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## Full length article

# Impact of alcohol–diesel fuel blends on soot primary particle size in a compression ignition engine

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## ABSTRACT

The use of alternative fuels, such as bio-alcohols, in advanced propulsion systems could be a feasible strategy to address several of the current issues associated with the use of internal combustion engines fuelled by carbonaceous fossil fuels. Particularly, soot particles, are one of the key pollutants emitted from compression ignition engines. Therefore, the development of soot formation prediction models providing new understanding on the impact of alternative fuels combustion in compression ignition engines become essential for soot mitigation purposes.

This study proposes a new semi-empirical model that predicts in-cylinder soot primary particle growth from an engine fuelled with alcohol–diesel fuel blends. The model uses macroscopic experimental measurements of engine parameters such as instantaneous in-cylinder pressure. Furthermore, an empirical correlation is presented predicting the mean soot primary particle size as a function of alcohol–diesel fuel blend properties and fuel/air ratio. The experimental measurement of primary soot particle mean size are obtained from High Resolution Transmission Electron Microscope (HT-TEM) micrographs obtained from soot particles collected via thermophoresis. Overall, the research findings presented in this work contribute to propose environmentally friendly fuel candidates for transportation.

## 1. Introduction

Environmental and human health effects of pollutant emissions have resulted in increasingly stringent regulations as well as significant research efforts to decrease pollutant levels in the atmosphere [1]. Vehicles propelled by compression ignition engines have advantages in terms of lower fuel consumption and CO<sub>2</sub> emissions with respect to their counterpart spark ignition engines, while they present the challenge of the simultaneous reduction of particulate matter (PM) and NO<sub>x</sub> emissions. Approaches which have been implemented to reduce global and local vehicular pollutant emissions include using alternative fuels, improving in-cylinder combustion and air management strategies and exhaust post-treatment technologies [2].

Alternative fuels have been proposed as a solution for vehicular propulsion systems to completely/partially replace conventional oil-derived. There are some key favourable characteristics such as their renewability, sustainability, lower carbon footprint, availability to supply the fuel demands and potential to reduce local and global pollutant emissions. Conventionally, biodiesel for compression ignition and bio-alcohols for spark-ignition engines are the most used alternative fuels. Bio-alcohols can be produced from lignocellulosic biomass using, for

example, agricultural residue and switch grass. There are some advantages in the properties of alcohol fuels such as the high H/C ratio [3], absence of aromatic components, high oxygen-containing component (in this case, the hydroxyl group, OH) as well as excellent cold-flow properties [4]. These properties position them as good candidates for compression ignition engines, despite the apparent limitations due to their poor autoignition capabilities, lubricant properties and limited solubility within diesel in alcohol–diesel fuel blends [5]. Emissions reductions, especially in mass and number of particles, have been reported when individually blending methanol [6–8], ethanol [7–9], propanol [10] and butanol [7,8,11] with diesel fuel. The absence of aromatics, longer ignition delay and the presence of oxygen (O<sub>2</sub>) in the alcohol fuel molecule have been reported as reasons for the observed particle reduction [9]. Results have also indicated that the presence of the OH group has a more significant particle reduction potential than that of the atomic oxygen within biodiesel [11].

The environmental and human health effects of particles do not only depend on the total mass and/or the number of emitted particles but also on particle size, morphology, and composition. For instance, smaller particles have larger surface/volume ratio and are more reactive,

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longer suspension residence time in the atmosphere and have higher deposition rates in the human respiratory system [12]. The shape of the particles emitted from compression ignition engines is chain-like composed of quasi-spherical primary particles [13,14]. Therefore, characteristics of the agglomerates such as shape, the number of primary particles, size of primary particles, and nano-structure are quantified to understand their formation, their potential effects on the environment and human health, as well as to provide guidelines for their abatement. Notably, the knowledge of primary particle size and the net growth rate of primary particles provide key information regarding in-cylinder formation process and particle reactivity. Also, primary particle size is a crucial input to feed models to determine soot agglomerates characteristics such as morphology and size as well as the greenhouse potential of particles [15,16]. Primary particle size distributions are commonly used to determine the number of primary particles per particle size. Primary particle size distributions are mathematically fitted to normal [17,18] and/or log-normal distribution functions [19], while other authors use an average primary particle size [20].

The effect of the engine operating condition on the primary particle size has been previously investigated. In-cylinder mass of fuel, partial pressure (concentration) of oxidant and temperature have been identified and included in models as critical parameters which control primary particles growth and oxidation [18,21]. Experimentally, the effect of in-cylinder temperature has been studied. There are some works which report that an increase in the in-cylinder temperature decreases primary particle size [22,23]. In contrast, other investigators have reported an increase in primary particle size [24–26] with the increase in temperature. The constant mean size of primary particles independently of the operating conditions, has been also reported [20, 27]. Explanations provided are that an increase in the in-cylinder temperature produces a twofold effect by (i) increasing the rate of nucleation and surface growth, increasing primary particle size and (ii) enhancing soot oxidation, decreasing the primary particle size. The net effect on the primary particle size will depend on the compromise between the formation/growth and oxidation of primary particles, which would depend on the specific in-cylinder conditions such as temperature level [28], in-cylinder oxidant concentration, nature of particles, etc.

The effect of oxygenated fuel blends in carbonaceous primary particle size emitted from compression ignition engines has also been studied. Most investigations have been carried out with oxygenated fuels such as biodiesel and alcohol fuel blends. Generally, the average sizes of primary particles emitted from biodiesel combustion are lower than those emitted with conventional diesel fuel [29–31]. Regarding the effect of alcohol–diesel fuel blends, there is an agreement in the cited literature that the incorporation of butanol [32–35] and pentanol [36] into the fuel blends reduce the size of primary particles. Most of the literature agrees that the oxygen content of butanol reduces the inception of particle precursors and carbonaceous components involved in the growth of primary particles and enhances the rate of oxidation of the particles already formed.

