	> 27	6.47	>22

260

261 Prior to engine tests, different ternary fuel blends consisting of DF, RO and DMF_{TPO} were prepared and tested for
 262 their flash point to verify the safety of fuel application. This indicated that to ensure a safe flash point (above 55°C
 263 according to EN 590), the DMF_{TPO} content cannot exceed 5%. Thus, ternary fuel blends were composed of different
 264 fractions of DF and RO with a constant DMF_{TPO} content of 5% on a mass basis. The ternary fuel blends subjected to
 265 further examinations were denoted as TPO₁ up to TPO₅, and composed according to Table 2.

266 To provide a baseline for the assessment of effects of the DMF_{TPO} addition, a binary blend of DF and RO (denoted
 267 as DR) with equal shares of both components was examined as well. This fuel was not, however, subjected to engine
 268 tests. It was noted that the addition of DMF_{TPO} positively influenced the viscosity, density and acid number of the
 269 ternary blends when compared with the DR sample. Nevertheless, despite a significant decrease in viscosity, the value
 270 of prepared ternary fuel blends exceeded the acceptable limit of 4.5 mm²/s, specified in EN 590. The viscosity ranged
 271 from 6.63 mm²/s to 11.56 mm²/s, as shown in Table 2. Furthermore, the content of sulphur in selected blends
 272 significantly exceeded the permissible content of that compound (10 mg/kg according to EN 590), and for that reason it
 273 is suggested to desulfurize the crude TPO before distillation.

274 Further engine tests were conducted using five selected ternary blends. To provide reference values, pure DF and a
 275 blend of rapeseed methyl ester and DF (20:80, v/v), denoted as Bio₂₀-DF₈₀, were used. Properties of all tested fuels are
 276 given in Table 2.

277

278 **Table 2.** The composition of individual fuel blends prepared for pilot analysis, along with most relevant physicochemical properties.

Samples	DR	DF	TPO ₁	TPO ₂	TPO ₃	TPO ₄	TPO ₅	Bio ₂₀ -DF ₈₀
composition DF/RO/ DMF * [% volume]	50/50/-	100/-/-	40/55/5	45/50/5	50/45/5	55/40/5	65/30/5	80/20/-
flash point [°C]	>100	57.0	54.5	55.0	56.0	56.5	57.0	57.0
viscosity at 40 °C [mm ² /s]	17.82	2.73	11.56	8.94	8.43	7.97	6.63	2.99
density at 15 °C [kg/m ³]	875	827	868	861	860	852	851	834
acid value [mg KOH/g]	0.81	0.07	0.68	0.73	0.63	0.62	0.63	0.20
sulphur content [mg/kg]	6.12	<0.1	271.6	277.5	274.5	276.1	140.3	4.8
oxidative stability [h]	9.25	> 22	> 5.86	> 5.86	6.02	8.84	6.63	> 20
Lower heating value [MJ/kg]	n.d.	44.5	39.5	39.6	40.1	40.7	41.1	43.8

* for Bio₂₀-DF₈₀ fuel sample RME is used as biocomponent instead of RO

279 2.3 Engine test setup and methodology

280 The fuel samples were tested on an engine test bench with a four-cylinder, medium-duty compression-ignition
 281 engine manufactured by Andoria-Mot Poland. The engine was equipped with a Bosch common-rail 2.0 fuel injection

282 system and controlled by a factory EDC1639 engine control unit. Technical specifications of the test engine are listed in
 283 Table 3 and its layout is illustrated in Fig. 3.

284 The engine was installed on a test bench and equipped with the following measurement equipment:

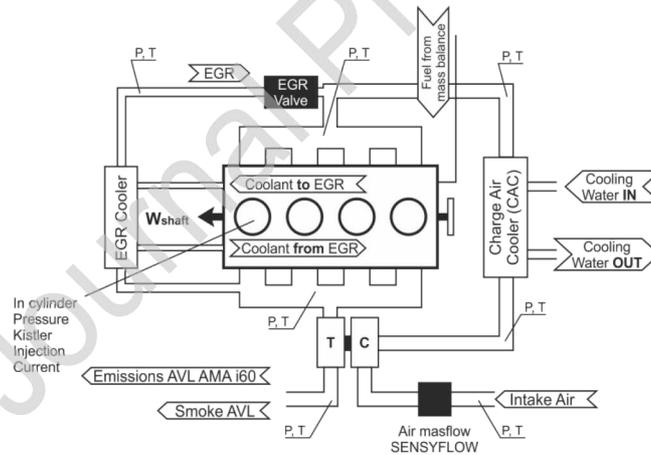
- 285 - eddy-current dynamometer (AVL DP 240),
- 286 - fuel balance AVL 735S with temperature conditioning,
- 287 - air mass flow meter SENSIFYLOW P from ABB,
- 288 - in-cylinder pressure measurement system (KISTLER),
- 289 - test stand control and data acquisition system (AVL PUMA Open),
- 290 - partial flow dilution emission measurement system (AVL AMA I60),
- 291 - smoke meter (AVL 552).

292 Additionally, a set of absolute pressure and temperature transducers was installed at various locations of the air and
 293 exhaust paths to monitor and control the media (cooling water, lube oil). A schematic diagram of the engine
 294 environment with the most important measurement points is shown in Fig. 3. Measurement accuracies of the
 295 instruments are given in Table 4.

296 **Table 3.** Technical data of the test engine.

Type	4-stroke, Compression-Ignition
Engine layout	4 cylinder inline, vertical
Cylinder diameter / piston travel	94 / 95 mm
Displacement volume	2636 cm ³
Compression ratio	17.5 : 1
Rated Power / rotational speed	85 kW / 3,700 rpm
Max. Torque / rotational speed	250 Nm / 1,800-2,200 rpm
Injection system	Bosch injection system CR 2.0
Turbocharger	radial, with exhaust extraction valve
EGR	High pressure system, pneumatic valve

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299

300 **Fig. 3.** Test engine layout with most important measurement points. Note that EGR valve was turned off in the present research.

301

302 The scope of the present paper includes analysis of emission, efficiency and selected performance parameters.
 303 Therefore, for the present analysis, only the relevant measurement systems will be discussed in detail. For further
 304 information on the engine test bench, the reader is referred to earlier works by the authors [37, 38]. For a detailed
 305 description of in-cylinder pressure measurements and thermodynamic analysis, refer to the second part of this work
 306 devoted to combustion analysis [17]. Here it is only relevant to mention that the in-cylinder pressure, along with the
 307 injection actuation current, were recorded with a CA resolution of 0.1°. The presented pressure and HRR curves are
 308 ensemble-averaged for 200 consecutive engine cycles.

309 Fuel consumption was measured using the AVL 735S fuel balance. The fueling system was equipped with an
 310 accurate thermal management unit that controlled fuel temperature on the intake and return lines via heat exchangers.
 311 The tested fuels were changed by switching the fuel tanks. Exceptional care was taken to ensure results reliability with
 312 such radically different fuels, purging the fuel system before each test sequence using a set of valves. The engine was
 313 then allowed to run on a new fuel with the injector pump return hose disconnected. Purging continued until a sufficient

amount of fuel was transferred through the engine fueling system as well as the measurement and conditioning devices.

The emission test bench consisted of the following analyzers:

- Flame Ionization Detector (FID) – for measurements of THC concentrations,
- Chemiluminescence Detector (CLD) – for measurements of NO_x concentrations,
- 2 x Infrared Detector (IRD) – calibrated for CO concentration,
- Paramagnetic Detector (PMD) – for O₂ concentration measurement.

All the sample lines leading to the exhaust analyzers were heated to 150 °C to avoid water condensation that might affect results. Additionally, EGO was measured using the AVL smoke meter (AVL 552).

The emission paths were carefully flushed with a high flux of pressurized air between different fuels, adhering to a procedure provided by the emission test bench manufacturer (AVL).

Table 4. List of the most relevant (low-frequency) parameters recorded directly, along with achieved maximum uncertainty.

Parameter	Engine rotational speed	Torque	Generated power	Air aspirated to the engine	Fuel consumption	Total hydrocarbons	Total nitrogen oxides	Carbon monoxide	Opacity
Symbol	N	Te	Pe	G _{air}	G _{fuel}	THC	NO _x	CO	EGO
Measurement device	AVL DP 240			SENSYFLOW P	AVL 735S	AVL AMA i60			AVL 439
Uncertainty level	± 5	± 2	± 0.2	± 0.5	± 0.1	± 11	± 19	± 13	± 0.9
Unit	RPM	Nm	kW	kg/h	kg/h	ppm	ppm	ppm	%

The research assessed the steady-state operation of the engine. For each of the operating points, after stabilization of the engine operating conditions (120 s), a measurement window was set to 180 s, during which the parameters listed in Table 4 were recorded. The sampling rate for the parameters was maintained constant (1 s), and time-averaged values are further analyzed in the Results section.

2.4 Calculation methodology

In the present study, the directly measured concentrations of toxic exhaust gas components and opacity were used to characterize the investigated fuels. Since the goal is to compare the environmental impact of different fuels at the same engine operating conditions, such an approach is more informative since it allows assessment of the emission output without introducing the bias resulting from engine efficiency. Thus, presented emission results are time-averaged direct outputs of the respective analyzers. Either the standard deviation calculated for a time series or the device accuracy (Table 4), whichever is higher, are taken as the maximum uncertainty of individual emission indexes.

Fuel efficiency analysis relies on the values of BTE, calculated as a ratio of power generated by the engine and energy input introduced with a specific fuel. Namely, using the directly measured quantities introduced in Table 4:

$$BTE[\%] = 100 \cdot \frac{Pe \cdot 3600}{G_{fuel} \cdot LHV_{fuel}} \quad (1)$$

Note that LHVs differ for the tested fuels due to differences in chemical composition. Thus, they were determined for each fuel, and are summarized in Table 2. The uncertainty level for the BTE was established from the maximum device accuracies of the directly measured inputs (Table 4) using the exact differential method, following the approach of Klien and McClintock [39].

