Analysis of cold-start NO_2 and NOx emissions, and the NO_2/NOx ratio in a diesel engine powered with different diesel-biodiesel blends

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Abstract

In the transportation sector, the share of biofuels such as biodiesel is increasing and it is known that such fuels significantly affect NOx emissions. In addition to NOx emission from diesel engines, which is a significant challenge to vehicle manufacturers in the most recent emissions regulation (Euro 6.2), this study investigates NO_2 which is a toxic emission that is currently unregulated but is a focus to be regulated in the next regulation (Euro 7). This manuscript studies how the increasing share of biofuels affects the NO_2, NOx, and NO_2/NOx ratio during cold-start (in which the after-treatment systems are not well-effective and mostly happens in urban areas). Using a turbocharged cummins diesel engine (with common-rail system) fueled with diesel and biofuel derived from coconut (10 and 20% blending ratio), this study divides the engine warm-up period into 7 stages and investigates official cold- and hot-operation periods in addition to some intermediate stages that are not defined as cold in the regulation and also cannot be considered as hot-operation. Engine coolant, lubricating oil and exhaust temperatures, injection timing, cylinder pressure, and rate of heat release data were used to explain the observed trends. Results showed that cold-operation NOx, NO_2, and NO_2/NOx ratio were 31-60%, 1.14-2.42 times, and 3-8% higher than the hot-operation, respectively. In most stages, NO_2 and the NO_2/NOx ratio with diesel had the lowest value and they increased with an increase of biofuel in the blend. An injection strategy change significantly shifted the in-cylinder pressure and heat release diagrams, aligned with the sudden NOx drop during the engine warm-up. The adverse effect of cold-operation on NOx emissions increased with increasing biofuel share.

Keywords: NOx emissions; NO_2 emissions; NO_2/NOx ratio; biodiesel; cold-start; engine warm-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 reason for higher NOx with biofuels, a significant downside of these alternative fuels frequently reported in the literature [11-13]. The role of biofuels such as biodiesel in NOx variations is controversial. A large number of studies claim increases in NOx emissions owing to the oxygen content of biodiesel but there are also a significant number of studies claiming otherwise [14-16].

Between vehicle emissions, NOx emissions are of significant importance due to their adverse effects on health and the environment [17, 18]. The term NOx is representative of several nitrogen compounds but is predominately comprised of nitrogen oxide (NO) and nitrogen dioxide (NO_2). Typically, NO is a product of the combustion process which forms within the combustion chamber; while, NO_2 can form in several locations in addition to in-cylinder combustion where it forms from the existing NO via a conversion reaction [19]. However, the different NO_2 formation pathways are an active area of research.

NO_2 is of importance not only because it can cause adverse health effects, particularly on the respiratory system [20], but also owing to how reacts in the atmosphere to form ozone and acid rain [21]. European Environmental Agency (EEA Report No 12/2018 Air quality in Europe) reported that a high NO_2 ratio in the exhaust emissions can impact the urban atmospheric chemistry, therefore the air quality. This report stated that the concentrations of ground-level ozone (O3) had an increase following the increase in diesel vehicles' NO_2 emissions. NO_2 is currently unregulated but there is a focus to be regulated in the upcoming emissions regulation (Euro 7).

The ratio of NO_2 in NOx plays an important role in modern vehicle after-treatment systems such as SCR-catalyst systems (SCR stands for selective catalytic reduction). SCR systems rely on a catalytic reaction with ammonia, the oxygen demand and fast reactions which are highly dependant on the proportion of NO_2 in NOx, otherwise known as the NO_2/NOx ratio [19, 22].

There are various strategies proposed in the literature to reduce NOx emissions such as using different additives [23, 24]. However, after-treatment systems are commonplace in the mitigation of NOx emissions [25, 26]. Praveena and Martin [27] reviewed different after-treatment techniques of NOx emissions reduction in CI engines. For example, they showed that a urea SCR can reduce NOx by 98-99% with a warmed-up engine. They also studied the effect of exhaust temperature on NOx control techniques, reporting that the performance of after-treatment systems depends on the engine operating condition, as well as the state. A study by Mera et al. [28] used a modern SUV diesel vehicle equipped with SCR and reported that during cold-start, NOx emissions were 2.7 times higher than the Euro 6 NOx emission limits, while with the warmed-up engine, cold-start emissions decreased by 92%. During cold-start operation, after-treatment systems are known to be not well-effective and emissions are largely untreated within this period. Car manufacturers can use different injection strategies to reduce NOx emissions during this period, which will be shown in this study; however, the NOx reduction is not as significant as when using SCRs.

During cold-operation, the temperatures of the engine block and components are not optimal, and the cold engine lubricating oil also has a subsequent high viscosity [29, 30]. These factors lead to higher friction losses, therefore more fuel is needed to maintain the output power. It has been frequently reported that cold-operation leads to higher fuel consumption [31, 32] and lower engine power [33, 34]. Subsequently, cold-operation leads to higher exhaust emission [35, 36].

It is known that the engine is cold when it is turned on after being parked for some hours over the night or during the day when the driver is in the office. That is the case for many vehicles in cities and cold-start operation is an inevitable part of their daily norm [37].

New vehicles need to be equipped with after-treatment technologies in order to comply with the type approval tests and receive the emissions certification. Given that a significantly high portion of harmful emissions can be removed by after-treatment systems, the cold-start period, within which the after-treatment systems are not working, contributes heavily to the total emissions. This, and the fact that cold-start usually takes place in urban areas (harmful to human health), and the increasing share of biofuels in the market all highlight the importance of understanding cold-operation with biofuels. Given that a relatively large portion of short trips occur when engines are cold, emissions from cold-start are of importance for urban driving conditions [38]. This is particularly significant when it comes to NO_2 and NOx emissions with biofuels during cold-operation, as there are not many fundamental studies on NOx (and no study on NO_2) during engine warm-up with biofuels. Also, most such studies are limited to the defined cold-operation period as most regulations (e.g. EU Directive 2012/46/EU) define the warm-up period from engine start (at ambient temperature after a proper engine-off time) either for the first 5 min of operation or the period in which the engine coolant temperature increases from ambient temperature to 70°C. Previous studies from our research group have shown that engine performance and emissions outside this narrowly defined boundary are still significantly impacted by sub-optimal engine temperature [39, 40].

