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1 **Analysis of cold-start NO₂ and NO_x emissions, and the NO₂/NO_x ratio in a diesel engine**
2 **powered with different diesel-biodiesel blends**

3

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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 NO_x emissions. In addition to NO_x 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 NO₂ 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 NO₂, NO_x, and NO₂/NO_x
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 NO_x, NO₂, and
40 NO₂/NO_x ratio were 31-60%, 1.14-2.42 times, and 3-8% higher than the hot-operation,
41 respectively. In most stages, NO₂ and the NO₂/NO_x 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 NO_x drop during the engine warm-up. The adverse effect of cold-operation on NO_x
45 emissions increased with increasing biofuel share.

46 Keywords: NO_x emissions; NO₂ emissions; NO₂/NO_x ratio; biodiesel; cold-start; engine warm-
47 up.

48 **1. Introduction**

49 The transportation sector contributes significantly to the pollution in cities through the
50 exhaust emissions of vehicles, such as CO, CO₂, HC, NO_x, PM, and PN. Exposure to such
51 pollutants may lead to serious health problems [1, 2]. In order to mitigate exposure, there are
52 incentives in place to restrict these harmful emissions through government regulations [3].
53 For example, in Europe, the emissions regulations progression from Euro 1 to Euro 6.2 has
54 successfully reduced emissions from the transport section by systematically reducing the
55 allowable thresholds on each emission [3]. Another regulated emissions control measure is
56 the use of alternative fuels, which can mitigate the adverse effect of fossil fuels and also
57 stimulate the economy. For example, the European Union targeted a 5.75% biofuel share in
58 fuel by 2010 (EC Directive 2003/30). This continued in Directive 2009/28/EC to increase the
59 share of biofuel to 10% in 2020. The result of these actions, in terms of vehicle fuels, was a
60 move from using neat diesel/petrol to gradually increasing the share of biofuel, today blends
61 of 10% biofuel with diesel/petrol are currently common [3].

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

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

71 reason for higher NO_x 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 NO_x
73 variations is controversial. A large number of studies claim increases in NO_x 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, NO_x emissions are of significant importance due to their adverse
77 effects on health and the environment [17, 18]. The term NO_x is representative of several
78 nitrogen compounds but is predominately comprised of nitrogen oxide (NO) and nitrogen
79 dioxide (NO₂). Typically, NO is a product of the combustion process which forms within the
80 combustion chamber; while, NO₂ 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 NO₂ formation pathways are an active area of research.

83 NO₂ 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 NO₂ 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' NO₂ emissions. NO₂ is
89 currently unregulated but there is a focus to be regulated in the upcoming emissions
90 regulation (Euro 7).

91 The ratio of NO₂ in NO_x 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 NO₂ in NO_x, otherwise known as the NO₂/NO_x ratio [19, 22].
95 There are various strategies proposed in the literature to reduce NO_x emissions such as using
96 different additives [23, 24]. However, after-treatment systems are commonplace in the
97 mitigation of NO_x emissions [25, 26]. Praveena and Martin [27] reviewed different after-
98 treatment techniques of NO_x emissions reduction in CI engines. For example, they showed
99 that a urea SCR can reduce NO_x by 98-99% with a warmed-up engine. They also studied the
100 effect of exhaust temperature on NO_x 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, NO_x emissions were 2.7 times higher than the Euro 6 NO_x 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 NO_x emissions during this period, which will be shown in this study;
108 however, the NO_x 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 NO₂ and NO_x emissions with biofuels during cold-operation, as there are not many
128 fundamental studies on NO_x (and no study on NO₂) 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 NO₂ and the NO₂/NO_x ratio during cold-start in a diesel

138 engine. And from these papers, only a few exist on the topics of NO₂ and the NO₂/NO_x ratio
139 during cold-start in a diesel engine using alternative fuels. For example, Lapuerta et al. [41]
140 evaluated the NO₂/NO_x 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 NO₂) 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 NO₂ during the cold-start section of different driving
145 cycles. There are also few more articles in this field reporting NO₂ and the NO₂/NO_x 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 NO₂ and the
148 NO₂/NO_x 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 NO_x, NO₂, and the NO₂/NO_x ratio.

156

157 **2. Methodology**

158 Given that this study aims to investigate the effect of engine temperature and fuel properties
159 on NO_x, NO₂ and the NO₂/NO_x 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.