This work develops a new semi-empirical model predicting the soot primary particle net growth (surface growth and oxidation) and the average net primary particle size of particles formed in compression ignition engines using conventional and alcohol–diesel fuel blends. The phenomenological soot primary particle net growth model is based on the Arrhenius equation incorporating key parameters including instantaneous in-cylinder pressure and temperature, the mass of fuel and air, as well as oxygen availability, which is distinguished between the oxygen provided by the intake air and the oxygen (in this case OH group) provided by the fuel. Butanol and pentanol have been chosen as non-cyclic long carbon chain alcohols due to their better blending stability, higher density, higher calorific value and higher cetane number compared to short-chain alcohols such as ethanol [10]. The effect of the inclusion of a cyclic group such as in the case of cyclopentanol has also been investigated. The outcomes of this investigation are supported by the already published literature which is limited to the effect of alcohol–diesel fuel blends on total engine output soot concentration [3,7,8,37] and average primary particle size [38].

**Table 1**

Test engine specifications [39].

Engine specification	Data
Number of cylinders	1
Bore	84 mm
Stroke	90 mm
Connecting rod length	160 mm
Compression ratio	16.1:1
Displacement volume	499 cm <sup>3</sup>
Maximum injection pressure	1500 bar
Emissions' standard	designed for Euro 5

## 2. Methodology

### 2.1. Experimental setup

In this research, a four-stroke single-cylinder research diesel engine was used as shown in Fig. 1. The engine technical data and specifications are summarised in Table 1. The four-stroke diesel engine is naturally aspirated, water-cooled, equipped with exhaust gas recirculation (EGR) and common rail direct injection fuel system. An alternating current (AC) electric dynamometer was used to motor and load the engine. The engine was fuelled with diesel fuel, as a reference fuel and three other fuels blended with diesel. Butanol, pentanol and cyclopentanol were purchased from Sigma Aldrich. Their blends with diesel and neat diesel as the baseline fuel were tested to study the influence of various alternative fuels with different molecular structures. The alternative fuels were tested at a 20%v/v ratio with diesel fuel. The engine operating conditions are summarised in Table 2; 1500 rpm with 2 bar and 4 bar IMEP (Indicated Mean Effective Pressure) were selected as the engine rotational speed and load respectively, to reproduce low-load driving conditions. The common rail fuel injection pressure was set at 550 bar and 650 bar at 2 and 4 bar IMEP, respectively. The pilot fuel injection was set to start at 15° bTDC (before Top Dead Centre) with the duration of 0.150 ms; whereas the main injection started at 3° bTDC with the variable duration of around 0.443 ms to have a constant IMEP. In the studied cases, there is not any post fuel injection [39].

An AVL GH13P pressure transducer mounted in the cylinder head was used to record in-cylinder pressure, and an AVL FlexiFEM 2P2 amplifier amplified its signal. Also, a digital shaft encoder producing 360 pulses per revolution measured the crank–shaft position [40]. The pressure and crank–shaft position data was combined to create an in-cylinder pressure trace [39]. The temperatures at different points, such as on the exhaust manifold were recorded by using k-type thermocouples and a Pico Technology TC-08 thermocouple data logger. To monitor the air/fuel ratio in all tested conditions, an airflow meter was used to measure the engine intake air-flow. Then  $\lambda$  as a ratio of actual air/fuel ratio to stoichiometric air/fuel ratio was calculated and checked for all tested conditions [39].

An in-house developed LabVIEW programme connected to a National Instruments PCI-6023E data acquisition device was used to monitor and control the engine operating settings, such as injection pressure, timing and duration. To confirm combustion stability and minimise cyclic variability, the coefficient of variation (COV) of the IMEP for 200 cycles was monitored and it was < 4% for all of the test conditions. The LabVIEW programme analyses the engine indicated mean effective pressure for each cycle [39,41].

In-cylinder pressure data was pegged to have the same in-cylinder pressure at the bottom dead centre of the intake stroke as that of the intake manifold [42]. With logged average data of the in-cylinder pressure in 200 engine operating cycles, the heat release rate was obtained. Also, from the instantaneous mean in-cylinder pressure and by using a zero-dimensional thermodynamic model within the combustion chamber [43,44], the instantaneous mean temperature inside the combustion chamber can be obtained.

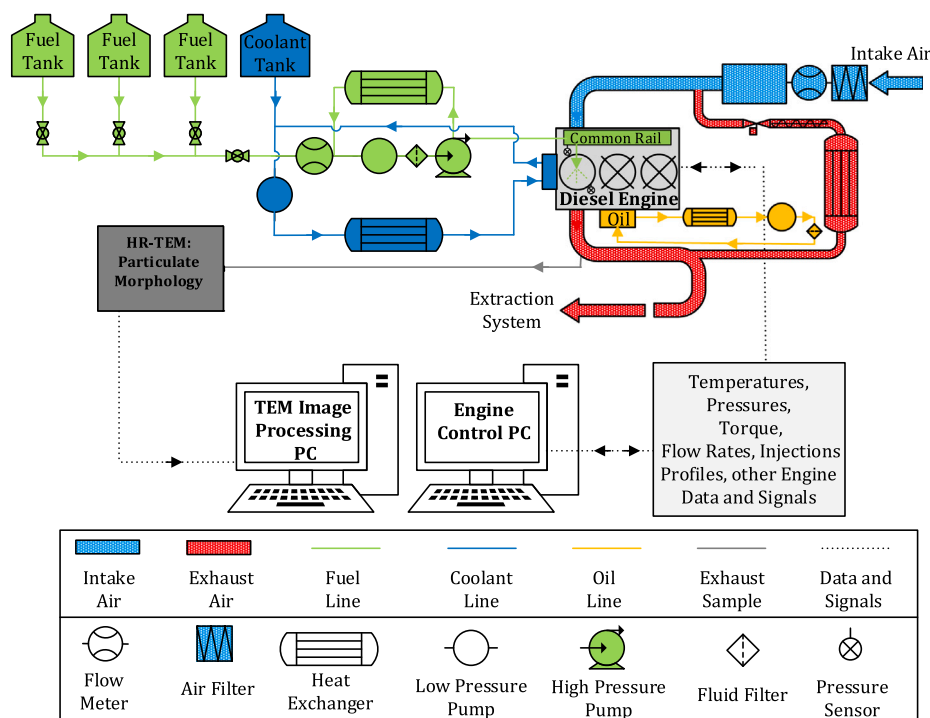


Fig. 1. Experimental set-up diagram.

