1   **Analysis of cold-start NO$_2$ and NOx emissions, and the NO$_2$/NOx ratio in a diesel engine**

2   **powered with different diesel-biodiesel blends**

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25   **Abstract**

26   In the transportation sector, the share of biofuels such as biodiesel is increasing and it is

27   known that such fuels significantly affect NOx emissions. In addition to NOx emission from

28   diesel engines, which is a significant challenge to vehicle manufacturers in the most recent

29   emissions regulation (Euro 6.2), this study investigates NO_2 which is a toxic emission that is

30   currently unregulated but is a focus to be regulated in the next regulation (Euro 7). This

31   manuscript studies how the increasing share of biofuels affects the NO_2, NOx, and NO_2/NOx

32   ratio during cold-start (in which the after-treatment systems are not well-effective and mostly

33   happens in urban areas). Using a turbocharged cummins diesel engine (with common-rail

34   system) fueled with diesel and biofuel derived from coconut (10 and 20% blending ratio), this

35   study divides the engine warm-up period into 7 stages and investigates official cold- and hot-

36   operation periods in addition to some intermediate stages that are not defined as cold in the

37   regulation and also cannot be considered as hot-operation. Engine coolant, lubricating oil and

38   exhaust temperatures, injection timing, cylinder pressure, and rate of heat release data were

39   used to explain the observed trends. Results showed that cold-operation NOx, NO_2, and

40   NO_2/NOx ratio were 31-60%, 1.14-2.42 times, and 3-8% higher than the hot-operation,

41   respectively. In most stages, NO_2 and the NO_2/NOx ratio with diesel had the lowest value and

42   they increased with an increase of biofuel in the blend. An injection strategy change

43   significantly shifted the in-cylinder pressure and heat release diagrams, aligned with the

44   sudden NOx drop during the engine warm-up. The adverse effect of cold-operation on NOx

45   emissions increased with increasing biofuel share.

46   Keywords: NOx emissions; NO_2 emissions; NO_2/NOx ratio; biodiesel; cold-start; engine warm-

47   up.

1. Introduction

The transportation sector contributes significantly to the pollution in cities through the exhaust emissions of vehicles, such as CO, CO_2, HC, NOx, PM, and PN. Exposure to such pollutants may lead to serious health problems [1, 2]. In order to mitigate exposure, there are incentives in place to restrict these harmful emissions through government regulations [3]. For example, in Europe, the emissions regulations progression from Euro 1 to Euro 6.2 has successfully reduced emissions from the transport section by systematically reducing the allowable thresholds on each emission [3]. Another regulated emissions control measure is the use of alternative fuels, which can mitigate the adverse effect of fossil fuels and also stimulate the economy. For example, the European Union targeted a 5.75% biofuel share in fuel by 2010 (EC Directive 2003/30). This continued in Directive 2009/28/EC to increase the share of biofuel to 10% in 2020. The result of these actions, in terms of vehicle fuels, was a move from using neat diesel/petrol to gradually increasing the share of biofuel, today blends of 10% biofuel with diesel/petrol are currently common [3].

In addition to regulations and legislation aimed at promoting alternative fuels and fossil fuels substitution, there is a need to divert energy subsidies toward biofuels as well. For instance, a study by Khatibi et al. [4] showed that fossil energy price subsidy encourages overconsumption and elevates air pollution while on the contrary, a 100% energy price hike in the investigated geographical region, could lead to a 62.9-million-ton reduction in air pollutants.

Using biofuel in combustion engines affects exhaust emissions [5, 6]. It has been frequently reported that PM emission decreases significantly with biofuels [7, 8]. This is because of the fuel oxygen content in biofuels [9, 10]. On the other hand, the fuel oxygen content is also a

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71 reason for higher NOx with biofuels, a significant downside of these alternative fuels

72 frequently reported in the literature [11-13]. The role of biofuels such as biodiesel in NOx

73 variations is controversial. A large number of studies claim increases in NOx emissions owing

74 to the oxygen content of biodiesel but there are also a significant number of studies claiming

75 otherwise [14-16].

76 Between vehicle emissions, NOx emissions are of significant importance due to their adverse

77 effects on health and the environment [17, 18]. The term NOx is representative of several

78 nitrogen compounds but is predominately comprised of nitrogen oxide (NO) and nitrogen

79 dioxide (NO_2). Typically, NO is a product of the combustion process which forms within the

80 combustion chamber; while, NO_2 can form in several locations in addition to in-cylinder

81 combustion where it forms from the existing NO via a conversion reaction [19]. However, the

82 different NO_2 formation pathways are an active area of research.

83 NO_2 is of importance not only because it can cause adverse health effects, particularly on the

84 respiratory system [20], but also owing to how reacts in the atmosphere to form ozone and

85 acid rain [21]. European Environmental Agency (EEA Report No 12/2018 Air quality in Europe)

86 reported that a high NO_2 ratio in the exhaust emissions can impact the urban atmospheric

87 chemistry, therefore the air quality. This report stated that the concentrations of ground-level

88 ozone (O3) had an increase following the increase in diesel vehicles' NO_2 emissions. NO_2 is

89 currently unregulated but there is a focus to be regulated in the upcoming emissions

90 regulation (Euro 7).

91 The ratio of NO_2 in NOx plays an important role in modern vehicle after-treatment systems

92 such as SCR-catalyst systems (SCR stands for selective catalytic reduction). SCR systems rely

93 on a catalytic reaction with ammonia, the oxygen demand and fast reactions which are highly

94 dependant on the proportion of NO_2 in NOx, otherwise known as the NO_2/NOx ratio [19, 22].

95 There are various strategies proposed in the literature to reduce NOx emissions such as using

96 different additives [23, 24]. However, after-treatment systems are commonplace in the

97 mitigation of NOx emissions [25, 26]. Praveena and Martin [27] reviewed different after-

98 treatment techniques of NOx emissions reduction in CI engines. For example, they showed

99 that a urea SCR can reduce NOx by 98-99% with a warmed-up engine. They also studied the

100 effect of exhaust temperature on NOx control techniques, reporting that the performance of

101 after-treatment systems depends on the engine operating condition, as well as the state. A

102 study by Mera et al. [28] used a modern SUV diesel vehicle equipped with SCR and reported

103 that during cold-start, NOx emissions were 2.7 times higher than the Euro 6 NOx emission

104 limits, while with the warmed-up engine, cold-start emissions decreased by 92%. During cold-

105 start operation, after-treatment systems are known to be not well-effective and emissions

106 are largely untreated within this period. Car manufacturers can use different injection

107 strategies to reduce NOx emissions during this period, which will be shown in this study;

108 however, the NOx reduction is not as significant as when using SCRs.

109 During cold-operation, the temperatures of the engine block and components are not

110 optimal, and the cold engine lubricating oil also has a subsequent high viscosity [29, 30]. These

111 factors lead to higher friction losses, therefore more fuel is needed to maintain the output

112 power. It has been frequently reported that cold-operation leads to higher fuel consumption

113 [31, 32] and lower engine power [33, 34]. Subsequently, cold-operation leads to higher

114 exhaust emission [35, 36].

115   It is known that the engine is cold when it is turned on after being parked for some hours over

116   the night or during the day when the driver is in the office. That is the case for many vehicles

117   in cities and cold-start operation is an inevitable part of their daily norm [37].

118   New vehicles need to be equipped with after-treatment technologies in order to comply with

119   the type approval tests and receive the emissions certification. Given that a significantly high

120   portion of harmful emissions can be removed by after-treatment systems, the cold-start

121   period, within which the after-treatment systems are not working, contributes heavily to the

122   total emissions. This, and the fact that cold-start usually takes place in urban areas (harmful

123   to human health), and the increasing share of biofuels in the market all highlight the

124   importance of understanding cold-operation with biofuels. Given that a relatively large

125   portion of short trips occur when engines are cold, emissions from cold-start are of

126   importance for urban driving conditions [38]. This is particularly significant when it comes to

127   NO_2 and NOx emissions with biofuels during cold-operation, as there are not many

128   fundamental studies on NOx (and no study on NO_2) during engine warm-up with biofuels.