The present work provides also some details concerning in-cylinder pressure analysis. The net IMEP was calculated by integrating the pressure signal across the whole 720 CA respectively. The coefficient of variation in IMEP (COV_{IMEP}) was introduced as an indicator for operational stability. This parameter was calculated for 200 subsequent engine cycles as a ratio of standard deviation and mean value. The average peak pressures and their standard deviations were used as measures for cycle-to-cycle variations.

The net IMEP was further used to calculate indicated efficiency

$$\eta_{net} = 100 \cdot \frac{^{1/2} \cdot IMEP_{net} \cdot V_{disp} \cdot N \cdot 3600}{G_{fuel} \cdot LHV_{fuel}} \quad (2),$$

where V_{disp} is the displaced volume and N denotes the engine rotational speed. Note that the differences between net indicated efficiency and BTE are the total friction losses. Combustion losses were calculated on the basis of recorded

356 THC and CO concentrations. This was done on a simplifying assumption that all unburned HCs account for n-heptane
 357 particles yet have the heating value of the corresponding fuel. Then, the combustion losses become:

$$358 \quad \eta_{comb} = \frac{G_{CO}LHV_{CO} + G_{THC}LHV_{fuel}}{G_{fuel} \cdot LHV_{fuel}} \quad (3),$$

359 where G terms with the subscripts CO and THC represent the concentrations of the corresponding species recalculated
 360 with the total exhaust flow rate to the adopted convention of mass flow as in Eq.1 and Eq. 2.

361 The injection current was recorded using the same sampling frequency as in-cylinder pressure. The first-order
 362 derivative of this signal was used to determine the SOA angle by means of a simple peak sensing routine. Thus, the
 363 maximum accuracy of this parameter was considered to be equal to twice the sampling rate (0.2 CA). For more
 364 information on the methodology of in-cylinder pressure analysis adopted in this research, the reader is referred to other
 365 works by Mikulski et. al. [37, 40, 41].

366 2.5 Scope of the research

367 Steady-state measurements were performed at two engine speeds: 1500 rpm and 3000 rpm. For both engine speeds,
 368 an engine-load sweep was performed by changing the Te value from 50 Nm to 200 Nm with a step size of 25. This
 369 covered the operational map up to 80% nominal engine load. The corresponding BMEP values ranged from 2.4 bar to
 370 9.5 bar for all operating points. Note that 100% rated diesel load point was not investigated in this study due to the
 371 inability of reaching this point for TPO₁ and TPO₂ samples. This was associated with limitations of the current injection
 372 aperture.

373 The research was performed without external EGR, using factory injection and turbocharger maps. This was done to
 374 assess the study's thesis that the combustion properties of raw vegetable oil – diesel mixtures can be significantly and
 375 positively altered by adding distilled pyrolytic oils.

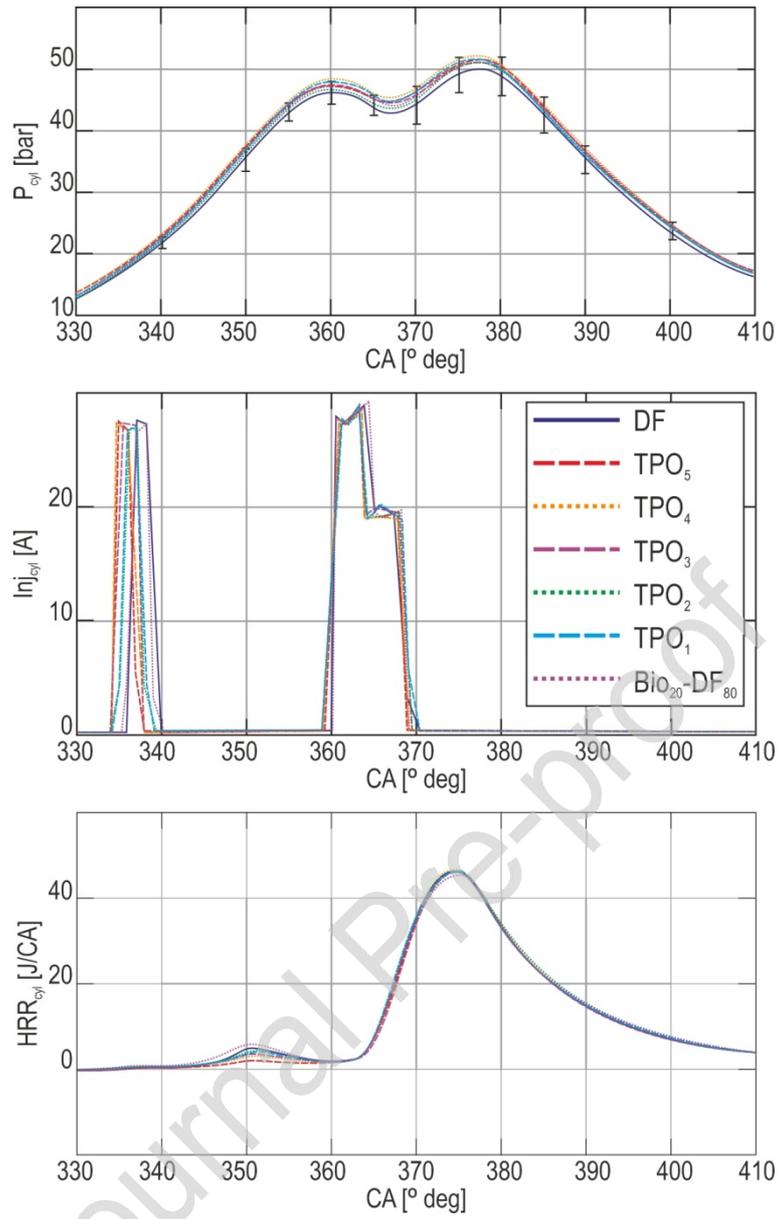
377 3 Results and discussion

378 The objective of the work is to provide the complete characterization of different ternary fuel mixtures containing
 379 distilled TPO in terms of combustion performance and emissions for a wide range of engine operating points, and to
 380 assess them with respect to DF and Bio₂₀-DF₈₀ references. Given the broad scope of the research, the details of
 381 combustion characteristics are not elaborated. It is however considered necessary for the reader to gain some
 382 understanding of the combustion strategy in general, so results of a detailed combustion analysis (in-cylinder pressure
 383 and HRR) for selected operating points are discussed in Subsection 3.1. A full factorial characterization is further
 384 performed based on selected efficiency (Subsection 3.2) and emission (Subsection 3.3) indicators. For a detailed
 385 combustion analysis accounting for the observed differences, the reader is referred to another work by the authors [17].

386 3.1 The combustion strategy

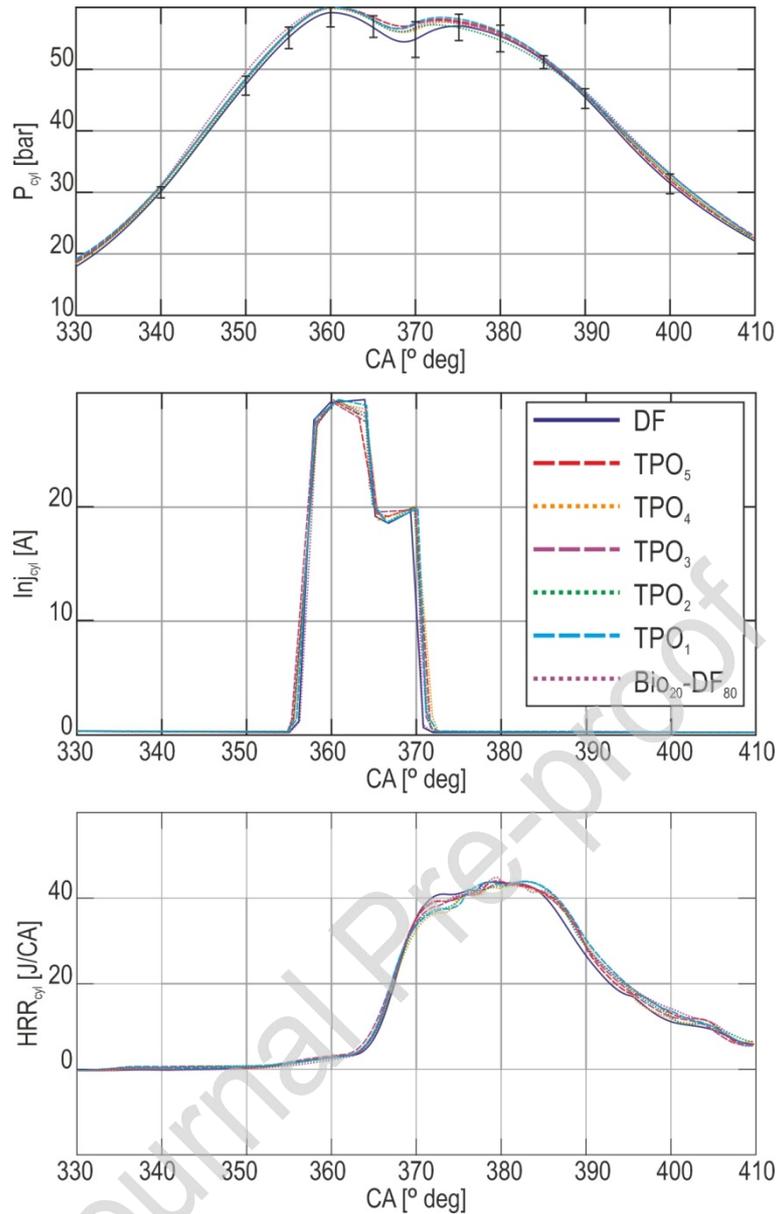
387 Figs. 5 and 6 show the results of processed injection current, in-cylinder pressure and heat release rate for two
 388 selected operating points from the experimental matrix. Namely, the figures refer to the same mid-load point of 6 bar
 389 BMEP (125 Nm) at the engine speed of 1500 rpm and 3000 rpm respectively.

