



Autoignition of blends of *n*-butanol and ethanol with diesel or biodiesel fuels in a constant-volume combustion chamber

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ABSTRACT

Recently, there is increasing interest in using butanol as a renewable component not only for gasoline but also for diesel fuels. This work investigates the effect of its concentration on diesel and biodiesel blends on the autoignition time, comparatively to equivalent blends with ethanol, in a constant-volume combustion chamber. The increase of alcohol content in diesel or biodiesel, led to an increase in autoignition times. Such increase was not linear but sharper for high alcohol contents, and was higher with ethanol than with butanol. For butanol blends, the increase in delay time was very similar when diesel or biodiesel were used. The maximum pressure during combustion decreases as the alcohol content was increased, especially in the case of ethanol, as a consequence of energy, chemical and dilution effects. However, for low ethanol or butanol concentrations, some increases in the pressure peaks were observed by a combination of compensating effects: increase in the amount of premixed combustion and increase in the flame speed. For 10% v/v alcohol blends in diesel or biodiesel, the delay times decreased as both the initial pressure and the initial temperature were increased, the latter effect being slightly higher with biodiesel compared to diesel.

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1. Introduction

The continued depletion of oil reserves, the fluctuating but net increase in fuel prices, the new policies promoting the use of advanced biofuels and the increasingly harder restrictions on emissions for vehicle engines, have led researchers to seek new forms of energy that reduce the dependence of fossil fuels. In this sense, new fuels from waste or lignocellulosic materials or alternative production techniques appear to be able to reduce life-cycle greenhouse emissions and thus to contribute to restrain global warming.

Diesel fuels can be blended with bioalcohols as a means to introduce a renewable fraction and to provide certain oxygen content. This renewable fraction could be additional to that already included in many diesel fuels with some biodiesel content, as it is usual in many countries. Some studies, performed in different setups and under different conditions, have reported reductions in

emissions of particulate matter and carbon monoxide when diesel engines operate with ethanol and butanol blends [1–4], although not unanimous trends have been reported in nitrogen oxides and unburned hydrocarbons especially at low loads [3,5–8]. The hydroxyl group of the alcohol molecule contributes to reduce soot formation and consequently particulate emissions, even more than other functional groups with similar oxygen content [9–13]. Among the alcohols to be used in diesel blends, ethanol and butanol have proved to have a significant potential to reduce life-cycle greenhouse gas emissions, as far as they can be produced from biological processes. Specifically, butanol can be produced from various methods, among which acetobutylicum fermentation (ABE) has superior interest, as far as the bio-acetone obtained as co-product is valued as such [14]. Ndaba et al. [15] suggest that some chemical conversion routes are preferable to the conventional ABE process, because the reaction proceeds more quickly compared to the fermentation route and fewer steps are required to produce *n*-butanol. Zheng et al. [16] made a review on the latest advances in butanol fermentation particularly from the perspective of genetic engineering and fermentation technology.

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A previous work was published about blending stability, lubricity, viscosity and cold filter plugging point as the key properties of ethanol and butanol blends (among others) with diesel fuel [17]. Additionally, among the properties affecting the combustion process, cetane number is a limiting one. Alcohols exhibit low cetane numbers, and therefore, only minor concentrations of these alcohols in the blends are recommended for use in unmodified diesel engines. The higher cetane number of butanol with respect to ethanol, together with its better miscibility, higher heating value and lower hydrophilic character, suggest that *n*-butanol is a better renewable component than ethanol in diesel blends [18,19], and consequently, its maximum concentration in diesel blends could be increased with respect to that recommended for ethanol.

Cetane number of a fuel is defined as the concentration of *n*-hexadecane in heptamethylnonane providing the same autoignition delay as that of the fuel. However, blends of these reference fuels do not provide autoignition times proportional to their concentrations. Similarly, blends of alcohols with diesel or biodiesel blends are not expected to provide autoignition times proportional to their composition. Instead, the most reactive components (those with shorter autoignition times) contribute to shorten the autoignition time more than the least reactive ones to enlarge it [20]. Therefore, experimental autoignition studies with these blends are necessary to evaluate their autoignition behavior.

Other studies have been previously published reporting autoignition results from alcohol blends in diesel or biodiesel fuels, or surrogates, in constant-volume combustion chambers, but far from modern diesel-like injection conditions [21–23].

The impact of ethanol and butanol concentrations on the autoignition time of diesel and biodiesel blends is analysed in this study. The effects of the initial temperature and pressure, as well as that of the equivalence ratio, are also studied for 10% alcohol blends.