129   Also, most such studies are limited to the defined cold-operation period as most regulations

130   (e.g. EU Directive 2012/46/EU) define the warm-up period from engine start (at ambient

131   temperature after a proper engine-off time) either for the first 5 min of operation or the

132   period in which the engine coolant temperature increases from ambient temperature to 70°C.

133   Previous studies from our research group have shown that engine performance and emissions

134   outside this narrowly defined boundary are still significantly impacted by sub-optimal engine

135   temperature [39, 40].

136   Many papers have been published on cold-start emissions from a diesel engine. Within these

137   papers, a small portion evaluated NO_2 and the NO_2/NOx ratio during cold-start in a diesel

138   engine. And from these papers, only a few exist on the topics of NO_2 and the NO_2/NOx ratio

139   during cold-start in a diesel engine using alternative fuels. For example, Lapuerta et al. [41]

140   evaluated the NO_2/NOx ratio in addition to different exhaust emissions during a drive cycle

141   (including a cold-start section) using a glycerol-derived advanced biofuel. Another study

142   evaluated cold-start idle emissions (including NO_2) in a diesel engine using ethanol and diethyl

143   ether blends [42]. Using hydrogenated vegetable oil and biodiesel, Pechout et al. [43]

144   reported different emissions including NO_2 during the cold-start section of different driving

145   cycles. There are also few more articles in this field reporting NO_2 and the NO_2/NOx ratio

146   emissions during cold-start engine operation using alternative fuels [44-46]. However, after

147   an extensive literature review, we could find no literature which investigates NO_2 and the

148   NO_2/NOx ratio with alternative fuels at different stages of engine warm-up including cold-

149   start and also phases outside the officially defined cold-start boundary (EU Directive

150   2012/46/EU) which cannot be considered as hot-start either. In engine calibration, after-

151   treatment systems and injection strategies are mostly based on the regulated cold-start

152   period. However, this study shows that the period in which engine emissions are negatively

153   affected is significantly longer when compared to the official cold-start boundary. This study

154   intends to investigate the effect of fuel properties and engine temperature at different stages

155   of engine warm-up on NOx, NO_2, and the NO_2/NOx ratio.

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157   **2. Methodology**

158   Given that this study aims to investigate the effect of engine temperature and fuel properties

159   on NOx, NO_2 and the NO_2/NOx ratio at different stages of the engine warm-up period, it was

160   opted to use an engine with no after-treatment systems (e.g. EGR, SCR, DPF) so that the

161 emissions are not dependent on such devices (type and performance) to better analyse the

162 actual engine and combustion dependent emissions [47, 48]. This experimental investigation

163 used a turbocharged Cummins ISBe220 engine. The highest power and torque of this engine

164 are 162 kW (at 2000 rpm) and 820 Nm (at 1500 rpm), respectively. Table 1 shows the

165 specifications of the engine.

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167 Table 1 Specifications of the engine used in this study

Model	Cummins ISBe220 31
Aspiration	Turbocharged & Aftercooled
Fuel injection	High-pressure common-rail
Capacity	5.9 L
Compression ratio	17.3:1
Cylinders	6 in-line
Number of valve per cylinder	4
Maximum torque	820 Nm @ 1500 rpm
Maximum power	162 kW @ 2500 rpm
Bore × stroke	102 × 120 (mm × mm)
CPL	2925
Automotive Engine Data Sheet	FR91210
Certification	ECE R24.03, 2001/27/EC (88/77/EEC)
Dynamometer	Hyraulic (Electornically-controlled)

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169 Figure 1 illustrates the test setup. Engine, emissions and dynamometer data were collected

170 from the dynamometer control system. For the emissions, a fraction of the exhaust gas from

171 the exhaust manifold was directed to a gas analyser via a copper tube fitted with a HEPA filter

172 and water trap which were placed in the sampling line as per the recommendation of the

173 analysers' manufacturer. It was necessary to use a filter in front of the gas meter, as without

174 it, the instrument would become contaminated in a one single measurement. The gas

175 adsorption and pressure loss of these filters are negligible given that they are designed to only

176 remove the moisture and particulate matter. Parker miniature coalescing HEPA filters (02F

177 series) were utilised in this study. These filters are highly efficient in removing the liquid

178 aerosols and submicron particulate matter. An air-water separator model P010A was used in

179 the sampling line to remove moisture. A water trap was used instead of a dryer as dryers are

180 mostly effective in a narrow window of flow rates and also losses are significant for dryers. In

181 general, dryers are not suitable for raw exhaust because of the very high temperature of the

182 raw exhaust, and also dryers would get dirty after a short sample making it difficult to do

183 continuous measurements [49].

184 NOx, NO_2 and NO were measured with a CAI-600 CLD NO/NOx analyser. A Kistler type 2614

185 crank angle sensor and a Kistler 6053CC60 pressure transducer were connected to a DT9832

186 A-to-D convertor to collect the in-cylinder data (crank angle, pressure and injection signal).

187 To determine the fuel injection timing an excitation offset was applied to the recorded

188 injector signal [50]. Refs. [51, 52] contains more specific information about the in-cylinder

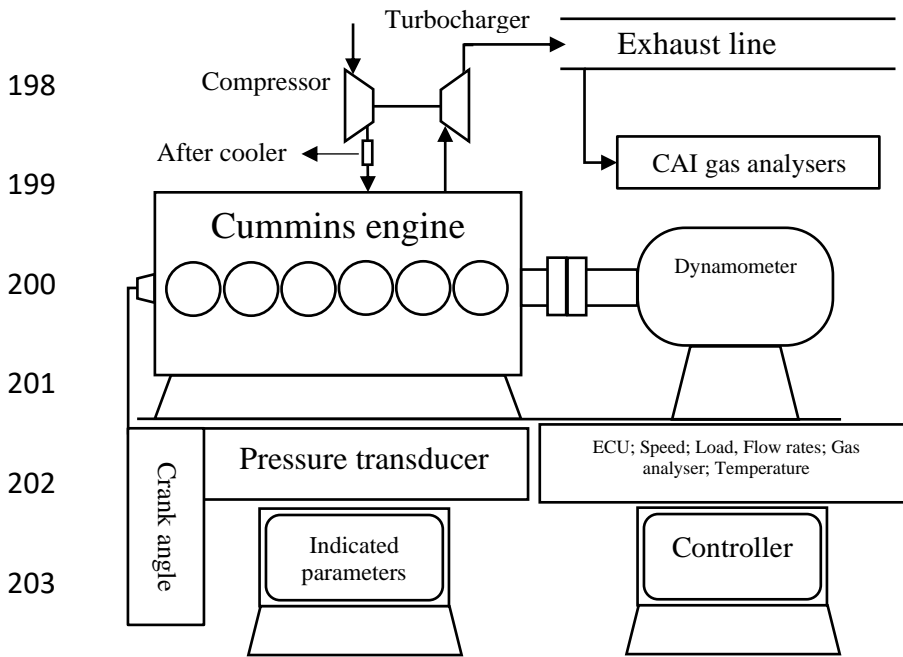189 data collection facility.

