Effect of equalising ignition delay on the combustion and soot emission characteristics of model fuel blends

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Abstract: This paper examines the effect of equalizing ignition delay in a compression ignition engine. Two sets of tests were conducted. A constant injection timing tests with start of fuel injection at 10° CAD BTDC and a constant ignition timing tests while also keeping the 10° CAD BTDC injection and adding ignition improver (2-ethylhexylnitrate -2EHN) to the fuel mixtures. Soot particles were characterised using DMS-500 instrument in terms of mass, size, and number. The experimental results showed that adding 2-EHN to the model fuel blends reduced the soot surface area, soot mass concentration and soot mean size. Replacing 20% (vol) of a C_7-heptane, with 20% of methyl-decanoate (an oxygenated C_{11} molecule) did not affect the ignition delay or rates of fuel air premixing, the peak in-cylinder pressure and heat release rates. Toluene addition (0 - 22.5% by vol) to heptane increased the mean size of the soot particles generated by only 3% while also resulting in a slight increase in the peak cylinder pressure and peak heat release rates. Blending toluene and methyl-decanoate into heptane without adding- 2EHN increased the premix phase fraction by at least 13%. However, adding 2EHN (400 -1500ppm), the premixed phase fraction decreased by at least 11%.

Key words: combustion characteristics, soot emission, compression ignition engine, ignition improver, premixed Phase

1.0 Introduction

For centuries now, compression engines fuelled with fossil diesel have been effective for power generation and heavy duty road transportation systems [1],[2]. Despite these significant contributions, they still suffer hugely from exhaust particulate emissions which degrade atmospheric air quality due to the toxicity of such particulates [3],[4,5]. Inhalation of particulate contaminated air has led and still leading to the rising global human morbidities and mortalities [6]. To control and reduce particulate emissions and their associated toxicities, there has been substantial body of research in the literature that employed several strategies. Such strategies have evolved from combusting fuels at low temperatures [7] or using diesel particulate filters [8] and to the reduction of toxic particulate precursors [9].

In recent days, the use of oxygenated fuels or biofuels have been investigated [10]. For example, Ning et al. [11] examined the effect of adding alcohols (methanol, ethanol and n-butanol) into diesel fuel on the emission and combustion characteristics in a direct injection diesel engine. They operated the engine at maximum speed of 2500rpm and a low indicated mean effective pressure (IMEP) of 0.75MPa. Ning et al. described that adding primary alcohols to diesel fuel did not only increase the combustion duration and ignition delay period but had also reduced particulate emissions. Huang et al. [12] investigated particle emission characteristics of a high-pressure common-rail engine under different EGR conditions. They used pure diesel (D100), 70%diesel30%gasoline, 70%diesel30%n-butanol and 70%diesel15%gasoline15%n-butanol for combustion. Their experimental results show that, with increasing EGR ratios, the in-cylinder pressure peak decreases and the heat release is delayed for the combustion of each fuel. In a computational perspective, Huang et al. [13] also developed and validated a new reduced diesel-n-butanol blends mechanism for engine applications. They confirmed that the proposed mechanism can be used to simulate the combustion of diesel or n-butanol-diesel blends in multi-dimensional CFD modelling.

Chen *et al.* [14] carried out comparative analysis of NOx emission of biodiesel and diesel. They reported that the biodiesel emitted more NOx than diesel at low and under low and medium speeds. In a related study, Chen *et al.* [15] studied the effects of blending 20%gasoline and 20%polyoxymethylene dimethyl ethers in diesel, named D80G20 and D80P20 respectively, on the combustion and emission characteristics of a common rail diesel engine. They found that, in comparison to diesel, D80P20 and D80G20 mostly reduced the duration of combustion, improved the brake thermal efficiency, increased the NOx emission and decreased the soot emissions and the number concentrations of ultrafine particles. In a recent study, Chen *et al.* [16] researched on the performance of a diesel–ethylene glycol (DEG) dual-fuel engine blend, with the blending ratio of ethylene glycol ranging from 0 – 15%. The combustion results showed that combustion process was highly affected by direct injection timing than by port injection timing.

Some recent studies have looked at how ignitability of fuels impact exhaust emissions. For example, Erman et al. [1] analysed the influence of cetane number of fuels on the combustion and exhaust emissions of seven fuel molecules in a compression ignition engine at a speed of 1200rpm and IMEP of 4 and 6 bar. They controlled the ignitability naturally using the seven fuels and by adding ignition improver into one fuel (hydrotreated non-dearomatized stream) to alter its ignition properties. Erman et. al reported that by varying the proportions of ignition improver, they observed an extended ignition delay at 6bar IMEP that caused the number of accumulation soot particles to increase.

Other studies have investigated the combinations of the two strategies employed by both Ning et al. [11] and Erman et al. [1]. For example, Qian *et al*. [17] proposed the combinations of post injection and the use of dimethyl carbonate (oxygenate) and exhaust gas recirculation (EGR) to produce low soot emissions. Qian *et al*. reported that due to low cetane number, the use of dimethyl carbonate delayed the combustion phase. However, when the cetane number was enhanced by adding an ignition improving additive, they reported that the delay in ignition duration decreased with slight increase in soot.