**Table 2**  
Engine test conditions abbreviations and colour codes.

Test abbreviation	Fuel blends with diesel (%v/v)	Engine speed (rpm)	Fuel injection pressure (bar)	IMEP (bar)	Injection timing bTDC-(CAD)	
					Pre	Main
D100L	Diesel 100%	1500	550	2	15	3
B20L	Butanol 20%	1500	550	2	15	3
P20L	Pentanol 20%	1500	550	2	15	3
CP20L	Cyclopentanol 20%	1500	550	2	15	3
D100M	Diesel 100%	1500	650	4	15	3
B20M	Butanol 20%	1500	650	4	15	3
P20M	Pentanol 20%	1500	650	4	15	3
CP20M	Cyclopentanol 20%	1500	650	4	15	3

Particle agglomerates were collected onto a formvar carbon film supported on a 3 mm diameter copper grid. A Talos<sup>TM</sup> F200X S/TEM coupled to a FEI Ceta 16M<sup>TM</sup> camera were utilised to obtain the high resolutions micrographs of particle agglomerates with a resolution up to 0.12 nm at a fast rate of 25 fps.

A bespoke digital image analysis software was utilised to measure 10 primary particles per agglomerate to a total of 30 agglomerates per fuel and engine operation condition. The conversion from pixels to nanometres was calibrated by comparison with standard latex spheres shadowed with gold.

Fig. 2.a shows a representative HR-TEM image from an agglomerate emitted from the combustion process of a fuel blend composed of 80% by volume of diesel and 20% of pentanol at low engine load. Fig. 2.b depicts how primary particles have been randomly selected from the agglomerate (marked with a red circle).

Fig. 3.a shows a typical agglomerate from the mid-load reference diesel engine tests, D100M. In the Figs. 3.b and 3.c two zones of the agglomerate are shown in which it can be appreciated how the growth is by graphite layers arranged as onion layers, tending to an almost spherical growth, as suggested by authors such as [45,46].

## 2.2. Fuels

The fuels used in this work are the reference diesel and three alcohol-type fuels, which are: butanol, pentanol and cyclopentanol. The main characteristics of neat fuels are shown in Table 3.

Alcohol fuels cannot be used in their neat state in conventional compression ignition engines, as they have poor autoignition properties. So, they were blended with the reference fuel in the proportion of 20% by volume of alcoholic fuel and 80% by volume of reference fuel. The mixture between diesel and butanol has been called B20, between diesel and pentanol has been called P20, and finally, between diesel and cyclopentanol has been called CP20. Relevant physicochemical characteristics of the studied fuel blends are shown in Table 4.

## 2.3. Model

There is not a single primary particle size within the same agglomerate (Figs. 2 and 3) as the size depends on multiple factors including fuel spatial distribution, local thermodynamic and mixing conditions around fuel spray formation, local dehydrogenation of the fuel, etc. It is therefore proposed to develop a growth model for the average primary particle size.



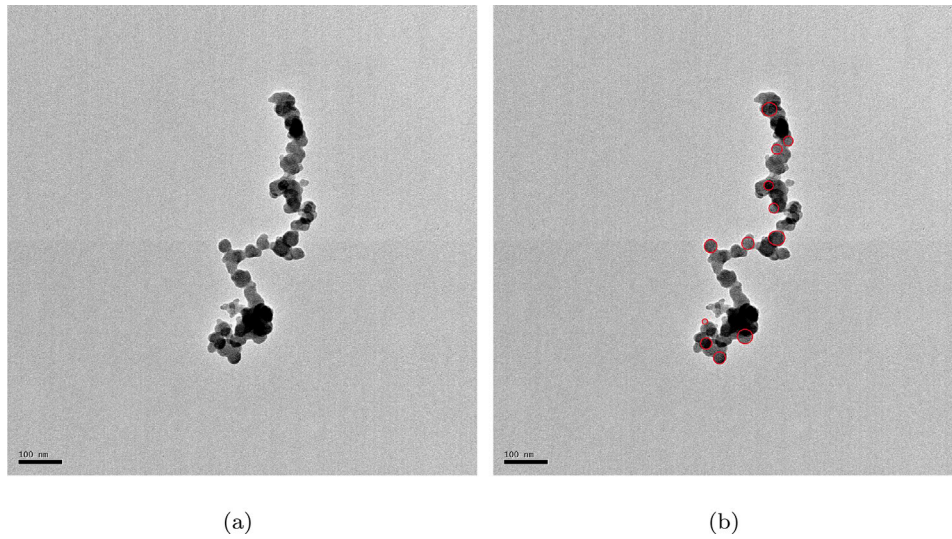


Fig. 2. Soot agglomerate from P20L tests (a) No primary particles indicated, (b) Primary particles indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

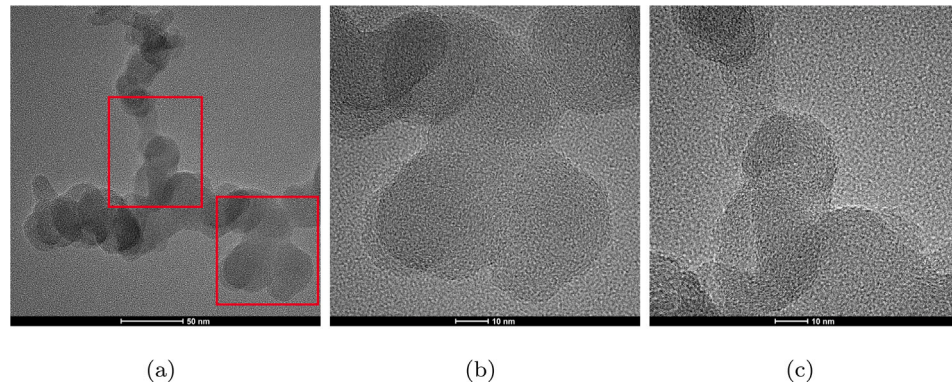


Fig. 3. Soot agglomerate from tests D100M.