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205 Figure 1 Test setup_schematic diagram of the experimental facility

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207 The tested fuels in this study were selected in such a way that they can cover past, current,

208 and future biofuel blending ratios likely to be on the market. Therefore, this study used diesel

209 (denoted as B00), a blend of 10% (by vol.) biofuel with diesel (denoted as B10) and a blend of

210 20% (by vol.) biofuel with diesel (denoted as B20). The biofuels were derived from coconut

211 oil. In terms of fuel properties, even a low blending ratio had a significant impact on the fuel

212 properties. For example, the density of the tested diesel (B00) in this study was 0.84 kg/m^3;

213 the density of B10 and B20 were 0.848 and 0.855 g/cc, respectively. The lower heating value

214 of B00 was 41.77 MJ/kg for B10 and B20 it was 41.17 and 40.58 MJ/kg, respectively. While

215 the changes in fuel properties were small, the literature reported that even these small

216 changes can notably affect engine performance and emissions [53-55]. The lower calorific

217 value and higher density of biofuels have negative impacts on engine power and increase fuel

218   consumption [56]. A critical fuel property that makes biofuel different is the fuel oxygen

219   content—diesel has no oxygen content. It has been frequently reported that this fuel property

220   is the reason for decreased PM [57, 58].

221   In terms of the engine operating conditions (load and speed) during cold-start tests, most

222   studies in the literature used a driving cycle (such as NEDC or WLTP) analysing the cold-start

223   section of the cycle as compared to the rest of the cycle. These driving cycles consist of abrupt

224   load and speed changes [59, 60]. NOx emissions are affected by different factors such as

225   engine load, speed, and injection parameters, this research aims to investigate the effect of

226   transient engine temperature and fuel properties during cold-start. In order to minimise the

227   number of variables, and therefore facilitate a fundamental investigation on the impact of the

228   engine state and fuel properties, this study used a constant speed (1500 rpm) and load (25%).

229   The experiments were conducted according to the regulation for cold-start test

230   preconditioning (EU Directive 2012/46/EU) which requires 12 hours of natural soaking at

231   ambient temperature (or 6 hours forced cool) before the engine starts. Before each test, the

232   engine lubricating oil and coolant temperatures were checked to make sure they were the

233   same as the ambient temperature in the engine lab (which was equipped with a ventilation

234   system). For each cold-start experiment, the engine ran for at least 30 min at a constant speed

235   (1500 rpm) under a quarter load. The collected data were classified into different categories,

236   as described below. For more information about the test repeatability, error analysis,

237   equipment accuracy and measurement uncertainty, please refer to Appendix.

238   In diesel engines, the formation of NOx depends on various parameters such as engine load,

239   speed, injection parameters, fuel properties, and after-treatment systems. Within the cold-

240   operation period, the after-treatment systems are not very effective, and the engine

241   temperature and fuel properties are the driving factors in NOx formation. Figure 2 shows

242   temperature change in the engine coolant and lubricating oil as the engine warmed up using

243   data from various temperature sensors collected with the engine control unit (ECU)—through

244   the controller area network (CAN) via the SAE J1939 standard.

245   The EU Directive 2012/46/EU regulation defines the cold-operation period from the engine

246   start for either for the first 5 min or until the temperature of coolant increases from ambient

247   temperature to 70°C. It can be seen in Figure 2 that after the defined cold-operation period,

248   the coolant and lubricating oil temperatures are still increasing, indicative that the engine

249   temperature is still not optimal. The lag between lubricating oil temperature and coolant

250   temperature during warm-up shows that even when the coolant temperature was optimal,

251   the engine temperature was not optimal because the lubricating oil temperature is still

252   increasing. There are some studies in the literature showing the effect of this lag and the sub-

253   optimal temperature outside the defined cold-operation boundary on engine performance

254   and emissions [39, 40]. Figure 2 also shows the start of injection data which is the time at

255   which the fuel injection into the combustion chamber begins. This parameter is typically

256   expressed in the crank angle domain. It can be seen in the figure that the injection strategy

257   of the tested engine, which is commanded by the ECU, changes when the engine coolant

258   temperature reaches 65°C by retarding the start of injection from 353 to 361 (crank angle

259   degree). Given that injection parameters significantly affect NOx emissions [26, 61], the

260   transition period also needs to be taken into consideration.

261   As discussed, and shown in Figure 2, during engine warm-up, there are several stages with

262   combinations of variables and characteristics. Therefore, to better analyse the influential

263   parameters, this study divides the warm-up period into several stages to minimise the

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264   number of variables in each stage. This is done by splitting the warm-up period into 7

265   consecutive stages (each two min).

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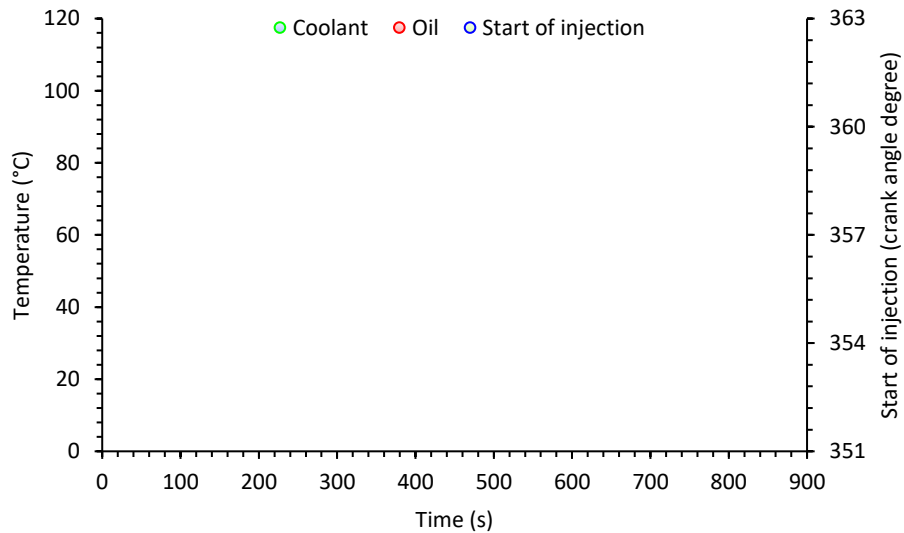
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268   Figure 2 Start of injection, engine lubricating oil temperature, and coolant temperature during
269   engine warm-up with B00

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271   **3. Results and Discussions**

272   This section studies NOx, NO_2, and the NO_2/NOx ratio during engine warm-up. As mentioned,

273   the engine warm-up period is split to 7 consecutive stages, each of two min. The difference

274   between stages shows the effect of engine temperature on different parameters. Exhaust

275   temperature can be representative of the combustion temperature showing how the engine

276   warms up. Apart from the engine load and speed, the combustion temperature depends on

277   different parameters such as temperatures of the engine block, cylinder wall, lubricating oil,

278   coolant, and fuel.

279   Figure 3 shows that the exhaust temperature increases as the engine warms up. This has been

280   reported in the literature [39, 62]. As can be seen, the exhaust temperature increased from

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281   Stage 1 to 5, and then stabilised during Stages 6 and 7. For example, with B20, the exhaust

282   temperature increased gradually from 290°C in Stage 1 to 350°C in Stage 5 and then stayed

283   at 358°C in Stages 6 and 7.

284   Stages 1 and 2 represent the cold-operation, these stages are within the initial 5 min of the

285   test and the temperature of engine coolant is lower than 70°C (Directive 2012/46/EU). Within

286   these two stages, the coolant temperature and lubricating oil temperature are sub-optimal.

287   Stages 3, 4 and 5 cannot be considered as cold-operation based on the definition in the

288   regulation (Directive 2012/46/EU). However, they cannot truly be considered as hot-

289   operation either as Figure 3. shows that within these stages the exhaust temperature is still

290   increasing.

