



Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

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

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ARTICLE INFO

Article history:

Received 30 April 2016

Received in revised form

22 September 2016

Accepted 21 October 2016

Available online xxx

Keywords:

Combustion

Delay time

Autoignition

Ethanol

n-butanol

Biodiesel

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].

Table 2
Methyl ester profile of biodiesel.

Methyl ester	Cn:db	%w/w
Lauric	C12:0	0.03
Myristic	C14:0	0.21
Palmitic	C16:0	15.62
Palmitoleic	C16:1	0.11
Margaric	C17:0	0.08
Margaroleic	C17:1	0.04
Stearic	C18:0	3.77
Oleic	C18:1	26.22
Linoleic	C18:2	47.26
α -linolenic	C18:3	5.39
Arachidic	C20:0	0.37
Gadoleic	C20:1	0.25
Behenic	C22:0	0.40
Lignoceric	C24:0	0.16

of use of biofuels proposed by European directives 2009/28/CE [30] and 1513/2015/CE [31], which will lead to a scenario where transport fuels will include 10% of advanced biofuels in 2020.

3. Results and discussion

3.1. Effect of alcohol content

The resulting values for ID_{CF} and ID_M and pressure peaks are listed in Table 3 for all tests. Also, standard deviations from the 15 cycles recorded for each blend are included for all the results presented hereinafter. In all cases they are small with respect to the variations found, proving the significance of the trends discussed. In this table, the equivalence ratio (defined as the ratio between the actual mass fuel/air ratio and the stoichiometric one, and denoted as relative F/A) is also listed for each test. As expected based on the cetane numbers, increasing the alcohol content always led to a significant increase in both ID_{CF} and ID_M as shown in Fig. 1, where the average pressure trace obtained from 15 individual pressure signals are displayed for each blend. Logarithmic scale is used in the horizontal axis for a better discrimination of pressure signals with low alcohol contents. The trends in both ignition delays are better observed in Fig. 2. Such an increase was not linear with the alcohol content, but was sharper at high alcohol contents, which is in agreement with other studies [3,9]. In the case of ethanol-diesel blends, no experimental results were obtained from 15% to 65% ethanol content, due to the weak miscibility of blends within this range, where emulsifiers would be necessary at room temperature. No tests could be done for higher ethanol contents because they resulted in delay times higher than 120 ms, which are the maximum data acquisition window. The result shown for Et65-D blend was obtained after heating the mixture up to 40 °C to reach enough miscibility.

Fig. 2c) and d) shows the same information as a) and b), respectively, at concentrations under 25%. For butanol blends, the increase in delay time was very similar when diesel or biodiesel were used in the blends. For the same alcohol content, the increase in ignition delay was always higher for ethanol than for butanol blends, consistently with the lower cetane number of ethanol. Two factors contribute to this trend: a) the lower carbon number of ethanol with respect to butanol and b) the lower equivalence ratio of the mixture of ethanol blends and air with respect to the corresponding butanol blends (see Table 3). If the delay time ID_M is compared for blend Et65-D and for net butanol (both with 0.28 equivalence ratio), it can be observed that the delay time for the ethanol blend is still much larger than that for butanol, proving that differences in equivalence ratio did not affect the observed trends

Table 3
Results of autoignition delay time for main combustion, ID_M , and cool-flame combustion, ID_{CF} , for different alcohol contents, initial temperatures and initial pressures.