A growth model based on the Hiroyasu–Nagle and Strickland model is proposed, in which there are a formation term and a reduction or disappearance term for the carbon layers [48]. Furthermore, it is assumed that both the growth and the reduction of the primary particles are made by means of thin spherical layers [18]. Eq. (1) shows that the instantaneous net growth of the outer surface of a mean primary particle,  $\overline{S_{net}}$ , is the balance between the instantaneous surface growth/formation,  $\overline{S_f}$ , by the effect of fuel dehydrogenation and subsequent precursor formation [49], and the instantaneous reduction of the outer surface by oxidation,  $\overline{S_{ox}}$ , [50].

$$\frac{d\overline{S_{net}}}{dt} = \frac{d\overline{S_f}}{dt} - \frac{d\overline{S_{ox}}}{dt} \quad (1)$$

The term soot formation mainly depends on the in-cylinder pressure and temperature [51]. Soot formation is modelled by an Arrhenius type expression where the pre-exponential term is dependent on the instantaneous mean in-cylinder pressure,  $p(t)$ , and the exponential term depends on instantaneous mean in-cylinder temperature,  $T(t)$ , as is shown in Eq. (2).

$$\frac{d\overline{S_f}}{dt} = A_f p(t)^{B_f} \exp\left(-\frac{E_f}{RT(t)}\right) \quad (2)$$

In Eq. (2)  $A_f$  and  $B_f$  are two constants,  $R$  is the gas constant and  $E_f$  is the activation energy of soot formation. In this case, the term  $E_f/R$  has been taken from the Refs. [52,53] and is equal to 12100 K.

The soot oxidation and formation terms depend on the in-cylinder pressure [51], and temperature and it is also modelled by an Arrhenius

expression [52]. In this case, a modified Arrhenius type expression will be used depending on the instantaneous mean pressure within the combustion chamber. Three more terms have been introduced: (i) one dependent on the instantaneous mean oxygen mass fraction within the combustion chamber,  $Y(t)_{O_2,ox}$ , (ii) another dependent on the instantaneous hydroxyl radical mass fraction of the fuel,  $Y(t)_{OH,fuel}$ , which must have a significant oxidising effect, (iii) a term that depends proportionally on the size of the particle to consider the larger outer surface of large particles. The soot oxidation term is shown in Eq. (3).

$$\frac{d\overline{S_{ox}}}{dt} = A_{ox} p(t)^{B_{ox}} \left(1 + C_{ox} Y(t)_{OH,fuel}\right) Y(t)_{O_2,ox}^{D_{ox}} \exp\left(-\frac{E_{ox}}{RT(t)}\right) \overline{S_{net}}^F \quad (3)$$

In Eq. (3) the coefficients  $A_{ox}$ ,  $B_{ox}$ ,  $C_{ox}$  and  $D_{ox}$  are constant. The variable  $E_{ox}$  is the soot oxidation activation energy. In this case the term  $E_{ox}/R$  has been taken from the Refs. [52,53] and is equal to 19680 K. The order of soot reaction as solid-state is 0.5, [54,55], so the constant  $F$  has been taken equal to 0.5.

The equation to be solved is obtained by replacing the Eqs. (2) and (3) in Eq. (1). All time-dependent terms in Eq. (2) have been included in the  $f(t)$  function, and equally, all time-dependent terms in Eq. (3) are grouped in the  $g(t)$  function. In addition, the mean surface area of the primary particle,  $\overline{S_{net}}$ , has been replaced by its diameter,  $\overline{d_{po}}$ . The Eq. (4) models the temporal evolution of the mean diameter of the primary particle.

$$\frac{d\overline{d_{po}}}{dt} = \frac{2}{\pi} f(t) - \frac{1}{\sqrt{\pi}} g(t) \overline{d_{po}} \quad (4)$$

**Table 3**  
Main properties of net fuels [47].

Property	Diesel	Butanol	Pentanol	Cyclopentanol
Molecular formula	$\sim C_{12}H_{22}$	$C_4H_9OH$	$C_5H_{11}OH$	$C_5H_9OH$
Molecular weight (g mol <sup>-1</sup> )	166.3	74.11	88.15	86.13
Purity (% v/v)	–	99	99	99
Density at 15 °C (kg m <sup>-3</sup> ) <sup>a</sup>	834.8	811.5	814.8	949
Viscosity at 40 °C (cSt) <sup>b</sup>	2.63	2.17	2.74	2.84
Lower heating value (MJ kg <sup>-1</sup> ) <sup>c</sup>	45.97	33.81	34.65	35.96
Heat of evaporation (kJ kg <sup>-1</sup> )	270–350	581.4	308.1	–
Lubricity at 60 °C (μm) <sup>d</sup>	463	628	579	452
Surface tension at 25 °C (mN m <sup>-1</sup> ) <sup>e</sup>	26.07	23.05	24.02	31.35
Cetane number <sup>f</sup>	53.0	15.9	18.2	9.8
H/C ratio	1.8	2.5	2.4	2.0
(Fuel/Air) <sub>st</sub> ratio	1/14.48	1/11.14	1/11.71	1/11.18
Carbon (%w/w)	86.44	64.87	68.18	69.76
Hydrogen (%w/w)	13.56	12.16	12.50	10.47
Hydroxyl radical (%w/w)	0	22.97	19.32	19.77
CFPP (° C) <sup>g</sup>	–20.0	–41.7	–47.0	–47.1
Water content (mg kg <sup>-1</sup> ) <sup>h</sup>	41.7	11.5	29.7	–
Boiling point (° C)	180–360	117.4	137.9	140.4
Cloud point (° C) <sup>i</sup>	–4.1	–115.5	–	–
Pour point (° C) <sup>j</sup>	–21	<–120.7	–	–
Flash point (° C)	68	35	49	51

<sup>a</sup>Method: EN ISO 3675.