For more accurate predictions of combustion phasing, characteristics of emissions and their chemical kinetics in engines, several combinations of model fuels have been used either computationally in a gasoline homogeneous charge compression ignition (HCCI) engine or experimentally in a diesel engine at high pressure. Classical model fuel blends used to represent gasoline include mixtures of normal, iso and cyclo-paraffins, olefins and aromatics [18]. While in a diesel engine, Pfahl and Adomeit [19] burnt a mixtures of n-decane, methylnaphthalene and di-methylether and Helier *et al.* [20] burnt a mixture of heptane/toluene in a compression ignition engine.

Despite these research developments, there is still much to be done in understanding how equalising ignition delays of fuels influence their combustion and soot emission processes. It is also imperative to examine whether making the combustion processes better by altering the ignition chemistry will impact the combustion and exhaust soot emissions in a compression ignition engine. More so, investigating the effect of ignition improving additive on the exhaust soot emissions and premixed burn fractions has been rarely carried out. To do this, heptane, toluene and methyl-decanoate were chosen as model fuels in comparison with diesel fuel, since the later has complex composition and its ignition chemistry is holistically intractable. The reason for this selection is in two-fold. Firstly, the cetane number of heptane and diesel fuel are similar. Secondly, the soot chemistry database for both heptane and toluene is significant in the literature [21,22]. Commercial diesel fuel is composed of many aromatics and toluene is a representative of one-ring aromatics. The blends of heptane/toluene have therefore been utilised as model fuels in diesel engines [23,24]. Methyl decanoate on the other hand was selected as biodiesel surrogate.

It is therefore the purpose of this paper to achieve the following objectives:

i) Assess the combustion characteristics of binary and tertiary model fuel blends at both constant injection and constant ignition timings.
ii) Evaluate the percentage of premixed and diffusion combustion phases from the combustion of heptane/toluene/methyl-decanoate blends.
iii) Characterise the particulates (using DMS 500 instrument) produced from the combustion of the fuel mixtures in terms of number, size, and mass
iv) Investigate the effect of ignition improving additive on the exhaust soot emissions and premixed burn fractions of the fuel blends.

2.0 Experimental

2.1 Fuels

The model fuels tested are the reference fossil diesel procured from Halter-mann Carless Ltd and heptane, toluene and methyl-decanoate procured from Sigma Aldrich, both in the United Kingdom. Tables 1and 2 show the molecular structures and the properties of the model fuels, respectively. It is worth mentioning that the model fuels (heptane and toluene) are not practical fuels but are intended to give an indication of influence of proportions of aromatic components in diesel fuel.

In view of the complex composition of the fossil diesel fuel, heptane was used for comparison with the results of fossil diesel fuel. Heptane has cetane number close to that of the diesel fuel and there is a significant body of information in the literature on soot chemistry for heptane as well as for toluene [21], [22]. Aromatics constitute substantial proportion of commercial diesel fuel and toluene is a model to several of these aromatics; therefore, heptane/toluene blends have been recommended as convenient model fuels for compression ignition engines [23], [24].

The proportions of aromatics in diesel fuel ranged from 15 – 22.5%, and the fossil diesel fuel used in this work had 22.2 % total aromatics and hence; the idea behind the blending ratio used in this work.

Table 1: Fuels and Additive [20,25,26]

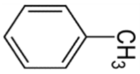
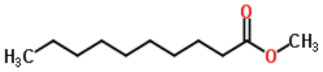
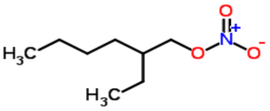
Fuel and Additive	Structure
Heptane	
Toluene	
Methyl-decanoate	
2 Ethylhexyl nitrate (2-EHN)	

Table 2: model fuel properties [20,25,26]

Fuel Properties	Diesel	Heptane	Toluene	Methyldecanoate	2-EHN
Assay (%)	-	99	> 99.8 (GC)	> 99	97
Fuel Nomenclature	Diesel	H	T	MD	2-EHN
H/C Ratio	1.771	2.28	1.143	2	2.125
PAH Content (% mass)	3.4	-	-	-	-
Boiling Point (°C)	271.0^{a}	98.3	110.6	224	210.9
Density (g/mL, 20 °C)	0.835	0.684	0.867	0.871	0.963
Cetane Number	52.7	54.4	7.4	51.6	-

Lower heating value (MJ/kg)	43.14	44.5	40.6	36.7	-

2.2 Experimental Conditions

Table 3 shows fuel blends which were made by volumetrically blending toluene and methyl-decanoate into heptane. It is noteworthy that 22.5 % (vol.) was the maximum proportion of toluene added into heptane and this proportion is similar to the mono-aromatics in most conventional diesel fuel [27]. Ignition delays of these fuel blends during combustion were recorded as shown in Table 3. Ignition delays were equalised by adding to the fuel blends, small quantities (in ppm) of an ignition improver (2-ethylhexylnitrate -2EHN). The ignition improver was added at ppm levels in order not to change the bulk fuel composition. The 2-ethylhexylnitrate equalised the ignition delays and only differed by the resolution of the engine shaft encoder (0.2 CAD) used for measuring engine in-cylinder pressure. The required dosages of the 2-EHN added to the fuel blends for ignition delay equalisation were established by iteration method. The iteration method for determining the required dosages of the 2-EHN added to the model fuel blends to achieve a given ignition delay duration involved adding a known volume (at ppm level) of 2-EHN to the model fuel blend. The fuel blend was then burn and the ignition delay duration was noted. The dosage of the 2-EHN added to the model fuels was then either increased or decreased depending on the ignition duration initially measured. When two readings of the dosages of 2-EHN and their corresponding ignition duration were recorded, the exact dosage of the 2-EHN needed to achieve a required ignition delay was then found by either lagrangian interpolation or extrapolation procedures.