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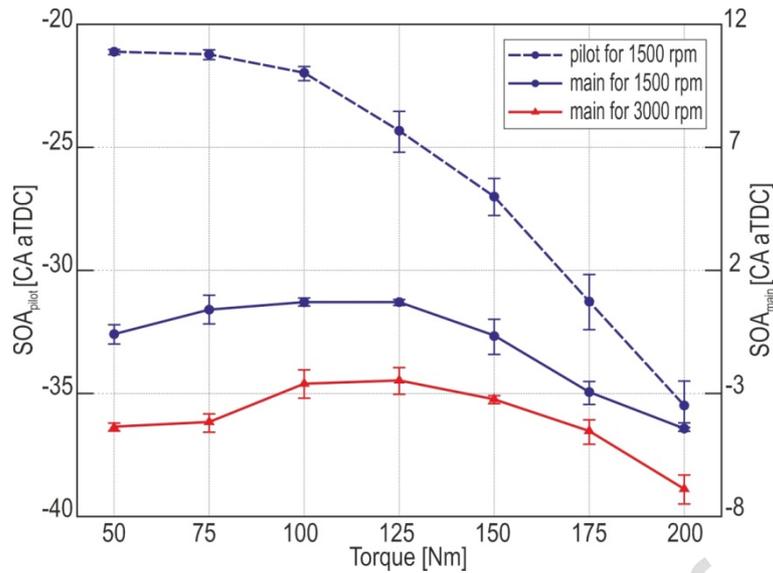
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Fig. 5. Cycle-averaged injection current, in-cylinder pressure and HRR; $N = 1500$ rpm, $T_q = 125$ Nm. Error bars for in-cylinder pressure denote cycle-to-cycle variations (for clarity plotted only for DF results).



394
 395 **Fig. 6.** Cycle-averaged injection current, in-cylinder pressure and HRR; $N = 3000$ rpm, $T_q = 125$ Nm. Error bars for in-cylinder
 396 pressure denote cycle-to-cycle variations (for clarity plotted only for DF results).

397 Comparing Fig. 5 and Fig. 6 one can immediately note that the engine realizes a different injection strategy for both
 398 operating points. This observation can be applied across the whole test matrix. Namely, split injection is realized for all
 399 cases with the engine speed of 1500 rpm, while at 3000 rpm the engine employs a single injection mode. The multi-
 400 pulse strategy with early injection of a relatively small pilot amount of fuel (around 10% of the overall fuel quantity
 401 independently of engine load) exhibits a clear premixed combustion phase, which can be seen in the HRR plot in Fig. 5.
 402 For the single injection, combustion is clearly diffusion-controlled by a developing spray which can be recognized by a
 403 distinctive flat HRR profile in Fig. 6. Note that in both analyzed cases the main combustion phase is significantly
 404 retarded, beyond the TDC. This strategy is often used as a NO_x emission-mitigation measure. It reduces peak in-
 405 cylinder temperatures while sacrificing indicated efficiency [42, 43]. Comparing the HRRs of individual fuels, one can
 406 note that combustion is not significantly affected by fuel choice. The in-cylinder pressure traces are also similar (within
 407 cycle-to-cycle variations) for both analyzed operating points. Note however that for the case presented in Fig. 5, the
 408 engine controller is able to maintain the preset combustion parameters adjusting on the pilot injection timing. The extent
 409 of changes in the injector SOA timing for all operating points and tested fuel samples is provided in Fig. 7.



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Fig. 7. Start of actuation of pilot injection and main injection for diesel fuel and all investigated conditions. Error bars denote maximum dispersion between different fuels. Note separate Y-axes for pilot and main injections.

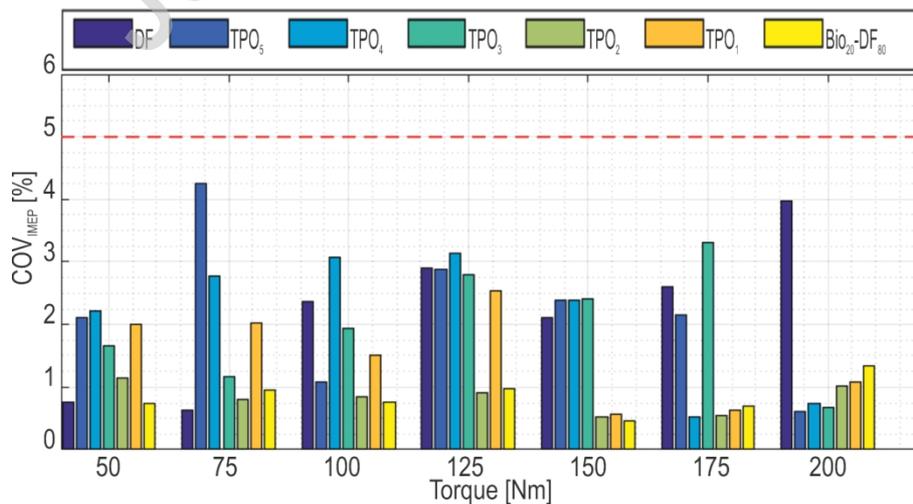
413 While analyzing the trends in SOA, one should keep in mind that the absolute, maximum error of determining the
414 timing was 0.2 CA. Cycle-to-cycle variations in SOA were not recorded in the present research.

415 From Fig. 7 one can observe that the pilot injection (when applied) is generally retarded with increasing engine load,
416 from around 21 CA bTDC at the lowest load up to 36 CA bTDC for the 200 Nm case. For the main injections, the
417 trends were non-monotonic in terms of both engine loads. Note however that the largest variations from fuel to fuel
418 were rather small and did not exceed 1.5 CA deg. With the small yet noticeable variations in engine operating
419 parameters, the extent to which the overall engine performance is affected by fuel can differ, depending on the
420 operating point. This is assessed in subsequent subsections with respect to combustion stability, thermal efficiency and
421 emissions.

422 3.2 Combustion stability and cycle-to-cycle variations

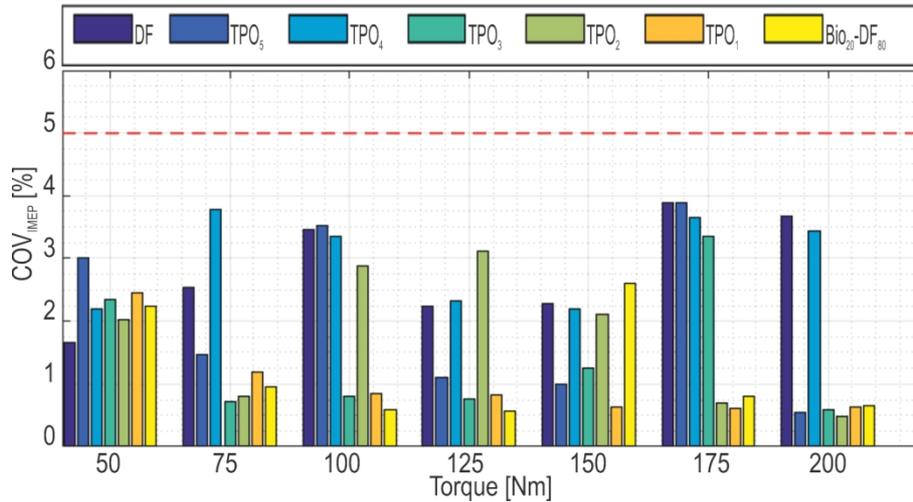
423 The COV_{IMEP} is a widely used indicator for assessing combustion stability. More accurately, it determines the
424 engine's capability for providing stable torque output, which is important in terms of drivability for vehicle applications
425 and efficiency [44]. More importantly, for power generation, torque instability will introduce frequency or current
426 output oscillations. A typically assumed stability limit for different applications is COV_{IMEP} that does not exceed 5%
427 [45, 46].

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Fig. 8. Coefficient of variation in IMEP for different fuels across the whole engine load sweep; N = 1500 rpm.

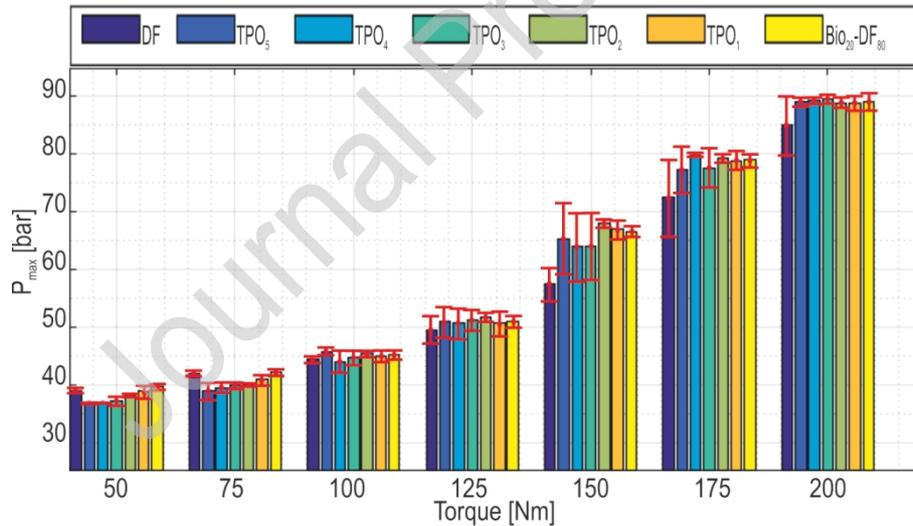


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Fig. 9. Coefficient of variation in IMEP for different fuels across the whole engine load sweep; N = 3000 rpm.