<sup>b</sup>Method: EN ISO 3104.

<sup>c</sup>Method: ASTM D240–02.

<sup>d</sup>Method: EN ISO 12156–1.

<sup>e</sup>Method: ASTM D971.

<sup>f</sup>Method: ASTM D6890.

<sup>g</sup>Method: EN 116.

<sup>h</sup>Method: EN ISO 12937.

<sup>i</sup>Method: EN 23015.

<sup>j</sup>Method: ASTM D97.

**Table 4**  
Main properties of fuel blends.

Property	B20	P20	CP20
Density at 15 °C (kg m <sup>-3</sup> ) <sup>a</sup>	830.1	830.8	857.6
Viscosity at 40 °C (cSt) <sup>b</sup>	2.27	2.60	2.75
Lower heating value (MJ kg <sup>-1</sup> ) <sup>c</sup>	43.54	43.99	43.97
Lubricity (μm) <sup>d</sup>	570	562	480
Surface tension at 25 °C (mN m <sup>-1</sup> )	25.48	24.78	26.30
(Fuel/Air) <sub>st</sub> ratio	1/13.83	1/13.94	1/13.75
Carbon (%w/w)	82.47	83.10	82.99
Hydrogen (%w/w)	13.04	13.11	12.64
Hydroxyl radical (%w/w)	4.49	3.79	4.37
CFPP (° C) <sup>e</sup>	–19.99	–20.06	–20.07

<sup>a</sup>Method: EN ISO 3675.

<sup>b</sup>Method: EN ISO 3104.

<sup>c</sup>Method: ASTM D240–02.

<sup>d</sup>Method: EN ISO 12156–1.

<sup>e</sup>Method: EN–116.

The Eq. (4) is an ordinary first-order differential equation, the general solution of which can be obtained from [56] and is:

$$\overline{d}_{po}(t) = \exp\left(-\int \frac{1}{\sqrt{\pi}} g(t) dt\right) \left[ \int \frac{2}{\pi} f(t) \cdot \exp\left(\int \frac{1}{\sqrt{\pi}} g(t) dt\right) dt + C \right] \quad (5)$$

In Eq. (5),  $C$  is the integration constant.

In Eq. (3), the term temporary mass fraction of oxygen within the combustion chamber has been modelled according to [57]. In this case, the exhaust gas recirculation and the gas escaping into the crankcase are assumed to be zero, so that the temporary oxygen mass fraction within the combustion chamber is:

$$Y(t)_{O_2,ox} = Y_{O_2,air} (1 - \phi HRF(t)) \quad (6)$$

In Eq. (6), the term  $Y_{O_2,air}$  is the mass fraction of oxygen in the air and is approximately equal to 0.23.  $HRF(t)$  is the time-dependent accumulated heat release fraction and  $\phi$  is the equivalence ratio.

And finally, in Eq. (3), the term temporary mass fraction of the hydroxyl radical released from the fuel inside the combustion chamber has been modelled as a function of the heat release rate.

$$Y(t)_{OH,fuel} = Y(t=0)_{OH,fuel} \left( \frac{(F/A)}{1 + (F/A)} \right) (1 - HRF(t)) \quad (7)$$

In Eq. (7), the term  $Y(t=0)_{OH,fuel}$  is the mass fraction of the hydroxyl radical in the fuel and  $(F/A)$  is the fuel/air ratio.

### 3. Results and discussion

#### 3.1. Test results

##### 3.1.1. Engine operating conditions

Table 5 shows the average fuel and air consumption, maximum in-cylinder pressure and equivalence ratio,  $\phi$ , for all the fuels at each engine operation condition, where engine speed and engine load are equal for all the fuels.

It can be seen in Table 5 that the fuel with the lowest absolute consumption is diesel, and this is due to its higher calorific value, as long as the same degree of load and engine speed is maintained, as is the case here. There is no clear trend for other fuel mixtures.

##### 3.1.2. Mean in-cylinder pressure

The instantaneous in-cylinder pressure is shown in Fig. 4.a for low load (IMEP~ 2 bar) and in Fig. 4.b for medium load (IMEP~ 4 bar) engine operation. The starting point for the model has been located when the combustion starts for each fuel.

Fig. 4.a and 4.b show how the evolution of in-cylinder pressure follow a similar pattern characteristic of conventional combustion for all the studied fuels. Generally, the combustion of the alcohol–diesel fuel blends produces a higher maximum in-cylinder pressure with

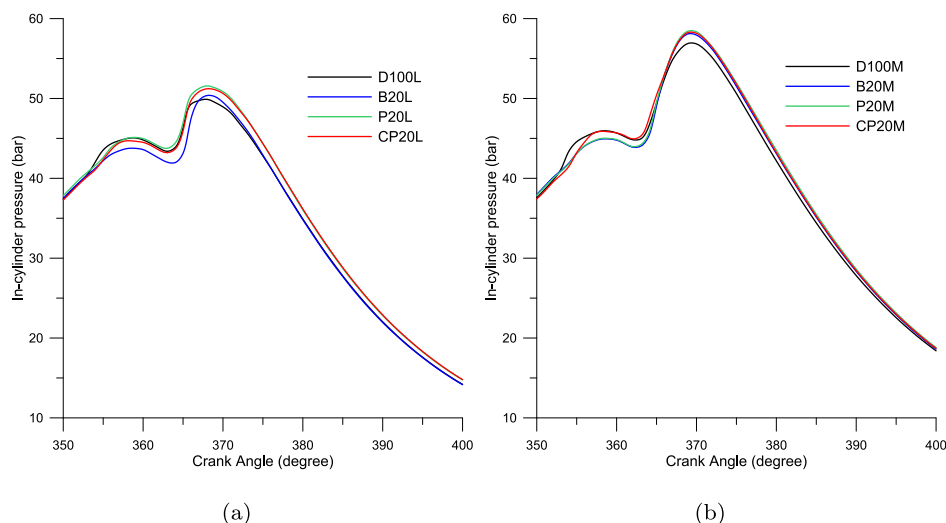


Fig. 4. Average pressure inside the combustion chamber vs. crank angle degree. (a) Low load Modes, *L*, (b) Medium load Modes, *M*.