291   Within Stages 3 and 4, the engine coolant and lubricating oil temperatures are still increasing.

292   Stage 5 analysis also showed that within this stage while the temperature of engine coolant

293   was optimal, the temperature of engine lubricant was still increasing. Therefore, results from

294   Stage 5 can show the effect of sub-optimal engine lubricating oil temperature [39, 40]. On the

295   other hand, within Stages 6 and 7, the temperatures of engine coolant and lubricating oil were

296   optimal; therefore, these two stages can represent hot-operation. The stability of the engine

297   temperature within Stage 6 and 7 can be seen in the exhaust temperature profile shown in

298   Figure 3, where the exhaust temperature did not change from Stage 6 to 7. It can be seen

299   that at all of the stages, B00 had the highest, and B20 had the lowest exhaust temperature

300   (except for Stage 1 in which B10 had a slightly lower value than B20, 288 and 289 °C). Also,

301   B10 had a less significant difference with B00 when compared to B20.

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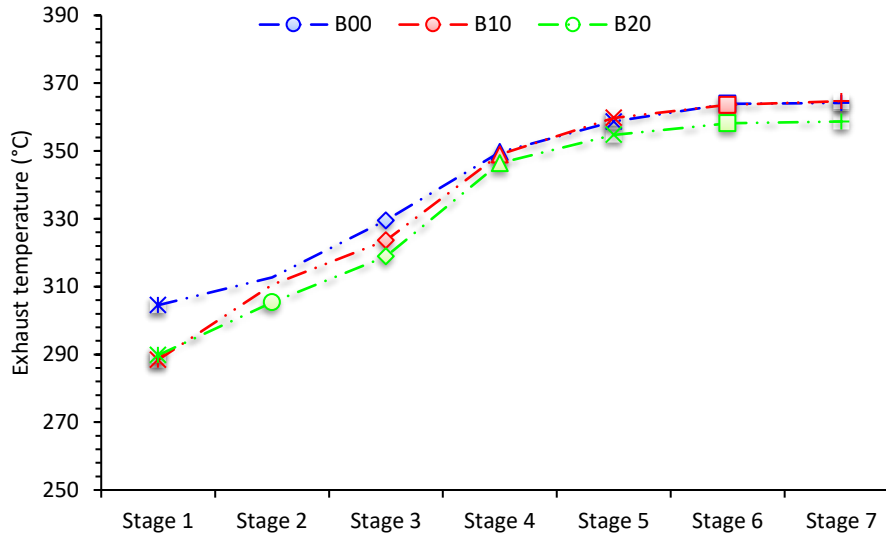
Figure 3 Exhaust temperature at different stages of engine warm-up with B00, B10 and B20

3.1 Nitrogen oxides

Figure 4 shows how NOx emissions change as the engine warms up. It can be seen that NOx emissions during cold-operation are significantly higher (31-60%) than during hot-operation. The higher NOx emissions during cold-start when compared to hot-start was reported frequently in the literature [63, 64]. It can also be seen that initially as the engine warmed up, NOx increased gradually, then dropped sharply, and finally stabilised at a low level, this trend was reported in the literature [31, 62]. For example, with B00, NOx was 30.9, 37.8, and 38% higher in Stages 1, 2 and 3, respectively, compared to Stage 7. In Stage 4, the NOx emissions dropped sharply by 48% to be 10% less than Stage 7. And finally, with a gradual increase in Stage 5, the NOx emissions stabilised in Stages 6 and 7. The graph also shows that the difference between cold-operation and hot-operation increases by increasing the share of biofuel in the fuel blend. For example, the NOx in Stage 1 with B00, B10 and B20 were 31%, 49%, and 60% higher than in Stage 7, respectively. This means that the adverse effect of cold-

319 operation on NOx emissions increases with biofuel share. This observation is similar to

320 another study in the literature [40].

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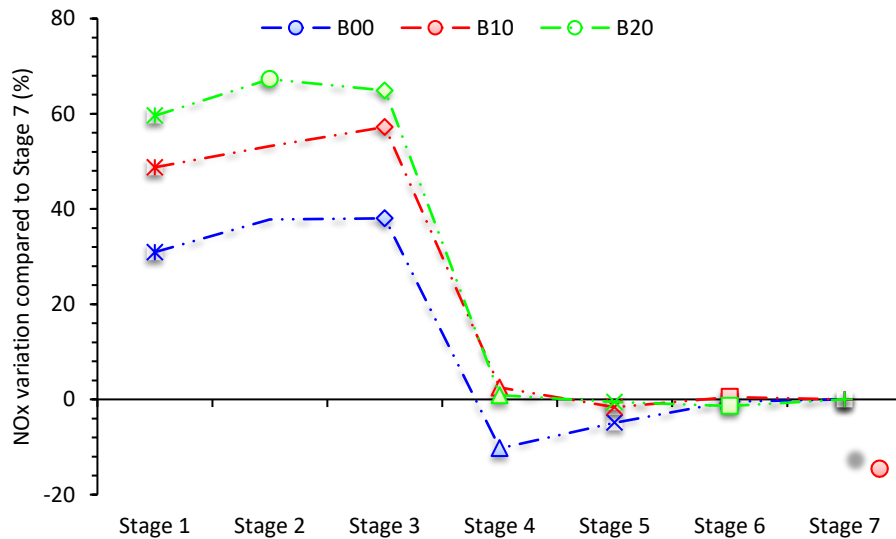
Figure 4 NOx variation compared to Stage 7 at different stages of engine warm-up with B00, B10 and B20

326 Within the cold-operation period, it can be seen in Figure 4 that NOx emissions increases as

327 the engine warms up from Stage 1 to 2. Across this period, For example, B20 NOx emissions

328 increased by 5%. It has been frequently reported that NOx emissions depend on combustion

329 temperature [26, 61]. It can be seen in Figure 3 that the exhaust temperature, which can be

330 taken as an indicator of the combustion temperature, increased within these two stages.

331 Therefore, increasing combustion temperature is the likely reason for the increasing NOx [62,

332 65]. This is the same for Stage 3, where NOx increased to a higher value. However, there is a

333 sharp drop after this stage.

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334   The observed sharp drop in NOx emissions is due to an injection strategy change [62]. It was

335   shown in Figure 2 that for the tested engine, during the engine warm-up period, when the

336   engine coolant temperature reached 65°C, the injection strategy commanded by the ECU

337   changed to a retarded injection mode [31, 39]. It can be seen that the injection strategy is a

338   significant influential factor on NOx emissions, as reported in the literature [66, 67]. When

339   the start of injection was constant during Stages 1 and 2, the main influential parameter was

340   the combustion temperature (shown by exhaust temperature in Figure 3). This is the same

341   from Stages 4 to 5, where the start of injection was stable at the retarded (compared to Stages

342   1 and 2) crank angle, NOx increased as the combustion temperature increased [15, 26].

343   However, the NOx graph shifted to lower values because of the retarded injection strategy .

344   During Stages 6 and 7, the start of injection was constant and the combustion temperature

345   stabilised, therefore NOx emissions did not change.

346   The gradual increase in combustion temperature, shown by the exhaust temperature in

347   Figure 3, is not well aligned with the trend of NOx within the stages in Figure 4, as NOx

348   increased, dropped and then increased before becoming stable. Therefore, the observed

349   trend warrants additional analysis, NOx emissions during engine warm-up are affected by

350   more than just engine temperature.

351   NOx emissions are significantly affected by the nature of combustion [26]. The in-cylinder

352   pressure profile provides insight into how combustion changes as the engine warmed up.