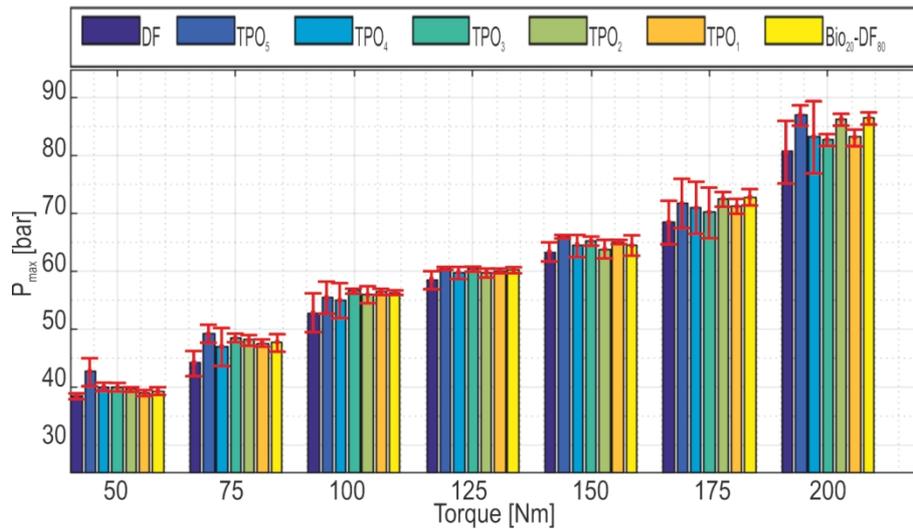
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Figs. 8 and 9 show how this parameter is influenced by a given fuel for the engine speeds of 1500 rpm and 3000 rpm, respectively. It can be seen that all fuel samples were able to meet the adopted stability criterion at all operating points, although at selected operating points the combustion variability was rather high and exceeded 3% COV_{IMEP}. Note however that this variability apparently can be attributed to the engine itself rather than the type of fuel used, since in the standard DF operation the COV_{IMEP} is equal or higher compared to other fuel samples. In effect, the stability results are rather stochastic in nature, even though the Bio₂₀-DF₈₀ showed more stable operation compared with diesel and all TPO mixtures. Consequently, the TPO samples with the lowest admixture of pure rapeseed oil have the physicochemical properties resembling those of diesel fuel, which resulted in the highest levels of variations.



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Fig. 10. Peak in-cylinder pressure for different fuels across the whole engine load sweep; N = 1500 rpm. Error bars denote standard deviation of P_{max} calculated over 200 cycles.



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Fig. 11. Peak in-cylinder pressure for different fuels across the whole engine load sweep; $N = 3000$ rpm. Error bars denote standard deviation of P_{max} calculated over 200 cycles.

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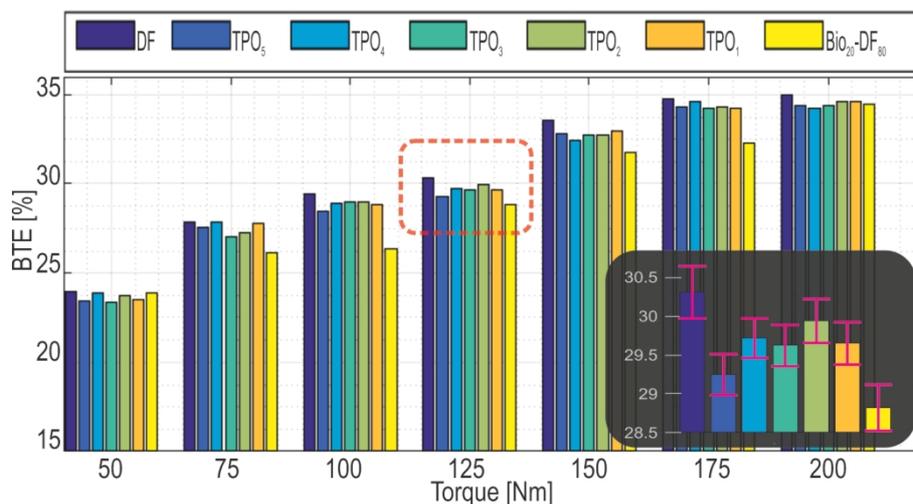
Figs. 10 and 11 show how the cycle-to-cycle oscillations translate into variability of peak in-cylinder pressure. The maximum peak pressure is one of the engine design constraints. Excessive pressures may exert mechanical and thermal stress on combustion chamber components, leading to engine failure. The peak in-cylinder pressures generally increase with engine load, which is obvious since more energy is released during combustion. One can note that all biofuels show generally similar peak pressures that are usually slightly higher than the reference diesel fuel's. The differences, however, always lie within the cycle-to-cycle variations showed by the error bars. Importantly, comparing Figs. 10 and 11 with Figs. 8 and 9 one can note that the peak pressure variations only partially correspond to the variations in IMEP. For instance, the 50 Nm case with 1500 rpm shows a similar COV_{IMEP} for TPO samples 5, 4 and 2, while for the latter sample the variations in P_{max} are substantially higher. Despite that, the peak pressure limit (130 bar for the given engine) was not exceeded for the tested fuels either in terms of cycle-averaged values or in individual cycles. The results presented in this subsection confirm that all tested biofuels can be operated on the engine without exceeding the stability tolerances.

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3.3 Efficiency breakdown analysis

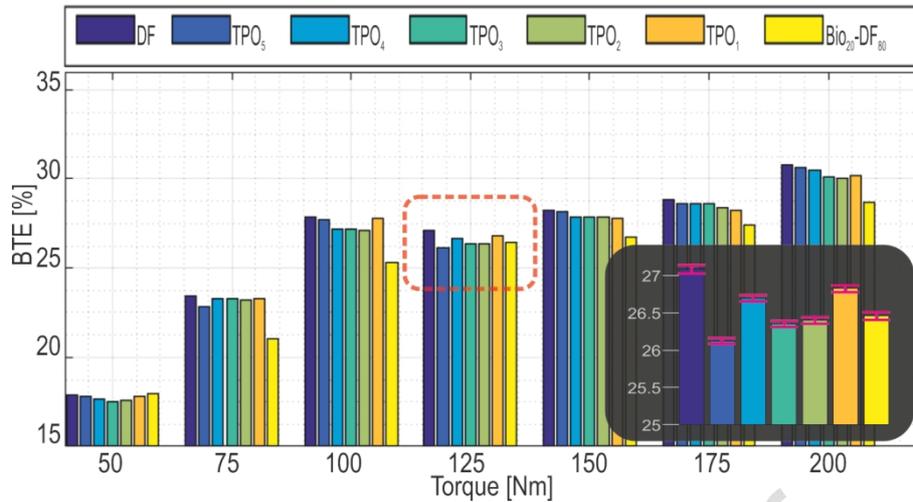
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Figures 14 and 15 present the results of BTE for the engine operated on different fuels. It is important to know that the maximum error of determining the BTE on the basis of measured fuel consumption and power output was below 0.6%, with its values consistently decreasing with increasing engine load. For example, for the highest power output (200 Nm / 3000 rpm) the absolute error did not exceed 0.06%. Due to this very small measurement uncertainty, error-bars are omitted in Figs. 12 and 13, but accuracy of BTE estimation is clearly indicated in the discussion of the results.



465

466 **Fig. 12.** Brake thermal efficiency; $N = 1500$ rpm. Error bars (for a chosen operating point) denote the maximum uncertainty.

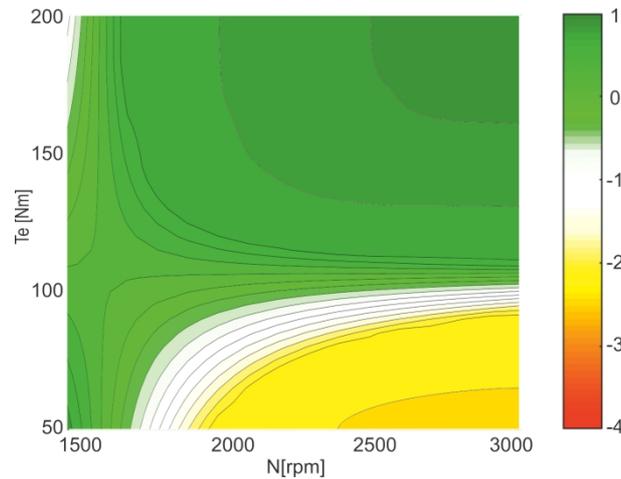


467
468 **Fig. 13.** Brake thermal efficiency; $N = 3000$ RPM, $T_q = 125$ Nm. Error bars (for a chosen operating point) denote the maximum
469 uncertainty.

470 Bearing the above remarks in mind, one can conclude that under the lowest load, for both tested engine-speeds,
471 efficiency differences between the tested biofuel mixtures and diesel are below the level of significance. For higher
472 loads however, the binary mixture of diesel and rapeseed oil showed considerable efficiency deterioration with respect
473 to the diesel reference. For instance, at 3000 rpm and 100 Nm the absolute difference in efficiency was as much as 2.2%
474 with an average uncertainty of 0.04%. For all TPO samples the efficiency was only slightly lower compared to diesel.
475 For instance, at the same operating point the TPO samples resulted in BTE values ranging from 27.2% to 27.8%, while
476 the diesel operation gave the thermal efficiency of 27.9%. There was no clear relationship between the addition of
477 biocomponent in the ternary mixture and efficiency loss. At one operating point, the sample TPO₅ (with 30% RO)
478 produced better efficiency than TPO₁ (55% RO), whereas at other operating points an opposite trend was observed.
479 Nevertheless, the maximum difference between all TPO samples did not exceed 0.6%. At the same time, the maximum
480 difference between a given TPO sample and DF was around 1.2% (TPO₄ vs DF at 150 Nm and 1500 rpm) with an
481 average uncertainty of 0.22%.