Table 3: Equalised ignition delay for the model fuel blends

Blend Number	Fuel/ Fuel Blend	Ignition Delay (CAD)	2-EHN Dosage (ppm)	Ignition Delay after addition of 2-EHN (CAD)
0	Diesel start	9.4	-	-
1	100%H	9.4	-	-
2	85%H15%T	9.8	400	9.4

3A	77.5%H22.5%T	10.8	850	9.8
3B			1500	9.4
4	65%H15%T20%MD	9.8	-	-
0	Diesel Finish	9.4	-	-

All the engine tests were conducted at a constant speed of 1200 rpm, a fixed fuel injection pressure of 450 bar, a uniform IMEP of 7 bar. The constant injection and constant ignition tests were both carried out at 10 crank-angle-degrees (CAD) before-top-dead-centre (BTDC) with the constant ignition tests achieved while the ignition delays were equalised by adding 2-EHN to the fuels.

2.3 Experimental Set-up

The engine used was a 4-stroke, single cylinder compression-ignition engine and Table 4 lists the specifications for the facility. Figure 1 shows the schematic of the engine facility. The in-cylinder gas pressure was measured using a Kistler 6056A piezoelectric pressure transducer in conjunction with a Kistler 5018 charge amplifier, 1800 pulse per revolution (ppr) shaft encoder and a digital data acquisition system. The resolution of the in-cylinder pressure was 0.2 CAD. Detail description of the experimental set-up can be found in [28].

Table 4: Engine Specifications

Description	**Specification**
Bore	86 mm
Stroke	86 mm
Swept volume	499.56 cm3
Compression ratio (geometric)	18.3 : 1
Maximum in-cylinder pressure	150 bar
Piston design	Central ω – bowl in piston
Fuel injection pump	Delphi single-cam radial-piston pump
High pressure common rail	Delphi solenoid controlled, 1600 bar max.
Diesel fuel injector	Delphi DFI 1.3 6-hole solenoid valve
Electronic fuel injection system	1 µs duration control
Crank shaft encoder	1800 ppr, 0.2 CAD resolution
Oil and coolant temperature	80 ± 2.5 °C

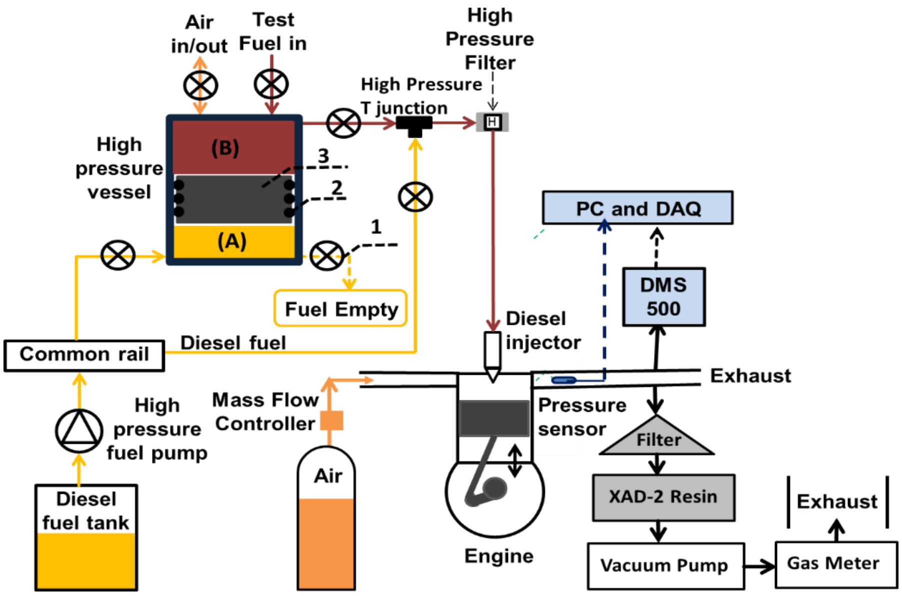


Figure 1: Schematics of the experimental facility

2.4 Sampling of soot particles

Soot particles were sampled from the engine exhaust using a stainless-steel tube (12mm diameter) connected to a vacuum pump. The soot sampling instruments are the DMS-500 and a customised soot sampling system connected to a vacuum pump. The schematics of these instruments are all depicted in Figure 1. The pump maintained a flow rate of 40 L/min through the soot sampling system. The sampling probe was thermally insulated to avoid condensation of water vapor. Detail description of generating and sampling particulates can be found in Dandajeh et al. [9], [29]

Soot particles were sampled on a glass micro fibre filter, its mass (M_s) and the total volume of gas (V_g) that passed through the filter were recorded. The sampling durations for the soot particles generated from the combustion of the model fuels was 15 min at all conditions tested. This duration was chosen after an optimisation exercise to trap enough mass of soot for subsequent Gas Chromatography-Mass Spectrometry (GC-MS) analysis to detect polycyclic aromatic hydrocarbons (PAHs) on the soot particles [28].