353   Figure 5 shows in-cylinder pressure diagrams at 7 stages of engine warm-up. As illustrated,

354   there are two different shapes for the in-cylinder pressure diagram. One is related to Stages

355   1, 2, and 3. Within these three stages, as the engine warmed up, the diagram slightly moved

356   toward lower crank angles, and the peak associated with combustion increased. However,

357 the change was not significant. After the injection strategy change, the motored peak (the

358 first peak, prior to combustion) became more obvious – the second peak is from combustion,

359 this shape is attributable to the retarded ignition strategy causing combustion to happen after

360 TDC. The systematic increase in the peak pressure of the motored peak (the first peak) is

361 indicative of the cylinder inside being warmer at the beginning of the cycle. The impact of this

362 change in injection strategy was also seen in Figure 4, where there was a significant drop in

363 NOx from Stage 3 to 4. The higher peak combustion pressure is indicative of a hotter in-

364 cylinder environment, hence a greater production of thermal NOx [26].

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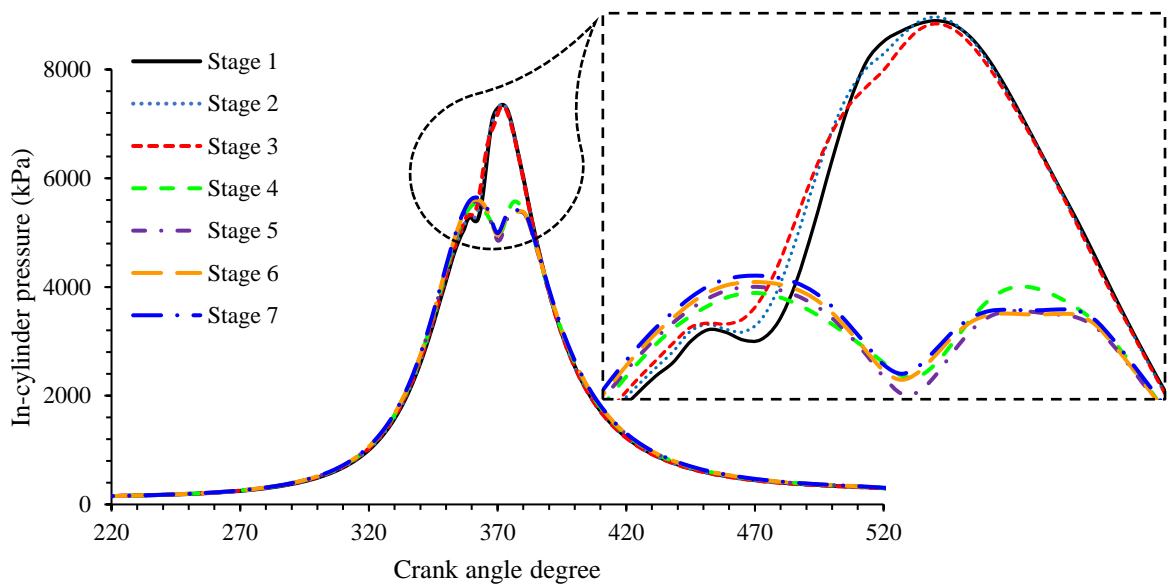
Figure 5 In-cylinder pressure during the engine warm-up with B00

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369 Figure 6 shows the heat release diagram at 7 stages of the engine warm-up period. Heat

370 release is another combustion characteristic parameter, commonly used to interpret NOx

371 emissions [65]. The heat release diagram can show four phases during combustion [65]. The

372 first one is the ignition delay period, which starts at the start of injection and ends at the start

373   of combustion. In this period, fuel is injected but it does not ignite. The heat release diagram

374   is negative in this period owing to fuel vaporisation and subsequent chemical reactions [65,

375   68]. The injected fuel also absorbs sensible energy due to the lower temperature of the fuel

376   compared to the in-cylinder environment, the so-called *cooling effect [65]*. The second phase

377   is premixed combustion, which is related to the initial combustion of the fuel/air mixture. In

378   this phase, the heat release diagram starts from zero (at the start of combustion), increases

379   to a maximum value, and then drops to an intermediate minimum value. In this phase, a high

380   proportion (typically a third) of the heat release happens. As can be seen, there are two

381   different shapes for the heat release diagram. The reason is the change in injection strategy

382   (retarded start of injection). The first shape is related to Stages 1, 2, and 3, where the start of

383   injection stays constant. It can be seen that within these three stages, as the engine warmed

384   up, the start of combustion occurred slightly earlier—the ignition delay decreased [69, 70].

385   This leads to a shorter time for the fuel to mix with the air and a subsequent decrease in the

386   number of potential ignition kernels. This results in a decrease in the first peak value, which

387   is caused by the rapid combustion of the premixed portion of the fuel as the engine warms.

388   Diffusion burning, or mixing-controlled combustion, is the third phase of combustion in which

389   the combustion of the available air/fuel mixture controls the burning rate. This phase can be

390   seen in the heat release diagram after the premixed combustion phase where the heat

391   release increases from the intermediate minimum point to the second peak value in the

392   diagram and then decreases gradually. Late combustion is the fourth phase in which there is

393   some possible energy release from unburned fuels. However, the heat release rate is low

394   within this phase due to the expanding volume causing a significant decrease in the in-cylinder

395   temperature. It can also be seen in Figure 6 that as the engine warmed up, the second peak

396   of the heat release diagram, which is related to the mixing-controlled combustion phase, was

397   increasing. Figure 4 showed that NOx increased gradually through these three stages as the

398   engine warmed up.

399   A similar trend and tendency of having a double peak in the heat release diagram can be seen

400   for the second shape which is related to Stages 4 to 7. Compared to the first shape (Stage 1

401   to 3), in Stages 4 to 7, there is a significant shift in the heat release diagram toward the higher

402   crank angles. This is because of the injection strategy change, this shift is also aligned with the

403   sharp drop in the NOx emissions shown in Figure 4. It can be seen in Figure 6 that on the heat

404   release diagram, with the new start of injection, as the engine warmed up through Stages 4

405   to 7, the first peak value decreased and the second peak increased. As with Stages 1 to 3, this

406   is associated with a systematic NOx increase. The reason could be that the increase in

407   diffusion combustion is prolonging the time the in-cylinder environment is at an elevated

408   temperature, thereby giving more opportunity to produce thermal NOx.

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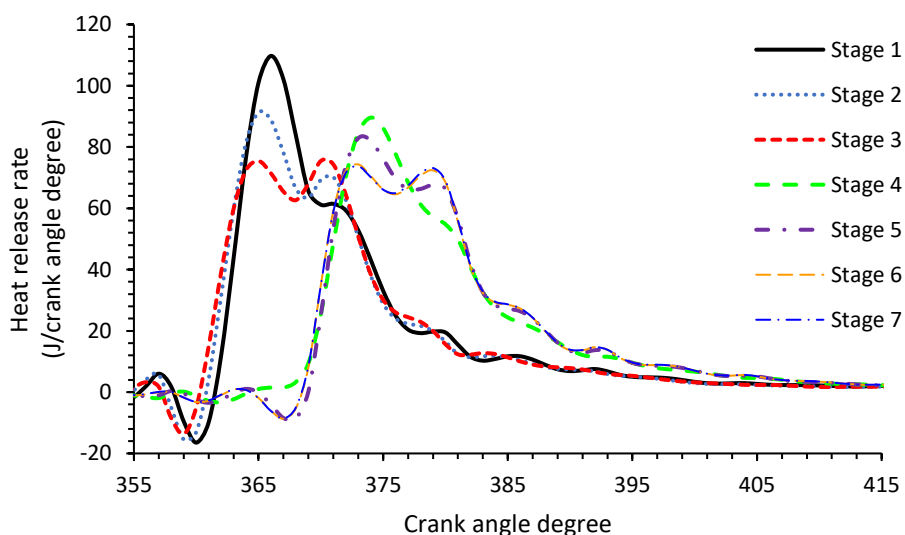
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411   Figure 6 Heat release rate at 7 stages of engine warm-up with B00

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20

413   The mechanisms of NOx formation in diesel engines are well known [65]. This includes

414   thermal NOx, fuel NOx, and prompt NOx [61, 65]. Between them, thermal NOx is the

415   dominant one in a diesel engine. The NOx umbrella covers various nitrogen compounds.