166

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	Hydraulic (Electronically-controlled)

168

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 NO_x, NO₂ and NO were measured with a CAI-600 CLD NO/NO_x 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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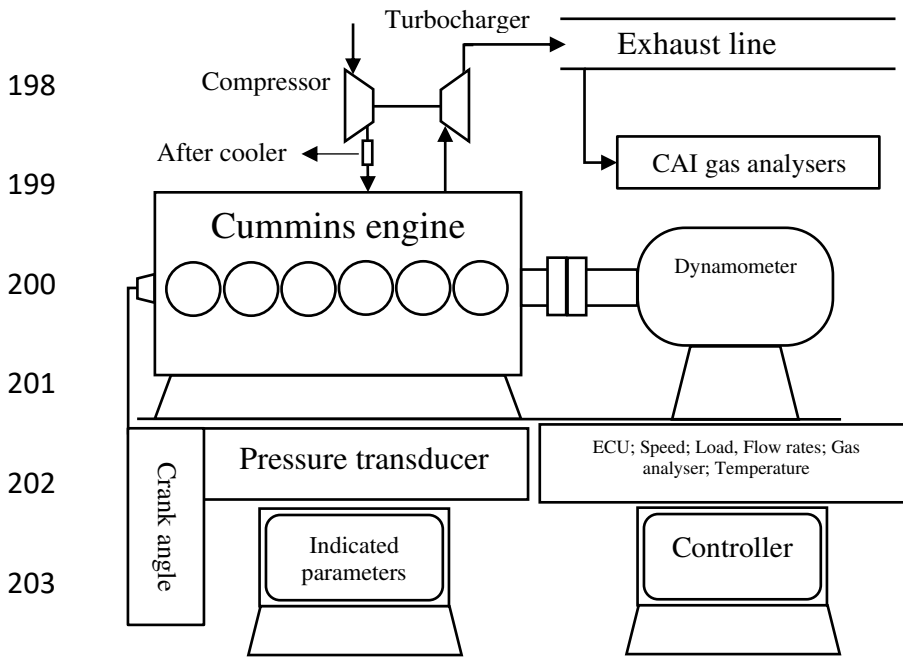
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205 Figure 1 Test setup_schematic diagram of the experimental facility

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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/m³;
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]. NO_x 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 NO_x 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

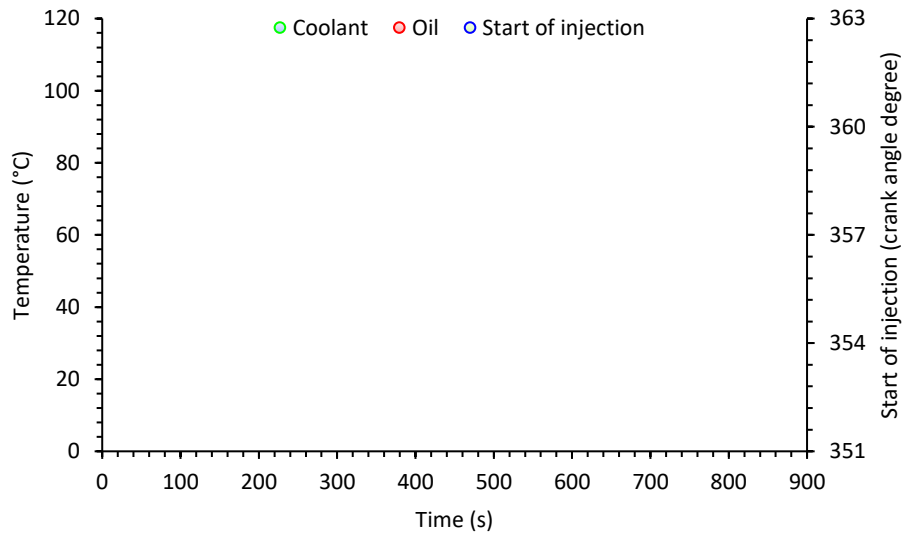
241 temperature and fuel properties are the driving factors in NO_x formation. Figure 2 shows
242 temperature change in the engine coolant and lubricating oil as the engine warmed up using
243 data from various temperature sensors collected with the engine control unit (ECU)—through
244 the controller 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 NO_x 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

264 number of variables in each stage. This is done by splitting the warm-up period into 7
265 consecutive stages (each two min).