Many papers have been published on cold-start emissions from a diesel engine. Within these papers, a small portion evaluated NO_2 and the NO_2/NOx ratio during cold-start in a diesel engine. And from these papers, only a few exist on the topics of NO_2 and the NO_2/NOx ratio during cold-start in a diesel engine using alternative fuels. For example, Lapuerta et al. [41] evaluated the NO_2/NOx ratio in addition to different exhaust emissions during a drive cycle (including a cold-start section) using a glycerol-derived advanced biofuel. Another study evaluated cold-start idle emissions (including NO_2) in a diesel engine using ethanol and diethyl ether blends [42]. Using hydrogenated vegetable oil and biodiesel, Pechout et al. [43] reported different emissions including NO_2 during the cold-start section of different driving cycles. There are also few more articles in this field reporting NO_2 and the NO_2/NOx ratio emissions during cold-start engine operation using alternative fuels [44-46]. However, after an extensive literature review, we could find no literature which investigates NO_2 and the NO_2/NOx ratio with alternative fuels at different stages of engine warm-up including cold-start and also phases outside the officially defined cold-start boundary (EU Directive 2012/46/EU) which cannot be considered as hot-start either. In engine calibration, after-treatment systems and injection strategies are mostly based on the regulated cold-start period. However, this study shows that the period in which engine emissions are negatively affected is significantly longer when compared to the official cold-start boundary. This study intends to investigate 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.

2. Methodology

Given that this study aims to investigate the effect of engine temperature and fuel properties on NOx, NO_2 and the NO_2/NOx ratio at different stages of the engine warm-up period, it was opted to use an engine with no after-treatment systems (e.g. EGR, SCR, DPF) so that the emissions are not dependent on such devices (type and performance) to better analyse the actual engine and combustion dependent emissions [47, 48]. This experimental investigation used a turbocharged Cummins ISBe220 engine. The highest power and torque of this engine are 162 kW (at 2000 rpm) and 820 Nm (at 1500 rpm), respectively. Table 1 shows the specifications of the engine.

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)

Figure 1 illustrates the test setup. Engine, emissions and dynamometer data were collected from the dynamometer control system. For the emissions, a fraction of the exhaust gas from the exhaust manifold was directed to a gas analyser via a copper tube fitted with a HEPA filter and water trap which were placed in the sampling line as per the recommendation of the analysers' manufacturer. It was necessary to use a filter in front of the gas meter, as without it, the instrument would become contaminated in a one single measurement. The gas adsorption and pressure loss of these filters are negligible given that they are designed to only remove the moisture and particulate matter. Parker miniature coalescing HEPA filters (02F series) were utilised in this study. These filters are highly efficient in removing the liquid aerosols and submicron particulate matter. An air-water separator model P010A was used in the sampling line to remove moisture. A water trap was used instead of a dryer as dryers are mostly effective in a narrow window of flow rates and also losses are significant for dryers. In general, dryers are not suitable for raw exhaust because of the very high temperature of the raw exhaust, and also dryers would get dirty after a short sample making it difficult to do continuous measurements [49].

NOx, NO_2 and NO were measured with a CAI-600 CLD NO/NOx analyser. A Kistler type 2614 crank angle sensor and a Kistler 6053CC60 pressure transducer were connected to a DT9832 A-to-D convertor to collect the in-cylinder data (crank angle, pressure and injection signal). To determine the fuel injection timing an excitation offset was applied to the recorded injector signal [50]. Refs. [51, 52] contains more specific information about the in-cylinder data collection facility.

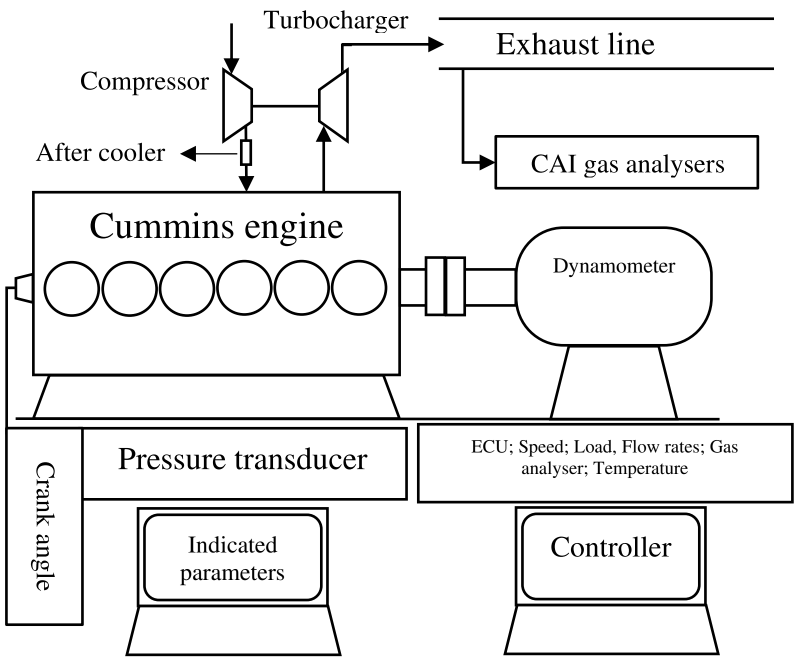

Figure 1 Test setup_schematic diagram of the experimental facility

The tested fuels in this study were selected in such a way that they can cover past, current, and future biofuel blending ratios likely to be on the market. Therefore, this study used diesel (denoted as B00), a blend of 10% (by vol.) biofuel with diesel (denoted as B10) and a blend of 20% (by vol.) biofuel with diesel (denoted as B20). The biofuels were derived from coconut oil. In terms of fuel properties, even a low blending ratio had a significant impact on the fuel properties. For example, the density of the tested diesel (B00) in this study was 0.84 kg/m^3; the density of B10 and B20 were 0.848 and 0.855 g/cc, respectively. The lower heating value of B00 was 41.77 MJ/kg for B10 and B20 it was 41.17 and 40.58 MJ/kg, respectively. While the changes in fuel properties were small, the literature reported that even these small changes can notably affect engine performance and emissions [53-55]. The lower calorific value and higher density of biofuels have negative impacts on engine power and increase fuel consumption [56]. A critical fuel property that makes biofuel different is the fuel oxygen content—diesel has no oxygen content. It has been frequently reported that this fuel property is the reason for decreased PM [57, 58].

In terms of the engine operating conditions (load and speed) during cold-start tests, most studies in the literature used a driving cycle (such as NEDC or WLTP) analysing the cold-start section of the cycle as compared to the rest of the cycle. These driving cycles consist of abrupt load and speed changes [59, 60]. NOx emissions are affected by different factors such as engine load, speed, and injection parameters, this research aims to investigate the effect of transient engine temperature and fuel properties during cold-start. In order to minimise the number of variables, and therefore facilitate a fundamental investigation on the impact of the engine state and fuel properties, this study used a constant speed (1500 rpm) and load (25%).