The cumulative volume of gas for each test was measured with the aid of volumetric gas meter. The soot mass measurements (M_s) and calculated soot mass concentration (M_s/V_g) of the test fuels without and with 2-EHN are shown in Tables 5 and 6, respectively. The filter was supported by two stainless steel wire meshes procured from The Mesh Company, UK to prevent filter damage at the high temperature, pulsating flow of the engine exhaust conditions. Exhaust soot particles were characterised using differential mobility spectrometer (DMS-500) instrument in terms real time outputs of mass, size, and number. To provide baseline data, diesel fuel was also analysed and compared with the results of the model fuel blends and the average value of two tests is reported here.

Table 5: Filter soot mass measurements without 2-EHN ignition improver

Fuel	**soot mass (M_s) (mg)**	**soot concentration (M_s/V_g) (mg/m^3)**	**particle mean diameter (D_P) (nm)**	**soot surface area (μm^2/cm^3)**
100%H	23.0	48.0	176	2720005
85%H15%T	19.3	40.0	178	1865106
77.5%H22.5%T	23.5	45.0	181	2367265
65%H15%T20%MD	6.90	13.7	160	1210826
Reference Diesel	28.7	58.0	177	1846044

Table 6: Filter soot mass measurements with 2-EHN ignition improver

Fuel + 2-EHN (ppm)	**soot mass (M_s) (mg)**	**soot concentration (M_s/V_g) (mg/m^3)**	**particle mean diameter (D_P) (nm)**	**Soot surface area (μm^2/cm^3)**
77.5%H22.5%T + 1500ppm	13.7	28.9	171	1889521
85%H15%T + 400ppm	16.6	34.3	171	1833473
77.5%H22.5%T + 850ppm	14.8	30.8	178	1841702

3.0 Results and Discussion

3.1 Combustion characterisation at constant injection timing

Figures 2a and b show the profiles of the in-cylinder pressures and apparent heat release rates for the test fuels respectively at a start of fuel injection (SOI) of 10 CAD before TDC. Table 7 shows an analysis of the main combustion parameters for the various fuels investigated. It can be seen from Figure 2a that the 85%H/15%T and 65%H15%T20%MD blends, both having ignition delay (ID) of 9.8 CAD (see Table 7), showed the highest peak in-cylinder pressure of 69.3 bar relative to the other fuels investigated. Also visible in Figure 2b, is the identical peak heat release rates (69.8 J/s) of the 85%H/15%T and 65%H15%T20%MD blends. As one might expect, the identical ignition delay of these fuels resulted in similar values of peak heat release rate and percentage of premixed fuel burned. These results suggest that replacing 20% by volume of a C_7-heptane, with 20% of methyl-decanoate (an oxygenated C_{11} molecule) does not affect the duration of ignition delay or rates of fuel air premixing and, therefore, the peak in-cylinder pressure and peak heat release rates.

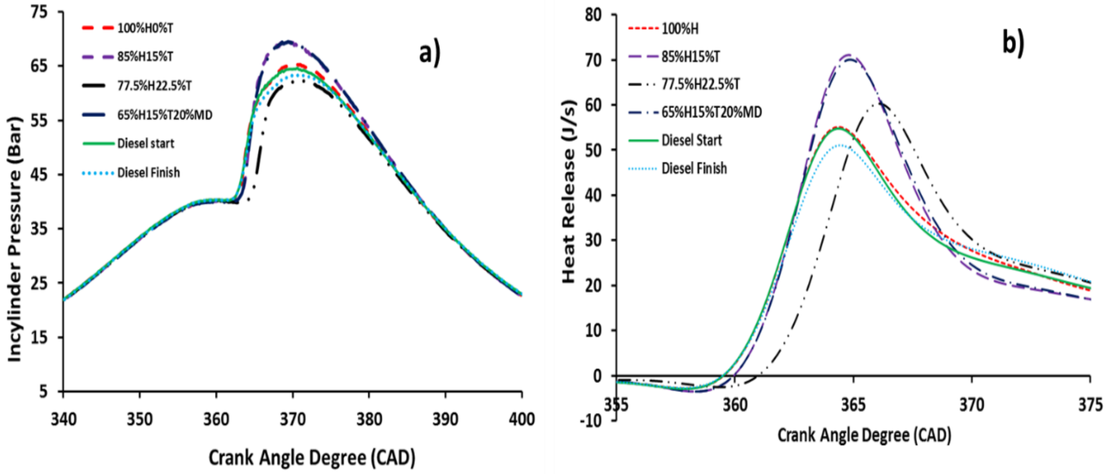


Figure 2: Profiles of: a) in-cylinder pressure (bar) b) apparent heat release rate (J/s) for the single/binary/tertiary fuel blends and a reference diesel fuel run in CI engine at speed of 1200 rpm and IMEP of 7 bar.

It can also be seen from Figure 2 that the binary mixtures of 77.5%H/22.5%T exhibited the least in-cylinder pressure (63.2 bar) and the second highest peak heat release rate (60.3 J/s), which are consistent with the observation in Table 7 that this mixture had the longest ignition delay of 10.8 CAD. Lower peak heat release rate of the 77.5%H/22.5%T blend can be attributed to a start of combustion after TDC, which resulted in heat release occurring at larger in-cylinder volumes and also at higher rates of heat transfer to the cylinder walls [20].