266



267

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

270

271 3. Results and Discussions

272 This section studies NO_x, NO₂, and the NO₂/NO_x 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.

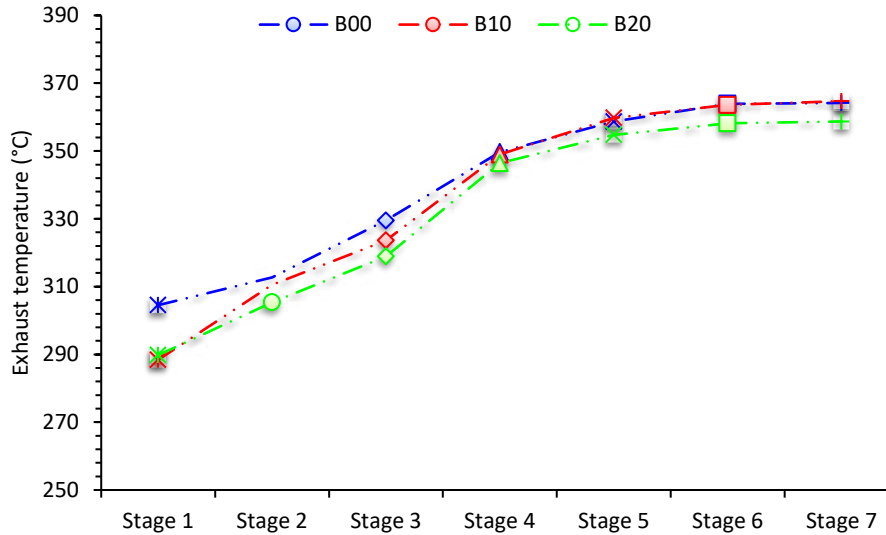
279 Figure 3 shows that the exhaust temperature increases as the engine warms up. This has been
280 reported in the literature [39, 62]. As can be seen, the exhaust temperature increased from

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.

302



303

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

305

306 3.1 Nitrogen oxides

307 Figure 4 shows how NOx emissions change as the engine warms up. It can be seen that NOx
 308 emissions during cold-operation are significantly higher (31-60%) than during hot-operation.

309 The higher NOx emissions during cold-start when compared to hot-start was reported
 310 frequently in the literature [63, 64]. It can also be seen that initially as the engine warmed up,
 311 NOx increased gradually, then dropped sharply, and finally stabilised at a low level, this trend
 312 was reported in the literature [31, 62]. For example, with B00, NOx was 30.9, 37.8, and 38%

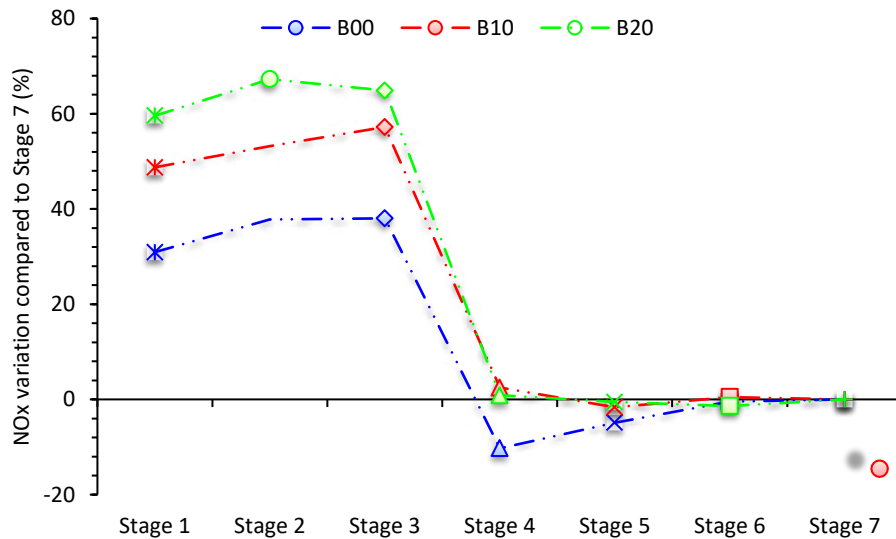
313 higher in Stages 1, 2 and 3, respectively, compared to Stage 7. In Stage 4, the NOx emissions
 314 dropped sharply by 48% to be 10% less than Stage 7. And finally, with a gradual increase in

315 Stage 5, the NOx emissions stabilised in Stages 6 and 7. The graph also shows that the
 316 difference between cold-operation and hot-operation increases by increasing the share of

317 biofuel in the fuel blend. For example, the NOx in Stage 1 with B00, B10 and B20 were 31%,
 318 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].

321



322

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

325

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.