2. Experimental procedure and fuels

The experiments were carried out in a Cetane ID510 by Herzog, which is basically a constant-volume combustion chamber, equipped with a common-rail diesel injector (operating at 1000 bar injection pressure) and with different temperature and pressure sensors: a dynamic pressure sensor to measure the chamber pressure, a static pressure sensor to correct the temperature offset

of the dynamic sensor, an injection pressure sensor, an inlet air pressure sensor and two thermocouples type K for the chamber inner wall and the cooling jacket. The experimental procedure proposed in Ref. [24] was followed, and pressure signals were recorded and analysed with a diagnostic model described in Ref. [25]. Initial chamber temperature and pressure were modified by modulating the previous heating/cooling of the combustion chamber jacket and the inlet air pressure reduction from the air bottles. The amount of fuel injected was modified with the injection pulse width. Most of the tests were done with injection pulse of 2.5 ms, and thus with approximately equal injected volume. Nevertheless, the exact volume injected per pulse was calibrated for each pure fuel. In all cases, the combustion process occurred in two stages, and therefore, two different ignition delays were defined: the first was denoted as ID_{CF} because it was associated to the cool flame stage, and the second, ID_M , is associated with the main combustion. The procedure to determine these times is described in Ref. [24].

The base fuels used for alcohol blending were diesel and biodiesel. Tests were made for blends of butanol and diesel (Bu-D), ethanol and diesel (Et-D), butanol and biodiesel (Bu-B), and ethanol and biodiesel (Et-B), at different alcohol concentrations, avoiding the use of emulsifiers. The nomenclature includes the volume percentage of alcohol in the blend. Thus, Et10-B refers to a blend of ethanol with 10% and 90% biodiesel. Table 1 shows the main properties of the four fuels used to prepare the blends. It should be noted that, despite the large differences between most of their properties, the derived cetane numbers are very similar for both diesel and biodiesel fuels, which permitted to concentrate the study on the effect of alcohols, rather than in that of the base fuels.

Diesel fuel was supplied by Repsol, and had zero oxygen content. The biodiesel fuel used was donated by Bio Oils and was produced from soybean and palm oils. Table 2 shows the methyl ester profile of the biodiesel fuel tested with indication of number of carbon atoms of the acid chain (*n*) and number of double bonds (*db*). Butanol was supplied by Green Biologics Ltd., as a member of the Consortium of ButaNext Project (see acknowledgements). Finally, ethanol was donated by Abengoa Bioenergy.

Blends with 10% alcohol (ethanol or butanol) were selected to study the effect of the initial pressure and temperature conditions and of the equivalence ratio. This choice is based on the promotion

Table 1
Properties of the fuels used for blends.

Properties	Method	Diesel ^a	Biodiesel ^a	Ethanol ^a	<i>n</i> -Butanol ^a
Purity (% v/v) ^b		~	~	>99.5	>99.5
Density at 15 °C (kg/m ³)	EN ISO 3675	842.0	883.5	792.0	811.5
Kinematic viscosity at 40 °C (cSt)	EN ISO 3104	3.00	4.19	1.13	2.27
Higher heating value (MJ/kg)	UNE 51123	45.77	40.19	29.67	36.11
Lower heating value (MJ/kg)	UNE 51123	42.93	37.64	26.84	33.20
C (wt %)		86.74	77.08	52.14	64.86
H (wt %)		13.26	11.91	13.13	13.51
O (wt %)		0	11.00	34.73	21.62
Water content (ppm wt)	EN ISO 12937	41.70	352.10	2024	1146
Molecular weight (kg/kmol)		208.20	291.26	46.07	74.12
Boiling point (°C)	ASTM D86	149–385	190–340	78.37	117.4
Standard enthalpy of vaporization (kJ/kg)		–	353.56 ^c	837.33 ^c	645.47 ^c
H/C atomic ratio		1.83	1.85	3	2.50
Stoichiometric fuel/air ratio		1/14.51	1/12.50	1/9.01	1/11.15
CFPP (°C)	EN 116	–20	–1	<–51	<–51
Lubricity (WS1.4) (µm)	EN ISO 12156-1	371.45	143.30	1057	571.15
Derived cetane number	ASTM D7668-14	52.65	52.48	8 ^d	15.92

^a Data measured at University of Castilla-La Mancha.

^b Data provided by supplier.

^c Estimated from the corresponding-state correlation proposed by Pitzer [26] with modified exponents as proposed in Ref. [27].

^d Taken from Refs. [28,29].

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