The experiments were conducted according to the regulation for cold-start test preconditioning (EU Directive 2012/46/EU) which requires 12 hours of natural soaking at ambient temperature (or 6 hours forced cool) before the engine starts. Before each test, the engine lubricating oil and coolant temperatures were checked to make sure they were the same as the ambient temperature in the engine lab (which was equipped with a ventilation system). For each cold-start experiment, the engine ran for at least 30 min at a constant speed (1500 rpm) under a quarter load. The collected data were classified into different categories, as described below. For more information about the test repeatability, error analysis, equipment accuracy and measurement uncertainty, please refer to Appendix.

In diesel engines, the formation of NOx depends on various parameters such as engine load, speed, injection parameters, fuel properties, and after-treatment systems. Within the cold-operation period, the after-treatment systems are not very effective, and the engine temperature and fuel properties are the driving factors in NOx formation. Figure 2 shows temperature change in the engine coolant and lubricating oil as the engine warmed up using data from various temperature sensors collected with the engine control unit (ECU)—through the controller area network (CAN) via the SAE J1939 standard.

The EU Directive 2012/46/EU regulation defines the cold-operation period from the engine start for either for the first 5 min or until the temperature of coolant increases from ambient temperature to 70°C. It can be seen in Figure 2 that after the defined cold-operation period, the coolant and lubricating oil temperatures are still increasing, indicative that the engine temperature is still not optimal. The lag between lubricating oil temperature and coolant temperature during warm-up shows that even when the coolant temperature was optimal, the engine temperature was not optimal because the lubricating oil temperature is still increasing. There are some studies in the literature showing the effect of this lag and the sub-optimal temperature outside the defined cold-operation boundary on engine performance and emissions [39, 40]. Figure 2 also shows the start of injection data which is the time at which the fuel injection into the combustion chamber begins. This parameter is typically expressed in the crank angle domain. It can be seen in the figure that the injection strategy of the tested engine, which is commanded by the ECU, changes when the engine coolant temperature reaches 65°C by retarding the start of injection from 353 to 361 (crank angle degree). Given that injection parameters significantly affect NOx emissions [26, 61], the transition period also needs to be taken into consideration.

As discussed, and shown in Figure 2, during engine warm-up, there are several stages with combinations of variables and characteristics. Therefore, to better analyse the influential parameters, this study divides the warm-up period into several stages to minimise the number of variables in each stage. This is done by splitting the warm-up period into 7 consecutive stages (each two min).

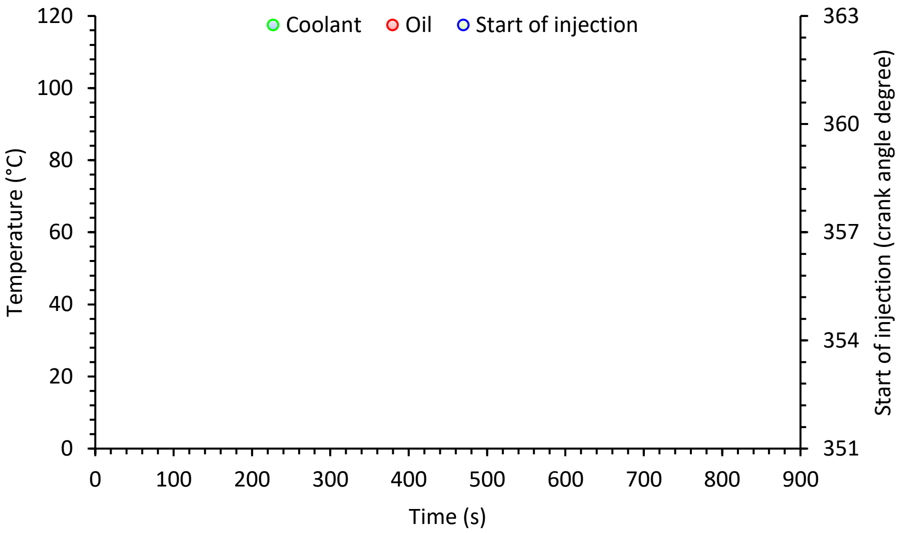

Figure 2 Start of injection, engine lubricating oil temperature, and coolant temperature during engine warm-up with B00

3. Results and Discussions

This section studies NOx, NO_2, and the NO_2/NOx ratio during engine warm-up. As mentioned, the engine warm-up period is split to 7 consecutive stages, each of two min. The difference between stages shows the effect of engine temperature on different parameters. Exhaust temperature can be representative of the combustion temperature showing how the engine warms up. Apart from the engine load and speed, the combustion temperature depends on different parameters such as temperatures of the engine block, cylinder wall, lubricating oil, coolant, and fuel.

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

Stage 1 to 5, and then stabilised during Stages 6 and 7. For example, with B20, the exhaust temperature increased gradually from 290°C in Stage 1 to 350°C in Stage 5 and then stayed at 358°C in Stages 6 and 7.

Stages 1 and 2 represent the cold-operation, these stages are within the initial 5 min of the test and the temperature of engine coolant is lower than 70°C (Directive 2012/46/EU). Within these two stages, the coolant temperature and lubricating oil temperature are sub-optimal. Stages 3, 4 and 5 cannot be considered as cold-operation based on the definition in the regulation (Directive 2012/46/EU). However, they cannot truly be considered as hot-operation either as Figure 3. shows that within these stages the exhaust temperature is still increasing.

Within Stages 3 and 4, the engine coolant and lubricating oil temperatures are still increasing. Stage 5 analysis also showed that within this stage while the temperature of engine coolant was optimal, the temperature of engine lubricant was still increasing. Therefore, results from Stage 5 can show the effect of sub-optimal engine lubricating oil temperature [39, 40]. On the other hand, within Stages 6 and 7, the temperatures of engine coolant and lubricating oil were optimal; therefore, these two stages can represent hot-operation. The stability of the engine temperature within Stage 6 and 7 can be seen in the exhaust temperature profile shown in Figure 3, where the exhaust temperature did not change from Stage 6 to 7. It can be seen that at all of the stages, B00 had the highest, and B20 had the lowest exhaust temperature (except for Stage 1 in which B10 had a slightly lower value than B20, 288 and 289 °C). Also, B10 had a less significant difference with B00 when compared to B20.