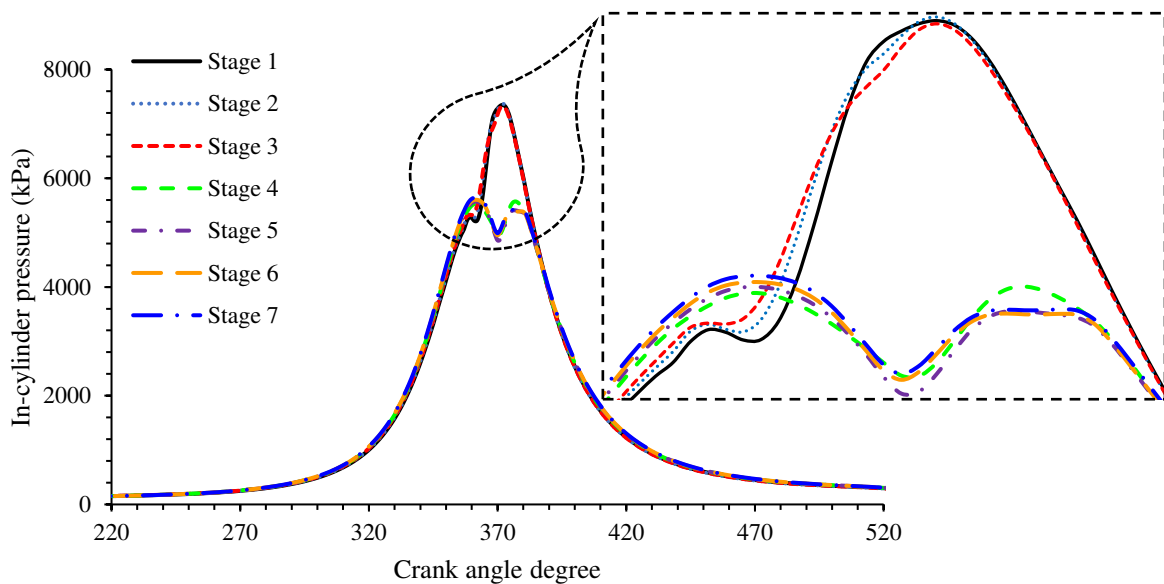
334 The observed sharp drop in NO_x emissions is due to an injection strategy change [62]. It was
335 shown in Figure 2 that for the tested engine, during the engine warm-up period, when the
336 engine coolant temperature reached 65°C, the injection strategy commanded by the ECU
337 changed to a retarded injection mode [31, 39]. It can be seen that the injection strategy is a
338 significant influential factor on NO_x 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, NO_x increased as the combustion temperature increased [15, 26].
343 However, the NO_x 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 NO_x 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 NO_x within the stages in Figure 4, as NO_x
348 increased, dropped and then increased before becoming stable. Therefore, the observed
349 trend warrants additional analysis, NO_x emissions during engine warm-up are affected by
350 more than just engine temperature.

351 NO_x 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].

365



366

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

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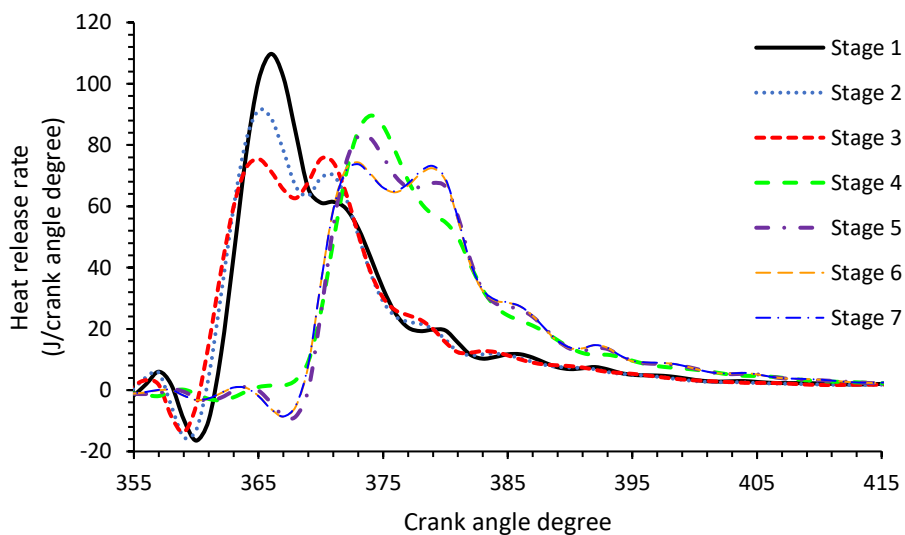
369 Figure 6 shows the heat release diagram at 7 stages of the engine warm-up period. Heat
 370 release is another combustion characteristic parameter, commonly used to interpret NOx
 371 emissions [65]. The heat release diagram can show four phases during combustion [65]. The
 372 first one is the ignition 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.