416   However, in engine NOx exhaust emissions, nitrogen monoxide (NO) and nitrogen dioxide

417   (NO_2) comprise the significant majority. Between NO and NO_2, NO is typically the dominant

418   one. However, in some modern engines, the ratio of NO_2 to NO has increased [71]. NO_2 can

419   also form from an already existing NO [19]. Despite this, in most diesel engine studies, NOx

420   formation can be accurately described from NO formation mechanisms, without an explicit

421   explanation for NO_2 [19]. Based on that, it is reasonable to assume that NO (and NO_2) will

422   show a similar trend to NOx. This study shows that NOx and NO_2 are higher during cold-

423   operation. However, they have a different trend when it comes to the effect of temperature

424   increase.

425   NO_2 can form from NO through the reaction of $NO + HO_2 \rightarrow NO_2 + OH$ [72]. This reaction is

426   between thermal NO, which forms in the hot flame front, and HO_2 which forms in relatively

427   cold regions of the unburnt fuel/air mixture near the flame front [19, 21, 73]. The NO to NO_2

428   conversion depends on the temperature of the mixture, and the NO and HO_2 concentrations;

429   however, the availability of HO_2 is the predominant factor [74]. HO_2 radicals form in the

430   relatively low-temperature regions of the unburned air/fuel mixtures before the mixture is

431   consumed by flame propagation. This explains the relatively high NO_2 formation during cold-

432   operation. However, as the engine warms up, thermal NO increases, but the decreased cold

433   regions of unburned air/fuel mixture can tend to lower HO_2 radicals, therefore reducing NO_2

434   formation [19].

435   The generated NO_2 can revert to NO via $NO_2 + OH \rightarrow NO + HO_2$ when the HO_2 concentration

436   is low, or via $NO_2 + H \rightarrow NO + OH$ reaction when the bulk temperature is high [19]. At low

437   temperatures, mixing the cool bulk mixture with the NO_2-contained mixture can quench the

438   NO_2 to NO conversion, therefore a portion of NO_2 can be retained [19]. For example, at the

439   early stages of cold- operation (Stage 1), the low temperature of the cylinder environment,

440   fuel, and air can lead to a high portion of cool bulk mixture far from the sprayed fuel plume,

441   which can quench the NO_2 conversion to NO, therefore more NO_2 retains. This can be seen

442   during the early stages of cold-operation where in addition to high NO_2 formation (because

443   of high NO and NOx formation), the NO_2/NOx ratio is high as well.

444

445   **3.2   Nitrogen dioxide**

446   Figure 7 (a) shows how NO_2 changes at different stages of engine warm-up. It can be seen

447   that similar to NOx (Figure 4), NO_2 during cold-operation is significantly higher than hot-

448   operation. For example, NO_2 during Stage 1 with B00, B10, and B20 was 2.42 times, 86%, and

449   1.14 times higher than Stage 7, respectively. Higher NO_2 emission during cold-start when

450   compared to hot-start was reported in the literature [75]. Figure 7 (a) shows that during

451   engine warm-up, NO_2 decreased from Stage 1 to 3 as the engine temperature increased,

452   dropped in Stage 4 because of injection strategy change, increased slightly in Stage 5 as the

453   engine warmed up and then stabilised in Stages 6 and 7. As the engine warmed up, the

454   difference decreased from 1.14 times higher (in Stage 1 compared to Stage 7) to 47% (Stage

455   2) and 32% (Stage 3). After that, NO_2 dropped to 55% lower than Stage 7 in Stage 4, and then

456   increased in Stage 5 and finally stabilised. Comparing Figure 4 to Figure 7 (a) shows that the

457   temperature increase within the first three stages of engine warm-up has a different effect

458   on NO_2 and NOx, as NOx increased and NO_2 decreased. This can be explained by looking at

459   the formation mechanism of NOx and NO_2.

460   Figure 7 (b) shows how the NO_2/NOx ratio varied at different stages of engine warm-up. It can

461   be seen that the NO_2/NOx ratio during Stage 1 was higher than at other stages. The NO_2/NOx

462   ratio during Stage 1 with B00, B10, and B20 was 8, 3, and 4% higher than Stage 7, respectively.

463   Further analysis showed that the NO_2 contribution in NOx was 13-17% during Stage 1, while

464   during Stage 7 it was 5-13%.

465   The trend shows that during engine warm-up, the NO_2/NOx ratio decreased from Stage 1 to

466   3 as the engine temperature increased, before increasing to become stable from Stage 5.

467   However, during Stage 4 in which the injection strategy changed, the NO_2/NOx ratio behaved

468   differently.

469   As the temperature increased, NOx formation increased because of the thermal NO

470   mechanism. While higher NO formation can lead to higher NO_2 formation, the increasing

471   engine temperature can lead to more conversion of NO_2 to NO, thereby causing a decrease

472   in the NO_2/NOx ratio. This can be a reason for the decreasing trend of NO_2/NOx ratio with

473   engine temperature. As seen, from Stage 1 to Stage 3, as the engine warmed up, the exhaust

474   temperature (Figure 3) and NOx increased (Figure 4), while NO_2 (Figure 7(a)) and the NO_2/NOx

475   ratio (Figure 7 (b)) decreased.