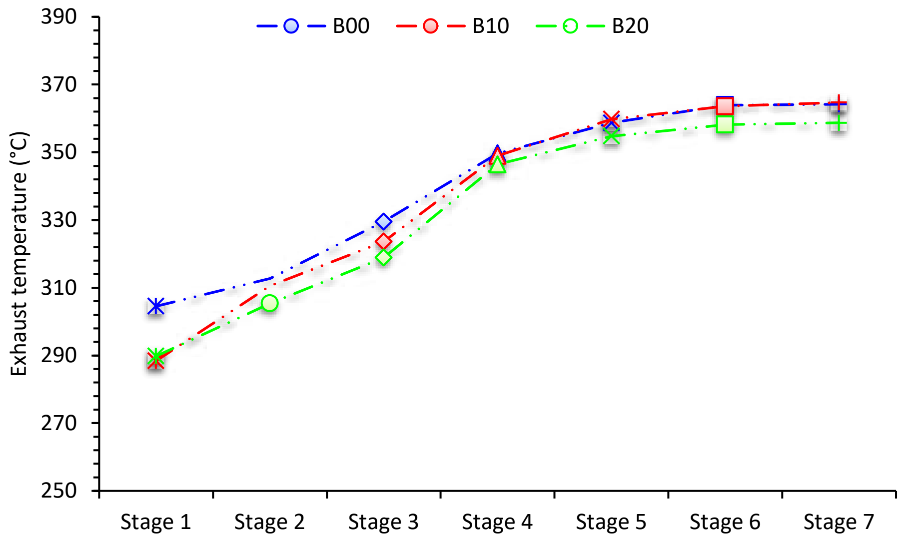

Figure 3 Exhaust temperature at different stages of engine warm-up with B00, B10 and B20

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-operation on NOx emissions increases with biofuel share. This observation is similar to another study in the literature [40].

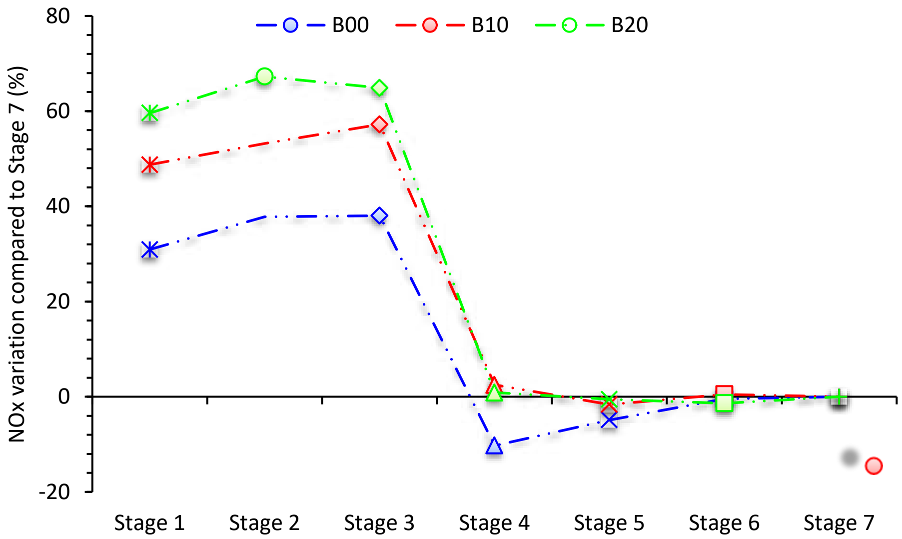

Figure 4 NOx variation compared to Stage 7 at different stages of engine warm-up with B00, B10 and B20

Within the cold-operation period, it can be seen in Figure 4 that NOx emissions increases as the engine warms up from Stage 1 to 2. Across this period, For example, B20 NOx emissions increased by 5%. It has been frequently reported that NOx emissions depend on combustion temperature [26, 61]. It can be seen in Figure 3 that the exhaust temperature, which can be taken as an indicator of the combustion temperature, increased within these two stages. Therefore, increasing combustion temperature is the likely reason for the increasing NOx [62, 65]. This is the same for Stage 3, where NOx increased to a higher value. However, there is a sharp drop after this stage.

The observed sharp drop in NOx emissions is due to an injection strategy change [62]. It was shown in Figure 2 that for the tested engine, during the engine warm-up period, when the engine coolant temperature reached 65°C, the injection strategy commanded by the ECU changed to a retarded injection mode [31, 39]. It can be seen that the injection strategy is a significant influential factor on NOx emissions, as reported in the literature [66, 67]. When the start of injection was constant during Stages 1 and 2, the main influential parameter was the combustion temperature (shown by exhaust temperature in Figure 3). This is the same from Stages 4 to 5, where the start of injection was stable at the retarded (compared to Stages 1 and 2) crank angle, NOx increased as the combustion temperature increased [15, 26]. However, the NOx graph shifted to lower values because of the retarded injection strategy . During Stages 6 and 7, the start of injection was constant and the combustion temperature stabilised, therefore NOx emissions did not change.

The gradual increase in combustion temperature, shown by the exhaust temperature in Figure 3, is not well aligned with the trend of NOx within the stages in Figure 4, as NOx increased, dropped and then increased before becoming stable. Therefore, the observed trend warrants additional analysis, NOx emissions during engine warm-up are affected by more than just engine temperature.

NOx emissions are significantly affected by the nature of combustion [26]. The in-cylinder pressure profile provides insight into how combustion changes as the engine warmed up. Figure 5 shows in-cylinder pressure diagrams at 7 stages of engine warm-up. As illustrated, there are two different shapes for the in-cylinder pressure diagram. One is related to Stages 1, 2, and 3. Within these three stages, as the engine warmed up, the diagram slightly moved toward lower crank angles, and the peak associated with combustion increased. However, the change was not significant. After the injection strategy change, the motored peak (the first peak, prior to combustion) became more obvious – the second peak is from combustion, this shape is attributable to the retarded ignition strategy causing combustion to happen after TDC. The systematic increase in the peak pressure of the motored peak (the first peak) is indicative of the cylinder inside being warmer at the beginning of the cycle. The impact of this change in injection strategy was also seen in Figure 4, where there was a significant drop in NOx from Stage 3 to 4. The higher peak combustion pressure is indicative of a hotter in-cylinder environment, hence a greater production of thermal NOx [26].