409



410

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

412

413 The mechanisms of NO_x formation in diesel engines are well known [65]. This includes
414 thermal NO_x, fuel NO_x, and prompt NO_x [61, 65]. Between them, thermal NO_x is the
415 dominant one in a diesel engine. The NO_x umbrella covers various nitrogen compounds.
416 However, in engine NO_x exhaust emissions, nitrogen monoxide (NO) and nitrogen dioxide
417 (NO₂) comprise the significant majority. Between NO and NO₂, NO is typically the dominant
418 one. However, in some modern engines, the ratio of NO₂ to NO has increased [71]. NO₂ can
419 also form from an already existing NO [19]. Despite this, in most diesel engine studies, NO_x
420 formation can be accurately described from NO formation mechanisms, without an explicit
421 explanation for NO₂ [19]. Based on that, it is reasonable to assume that NO (and NO₂) will
422 show a similar trend to NO_x. This study shows that NO_x and NO₂ are higher during cold-
423 operation. However, they have a different trend when it comes to the effect of temperature
424 increase.

425 NO₂ can form from NO through the reaction of $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ [72]. This reaction is
426 between thermal NO, which forms in the hot flame front, and HO₂ which forms in relatively
427 cold regions of the unburnt fuel/air mixture near the flame front [19, 21, 73]. The NO to NO₂
428 conversion depends on the temperature of the mixture, and the NO and HO₂ concentrations;
429 however, the availability of HO₂ is the predominant factor [74]. HO₂ 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 NO₂ 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 HO₂ radicals, therefore reducing NO₂
434 formation [19].

435 The generated NO_2 can revert to NO via $\text{NO}_2 + \text{OH} \rightarrow \text{NO} + \text{HO}_2$ when the HO_2 concentration
436 is low, or via $\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$ 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 NO_x formation), the NO_2/NO_x 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 NO_x (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

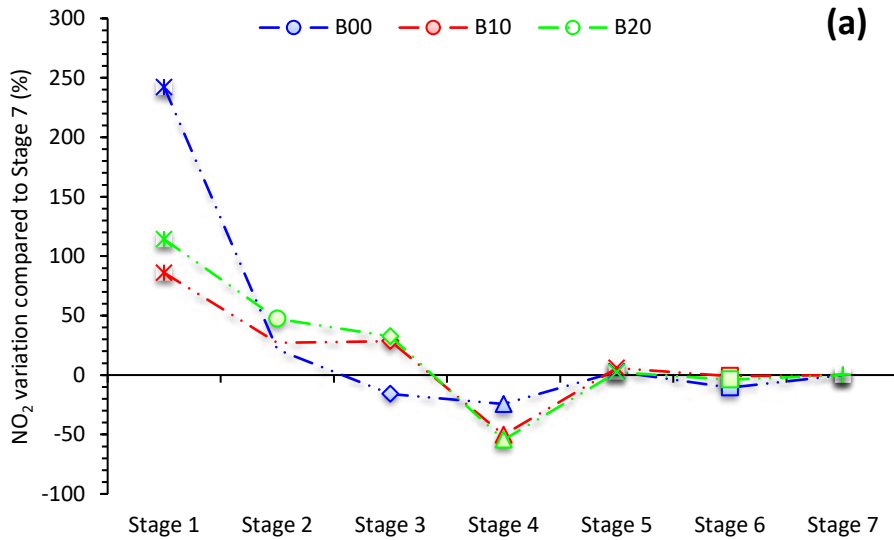
458 on NO₂ and NO_x, as NO_x increased and NO₂ decreased. This can be explained by looking at
459 the formation mechanism of NO_x and NO₂.

460 Figure 7 (b) shows how the NO₂/NO_x ratio varied at different stages of engine warm-up. It can
461 be seen that the NO₂/NO_x ratio during Stage 1 was higher than at other stages. The NO₂/NO_x
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 NO₂ contribution in NO_x was 13-17% during Stage 1, while
464 during Stage 7 it was 5-13%.