Table 5

Engine operating conditions.

Operating mode	Fuel (kg/h)	Air (kg/h)	$p_{max}$ (bar)	$\phi$
D100L	0.366	17.42	49.90	0.3041
B20L	0.407	17.05	50.37	0.3299
P20L	0.414	17.42	51.58	0.3310
CP20L	0.434	17.35	51.22	0.3438
D100M	0.649	17.27	56.92	0.5439
B20M	0.659	17.42	58.11	0.5228
P20M	0.678	17.13	58.46	0.5513
CP20M	0.668	17.13	58.28	0.5359

respect to the maximum in-cylinder pressure resulting from diesel fuel combustion for each engine operation load. This is well supported by the lower autoignition tendency of the alcohol fuel which slightly delays the start of combustion increasing the quantity of fuel burnt in premixed combustion phase and thus the maximum in-cylinder pressure [11].

Fig. 5 shows as a representative example, from the results derived from the combustion process of the butanol–diesel fuel blend for both engine operation conditions. Instantaneous mean in-cylinder pressure (black), rate of heat release (green), in-cylinder oxygen fraction due to the air (red) calculated using Eq. (6) and mass fraction of the hydroxyl radical (blue) calculated using Eq. (7) are shown in Fig. 5. Similar patterns are obtained for the rest of fuel blends, but are not shown for the clarity of the results. The main difference between the fuels is the mass fraction of the hydroxyl radical.

Comparing Fig. 5.a with 5.b shows how an increase in the final oxygen mass fraction in the chamber is obtained with the decrease of engine load.

### 3.1.3. Measured primary particles

A minimum of 30 photographs obtained in HR-TEM have been taken as the image shown in Fig. 2 of each engine operating mode and for each fuel. For each photograph a minimum of 10 primary particles has been measured, so that for each engine operating mode and for each fuel tested, there is a population of no less than 300 primary particles. The histogram shown in Fig. 6 has been obtained from this population.

All samples were subjected to the nonparametric Kolmogórov–Smirnov normality test enhanced with the Lilliefors test. In all cases, the distribution obtained is normal, as shown in Fig. 6.

The average size of primary particles formed during the combustion process of alcohol–diesel fuel blends is always smaller than the size of those emitted under diesel fuel combustion for the two studied engine

loads. It is thought that the higher H/C ratio, the longer the ignition delay and the presence of fuel-borne oxygen (in this case OH) contribute to this result, as it has been previously reported in [32–36,38].

In Fig. 6 it is observed that with the increase of engine load, there is a greater dispersion of the sizes of the primary particles when the engine works with the mixtures of alcoholic fuels. In the case of an engine operating on pure diesel, the dispersion of the primary particle sizes does not change significantly. This effect may be because the mass increase of alcoholic fuel within the combustion chamber can significantly change the local conditions in which soot precursors are produced, causing both small and large soot particles to be generated in similar proportions.

Also, in Fig. 6, it is observed that the greater the engine load, the greater the average diameter of the primary particles for all fuels. This effect may be because the greater the engine load, the greater the fuel/air ratio, and the greater the mass of fuel injected, thus increasing the likelihood of generating new soot precursors [58]. This is also supported by the fact that an increase in the in-cylinder temperature promotes primary particle growth more than particle oxidation, as it has been reported for low-temperature levels, as in this case (low and medium load conditions) [28].

From the data shown in the Tables 3–5 a multiparametric correlation has been obtained with a very high adjustment coefficient,  $R^2 = 0.960$ . So, there is an almost linear relationship between the mean diameter of the primary particles and the independent variables shown in Eq. (8).

$$\overline{d_{po}} = 984.226 - 11.255 Y_{OH, fuel} - 15.982 H_p - 16.360 Y_{H, fuel} - 0.147 \frac{A}{F} \quad (8)$$

In the correlation shown in Eq. (8) the appearance of independent variables have been ordered according to which effect is more predominant,  $Y_{OH, fuel}$ , or less predominant,  $(A/F)$ , on the mean diameter of the primary particles.

So, the larger the mass fraction of hydroxyl group in the fuel, the greater the probability that the mean diameter of the primary particles will be smaller. This may be due to the lower probability of generating precursors due to the oxidising effect of the hydroxyl radical. The greater the heating value of the fuel, the smaller quantity of fuel injected to maintain the same load (particularly for this study as indicated/brake thermal efficiency is similar for all fuels) and the greater the average temperature in the combustion chamber both reducing particle formation in the studied conditions [50]. The lower the hydrogen content in the fuel the greater the probability of generating larger primary particles. This may be because the lower the mass of hydrogen in the fuel the less energy there is to dehydrogenate the fuel