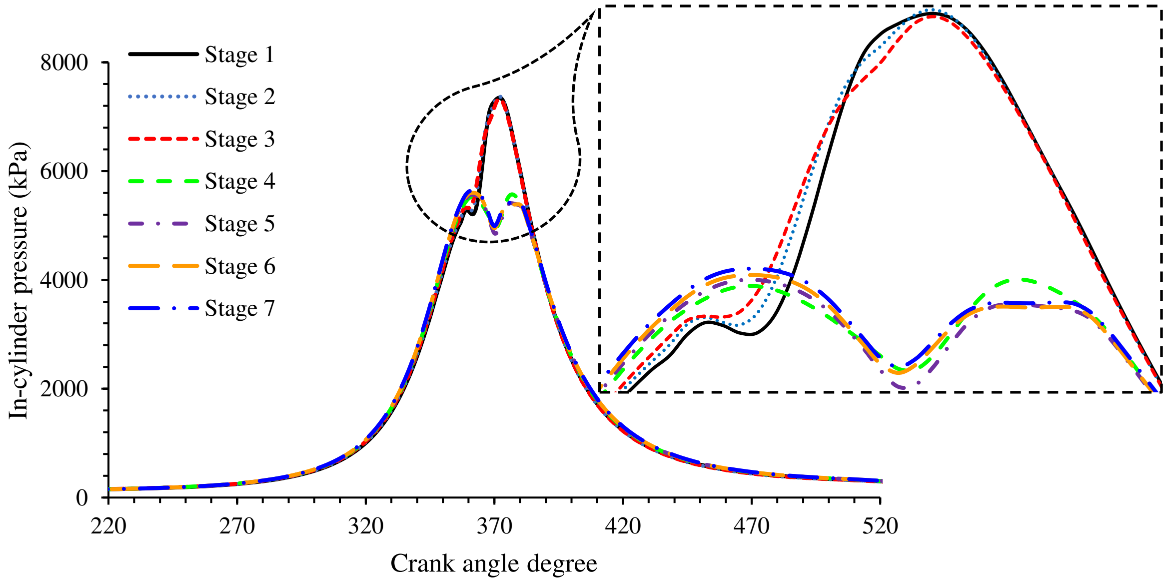

Figure 5 In-cylinder pressure during the engine warm-up with B00

Figure 6 shows the heat release diagram at 7 stages of the engine warm-up period. Heat release is another combustion characteristic parameter, commonly used to interpret NOx emissions [65]. The heat release diagram can show four phases during combustion [65]. The first one is the ignition delay period, which starts at the start of injection and ends at the start of combustion. In this period, fuel is injected but it does not ignite. The heat release diagram is negative in this period owing to fuel vaporisation and subsequent chemical reactions [65, 68]. The injected fuel also absorbs sensible energy due to the lower temperature of the fuel compared to the in-cylinder environment, the so-called *cooling effect [65]*. The second phase is premixed combustion, which is related to the initial combustion of the fuel/air mixture. In this phase, the heat release diagram starts from zero (at the start of combustion), increases to a maximum value, and then drops to an intermediate minimum value. In this phase, a high proportion (typically a third) of the heat release happens. As can be seen, there are two different shapes for the heat release diagram. The reason is the change in injection strategy (retarded start of injection). The first shape is related to Stages 1, 2, and 3, where the start of injection stays constant. It can be seen that within these three stages, as the engine warmed up, the start of combustion occurred slightly earlier—the ignition delay decreased [69, 70]. This leads to a shorter time for the fuel to mix with the air and a subsequent decrease in the number of potential ignition kernels. This results in a decrease in the first peak value, which is caused by the rapid combustion of the premixed portion of the fuel as the engine warms. Diffusion burning, or mixing-controlled combustion, is the third phase of combustion in which the combustion of the available air/fuel mixture controls the burning rate. This phase can be seen in the heat release diagram after the premixed combustion phase where the heat release increases from the intermediate minimum point to the second peak value in the diagram and then decreases gradually. Late combustion is the fourth phase in which there is some possible energy release from unburned fuels. However, the heat release rate is low within this phase due to the expanding volume causing a significant decrease in the in-cylinder temperature. It can also be seen in Figure 6 that as the engine warmed up, the second peak of the heat release diagram, which is related to the mixing-controlled combustion phase, was increasing. Figure 4 showed that NOx increased gradually through these three stages as the engine warmed up.

A similar trend and tendency of having a double peak in the heat release diagram can be seen for the second shape which is related to Stages 4 to 7. Compared to the first shape (Stage 1 to 3), in Stages 4 to 7, there is a significant shift in the heat release diagram toward the higher crank angles. This is because of the injection strategy change, this shift is also aligned with the sharp drop in the NOx emissions shown in Figure 4. It can be seen in Figure 6 that on the heat release diagram, with the new start of injection, as the engine warmed up through Stages 4 to 7, the first peak value decreased and the second peak increased. As with Stages 1 to 3, this is associated with a systematic NOx increase. The reason could be that the increase in diffusion combustion is prolonging the time the in-cylinder environment is at an elevated temperature, thereby giving more opportunity to produce thermal NOx.