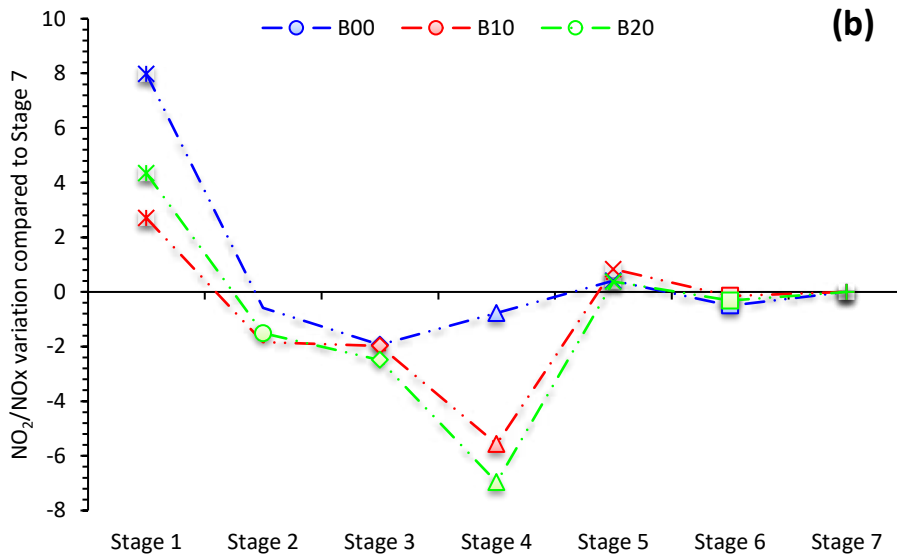
465 The trend shows that during engine warm-up, the NO₂/NO_x ratio decreased from Stage 1 to
466 3 as the engine temperature increased, before increasing to become stable from Stage 5.
467 However, during Stage 4 in which the injection strategy changed, the NO₂/NO_x ratio behaved
468 differently.

469 As the temperature increased, NO_x formation increased because of the thermal NO
470 mechanism. While higher NO formation can lead to higher NO₂ formation, the increasing
471 engine temperature can lead to more conversion of NO₂ to NO, thereby causing a decrease
472 in the NO₂/NO_x ratio. This can be a reason for the decreasing trend of NO₂/NO_x 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 NO_x increased (Figure 4), while NO₂ (Figure 7(a)) and the NO₂/NO_x
475 ratio (Figure 7 (b)) decreased.

476



477



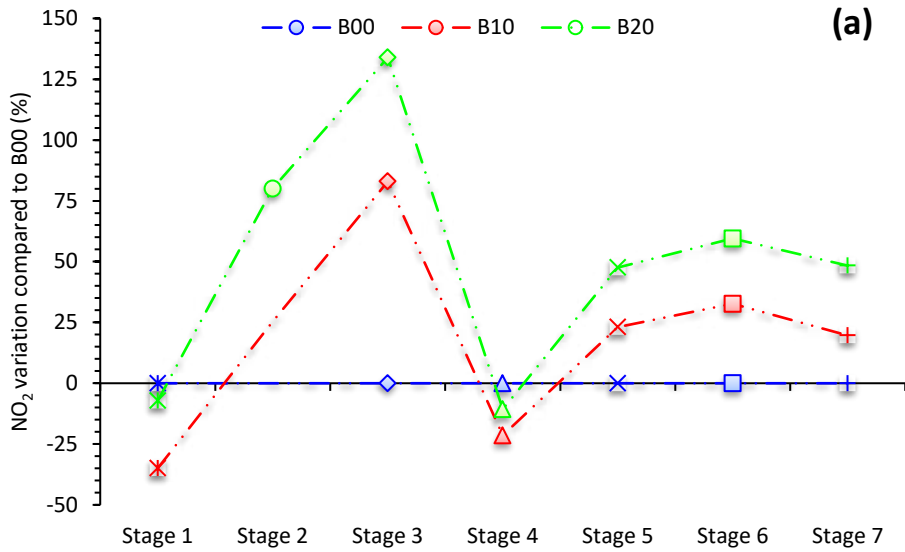
478

479 Figure 7 NO₂ (a) and NO₂/NO_x (b) variations compared to Stage 7 at different stages of engine warm-up with B00, B10 and B20
480