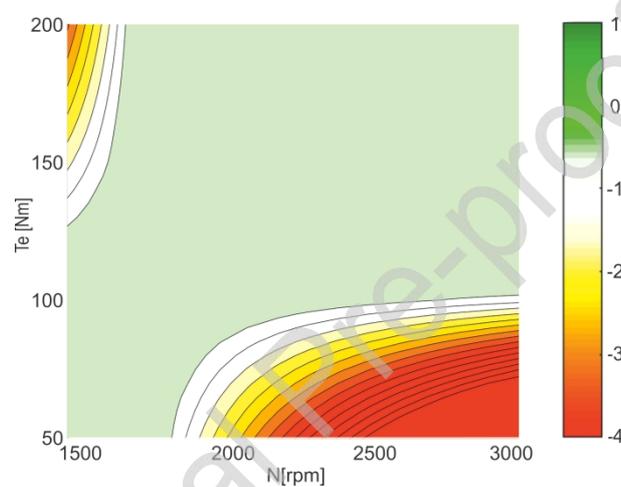
482 Summarizing the above discussion, the obtained TPO samples showed significantly better performance compared to
483 the binary fuel blend with RME. The 5% addition of pyrolytic oil enables the share of the inexpensive raw
484 biocomponent in diesel fuel to be as much as 55%, with only slight overall performance deterioration compared to DF.
485 Since a detailed combustion analysis is beyond the scope of the present paper, only brief remarks on the causes of the
486 observed differences in BTE are provided below. For a more detailed analysis of combustion of fuels containing TPO,
487 refer to a different work by the authors [17].

488 Further insight into the causes of the observed performance differences between diesel, ternary TPO samples and
489 binary sample (Bio₂₀-DF₈₀) can be gained by analyzing the net indicated efficiency trends. For consistency, this is
490 visualised by mapping the differences in net indicated efficiency between diesel and TPO₃ in Fig. 14. A corresponding
491 map for the binary Bio₂₀-DF₈₀ sample is shown in Fig. 15. Note that for the purpose of mapping, the results of the
492 engine-load sweeps at intermediate speeds of 2000 and 2500 rpm are also included.



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Fig. 14. Delta between net indicated efficiency of the engine operated on TPO₃ and DF. The negative values indicate favorable results for DF.



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Fig. 15. Delta between net indicated efficiency of the engine operated on Bio₂₀-DF₈₀ and DF. The negative values indicate favorable results for DF.

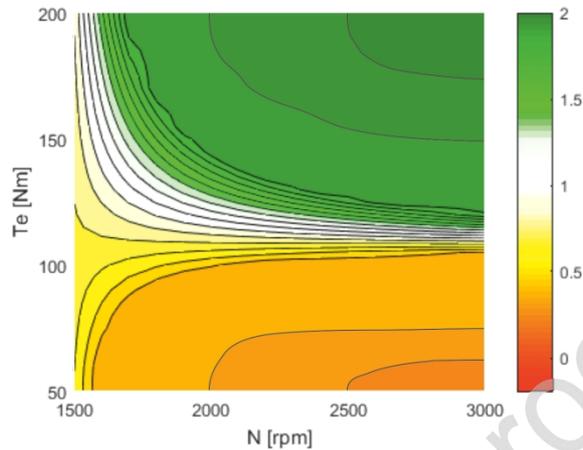
499 Figure 14 indicates that, despite the overall BTE being lower for the TPO₃ sample than for diesel, the net indicated
500 efficiency can sometimes slightly favour TPO₃. With low engine speeds this occurs at low engine loads, where the
501 efficiency is approximately 1 percentage point (pp) higher than with diesel, with a deteriorating trend towards high
502 loads. The trend is opposite for higher engine speeds, with TPO₃'s partial loads' performance being 2 pp lower than the
503 diesel baseline. Note that the corresponding maps for all TPO samples are in general alike.

504 The trends in relative indicated efficiency for the Bio₂₀-DF₈₀ sample shown in Fig. 15 are generally the same as
505 those for the TPO samples shown in Fig. 14. The magnitude of efficiency deterioration is however generally much more
506 significant. In the particularly sensitive regions (low load /high engine speed and high load /low engine speed), the net
507 indicated efficiency is between 3 pp – 4 pp lower than the baseline diesel operation. In other regions of the map, where
508 TPO showed increased performance, the net indicated efficiency for Bio₂₀DF₈₀ is nearly the same as for the diesel
509 reference.

510 Analysis of Figs. 14 and 15 suggests that the 5% TPO addition facilitates good combustion at a wide range of
511 operating points of the engine and for a wide range of biocomponent shares (up to 50% by volume). Without the TPO
512 addition, only a 20% admixture of RME to diesel causes significant deterioration of indicated efficiency. Note that the
513 pumping losses were found to be independent of the kind of fuel used. Thus, the deterioration comes from incomplete
514 combustion and worsened combustion phasing of the Bio₂₀DF₈₀ sample compared to both the diesel reference and TPO
515 samples. Running the engine on Bio₂₀-DF₈₀ generally increased THC and CO emissions (refer to the following section
516 for details), but the combustion losses calculated on the basis of both emission factors did not exceed the value of 0.3%
517 for any of the operating points. Thus, the shifted combustion phasing is suspected to play a vital role in the indicated
518 efficiency changes between Bio₂₀-DF₈₀ and other tested fuels. More insight into the effect of different biofuels on

519 combustion phasing can be found in other works by the authors [17, 37, 38].

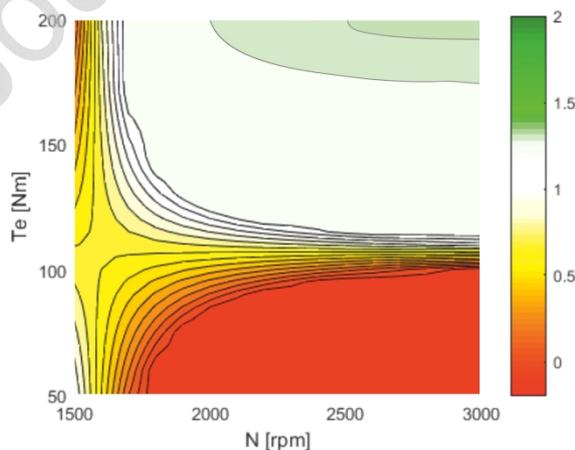
520 An interesting observation can be made by comparing Fig. 14, which shows the indicated efficiency for TPO₃
 521 (in relation to diesel), with the corresponding BTE values in Figs. 12 and 13. Note that the difference between the net
 522 indicated efficiency and BTE can be interpreted as total friction losses due to both mechanical and parasitic resistance.
 523 The generally lower values of BTE achieved for the TPO samples at all operating points (Figs. 12 and 13), despite their
 524 better results of indicated efficiency (at selected operating points), suggest that friction significantly increased during
 525 TPO₃ operation compared to the diesel reference. This is explicitly shown in Fig. 16.
 526



527 **Fig. 16.** Delta between friction losses of the engine operated on TPO₃ and DF. The negative values indicate lower friction for
 528 DF.
 529

530 Detailed analysis of Fig. 16 reveals a nearly 2 pp increase in friction for the TPO₃ sample at high engine loads. At
 531 low engine loads the friction increase can hardly be observed. This can be attributed to increased parasitic losses in the
 532 fuel injection equipment caused by higher viscosity of the TPO fuels compared with DF (see Table 2 for reference). The
 533 friction loss for highly viscous fuels is compounded by their lower heating value (Table 2). With this, more fuel needs
 534 to be transferred through the fuel system to attain the same power output. Finally, the TPO samples with the highest
 535 biocomponent share exhibit the largest increase in friction. For the same reasons, the increase in friction losses for the
 536 ternary mixtures maximizes at high loads and high rpm.

537 For the Bio₂₀-DF₈₀ sample the increase in friction is just slightly above the level of significance at higher engine
 538 loads (taking into account the accuracy of BTE calculation), which correlates with the fact that its viscosity, density and
 539 heating values deviate less from the diesel reference (Table 2). Details of this are presented in Fig. 17 for reference.



540 **Fig. 17.** Delta between friction losses of the engine operated on Bio₂₀-DF₈₀ and DF. The negative values indicate lower
 541 friction for DF.
 542

543 The slightly negative values in Fig. 17 at partial loads indicating lower friction for DF can be interpreted as
 544 insignificant. For instance, for DF at 50 Nm and 3000 rpm, the friction amounts to around 18% of total energy. Thus,

545 the relative friction difference between Bio₂₀-DF₈₀ and DF at this particular operating point is lower than 1%. In
546 contrast, the almost 2 pp difference in friction observed in Fig. 16 at high loads accounts for more than a 22% relative
547 increase in friction losses for TPO₃ operation over baseline diesel.

548 The observations made here are somewhat consistent with the results obtained in the earlier work by Koc and
549 Abdullah [33], who examined a ternary blend of 5% bio-diesel, 5% TPO and 90% DF on a legacy engine with
550 mechanically-driven injection equipment. The above authors noted that at lower engine speeds (from 1000 rpm to 2400
551 rpm), the engine operation on this ternary fuel mixture was characterized by lower BTE values compared to the
552 reference DF sample, while above 2400 rpm the trend was reversed [33]. In turn, the cited research revealed that the
553 blends with increased share of bio-diesel and TPO (10% each, respectively) resulted in significantly lower BTE values
554 than in the case of mineral fuel at higher engine speeds (above 2000 rpm). The observed tendency was explained by
555 higher viscosity and density of TPO blends, which – according to the authors – contributed to improper combustion.
556 However, the exact identification of engine losses was not provided in the above-mentioned work.

557 3.4 Exhaust emissions

558 Exhaust emissions indicators, except for opacity, were presented as concentrations on a volumetric basis. These
559 quantities were chosen because they can be better referred to in-cylinder concentrations and thermal parameters than
560 specific emission factors that are biased by thermal efficiency. The concentrations are thus presented as raw
561 measurement values averaged over the measurement window. The THC concentrations are expressed as C₁, as
562 displayed by Flame Ionization Detector.