It is noteworthy that increasing the amount of toluene from 15% to 22.5% in the heptane/toluene mixture increased the ignition delay by 0.4 CAD due to decrease in reactivity of the mixture with increased toluene. Toluene has higher density and boiling point than heptane (see Table 2). The increased ignition delay is consistent with results from previous studies [20,30,31], [32]. For example, Hellier et al. [20]

researched binary mixtures of heptane/toluene blends in a direct injection compression ignition engine at toluene levels up to 52% (wt/wt). They reported increased ignition delay by 0.5 CAD due to increase in amount of toluene from 10 to 20% in heptane/toluene blends. Di-Sante [30] also reported increased ignition delay times with increasing volume of toluene in heptane/toluene mixture measured in a rapid compression machine.

Observations during the experiments showed consistently that increasing toluene level up to 22.5% into the heptane inhibited the ignition process and this resulted in greater ignition delay. This inhibition of ignition due to toluene addition can be explained using the results of previous studies [32,33]. It was reported that toluene can be oxidised at low temperatures through abstraction of hydrogen atom (H) by either OH radicals or oxygen molecule (O_2) to leave benzyl radicals [32]. These reactions are shown below in R_1 and R_2 respectively. The benzyl radicals react further with oxygen atom (O) to form phenyl radicals in reaction R_3 [33].

$C_6H_5CH_3 + OH \rightarrow C_6H_5CH_2$ (benzyl) $+ H_2O$ R_1

$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH_2$ (benzyl) $+ HO_2$ R_2

$C_6H_5CH_2 + O \rightarrow C_6H_5 + CH_2O$ R_3

$C_7H_{16} + O_2 \rightarrow C_7H_{15}O + OH$ R_4

It may appear therefore that H-abstraction from n-heptane by O_2, shown in reaction R_4, could be the only possible source of OH radicals that was consumed by toluene in R_1. Reaction R_4 is considered to be the first step in radical branching, which is important part of ignition chemistry of long alkyl chains and which marks the start of large increase in heat release and ignition of the air/fuel mixture [34]. Inferences from the preceding reactions suggest that toluene can delay the start of combustion by consuming radicals in reaction R_1 which would otherwise be used to propagate the reaction of heptane in the heptane/toluene blend.

Returning now to Figure 2, fossil diesel and 100%H (pure heptane) in Figures 2a and b exhibited the same peak in-cylinder pressure and peak heat release rate and identical ignition delay of 9.4 CAD. This result was also reported in previous studies [20] and was expected, since both the reference fossil diesel fuel and pure heptane have cetane numbers and lower heating values which were way close to each other (see Table 2). However, the reference diesel, which was run at the end of each daily test schedule, demonstrated slightly lower in-cylinder pressure and heat release rates; 1.2 bar and 4J/s, respectively, lower than those of the fossil diesel. These small differences are believed to be largely due to the daily drift in the engine performance.

Taking Figure 2, it is apparent that increasing the volume of toluene in the heptane/toluene mixture from 0 to 15%, resulted in a slight increase in the peak cylinder pressure and peak heat release rate by approximately 4 bar and 16 J/s respectively. Additional increase in the proportion of toluene from 15% to 22.5% in the heptane/toluene mixture, slightly decreased the peak cylinder pressure and peak heat release rate by approximately 7 bar and 11 J/s respectively. These results are consistent with the corresponding increase in ignition delay, as the percentage of toluene in the blends was increased, and are in agreement with the results of previous studies at constant injection timings [20].

An increased duration of ignition delay allows more time for fuel and air pre-mixing prior to the start of combustion and thus, larger premixed burn fraction. Proportions of premixed and diffusion phases were calculated using equations Eq.1 and Eq.2 below, respectively. Table 7 shows a trend of increasing proportions of premixed phase and decreasing diffusion phase when the percentage of toluene blended into heptane was increased. The main reason for this increase is the increasing ignition delay which allows for greater period for air/fuel mixing to occur and a greater amount of premixed mixture to be ready for combustion upon ignition. In contrast, higher viscosity and density of toluene, in comparison with heptane, was reported to decrease the rate of air and fuel mixing for toluene [20], hence, increased resulting in an increased proportion of premixed burn fraction for heptane.

Table 7: Proportions of premixed and diffusion phases of fuels without 2-EHN

Fuels with no EHN	**ID**	**CAD$_{switch}$**	**CHRR$_{switch}$**	**CHRR$_{max}$**	**%Premixed**	**%Diffusion**
100%H	9.4	370.8	2628	4325	61	39
85%H15%T	9.8	372.6	2992	4323	69	31

77.5%H22.5%T	10.8	373.2	3096	4360	71	29
65%H15%T20%MD	9.8	372.6	3021	4319	70	30
Diesel Start	9.4	370.2	2503	4394	57	43
Diesel Finish	9.4	370.8	2526	4380	58	44

$$\text{Premixed Phase (\%)} = \frac{\mathrm{CHRR_{swich}}}{\mathrm{CHRR_{max}}} \text{ x } 100 \tag{1}$$

$$\text{Diffusion phase (\%)} = \frac{\mathrm{CHRR_{max}} - \mathrm{CHRR_{swich}}}{\mathrm{CHRR_{max}}} \text{ x } 100 \tag{2}$$

Where; $\mathrm{CAD_{switch}}$ is the crank angle degree at the point of switch from premixed to diffusion phase, $\mathrm{CHRR_{switch}}$ is the cumulative heat release rate at the point of switch from premixed to diffusion phase and $\mathrm{CHRR_{max}}$ is the maximum cumulative heat release rate.