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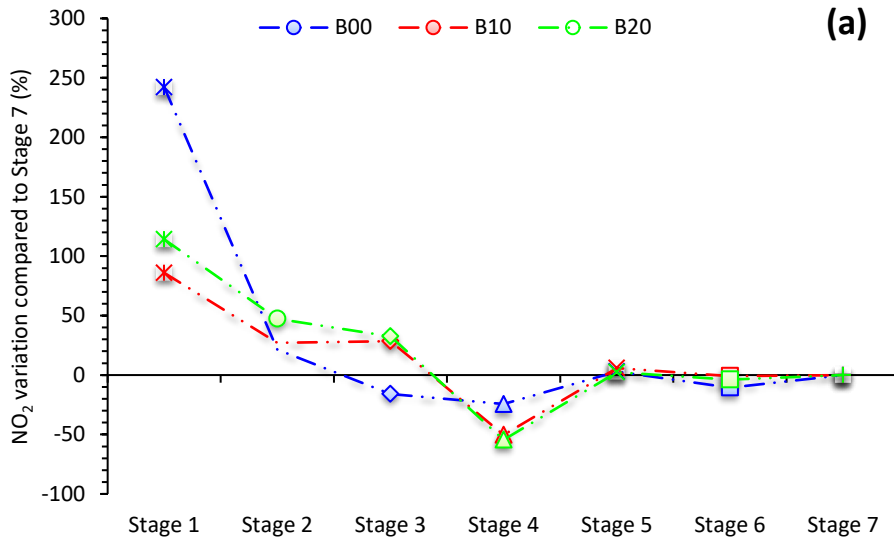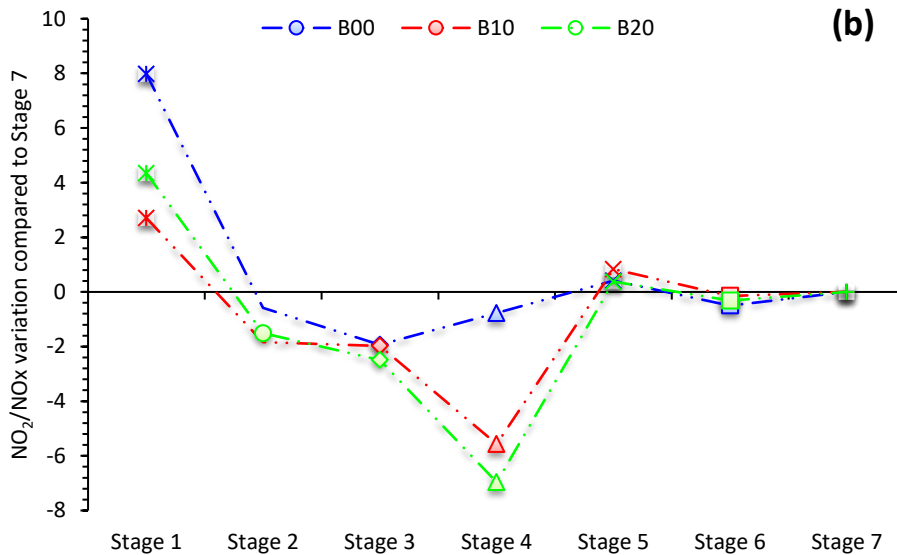
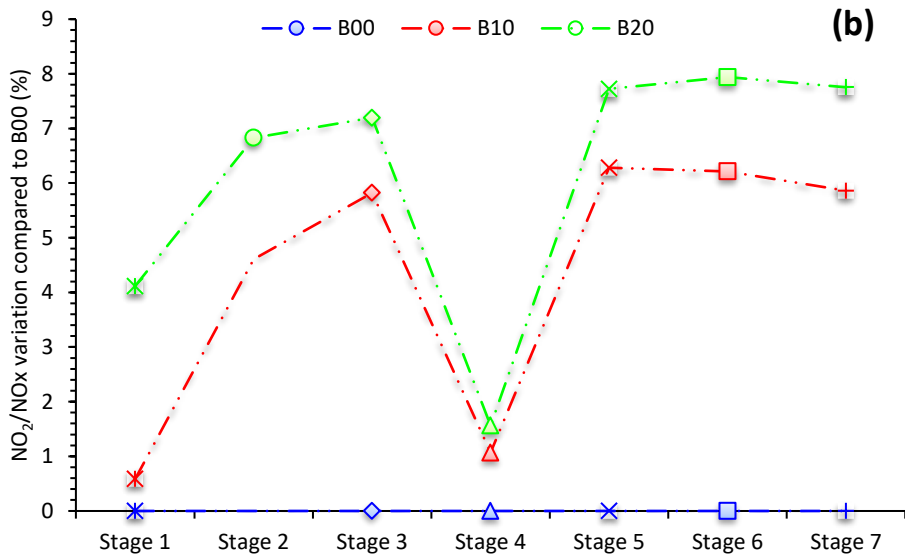Figure 7 NO_2 (a) and NO_2/NOx (b) variations compared to Stage 7 at different stages of engine warm-up with B00, B10 and B20

Figure 8 (a) shows the NO_2 changes with different fuels, as compared to B00. The figure shows

that except for Stage 1 and 4, in all of the other stages, NO_2 with diesel (B00) is the lowest

and it increases with an increase of biofuel in the blend. Similar to NO_2, Figure 8 (b) shows

that the NO_2/NOx ratio increased as the share of biofuel in the fuel blends increased. This

increasing trend happened in all of the Stages. It can also be seen that as the engine warmed

487   up, the NO_2/NOx ratio difference between B00 and the biofuel blends increased. The reason

488   for this could be because adding biofuel to the blend increases the fuel oxygen content and

489   decreases the calorific value of the fuel enlarging the cooler regions which leads to more NO_2

490   from the reaction of NO and HO_2 [76], given that the NO to NO_2 conversion depends on the

491   temperature of the mixture [19, 74]. It also adversely impacts the NO_2 destruction reaction

492   from NO [65]. Also, biofuel being oxygenated is of importance as the oxygen release from the

493   fuel readily oxidizes with nitrogen and NO.
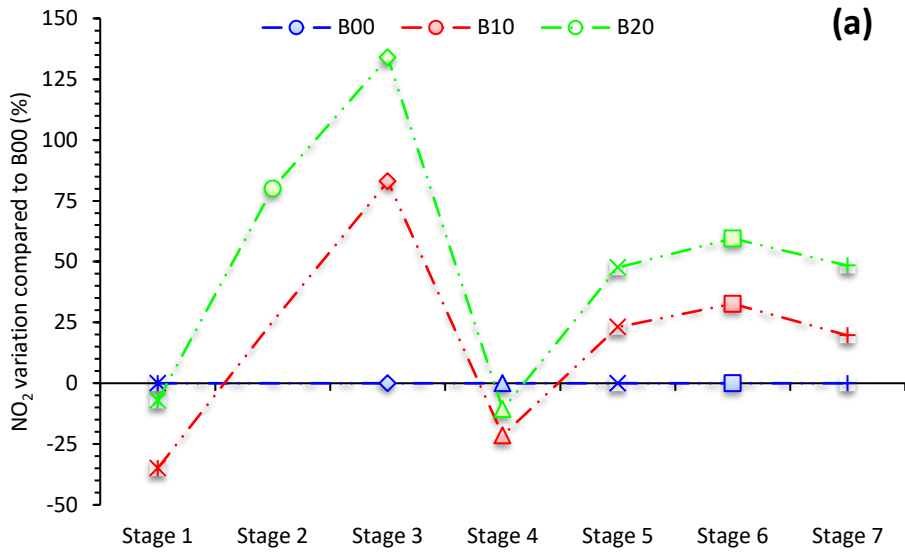
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496   Figure 8 NO$_2$ (a) and NO$_2$/NOx ratio (b) variations compared to B00 at different stages of engine
497   warm-up with B00, B10 and B20

498

3.3   Practical implications of this study and limitations

499

500   Because of the adverse health impacts and high cost of diesel/petrol, there are plans and

501   measures in place to increase the share of biofuels such as biodiesel. However, vehicle

502   emissions are an issue, and authorities and decision-makers have been limiting emissions by

503   tightening the permissible emission thresholds in the regulations (such as Euro1-6). This

504   research shows that when it comes to NOx emissions, the current increasing share of biofuels

505   can have more adverse effects, especially during cold-operation—which is a part of the daily

506   driving norm for many vehicles in cities—where the after-treatment systems are not well-

507   effective [28]. Emissions from the cold-start period are important as this period is within the

508   first 5 min of starting a vehicle, during which time many vehicles are still near urban areas

509   [38]. Results from this study highlight the negative effects of this period on regulated and

510   unregulated exhaust emissions, which need to be taken into consideration. This study shows

511   the importance of regulating NO_2 emissions in future regulations, or even in the new

512   amendments of the current regulations. In addition to that, in engine calibration, after-

513   treatment systems and injection strategies are mostly based on the regulated cold-operation

514   period. However, this study shows that the period in which the engine emissions are

515   negatively affected is significantly longer than the official cold-start boundary.

516   Different fuels have different chemistry, therefore, different effects on combustion behavior,

517   which consequently affects emissions. Studying more types of biofuels with different

518   properties can help the literature in this area. Another limitation of such studies can be

519   related to engines. Due to fuel chemistry influences prior to combustion, engines with

520   different injection strategies and in-cylinder pressure profiles are likely to exhibit different

521   combustion behavior [52, 77]. This is a common limitation of any fuel study, however, to some

522   extent, this has been controlled in our experiment by reducing variables and using a mid-sized

523   multi-cylinder engine with a modern fuel system that uses a single pulse for injection, rather

524   than a complex delivery strategy which would limit the applicability of the results in a general

525   sense.