563 3.4.1. Total unburned hydrocarbons

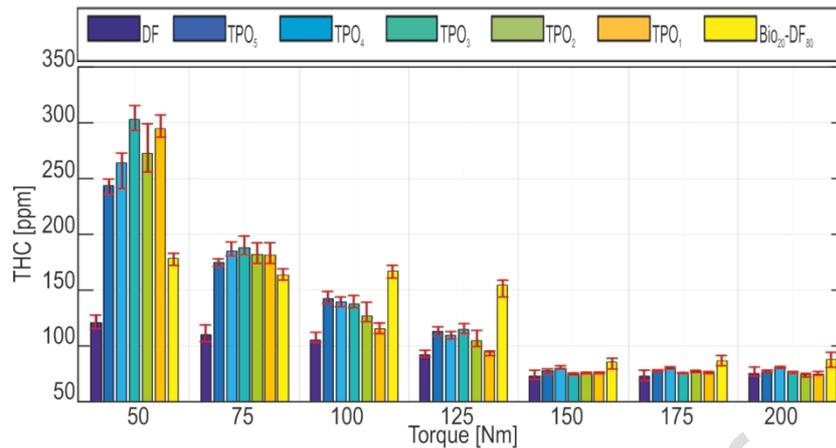
564 Emissions of unburned hydrocarbons are the direct result of incomplete combustion of fuels [34]. The reasons for
565 incomplete combustion and formation of unburned hydrocarbons are primarily related to global or local oxygen
566 deficiency and wall/crevice mixture interactions. However, due to the inhomogeneous nature of diesel combustion,
567 mixture formation, fuel vaporization, its composition and, finally, burn rate, should all be considered when clarifying
568 trends in emissions. The complexity of hydrocarbon emission trends for the tested fuels is demonstrated in Fig. 18 and
569 Fig. 19. Comparing the ternary fuel samples with the binary and DF samples, it was noted that significantly lower THC
570 concentrations were generated for the mineral fuel under the tested loads at both engine speeds. Furthermore, it was
571 found that the significantly higher THC emissions were generated at low-load regime for all tested samples, at both
572 engine speeds, which is consistent with the results obtained by Murugan et al. [21] and Bhaskar et al. [47]. The above
573 authors explained that the higher THC emissions observed at low loads resulted from incomplete combustion, caused
574 by the production of locally over-lean mixtures during the longer ignition delay period. Moreover, the THC emission
575 for all analyzed samples gradually decreased between 50 and 150 Nm measurement points (at 1500 rpm), while above
576 150 Nm it remained at almost the same level.

577 It was also observed that at the first two measurement points (50 Nm and 75 Nm) significantly higher amounts of
578 total unburned hydrocarbons were formed by combustion of the ternary blends. This probably resulted from a longer
579 time needed for fuel vaporization and preparation of the combustible mixture, because crude rapeseed oil is mainly
580 composed of fatty acids that consist of long hydrocarbon chains. As a result, the combustion rates of raw oil are too low
581 to provide complete combustion before it is terminated by the dropping temperature during the expansion stroke [48].
582 The presence of unsaturated hydrocarbons in a distilled fraction of TPO further leads to reduction of combustion rates.
583 Murugan et al. [49] and Kidoguchi et al. [50] pointed out that TPO hydrocarbon chains can turn out to be unbreakable
584 under the conditions of typical diesel combustion. Furthermore, the increased emissions of THC for ternary blends
585 could be related to the creation of an overly premixed (and thus too lean) mixture. This effect was quantified by
586 Kidoguchi et al. [50], who demonstrated a significant increase in THC concentrations at low load for low cetane-
587 number fuels as a result of increased mixing time.

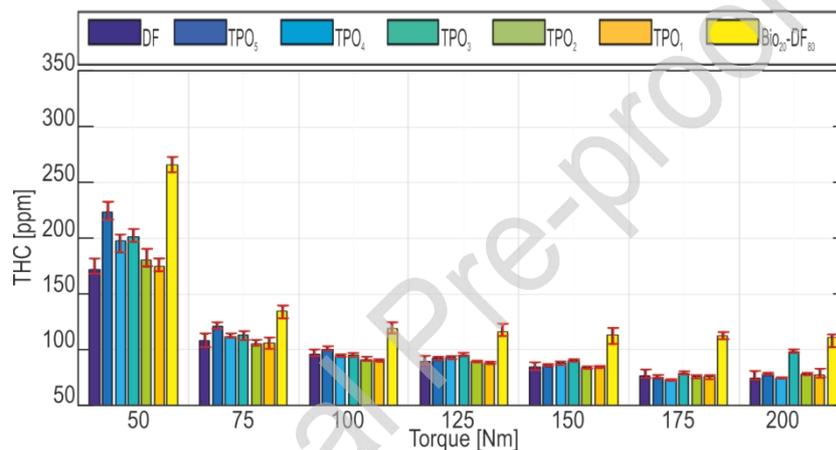
588 The above reasoning is supported by the trend in the relative THC emissions shown in Fig. 18. The differences
589 diminish with increasing engine load because the increase in fuel concentration itself reduces the auto-ignition delay,
590 and, additionally, higher combustion temperatures reduce the time of fuel vaporization and thus accelerate the
591 combustion of mixing controlled phase.

592 Interestingly, the relative THC emissions for Bio₂₀-DF₈₀ change with engine load, as shown in Fig. 18. Namely, for
593 low load the emissions are substantially lower than for other blends, whereas for higher load the emissions are relatively

596 higher. This trend might be associated with wider spray propagation when the fuel contains a biodiesel component.
 597 Consequently, fuel hydrocarbons are concentrated near the combustion chamber walls, enhancing the side-wall effect.
 598 Additionally, gaseous fuel penetrates into the crevice volume and is left in an unburned form [51].



599 **Fig. 18.** THC emissions for tested fuels; N = 1500 rpm.
 600



601 **Fig. 19.** THC emissions for tested fuels; N = 3000 rpm.
 602
 603

604 Comparing THC emissions for the two investigated engine speeds, one cannot neglect the different injection
 605 strategies. At 1500 rpm, split fuel-injection was realized, whereas at 3000 rpm fuel was injected in a single dose. At the
 606 higher speed, the highest THC emissions were achieved for the binary blend independently of engine load, as shown in
 607 Fig. 19. This supports the thesis that increased THC emissions for the binary blend result from deeper spray propagation
 608 towards the combustion chamber walls. This thesis suggests that in a single dose more fuel is injected at a time, so the
 609 propagation distance increases and THC emissions are substantially increased, even for low loads. Under these
 610 conditions, however, the emissions produced by ternary blends are comparable to those of diesel fuel.

611 Though THCs are increased for the TPO samples, in terms of absolute values they are still very low (characteristic
 612 for diffusion flame combustion). Note however that aside from the quantitative effect, the composition of HCs may
 613 significantly differ for TPO. Here especially the PAHs might be an issue: some of them have been identified as
 614 carcinogenic and mutagenic [52]. Williams et al. [16] provided detailed composition of TPO showing total PAH content
 615 of 9.2% where the main constituents were naphthalene, fluorene and phenanthrene and their alkylated derivatives.
 616 Although the PAH concentration was approximately three times higher than with typical DF, it did not exceed the limit
 617 set by the EN590 standard, which is 11% on a mass basis. Moreover, composition of TPO depends on feedstock and the
 618 pyrolysis process conditions. For example, Frigo et al. [22] reported PAH content of 7.8%. Finally, it should be noted
 619 that in the current study only 5% admixture of TPO was used, while high fractions of bio-oil did not contain any PAHs.
 620

621 3.4.2. Nitrogen oxides

622
 623 The main factors determining the level of NO_x formation in a CI engine are the temperature of combustion and the
 624 availability of oxygen [30, 53]. However, due to some nitrogen in TPO, the production of NO_x can be increased for that

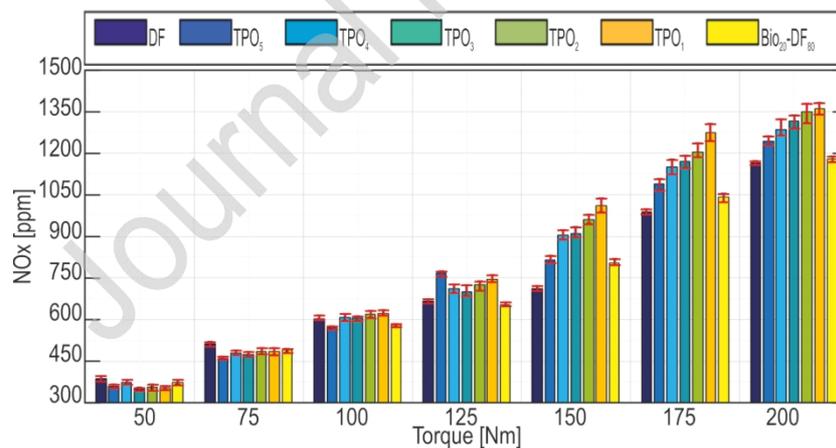
625 fuel [16]. Intensities of NO_x production, shown in Figs. 20 and 21, reveal a general trend that the higher the engine
 626 load, the higher the emissions of NO_x . This dependence is well-understood and was explained by Sharma and Murugan
 627 [30] and Tan et al. [53]. Namely, NO_x production increases due to the fact that with increasing fuelling rates, the
 628 temperature in the combustion chamber increases, creating favorable conditions for thermal NO_x formation [30].

629 A comparison of Figs. 20 and 21 reveals an interesting tradeoff. For low-load conditions (50 Nm), the NO_x
 630 concentrations are lower for 1500 rpm than for 3000 rpm. However, at high loads the relation is opposite. To explain
 631 this behavior, injection strategies should be taken into consideration. The split-injection strategy with fixed pilot
 632 injection fuel quantity provides a high fraction of premixed low-temperature combustion which hardly produces NO_x .
 633 However, split injection can lead to increased NO_x production at high loads because the combustion of pilot injection
 634 advances the combustion of the main fuel dose, which contributes to higher peak temperatures. These trends are
 635 consistent with those observed for peak pressure, shown in Figs. 10 and 11. In contrast, for the single fuel injection at
 636 high loads, the NO_x content is lower than for the split injection due to a high fuel concentration in the flame zone and a
 637 higher fraction of fuel burned by diffusion-controlled combustion.