The proportions of premixed and diffusion phases as enumerated by Eqs 1 and 2 were determined from the graph of the cumulative heat release rate against crank angle as reported by Heywood [35]. These equations were developed based on the maximum value of the cumulative heat release rates and the point at which the premixed and the diffusion phases switch over.

3.2 Combustion characteristics at constant ignition timing

To isolate the effect of ignition delay with the heptane/toluene mixtures, an ignition improving additive 2-ethylhexyl nitrate (2-EHN) was used to equalise the ignition delays of the various heptane/toluene blends. Dosages of 2-EHN added to the heptane/toluene mixtures to achieve very nearly the same ignition delays are shown in Table 3.Equalising ignition delays imply removing the influence of varying periods of ignition delay allows other effects such as those of the physical properties of the fuels to be investigated and highlighted. With equalising ignition delay, Hellier et al. [20] also reported the effect of adiabatic flame temperature on NOx production using heptane/toluene fuel blends. There are other effects of equalising ignition delay beyond the scope of this work; especially on the formation and emission characteristics of polycyclic aromatic hydrocarbons (PAHs).

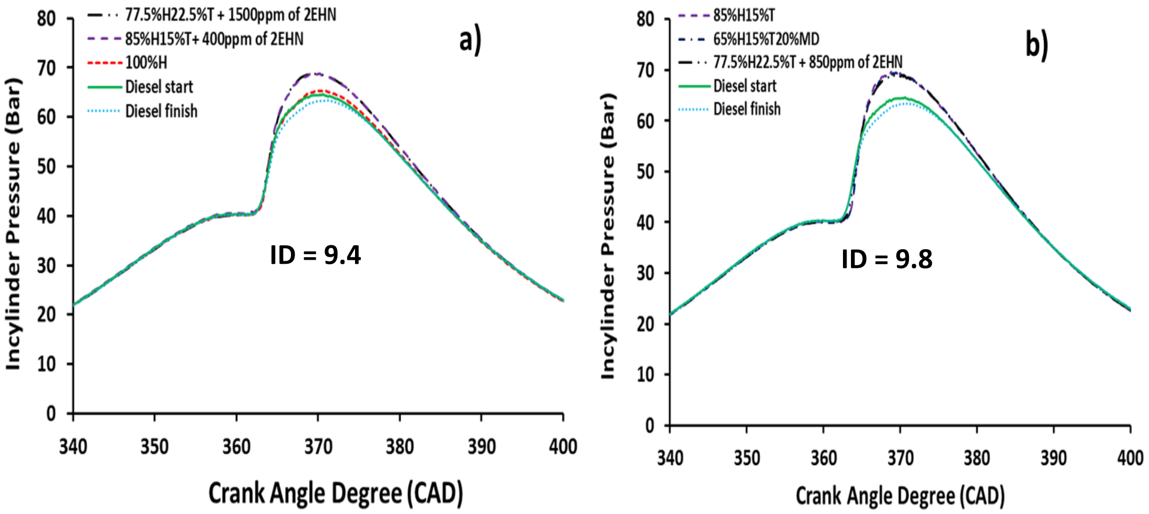


Figure 3: Profiles of in-cylinder pressures (bar) at constant ignition delays (ID): a) ID = 9.4 b) ID = 9.8.

Figures 3a and b show the profiles of in-cylinder pressure at very nearly constant ignition delays of 9.4 and 9.8 respectively. In Figure 3, Diesel start and Diesel finish mean readings for diesel fuel combustion at the start and the end of each daily tests respectively. The figures show that equalising the ignition delay of the heptane/toluene blends resulted in identical peak in-cylinder pressures. For example, the peak in-cylinder pressure in Figures 3a and b at ignition delays of 9.4 and 9.8 CAD are 69.2 and 68.8 bar respectively. This feature of equal peak in-cylinder pressures (as well as pressure profiles) suggest that the pressure profile and its peak pressure are influenced primarily by ignition delay and, thereby, the percentage of premixed combustion, with other fuel properties (such as physical properties) having only a secondary role.

Figures 4a and b show the profiles of heat release rates at very nearly constant ignition delays of 9.4 and 9.8 CAD respectively. As it was observed previously, in the case of in-cylinder pressure, it can also be seen in Figure 4 that peak heat release rates of the heptane/toluene blends with 2-EHN were also similar, but this does not seem to apply in the case of fuels with ID of 9.8 CAD.

Comparing Figure 2a and Figures 3a and b, it can be observed that, under high load (IMEP of 7bar), the peak in-cylinder pressure was slightly higher in those fuel mixtures with 2-EHN. This finding was also observed by Li et al. [36] in methanol/biodiesel blend and was anticipated since 2-EHN could produce chain initiation/pre-ignition radicals via thermal decomposition [37].