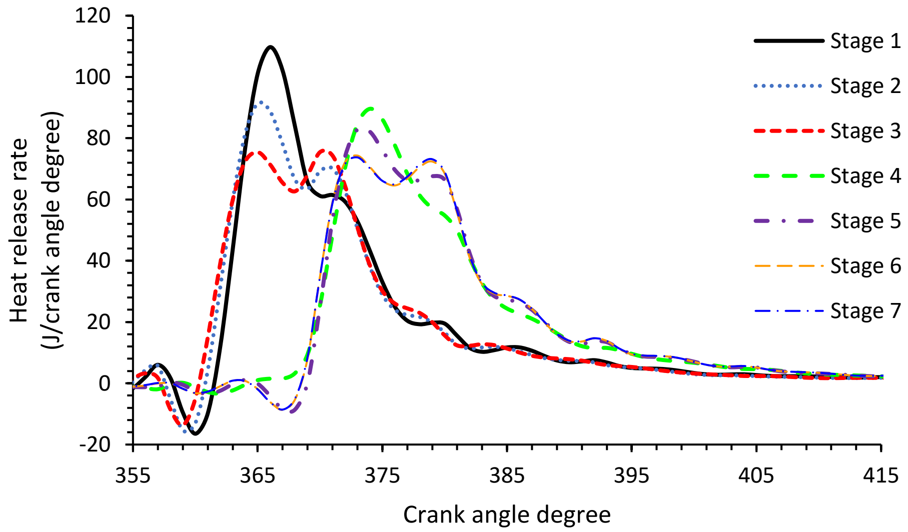

Figure 6 Heat release rate at 7 stages of engine warm-up with B00

The mechanisms of NOx formation in diesel engines are well known [65]. This includes thermal NOx, fuel NOx, and prompt NOx [61, 65]. Between them, thermal NOx is the dominant one in a diesel engine. The NOx umbrella covers various nitrogen compounds. However, in engine NOx exhaust emissions, nitrogen monoxide (NO) and nitrogen dioxide (NO_2) comprise the significant majority. Between NO and NO_2, NO is typically the dominant one. However, in some modern engines, the ratio of NO_2 to NO has increased [71]. NO_2 can also form from an already existing NO [19]. Despite this, in most diesel engine studies, NOx formation can be accurately described from NO formation mechanisms, without an explicit explanation for NO_2 [19]. Based on that, it is reasonable to assume that NO (and NO_2) will show a similar trend to NOx. This study shows that NOx and NO_2 are higher during cold-operation. However, they have a different trend when it comes to the effect of temperature increase.

NO_2 can form from NO through the reaction of $NO + HO_2 \rightarrow NO_2 + OH$ [72]. This reaction is between thermal NO, which forms in the hot flame front, and HO_2 which forms in relatively cold regions of the unburnt fuel/air mixture near the flame front [19, 21, 73]. The NO to NO_2 conversion depends on the temperature of the mixture, and the NO and HO_2 concentrations; however, the availability of HO_2 is the predominant factor [74]. HO_2 radicals form in the relatively low-temperature regions of the unburned air/fuel mixtures before the mixture is consumed by flame propagation. This explains the relatively high NO_2 formation during cold-operation. However, as the engine warms up, thermal NO increases, but the decreased cold regions of unburned air/fuel mixture can tend to lower HO_2 radicals, therefore reducing NO_2 formation [19].

The generated NO_2 can revert to NO via $NO_2 + OH \rightarrow NO + HO_2$ when the HO_2 concentration is low, or via $NO_2 + H \rightarrow NO + OH$ reaction when the bulk temperature is high [19]. At low temperatures, mixing the cool bulk mixture with the NO_2-contained mixture can quench the NO_2 to NO conversion, therefore a portion of NO_2 can be retained [19]. For example, at the early stages of cold- operation (Stage 1), the low temperature of the cylinder environment, fuel, and air can lead to a high portion of cool bulk mixture far from the sprayed fuel plume, which can quench the NO_2 conversion to NO, therefore more NO_2 retains. This can be seen during the early stages of cold-operation where in addition to high NO_2 formation (because of high NO and NOx formation), the NO_2/NOx ratio is high as well.

3.2 Nitrogen dioxide

Figure 7 (a) shows how NO_2 changes at different stages of engine warm-up. It can be seen that similar to NOx (Figure 4), NO_2 during cold-operation is significantly higher than hot-operation. For example, NO_2 during Stage 1 with B00, B10, and B20 was 2.42 times, 86%, and 1.14 times higher than Stage 7, respectively. Higher NO_2 emission during cold-start when compared to hot-start was reported in the literature [75]. Figure 7 (a) shows that during engine warm-up, NO_2 decreased from Stage 1 to 3 as the engine temperature increased, dropped in Stage 4 because of injection strategy change, increased slightly in Stage 5 as the engine warmed up and then stabilised in Stages 6 and 7. As the engine warmed up, the difference decreased from 1.14 times higher (in Stage 1 compared to Stage 7) to 47% (Stage 2) and 32% (Stage 3). After that, NO_2 dropped to 55% lower than Stage 7 in Stage 4, and then increased in Stage 5 and finally stabilised. Comparing Figure 4 to Figure 7 (a) shows that the temperature increase within the first three stages of engine warm-up has a different effect on NO_2 and NOx, as NOx increased and NO_2 decreased. This can be explained by looking at the formation mechanism of NOx and NO_2.

Figure 7 (b) shows how the NO_2/NOx ratio varied at different stages of engine warm-up. It can be seen that the NO_2/NOx ratio during Stage 1 was higher than at other stages. The NO_2/NOx ratio during Stage 1 with B00, B10, and B20 was 8, 3, and 4% higher than Stage 7, respectively. Further analysis showed that the NO_2 contribution in NOx was 13-17% during Stage 1, while during Stage 7 it was 5-13%.

The trend shows that during engine warm-up, the NO_2/NOx ratio decreased from Stage 1 to 3 as the engine temperature increased, before increasing to become stable from Stage 5. However, during Stage 4 in which the injection strategy changed, the NO_2/NOx ratio behaved differently.

As the temperature increased, NOx formation increased because of the thermal NO mechanism. While higher NO formation can lead to higher NO_2 formation, the increasing engine temperature can lead to more conversion of NO_2 to NO, thereby causing a decrease in the NO_2/NOx ratio. This can be a reason for the decreasing trend of NO_2/NOx ratio with engine temperature. As seen, from Stage 1 to Stage 3, as the engine warmed up, the exhaust temperature (Figure 3) and NOx increased (Figure 4), while NO_2 (Figure 7(a)) and the NO_2/NOx ratio (Figure 7 (b)) decreased.