638 Furthermore, it was observed that at lower loads (from 50 Nm to 100 Nm) at 1500 rpm, the composition of
 639 investigated blends did not significantly affected the level of NO_x emissions, as shown in Fig. 20. In turn, at higher load
 640 levels (above 100 Nm), the ternary blends generated higher amounts of nitrogen oxides, with a clear trend showing that
 641 the content of rapeseed oil enhances NO_x production. This effect can be attributed to two factors: (i) oxygen content in
 642 biofuel, and (ii) nitrogen content in TPO. The significant effect of the elementary composition of fuel on NO_x
 643 formation was quantified by Vihar et al. [54]. The fuel-bound nitrogen was identified as a precursor of increased NO_x
 644 emissions from TPO resulting from the fuel NO production mechanism. The above authors also stated that the
 645 contribution of fuel mechanism to total NO_x production increases with engine load due to decreasing dilution combined
 646 with lack of the excess air ratio effect. Additionally, Murugan et al. [21] found that the use of higher doses of TPO
 647 characterized by significant aromatics content might further lead to increased NO_x emissions of TPO blends.

648 Interestingly, for the single-injection case (3000 rpm), there is no clear trend of NO_x emissions versus tested fuel
 649 blends, as shown in Fig. 21. It could be attributed to longer ignition delay and more rapid start of combustion rather
 650 than to the split-injection case, as one can observe by comparing Figs. 5 and 6. Such conditions favor thermal NO_x
 651 formation rather than fuel mechanism. As a result, the production of NO_x was not affected by fuel composition.

652



653

654 **Fig. 20.** NO_x emissions for tested fuels; N = 1500 rpm.

655

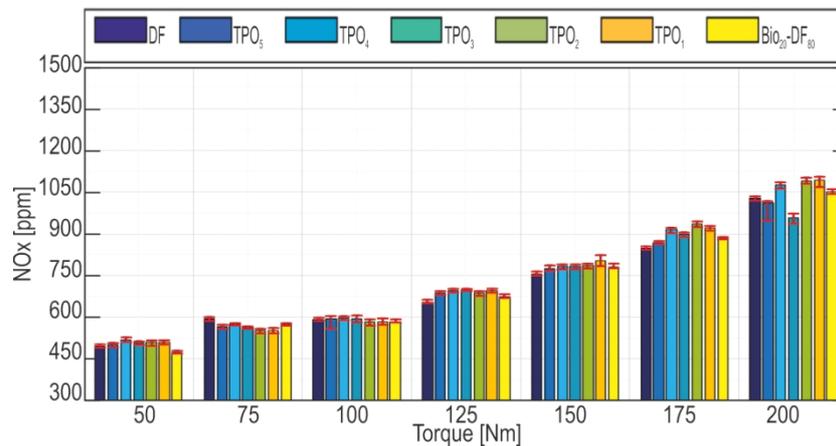


Fig. 21. NO_x emissions for tested fuels; N = 3000 rpm.

3.4.3. Carbon monoxide

An analysis of CO emissions at 1500 rpm demonstrated a different profile of gas formation in different load ranges, as shown in Figs. 22 and 23. For the lower investigated engine speed (Fig. 22), it can be observed that at lower engine loads (50-100 Nm), the ternary samples are characterized by higher CO emissions in comparison to the binary and DF samples. This trend resembles that observed for THC, shown in Fig. 18, and – similarly to the previous discussion – the increased CO emissions can be attributed to a longer mixture formation time, which results in the creation of lean premixed mixture areas [49, 50]. What is more, the blends with a higher DF share examined at 50 and 75 Nm measurement points generated higher emissions of CO, while at higher loads (100-125 Nm) the opposite tendency was observed. In contrast, at both 125 Nm and 200 Nm operating points, higher CO emission was observed for the DF sample and binary blend. Between the aforementioned engine-load points, the concentrations for all tested fuels were nearly the same. Moreover, it should be noted that the emissions were generally lower than for other engine loads. This non-monotonic trend in CO emissions results from a balance between the combustion temperature and the local excess air ratio. In other words, at low-load regime, the combustion temperature is low and CO oxidation can be terminated. In contrast, at high loads the temperature is high enough, but oxygen deficiency can occur locally.

The above reasoning is also supported by the results for 3000 rpm. In the latter case, however, the minimum CO emissions are observed for the 100 Nm load. This is plausible because in contrast to the 1500 rpm operation, the injection is single in this case, and thus fuel is more concentrated in the combustion chamber.

In general, for higher loads at 1500 rpm and for the entire load range at 3000 rpm, the ternary samples show a noticeable trend that as the fuel's RO content increases, the lower the CO emissions become. It should be noted that among the tested fuel components, RO contain the most oxygen. These observations are in agreement with the findings of Xiao et al. [55], who proved that fuel blends with higher oxygen content produce lower CO emissions. However, it should be noted that in low-load regime and at 1500 rpm the opposite tendency was observed. The discrepancy between the results for the two engine speeds can result from different mixture formation strategies. It could be concluded that the oxygen content in fuel reduces CO concentration if it originates from high fuel concentrations and locally rich mixture. For a more-premixed mixture (less fuel and split injection), the effect is opposite, because the oxygen content in fuel makes the mixture leaner and thus reduces its combustion temperature.

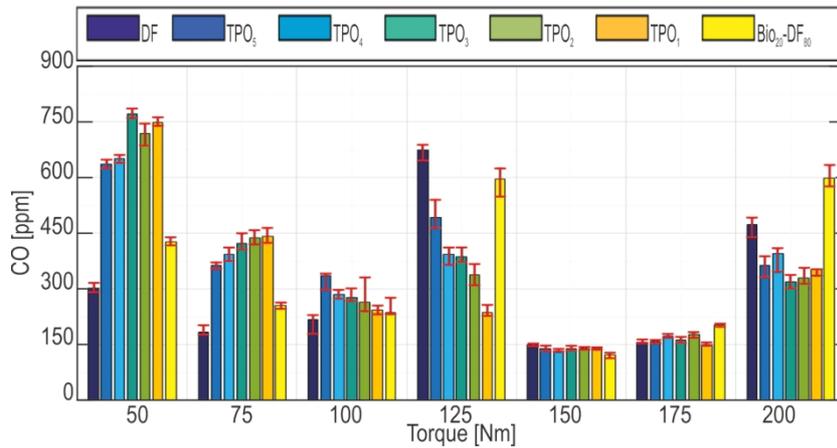


Fig. 22. CO emission for tested fuels; N = 1500 rpm.

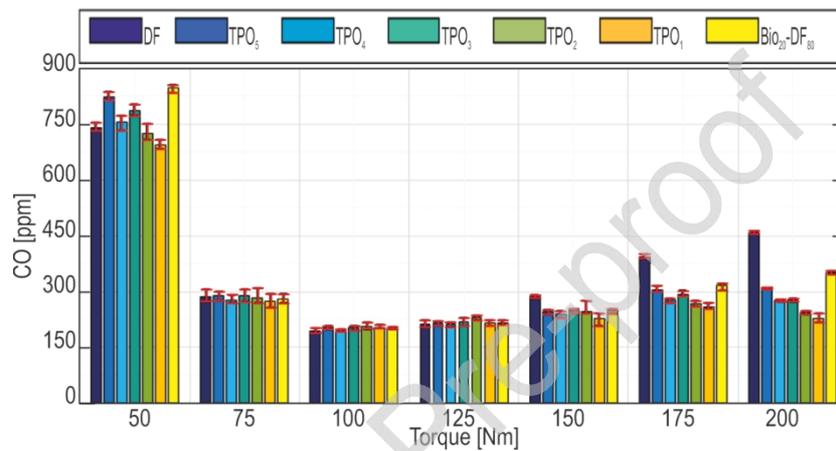
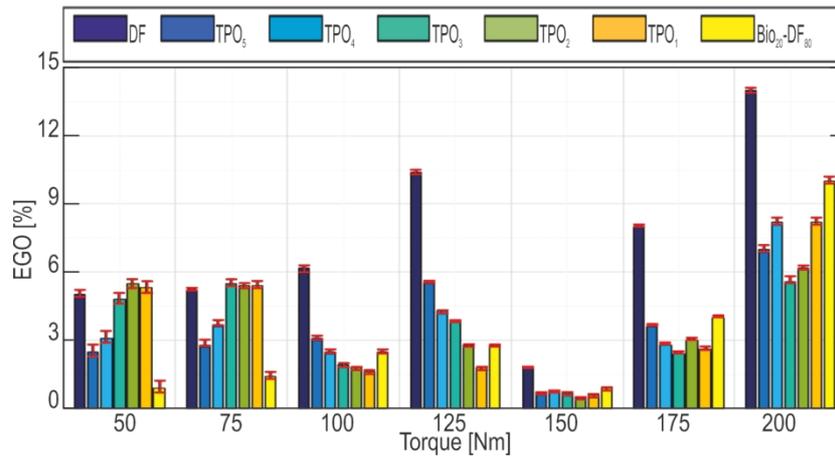


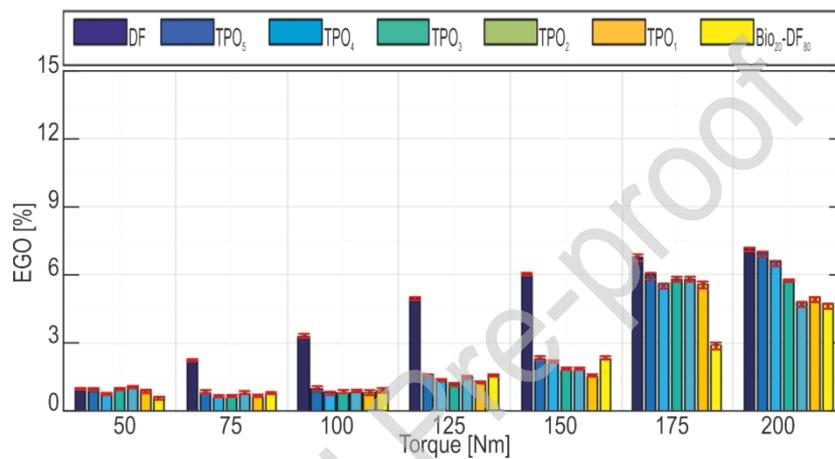
Fig. 23. CO emission for tested fuels; N = 3000 rpm.