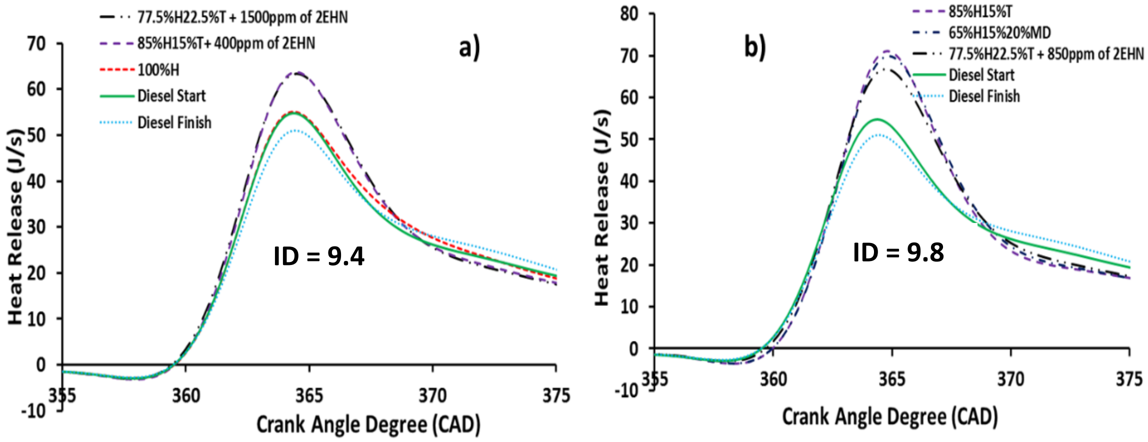


Figure 4: Profiles of heat release rates at constant ignition delays (ID): a) ID = 9.4 b) ID = 9.8

Typically, the C-H and C-C bonds in the heptane/toluene blends have higher bond energies than those of C-O and N-O in the 2-EHN [36]. After addition of 2-EHN to the heptane/toluene blend, the C-O and N-O bonds in the 2-EHN may have dissociated prior to the C-H and C-C bonds in the fuel blend, thereby culminating in earlier ignition reactions with liberation of large amount of energy [38–40].

Table 7 shows that the fuel blends with equal ignition delays exhibited very similar percentages of premixed burnt fraction (within 1% difference). For instance, fuel blends with ID of 9.4 CAD, exhibited a proportion of premixed phase within the range of 61 - 62%, while those with ID of 9.8 CAD showed a proportion of premixed phase within the range of 69 - 70%. Comparing the results of the percentage of premixed phase in Tables 7 and 8, it can be deduced that adding 2-EHN to the fuel blends did not only lower the ignition delay, but also shortened the proportions of premixed burnt fraction. This result agrees well with other earlier works [41].

Table 8: Proportions of premixed and diffusion phases of fuels with 2-EHN

Fuels + 2-EHN (ppm)	**ID**	**$\text{CAD}_{\text{switch}}$**	**$\text{CHRR}_{\text{switch}}$**	**CHRR_{max}**	**%Premixed**	**%Diffusion**
77.5%H22.5%T + 1500ppm	9.4	370.2	2694	4363	61	39
85%H15%T + 400ppm	9.4	370.2	2724	4367	62	38
100%H	9.4	370.8	2628	4325	61	39
77.5%H22.5%T + 850ppm	9.8	372.8	3013	4335	70	30
85%H15%T	9.8	372.6	2992	4323	69	31

65%H15%20%MD	9.8	372.6	3021	4319	70	30

3.3 Soot emissions characterisation at constant injection and ignition timings

Figure 5 shows soot particle number concentrations profiles for the model fuel blends as sampled using the DMS500. Figures 5a and b present soot particle number concentrations for the fuels without 2-EHN and with 2-EHN, respectively. In Figure 5a, the sizes of the soot particles for the fuel blend ranged from 30 – 360 nm when 2-EHN was not added and, similarly, the soot particle size range was 13 – 316 nm with 2-EHN in the fuel blends.

Tables 5 and 6 show the soot particle mean sizes and surface area normalised by soot volume (μm^2/cm^3) of test blends with 2-EHN and without 2-EHN respectively. It can be observed from Table 5 that adding toluene into heptane increased the mean size of the soot particles slightly. From 176 nm for 100%H to 178 nm for 85%H15%T and 181 nm for 77.5%H22.5%T fuel blends. Wei et al. [23] also reported that in-cylinder soot mean particle sizes increased when toluene was added into heptane in a diesel engine. The soot particle mass-filter measurements are also shown in Table 5. It is noteworthy here that the trends in Table 5 of the calculated soot mass concentration from soot-mass filter measurements are like those of soot mass concentration reported by the DMS 500 measurements.