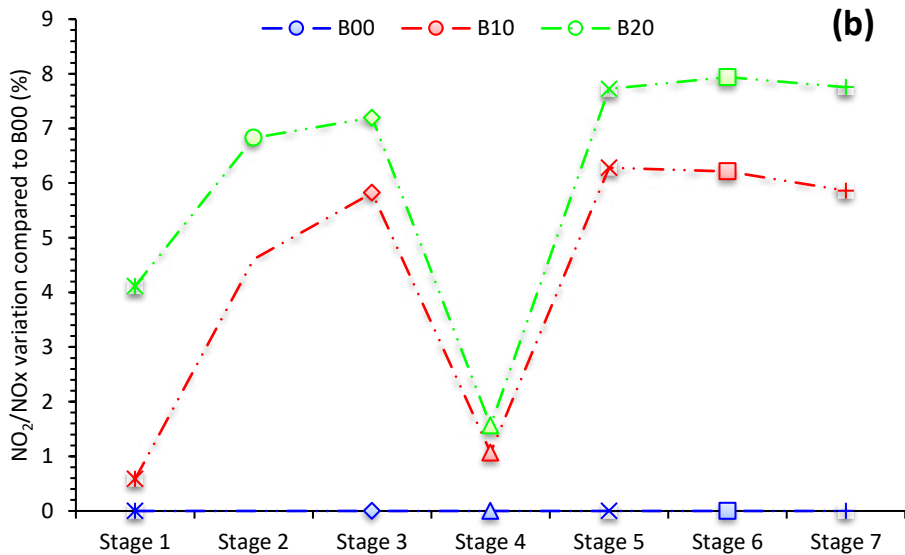
481

482 Figure 8 (a) shows the NO₂ changes with different fuels, as compared to B00. The figure shows
483 that except for Stage 1 and 4, in all of the other stages, NO₂ with diesel (B00) is the lowest
484 and it increases with an increase of biofuel in the blend. Similar to NO₂, Figure 8 (b) shows
485 that the NO₂/NO_x ratio increased as the share of biofuel in the fuel blends increased. This
486 increasing trend happened in all of the Stages. It can also be seen that as the engine warmed

487 up, the NO_2/NO_x 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 .



494



495

496 Figure 8 NO₂ (a) and NO₂/NO_x ratio (b) variations compared to B00 at different stages of engine
 497 warm-up with B00, B10 and B20

498

499 **3.3 Practical implications of this study and limitations**

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 NO_x 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 NO₂ 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.

526 4. Conclusions and future directions

527 This study investigated the effect of fuel properties and engine temperature at different
528 stages of engine warm-up on NO_x, NO₂, and the NO₂/NO_x ratio using diesel and biofuel blends
529 (10 and 20%). The experiments were conducted on a 6-cylinder, turbocharged, common-rail
530 Cummins engine. The engine warm-up period was divided into 7 stages to study the official
531 cold-operation and hot-operation periods in addition to the intermediate stages which are
532 not defined as cold-operation in the (EU) regulation and also cannot be considered as hot-
533 operation owing to non-stable engine temperature. To better describe and analyse the
534 observations, this study used coolant, lubricating oil and exhaust temperatures, the start of
535 injection, cylinder pressure and the rate of heat release data. Results showed that:

- 536 • Cold-operation NO_x was 31-60% higher than hot-operation, largely because of
537 differences in the injection strategy (the injection timing retarded once the engine
538 coolant reached 65°C). As the engine warmed up, NO_x ascended with temperature,
539 had a sharp drop because of the injection strategy change, then increased slightly with
540 temperature before stabilising. The adverse effect of cold-operation on NO_x emissions
541 increased with an increasing biofuel share, as the difference between cold- and hot-
542 operation was 31% with diesel, but 49 and 60% with 10 and 20% biofuel in the blend.
- 543 • There were two different shapes for the in-cylinder pressure and heat release
544 diagrams because of the retarded injection strategy corresponding to NO_x emissions
545 decrease.
- 546 • Cold-operation NO₂ was 1.14-2.42 times higher than hot-operation. Cold-operation
547 NO₂/NO_x ratio was 3-8% higher than hot-operation. As the engine warmed up, NO₂
548 and the NO₂/NO_x ratio decreased with increasing engine temperature, dropped

549 because of the injection strategy change, increased slightly and then stabilised. With
550 different fuels, the NO₂ contribution in NO_x was 13-17% during cold-operation, while
551 during hot-operation it was 5-13%.

552 • During cold-operation, with diesel, the effect on NO₂ was significantly higher when
553 compared to other fuels.

554 • In most stages, NO₂ and the NO₂/NO_x ratio with diesel were lower than the biofuel
555 blends, with both NO₂ and the NO₂/NO_x 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

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564

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836 Appendix

837 Table A1 shows the accuracy of the equipment used in this study. Table A2 analyses the test
838 repeatability of the experiments using average and coefficient of variation (CV) parameters.
839 As shown, a significantly low difference between tests (less than 1.5%) can be an indication
840 of test repeatability. In addition to these parameters, Table A3 presents the CO₂ repeatability.
841 This experiment utilised a quality CO₂ gas analyser (non-dispersive infrared CAI-600)—high-
842 tech equipment commonly utilised by research groups and the automotive industry. It is
843 worth highlighting that using a correlation engine/car to measure CO₂ in repeated
844 experiments and checking the variation is a trustworthy repeatability check and uncertainty
845 measurement method utilised in emissions laboratories within the automotive industry.