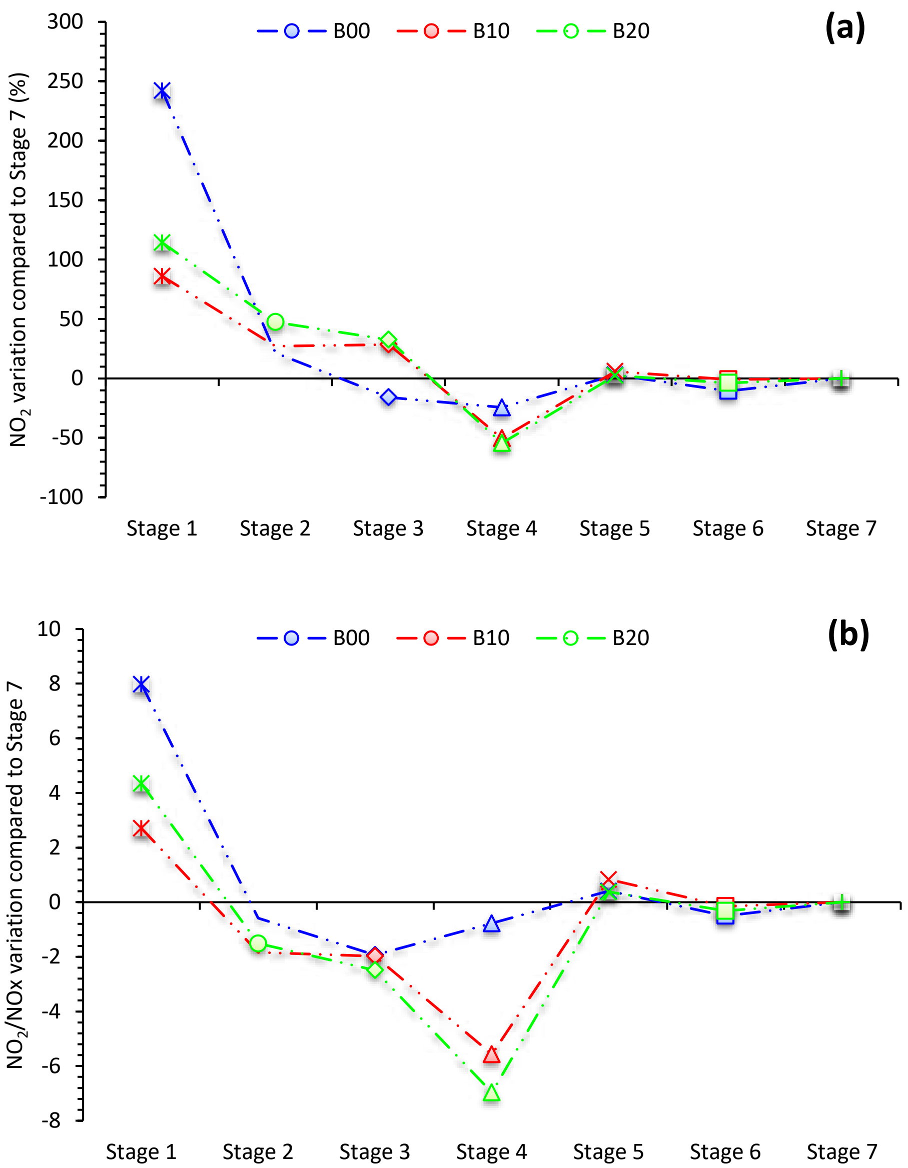

Figure 7 NO_2 (a) and NO_2/NOx (b) variations compared to Stage 7 at different stages of engine warm-up with B00, B10 and B20

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 up, the NO_2/NOx ratio difference between B00 and the biofuel blends increased. The reason for this could be because adding biofuel to the blend increases the fuel oxygen content and decreases the calorific value of the fuel enlarging the cooler regions which leads to more NO_2 from the reaction of NO and HO_2 [76], given that the NO to NO_2 conversion depends on the temperature of the mixture [19, 74]. It also adversely impacts the NO_2 destruction reaction from NO [65]. Also, biofuel being oxygenated is of importance as the oxygen release from the fuel readily oxidizes with nitrogen and NO.

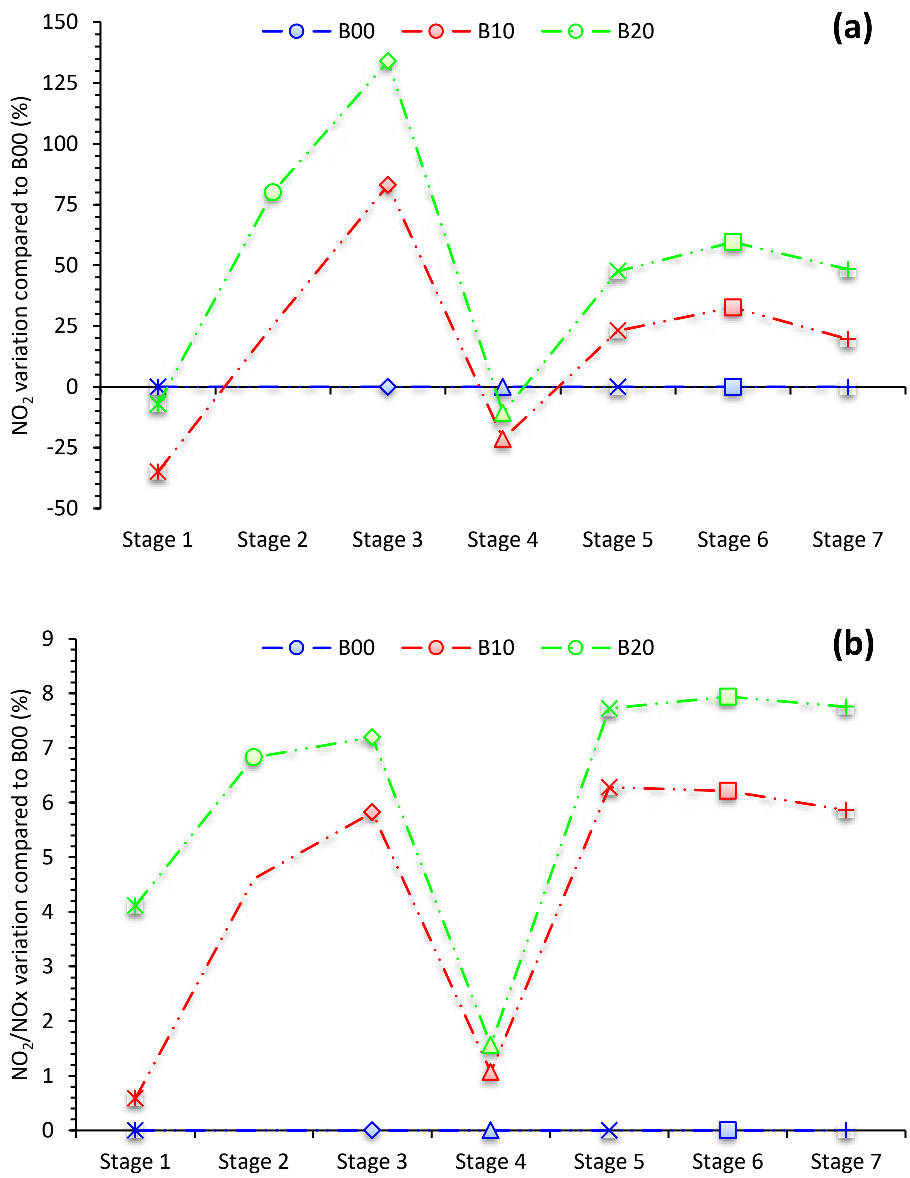

Figure 8 NO_2 (a) and NO_2/NOx ratio (b) variations compared to B00 at different stages of engine warm-up with B00, B10 and B20