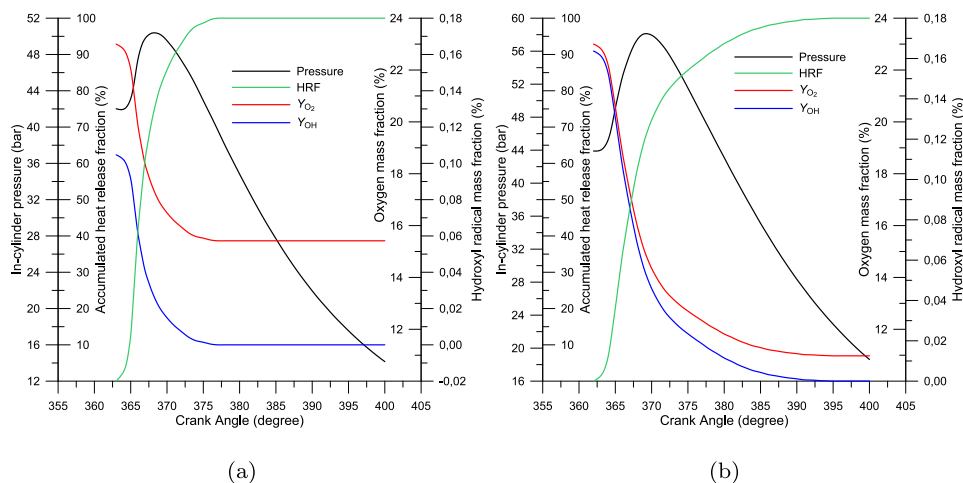


Fig. 5. Time evolution of pressure, HRF,  $Y_{O_2}$  and  $Y_{OH}$  vs. crank angle degree. (a) B20L, (b) B20M.

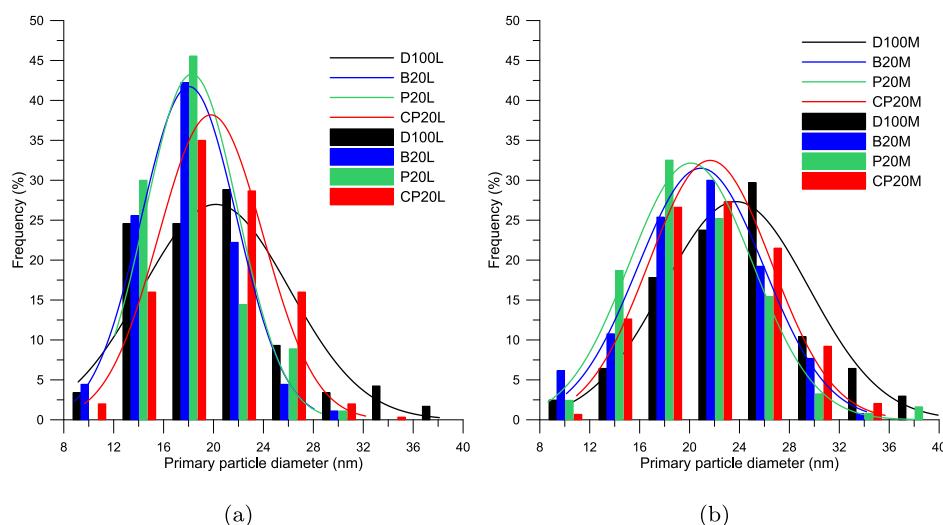


Fig. 6. Histograms of mean diameters of primary particles measured experimentally. (a) Low load Modes, L, (b) Medium load Modes, M.

and the greater the likelihood of soot precursor generation. As for the effect of the air/fuel mass ratio is the least significant of all, so the greater the mass of fuel injected or the smaller the mass of air introduced into the combustion chamber, the greater is the probability of generating new graphite layers, producing soot precursors and carbon components and therefore greater will be the average diameter of the primary particles [25].

### 3.2. Application of the model

The model coefficients have been obtained, minimising the mean quadratic error between modelled primary particle size obtained by Eq. (1) and average experimental primary particle size shown in Fig. 6. In this case, a minimum mean quadratic error of 0.3210 has been obtained for the coefficients:  $A_f = 509366$ ,  $A_{ox} = 19731$ ,  $B_f = 2.667$ ,  $B_{ox} = 4.429$ ,  $C_{ox} = 9869$  y  $D_{ox} = -0.046$ . For other engine size configurations, injector and combustion chamber geometry, engine operating conditions such as engine speed, load, EGR, etc., these coefficients must be re-fitted.

Fig. 7 depicts the temporal evolution of mean size of primary particles applying the model shown in Eq. (5) using the optimised constant values for the fitting parameters (represented by a thick continuous line in the plot). The net rate of primary particle size growth/oxidation has

also been obtained by calculating the temporal derivate, shown as thin continuous lines in Fig. 7.

Fig. 7.a shows the primary particles results for low load engine operation, while Fig. 7.b shows the results for engine medium load. In all cases, the time derivative of the diameter terminates in zero for crank angles above  $440^\circ$ , meaning that the primary particles do not evolve from that point. It should be noted that when combustion begins, the growth rate of the primary particles for the case of 100% diesel, D100, is very high, until the average temperature rises and the reduction of the graphite layers on the periphery of the soot are oxidised. This effect is best seen in Fig. 7.b which corresponds to the case of D100M, at medium load, in which the thermal effect is seen as predominant from about  $367^\circ$  CAD, in which the rate of decrease is in the order of the preliminary growth rate. From there, the growth of the primary particles is sustained with a relatively low growth rate and decreases until becoming zero.

For alcohol–diesel fuel blends, it can be observed that the growth of primary particles is suppressed by oxidation of the hydroxyl radical in the first stages of the formation of the graphene layers. This effect is best appreciated in medium load conditions, Fig. 7.b, in which the delay in forming primary particles with diameters of 1 nm on average reaches  $370^\circ$  CAD. From these CAD angles, the growth rate of soot formed when the engine operates on alcohol–diesel fuel blends is higher than when the fuel is pure diesel, and this may be because, for the same