4. Conclusions and future directions

This study investigated the effect of fuel properties and engine temperature at different stages of engine warm-up on NOx, NO_2, and the NO_2/NOx ratio using diesel and biofuel blends (10 and 20%). The experiments were conducted on a 6-cylinder, turbocharged, common-rail Cummins engine. The engine warm-up period was divided into 7 stages to study the official cold-operation and hot-operation periods in addition to the intermediate stages which are not defined as cold-operation in the (EU) regulation and also cannot be considered as hot-operation owing to non-stable engine temperature. To better describe and analyse the observations, this study used coolant, lubricating oil and exhaust temperatures, the start of injection, cylinder pressure and the rate of heat release data. Results showed that:

- Cold-operation NOx was 31-60% higher than hot-operation, largely because of differences in the injection strategy (the injection timing retarded once the engine coolant reached 65°C). As the engine warmed up, NOx ascended with temperature, had a sharp drop because of the injection strategy change, then increased slightly with temperature before stabilising. The adverse effect of cold-operation on NOx emissions increased with an increasing biofuel share, as the difference between cold- and hot-operation was 31% with diesel, but 49 and 60% with 10 and 20% biofuel in the blend.

- There were two different shapes for the in-cylinder pressure and heat release diagrams because of the retarded injection strategy corresponding to NOx emissions decrease.

- Cold-operation NO_2 was 1.14-2.42 times higher than hot-operation. Cold-operation NO_2/NOx ratio was 3-8% higher than hot-operation. As the engine warmed up, NO_2 and the NO_2/NOx ratio decreased with increasing engine temperature, dropped

28

549 because of the injection strategy change, increased slightly and then stabilised. With

550 different fuels, the NO_2 contribution in NOx was 13-17% during cold-operation, while

551 during hot-operation it was 5-13%.

552 • During cold-operation, with diesel, the effect on NO_2 was significantly higher when

553 compared to other fuels.

554 • In most stages, NO_2 and the NO_2/NOx ratio with diesel were lower than the biofuel

555 blends, with both NO_2 and the NO_2/NOx ratio increasing with the blend ratio.

556 The future research direction can be toward studying more types of biofuels with different

557 properties. Also, calibration of the engine based on each fuel blend could be another

558 direction.

559

564

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Appendix

Table A1 shows the accuracy of the equipment used in this study. Table A2 analyses the test

repeatability of the experiments using average and coefficient of variation (CV) parameters.

As shown, a significantly low difference between tests (less than 1.5%) can be an indication

of test repeatability. In addition to these parameters, Table A3 presents the CO_2 repeatability.

This experiment utilised a quality CO_2 gas analyser (non-dispersive infrared CAI-600)—high-

tech equipment commonly utilised by research groups and the automotive industry. It is

worth highlighting that using a correlation engine/car to measure CO_2 in repeated

experiments and checking the variation is a trustworthy repeatability check and uncertainty

measurement method utilised in emissions laboratories within the automotive industry.

Table A1: Accuracy of instruments used in this study

Instrument	Accuracy
Kistler 6053CC60	Sensitivity of ≈ -20 pC/bar (manufactured stated)
Kistler type 2614	Resolution of 0.5 crank angle degrees (manufacture stated)
CAI-600 NDIR CO_2 analyser	Repeatability > 1% of full scale / Linearity > 0.5% of full scale and
CAI-600 CLD NO/NOx analyser	Repeatability > 0.5% of full scale / Linearity > 0.5% of full scale / Convertor efficiency: 98%

849   Table A2: Test repeatability: statistical analysis

		Engine torque (Nm)		Engine speed (rpm)	
		Mean	CV (%)	Mean	CV (%)
Warm-start	Test I	238.28	1.34	1498.94	0.15
	Test II	242.02	1.00	1499.49	0.14
	Difference	1.5%		0.04%	
Cold-start	Test I	225.28	3.74	1498.87	0.15
	Test II	227.20	5.42	1499.19	0.13
	Difference	0.82%		0.02%	

850

851   Table A3: CO_2 correlation test to confirm the test repeatability:

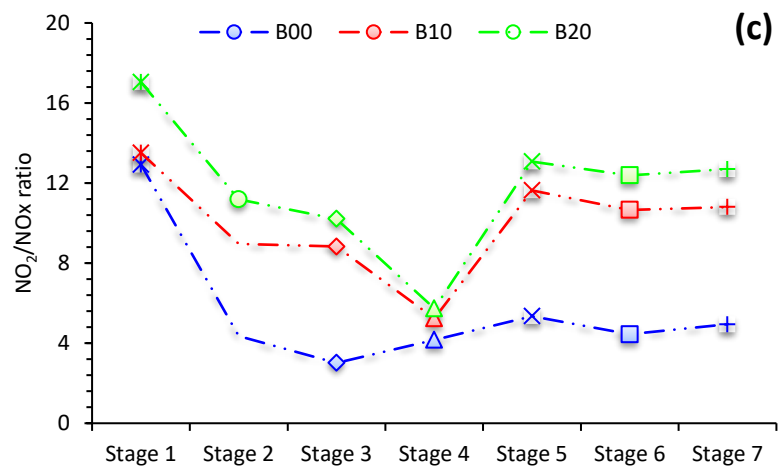|		Mean	CV (%)
Warm-start	Test I	6.47	0.51
	Test II	6.64	0.36
	Difference	0.17%	
Cold-start	Test I	6.36	0.97
	Test II	6.51	2.27
	Difference	0.12%	

852

853   Figure A1 shows NOx and NO_2 concentrations and NO_2/NOx ratio.
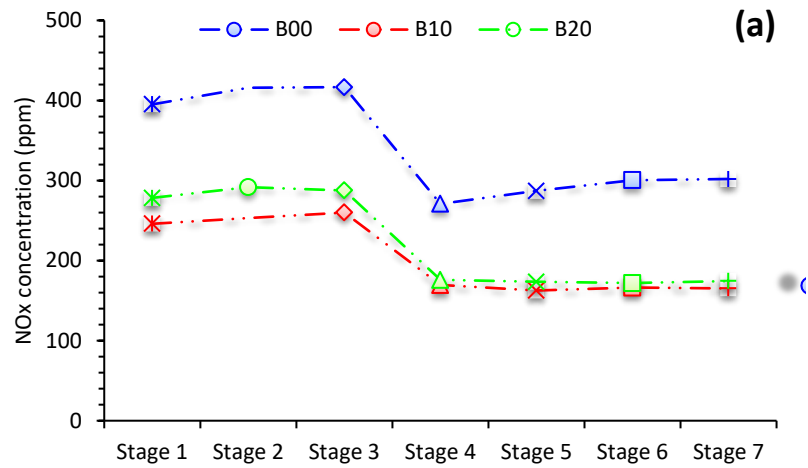
854
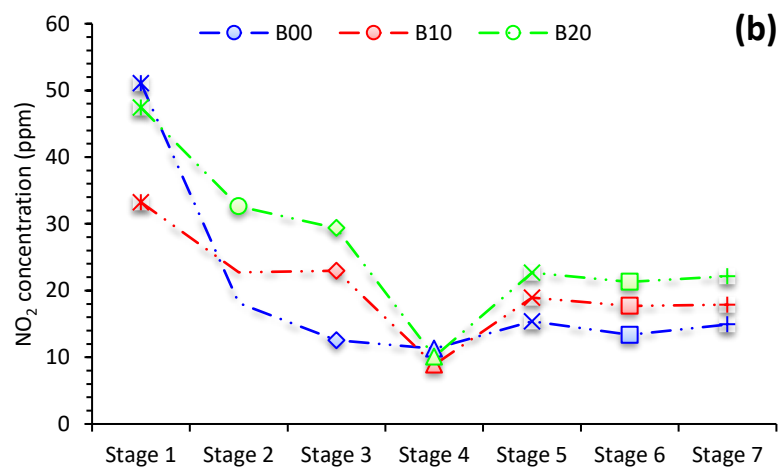
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856

857   Figure A1 NOx and NO₂ concentrations and NO₂/NOx ratio at different stages of engine

858   warm-up with B00, B10 and B20

859