846

847 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/NO _x analyser	Repeatability > 0.5% of full scale / Linearity > 0.5% of full scale / Convertor efficiency: 98%

848

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%

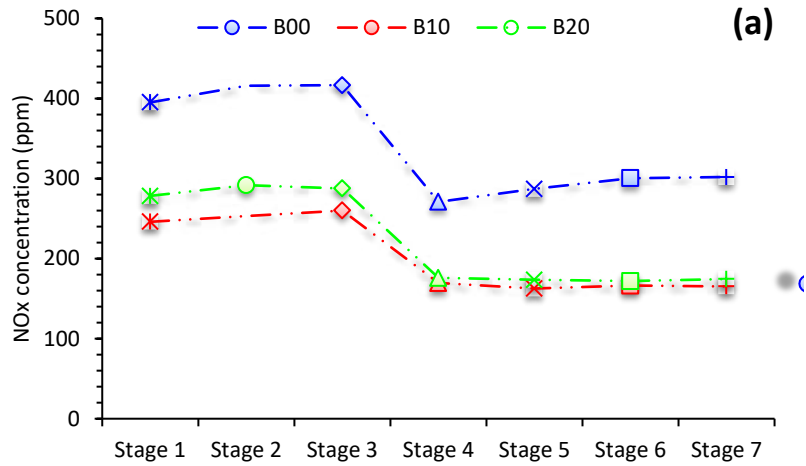
850

851 Table A3: CO₂ correlation test to confirm the test repeatability:

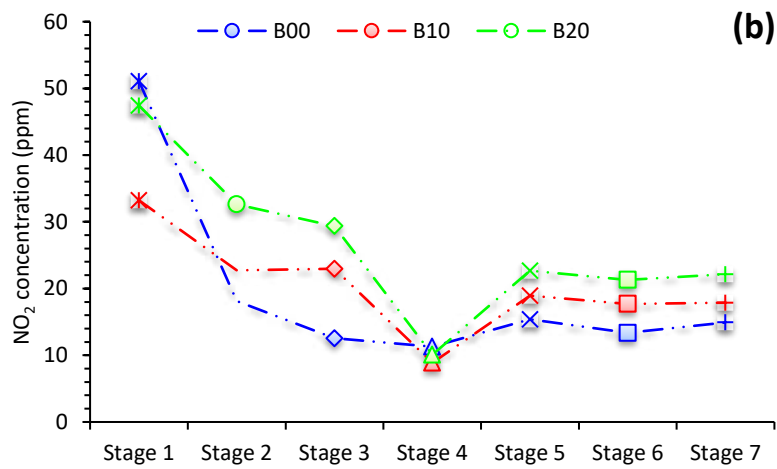
		Mean	CV (%)
Warm-start	Test I	6.47	0.51
	Test II	6.64	0.36
	Difference		0.17%
Cold-start	Test I	6.36	0.97
	Test II	6.51	2.27
	Difference		0.12%

852

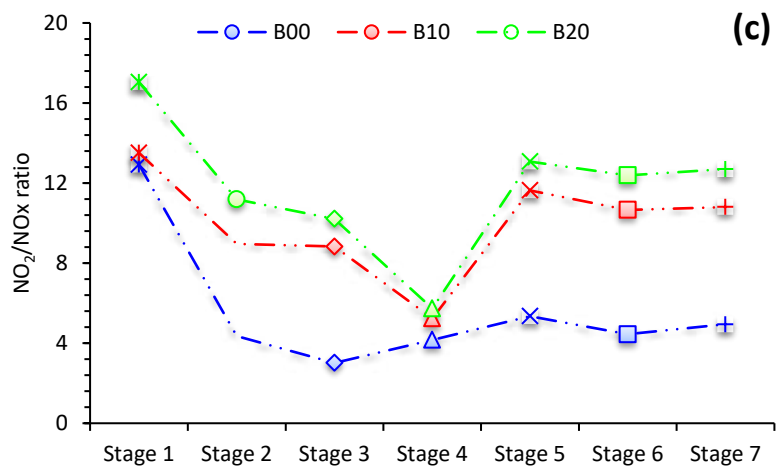
853 Figure A1 shows NO_x and NO₂ concentrations and NO₂/NO_x ratio.



854



855



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