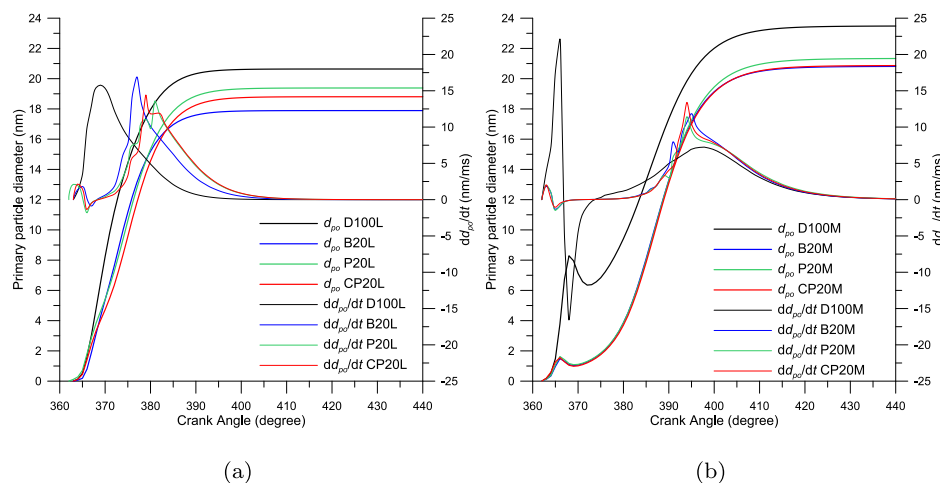


Fig. 7. Temporal evolutions of the mean diameter of the primary particles and their temporal derivative vs. crank angle degree.

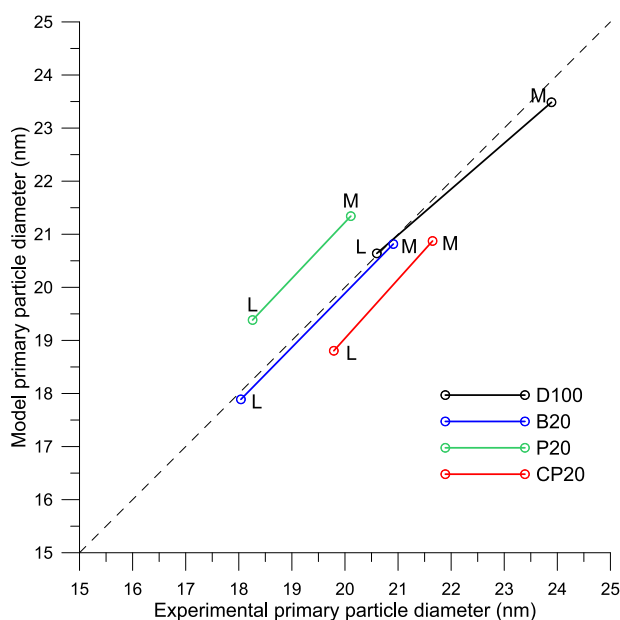


Fig. 8. Mean diameters of the primary particles obtained by the proposed model vs. the experimental ones.

CAD angles, the primary soot particles are much smaller for alcohol-diesel fuel blends and therefore fewer soot precursors are needed to form the same graphite layers as the pure diesel engine, since the surface area of the primary particles is smaller.

In Fig. 8 is shown the mean diameters of the primary particles measured experimentally versus those obtained by the model shown in Fig. 7.

Fig. 8 represents the modelled concerning the experimental primary particle sizes. It can be seen that all results are close to the bisecting line, represented by a dashed line in the figure.

#### 4. Conclusions

The size of the primary particles generated by a compression ignition engine running at low and medium loads with four different fuels has been measured experimentally. Pure diesel and three fuel blends composed of 80% diesel (by volume) with 20% of butanol, pentanol and cyclopentanol have been investigated. Based on these experimental measures and the physical and chemical characteristics of the fuels,

a correlation has been obtained that predicts accurately the average diameter of the primary particles emitted, which depends mainly (in decreasing order of their effect) on the mass fraction of the hydroxyl group in the fuel, on the mass fraction of hydrogen in the fuel and on the air/fuel ratio. In all cases, the larger any of these variables, the smaller the average primary particle diameter.

A new semi-empirical model has been developed predicting the instantaneous soot primary particle net growth, and thus, average primary particle size depending on engine condition and fuel properties. For alcohol-diesel blends, it can be observed that the growth of primary particles is suppressed by oxidation of the hydroxyl radical in the first stages of forming the graphene layers. The model is based on the mean in-cylinder pressure and temperature and fuel oxygen content as major inputs and geometric engine characteristics such as engine displacement, stroke, piston diameter and compression ratio. The model can reproduce the smaller primary particle size for diesel-alcohol blends concerning diesel fuel combustion and the larger primary particle size of medium load concerning low load engine operation. This investigation provides new knowledge and tools which contribute to propose environmentally friendly fuel candidates for transportation.

#### CRediT authorship contribution statement

**F.J. Martos:** Conceptualisation, Methodology, Formal analysis, Investigation, Supervision, Writing – original draft, Writing – review & editing. **O. Doustdar:** Investigation, Formal analysis, Writing – original draft. **S. Zeraati-Rezaei:** Investigation, Formal analysis, Writing – original draft. **J.M. Herreros:** Investigation, Resources. **A. Tsolakis:** Project administration, Conceptualization, Methodology, Funding acquisition, Supervision, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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## Appendix. Nomenclature

$A$	air
$A$	constant
$B$	constant
$C$	constant
$C$	carbon
$d$	diameter
$D$	constant
$E$	activation energy
$f$	function
$F$	constant
$F$	fuel
$g$	function
$H$	hydrogen
$H_p$	lower heating value
$HRF$	accumulated heat release fraction
$L$	low
$M$	medium
$p$	pressure
$O_2$	oxygen
$R$	gas constant
$S$	surface
$t$	time
$T$	temperature
$v$	volume
$w$	weight
$Y$	mass fraction
$\lambda$	inverse equivalence ratio
$\phi$	equivalence ratio

## Subscripts

$air$	air
$f$	formation
$fuel$	fuel
$H$	hydrogen
$max$	maximum
$net$	net
$po$	primary particle
$O_2$	oxygen
$OH$	hydroxyl group
$ox$	oxidation
$po$	primary particle
$sth$	stoichiometric

## Acronyms

AC	Alternating current
bTDC	Before top dead centre
CAD	Crank angle degree
COV	Coefficient of variation
EGR	Exhaust gas recirculation
HR-TEM	High resolution transmission electronic microscopy
IMEP	Indicated mean effective pressure
PM	Particulate matter

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