3.4.4. Exhaust gas opacity

The investigations showed that in most cases, the soot produced from diesel fuel combustion, represented in the results by EGO, is higher than that from the blends containing biofuel components, as shown in Figs. 24 and 25. These results correlate with the findings of Corosini et al. [48], who found that less soot is produced in the combustion of biofuels due to oxygen content in the fuel. The exception was observed only at 50 and 75 Nm measurement points for 1500 rpm speed, where the EGO from DF was similar to the TPO₁-TPO₃ blends, as shown in Fig. 24. However, under these conditions the binary blend was characterized by a significantly lower EGO. Another exception can be noted at 150 Nm load point and 1500 rpm, where, generally, a significant reduction in EGO is observed for all tested samples. This result can be attributed to the change of injection strategy at this measurement point, as shown in Fig. 7, i.e. the advance of main fuel injection. A further increase in opacity despite the advanced injection is a result of increasing fuel concentration [31]. At the maximum load for 1500 rpm, the higher EGO was observed for the DF sample and binary blend, in contrast to other cases. As for the ternary blends, it was found that at 1500 rpm they generated a varied EGO at individual measurement points. At lower loads (50 and 75 Nm), the blends with higher rapeseed oil contents generated a higher EGO than the mixtures with lower contents of this component. In turn, at 100 and 125 Nm measurement points, the trend was opposite, whereas at higher loads no clear trend could be detected. In the case of engine tests conducted at 3000 rpm, it was observed that with increasing load (from 50 to 200 Nm), the EGO concentration gradually increased for all analyzed samples, as shown in Fig. 25. Moreover, at higher loads, for all blends except for Bio20-DF80, one can observe a trend that greater content of biofuel component leads to lower opacity.



713
714 **Fig. 24.** EGO for tested fuels; N = 1500 rpm.
715



716
717 **Fig. 25.** EGO for tested fuels; N = 3000 rpm.
718

719 Due to the broad scope of the present research, PM emissions through direct gravimetric measurements were not
720 considered here. For a conventional CI engine, however, due to the fact that HC emission is relatively low, EGO is
721 almost linearly correlated with PM concentrations [56]. To this, trend-wise observations are considered transferable and
722 the generally lower PM content is recognized for oxygenated fuels. Particular differences between subsequent biofuel
723 samples are generally not constant and both EGO and PM mass is influenced rather by the net effect of physical
724 properties of the fuel on combustion parameters. The differences in chemical composition of the fuel, including the
725 increased sulphur content of the TPO, do not translate towards distinguishable effect on EGO or PM mass. However,
726 more profound differences may occur in particulates size distribution when fuels of different feedstock are used [57,
727 58]. This issue might affect the feasibility of crude oils with TPO addition as drop-in fuels and should be addressed in
728 dedicated research.
729

730 3.5 Discussion and future outlook

731 Since the research scope of this work is broad and exploratory, it is not strictly aimed at providing insight into the
732 actual phenomena causing differences in efficiency and emissions between individual fuel samples. However, the
733 study's results do point towards some general observations that bridge the knowledge gap and indicate further research
734 directions.

- 735 1. When using highly viscous fuel components (as raw RO), parasitic losses in the fuel injection equipment play an
736 increasingly important role in the overall energy balance of the engine. This can contribute to as much as 2% loss at
737 high load operation for fuel samples with high shares of RO. To mitigate these losses, further research should be
738 conducted into an optimized fuel composition which takes into account the flashpoint-viscosity tradeoff.

- 739 2. The methyl ester-based biofuel, without TPO addition, exhibited significant deterioration in indicated efficiency,
 740 especially at high engine speeds and low loads. The addition of biocomponent alone is known to cause a significant
 741 delay in auto-ignition and extended combustion duration. The samples with TPO showed considerable efficiency
 742 improvement over Bio₂₀-DF₈₀ despite higher shares of unrefined biocomponent. This indicates that in terms of
 743 efficiency, adding TPO to fuel produces benefits derived from the mixture's improved auto-ignition properties and
 744 burn rate.
- 745 3. The study demonstrated that the effects of ternary fuel composition on emissions are complex, with several
 746 contributing factors including spray characteristics, mixture and temperature distribution and the fuel's
 747 physicochemical properties. The relationships between fuel properties and emissions greatly depend on the mixture
 748 formation strategy that is used (single injection or split injection). Consequently, research should be continued by
 749 designing controlled experiments investigating the sensitivity of exhaust emissions to fuel-injection strategies under
 750 the same conditions.
- 751 4. The detailed speciation of THCs and PM size distribution should be further researched, as reported to be
 752 significantly different for TPO admixed fuels, compared to other alternatives. In particular, the presence of specific
 753 carcinogenic species (PAHs) can influence the feasibility of developed fuels and should be addressed. For TPO
 754 admixed fuels, this is foreseen in a dedicated endeavor and covered together with other relevant legislative emission
 755 components, like N₂O which can majorly affect the GHG footprint.
- 756 5. In the study we postulate that direct use of cold-pressed rapeseed oil as bio component admixed with distilled tyre
 757 pyrolytic oil could be an energy-efficient alternative to commonly considered methyl ester-based mixtures. Though
 758 in-depth analysis of this assumption was not performed at this stage, there are a number of convincing arguments to
 759 support it. Note, that the costs of FAME produced from conventional materials can be even 50% higher than fossil
 760 diesel (without taxes and additional costs) [59]. Furthermore, the market cost of edible-grade rapeseed oil is around
 761 20% lower than the cost of diesel, giving a solid advantage for the main fuel component considered in this study.
 762 Regarding TPO, although its production is energetically demanding, it is fully sustainable due to the off-pyrolytic
 763 gases [60]. A recent pilot project on technological and economic feasibility of a 40,000 t/y TPO pyrolysis plant
 764 reported the production costs 40% lower than diesel market prices [60]. Although these arguments demonstrate a
 765 clear economic advantage over FAME and mineral fuel, a full techno-economic feasibility study should be
 766 conducted. It should include feedstock availability, well-to-wheel economy and emission factors of the new fuels,
 767 comparing them with other feasible alternatives.
- 768 6. Finally, even a small addition of TPO caused the fuel's sulphur content to exceed the limit for automotive-grade
 769 fuels (10 mg/kg according to EN 590). Desulphurisation should be included in the TPO-based additive production to
 770 mitigate this issue. The above arguments on production costs suggest that there is sufficient room for further post-
 771 processing of the TPO, while maintaining its economic feasibility as a fuel component.

773 4. Conclusions

774
 775 This study investigated whether raw vegetable oil can be used as an inexpensive fuel biocomponent for modern
 776 diesel engines if a small fraction of distilled TPO is also used as an additive. Different mixtures of DF and RO with 5%
 777 addition of distilled TPO were subjected to engine tests. Note that fuel samples with TPO content above 5% or RO
 778 fractions lower than 30% did not satisfy the handling safety criterion for diesel engine fuels (flash point above 53 °C),
 779 and so were therefore excluded. Additionally, pure DF and DF with a 20% addition of rapeseed methyl ester (Bio₂₀-
 780 DF₈₀) were examined as reference fuels.

781 General conclusions regarding efficiency and emissions confirm the main thesis of this work, showing that TPO
 782 addition allows the use of fuels with large shares of unrefined biocomponent. These conclusions can be formulated as
 783 follows:

- 784 1. On the factory engine-maps the use of fuel samples with up to 55% of RO and 5% of TPO led to only minor
 785 deterioration of brake thermal efficiency when compared to that obtained for DF. The maximum deterioration did
 786 not exceed 1.2%, with no significant trends over the operating regime nor for the fuel mixtures containing TPO. In
 787 contrast, the reference biofuel Bio₂₀-DF₈₀, without TPO but with a transesterified biocomponent, showed efficiency
 788 deterioration of above 2% under the same conditions.
- 789 2. No abnormal combustion or misfire was observed for any of the tested fuels. The coefficient of variation in IMEP
 790 did not exceed the commonly accepted limit of 5% at any operating point. A further increase in the RO share above

791 50% was mainly limited by significantly reduced heating value of the fuel, preventing achievement of full-load
 792 characteristics due to fuel injection equipment limitations.

- 793 3. THC and CO exhaust concentrations significantly increased for the ternary mixtures compared to DF, but only at
 794 low load and split fuel injection at 1500 rpm (as much as 3-fold increase at near-idle load). Note that the reference
 795 Bio₂₀-DF₈₀ fuel suffered from the same drawback, and also performed worse in terms of combustion efficiency in all
 796 operating conditions.
- 797 4. Elevated NO_x emission is an inherent drawback of using oxygenated fuels. The tested fuels, however, exhibited
 798 increased NO_x concentrations (above the level of significance) only at high load and low engine-speed regime. This
 799 region of the operating map is characterized by high combustion temperatures and long residence times, and thus is
 800 particularly challenging for mitigation of engine-out emissions. Under such conditions, the increase in NO_x
 801 emissions almost linearly corresponded to the increased biocomponent share in the fuel. The maximum increase of
 802 25% over the baseline diesel NO_x emissions was noted for the ternary fuel sample containing 55% of RO.

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Highlights:

1. Tire pyrolytic oil and its tailor-made blends with diesel and rapeseed oil examined
2. Best ternary fuel samples subjected to test-bench runs on a modern CRDI engine
3. Efficiency and emission factors determined and assessed w.r.t. measurement accuracy
4. Slight deterioration of efficiency and emission w.r.t. diesel baseline
5. Superior performance w.r.t. RME-based biofuels

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