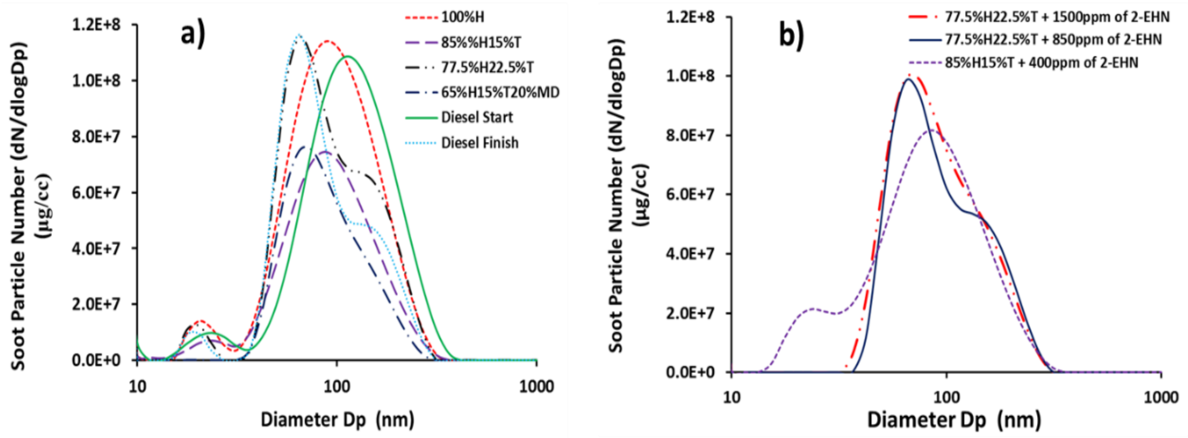


Figure 5: Distribution of soot particle number concentrations (μg/cm^3) for the fuel blends and reference diesel fuel a) without 2-EHN b) with 2-EHN

Table 5 shows that the calculated soot mass concentration increased from 40 to 45 mg/m^3 when the fuel blend was changed from 85%H15%T to of 77.5%H22.5%T. It is imperative to note that the soot mass concentration of 100%H was surprisingly 48 mg/m^3. This value of soot mass concentration of 100%H was high and need to be used with caution. Furthermore, one can notice in Table 5, reduction of 66% in soot mass concentration , 10% in mean particle size, and 35% in soot surface area, when the 20% (vol) of a heptane (a C_7 molecule) in the blend of 85%H15%T was substituted with 20% (vol) of a methyl-deconoate (a C_{11} ester molecule). The results of the reduction in these parameters was not surprising since similar studies [42,43] had reported that oxygen bearing fuels produced lower soot particles when burn in diesel engines in comparison to their hydrocarbon counterparts.

Pyrolysing 100%H usually generate substantial amount of C_2- C_6 species. Such species include acetylene (C_2H_2) and propargyl radicals (C_3H_3) and are the building block of making the first aromatic ring [44,45] that lead to growth of soot precursors (PAHs) and the soot particles themselves. These findings can be supported using the work of Alexiou and Williams [46], who reported reduction in the soot emissions of toluene by adding heptane in a reflected shock-tube pyrolysis.

Toluene generally produce large quantity of soot because of the exponential relationship of its nucleation rate with rising temperature [47]. Additionally, toluene pyrolysis is associated with abundance of C_2 - C_6 radicals including acetylene, propargyl and phenyl radicals [48] and blending it into heptane can be expected to increase the radical pool that provides the soot precursors; hence the subsequent increase in soot yield.

Furthermore, the fact that toluene is an abundant source of phenyl-radicals, via de-methylation, could trigger PAH growth by the phenyl-addition and cyclisation (PAC) pathway [49] and consequently accelerate the soot yield of the resulting heptane/toluene blend. Large quantities of acetylene produced while pyrolysing toluene could speed-up the growth of soot precursors (PAHs) and soot surface growth via the well-known hydrogen-abstraction, acetylene-addition mechanism (HACA) [50]. Similarly, Ladommatos et al. [51] reported toluene having higher soot propensity (18.5 times) as compared to heptane in a diffusion flame.

Looking closely at Table 6, it can be observed that that adding 850ppm of 2-EHN to 77.5%H22.5%T blend decreased the mean soot particle diameter by 1.7%, soot surface area by 22% and soot mass concentration by 32%. Moreover, increasing the quantity of the 2-EHN from 850 - 1500ppm in 77.5%H22.5%T blend further decreased the mean soot particle diameter by 5.5%, soot surface area by 20% and soot mass concentration by 36%. It is pertinent to note that the results of soot mass concentration decreasing by adding 2-EHN to the fuel blends is inconsistent with the previous works [40,51]. This is somewhat due to the different experimental conditions from those of the previous works. These works rather reported increased soot mass concentration when while adding ignition improver to fuels.

4.0 Conclusions

Analyses into the experimental combustion and soot emissions characteristics of single/binary/tertiary fuel blends formulated by blending toluene and methyl-decanoate into heptane with ignition improver was investigated. Two sets of tests were conducted. A constant injection timing tests with start of fuel injection at 10^o CAD BTDC and a constant ignition timing tests while also keeping the 10^o CAD BTDC injection and adding ignition improver (2-ethylhexylnitrate -2EHN) to the fuel mixtures. Soot particles were characterised using DMS-500 instrument in terms of mass, size, and number.

The following inferences can be drawn.

1) Replacing 20% (vol) of a C_7-heptane, with 20% of methyl-decanoate (an oxygenated C_{11} molecule) was did not affect the duration of ignition delay or rates of fuel air premixing and the peak in-cylinder pressure and peak heat release rates.

2) Adding 2-ethylhexylnitrate ignition improver to the fuel blends decreased the mean soot particle diameter, soot surface area and, surprisingly, gravimetric filter soot mass concentration
3) Toluene addition (0 - 22.5% by vol) to heptane increased the mean size of the soot particles generated by only 3%. Increasing the proportion of toluene into heptane resulted in a slight increase in the peak cylinder pressure and peak heat release rates.

4) Blending toluene and methyl-decanoate into heptane without adding- 2EHN was to increase the premixed phase by at least 13%. However, by adding 2EHN (400 -1500ppm), the premixed phase decreased by at least 11%.

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