3.3 Practical implications of this study and limitations

Because of the adverse health impacts and high cost of diesel/petrol, there are plans and measures in place to increase the share of biofuels such as biodiesel. However, vehicle emissions are an issue, and authorities and decision-makers have been limiting emissions by tightening the permissible emission thresholds in the regulations (such as Euro1-6). This research shows that when it comes to NOx emissions, the current increasing share of biofuels can have more adverse effects, especially during cold-operation—which is a part of the daily driving norm for many vehicles in cities—where the after-treatment systems are not well-effective [28]. Emissions from the cold-start period are important as this period is within the first 5 min of starting a vehicle, during which time many vehicles are still near urban areas [38]. Results from this study highlight the negative effects of this period on regulated and unregulated exhaust emissions, which need to be taken into consideration. This study shows the importance of regulating NO_2 emissions in future regulations, or even in the new amendments of the current regulations. In addition to that, in engine calibration, after-treatment systems and injection strategies are mostly based on the regulated cold-operation period. However, this study shows that the period in which the engine emissions are negatively affected is significantly longer than the official cold-start boundary.

Different fuels have different chemistry, therefore, different effects on combustion behavior, which consequently affects emissions. Studying more types of biofuels with different properties can help the literature in this area. Another limitation of such studies can be related to engines. Due to fuel chemistry influences prior to combustion, engines with different injection strategies and in-cylinder pressure profiles are likely to exhibit different combustion behavior [52, 77]. This is a common limitation of any fuel study, however, to some extent, this has been controlled in our experiment by reducing variables and using a mid-sized multi-cylinder engine with a modern fuel system that uses a single pulse for injection, rather than a complex delivery strategy which would limit the applicability of the results in a general 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

because of the injection strategy change, increased slightly and then stabilised. With different fuels, the NO_2 contribution in NOx was 13-17% during cold-operation, while during hot-operation it was 5-13%.

- During cold-operation, with diesel, the effect on NO_2 was significantly higher when compared to other fuels.
- In most stages, NO_2 and the NO_2/NOx ratio with diesel were lower than the biofuel blends, with both NO_2 and the NO_2/NOx ratio increasing with the blend ratio.

The future research direction can be toward studying more types of biofuels with different properties. Also, calibration of the engine based on each fuel blend could be another direction.

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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%

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%	

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%	

Figure A1 shows NOx and NO_2 concentrations and NO_2/NOx ratio.

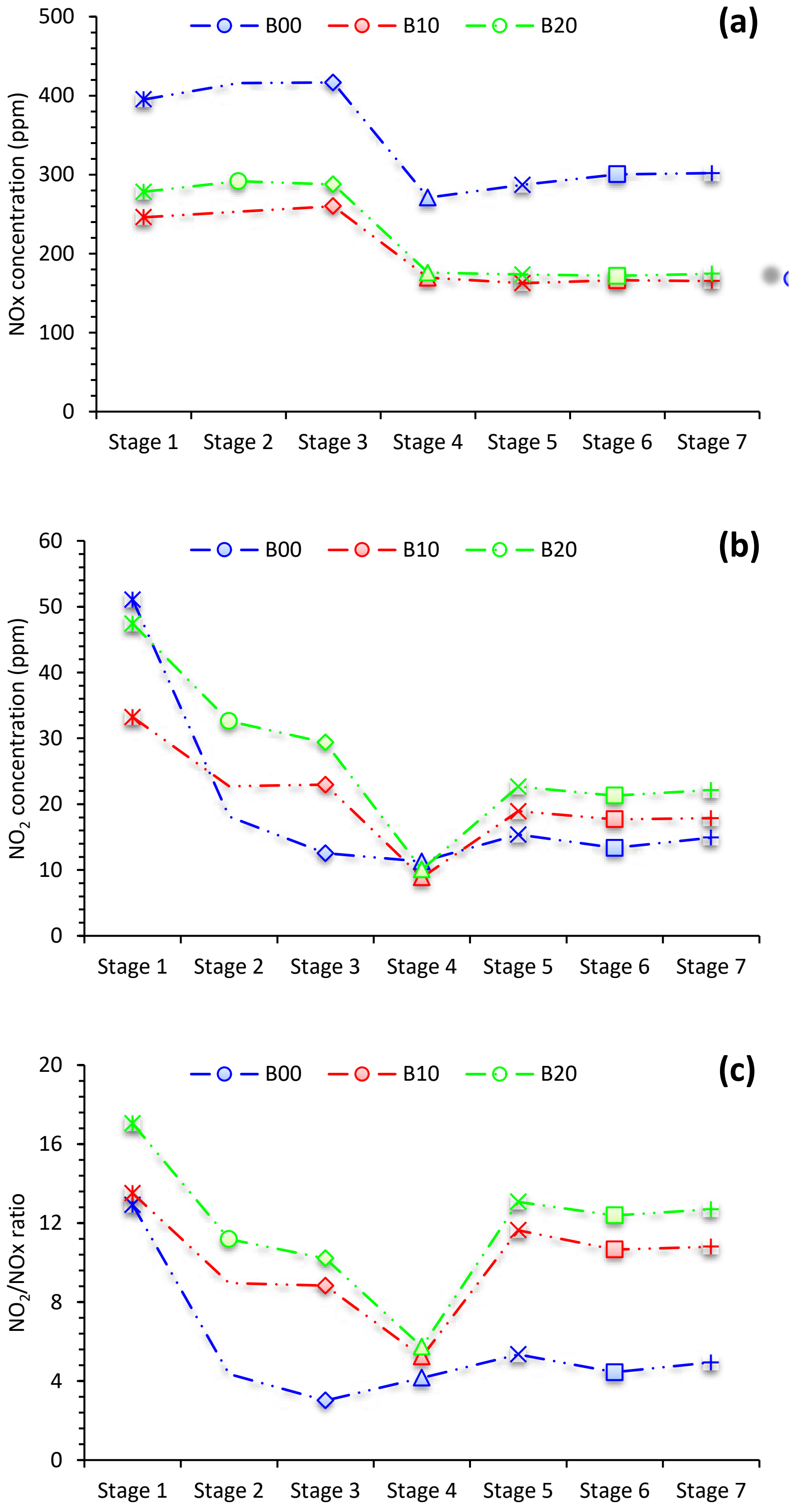

Figure A1 NOx and NO_2 concentrations and NO_2/NOx ratio at different stages of engine warm-up with B00, B10 and B20