Alcohol cont. %v/v	p_0 (bar)	T_0 (°C)	Inj. Dur. (ms)	Butanol-Diesel				Ethanol-Diesel			
				Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)	Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)
0	21	602.5	2.50	0.3849	2.4435 ± 0.0250	3.5793 ± 0.0591	42.0703 ± 0.0681	0.3849	2.4435 ± 0.0250	3.5793 ± 0.0591	42.0703 ± 0.0681
2.5	21	602.5	2.50	0.3820	2.5705 ± 0.0318	3.7352 ± 0.0439	41.9711 ± 0.1833	0.3782	2.5496 ± 0.0270	3.8676 ± 0.0619	42.0053 ± 0.1734
5	21	602.5	2.50	0.3800	2.6551 ± 0.0370	3.8606 ± 0.0628	41.9487 ± 0.1094				
7.5	21	602.5	2.50	0.3770	2.7821 ± 0.0351	4.0139 ± 0.0502	42.5531 ± 0.1279				
10	21	602.5	2.50	0.3763	2.9747 ± 0.0435	4.2033 ± 0.0485	42.3143 ± 0.1151				
15	21	602.5	2.50	0.3696	3.1201 ± 0.0421	4.4239 ± 0.0610	42.5473 ± 0.0412	0.3701	2.8188 ± 0.0214	4.3022 ± 0.0533	41.8916 ± 0.1524
20	21	602.5	2.50	0.3646	3.3802 ± 0.0722	4.7710 ± 0.1001	42.4115 ± 0.0729	0.3620	3.3524 ± 0.0433	5.0943 ± 0.0749	41.6515 ± 0.1578
30	21	602.5	2.50	0.3546	4.1125 ± 0.0599	5.8072 ± 0.0719	42.2406 ± 0.0801	a	a	a	a
40	21	602.5	2.50	0.3447	5.1513 ± 0.0929	7.3952 ± 0.1673	41.9214 ± 0.0841	a	a	a	a
50	21	602.5	2.50	0.3347	6.4770 ± 0.0781	9.8283 ± 0.1714	41.5374 ± 0.0674	a	a	a	a
65	21	602.5	2.50					0.2813	34.5444 ± 1.8453	129.2191 ± 2.6835	35.6908 ± 0.1705
75	21	602.5	2.50	0.3098	13.2890 ± 0.2779	24.8852 ± 0.4958	39.9949 ± 0.1002	b	b	b	b
100	21	602.5	2.50	0.2850	51.8662 ± 0.6234	88.1821 ± 1.4783	38.1606 ± 0.1195	b	b	b	b
10	21	535.0	2.50	0.3473	7.7148 ± 0.1590	9.8832 ± 0.4105	7.9622 ± 0.1503	0.3415	7.9622 ± 0.1503	10.3803 ± 0.3765	
10	21	550.0	2.50	0.3537	5.7452 ± 0.1156	7.3480 ± 0.2478	5.7565 ± 0.1375	0.3479	5.7565 ± 0.1375	7.5867 ± 0.1712	
10	21	570.0	2.50	0.3623	4.2109 ± 0.0673	5.4300 ± 0.1113	4.3243 ± 0.0708	0.3564	4.3243 ± 0.0708	5.7794 ± 0.1087	
10	21	625.0	2.50	0.3859	2.4017 ± 0.0287	3.7028 ± 0.0693	2.4510 ± 0.0823	0.3796	2.4510 ± 0.0823	3.7800 ± 0.1069	
10	21	650.0	2.50	0.3967	2.1065 ± 0.0280	3.1818 ± 0.0644	2.2071 ± 0.0242	0.3901	2.2071 ± 0.0242	3.5488 ± 0.0390	
10	6	602.5	2.50	1.3109	5.1788 ± 0.2836	10.3682 ± 0.2884	4.4568 ± 0.0564	1.2954	4.4568 ± 0.0564	11.979 ± 0.0785	
10	9	602.5	2.50	0.8780	3.2979 ± 0.0246	6.3902 ± 0.0670	3.3806 ± 0.0427	0.8636	3.3806 ± 0.0427	6.9951 ± 0.0602	
10	11	602.5	2.50	0.7150	3.1649 ± 0.0561	5.6579 ± 0.0707	3.2853 ± 0.0291	0.7066	3.2853 ± 0.0291	6.1978 ± 0.0770	
10	16	602.5	2.50	0.4938	2.8266 ± 0.0427	4.5874 ± 0.0460	2.9200 ± 0.0320	0.4858	2.9200 ± 0.0320	4.8981 ± 0.0541	

(continued on next page)

Table 3 (continued)

Alcohol cont. %v/v	p_0 (bar)	T_0 (°C)	Inj. Duration (ms)	Butanol-Diesel				Ethanol-Diesel			
				Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)	Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)
10	6	602.5	0.71	0.3763	4.3492 ± 0.0733	40.5963 ± 1.7400		0.3701	4.7971 ± 0.1532	47.6256 ± 1.9486	
10	9	602.5	1.07	0.3763	3.3058 ± 0.0366	11.1459 ± 0.6504		0.3701	3.6966 ± 0.0270	14.0849 ± 0.9087	
10	11	602.5	1.31	0.3763	3.1926 ± 0.0318	7.6031 ± 0.4625		0.3701	3.3751 ± 0.0425	7.9220 ± 1.3046	
10	16	602.5	1.91	0.3763	2.8538 ± 0.0465	4.6135 ± 0.0881		0.3701	2.9655 ± 0.0361	5.0432 ± 0.0952	
Alcohol cont. %v/v	p_0 (bar)	T_0 (°C)	Inj. Duration (ms)	Butanol-Biodiesel				Ethanol-Biodiesel			
				Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)	Relative F/A	ID_{CF} (ms)	ID_M (ms)	p_{MAX} (bar)
0	21	602.5	2.50	0.3474	2.7100 ± 0.0454	3.5749 ± 0.0434	39.9829 ± 0.1127	0.3474	2.7100 ± 0.0454	3.5749 ± 0.0434	39.9829 ± 0.1127
2.5	21	602.5	2.50	0.3459	2.7621 ± 0.0408	3.6362 ± 0.0711	40.0067 ± 0.0981	0.3451	2.8990 ± 0.0353	3.7999 ± 0.0609	40.0778 ± 0.0639
5	21	602.5	2.50	0.3454	2.7967 ± 0.0383	3.7242 ± 0.0549	39.9871 ± 0.1305	0.3428	2.9183 ± 0.0383	3.8660 ± 0.0497	39.8805 ± 0.1443
7.5	21	602.5	2.50								
10	21	602.5	2.50	0.3413	2.9527 ± 0.0328	3.9305 ± 0.0539	40.0579 ± 0.0962	0.3381	3.1462 ± 0.0531	4.2318 ± 0.0627	39.7427 ± 0.1154
15	21	602.5	2.50	0.3383	3.0996 ± 0.0651	4.1284 ± 0.0712	40.1327 ± 0.0780	0.3323	3.2819 ± 0.0457	4.5452 ± 0.0664	39.7704 ± 0.1119
20	21	602.5	2.50	0.3352	3.3181 ± 0.0461	4.4147 ± 0.0719	40.0175 ± 0.1296	0.3283	3.9276 ± 0.0554	5.4263 ± 0.1183	39.7497 ± 0.0872
30	21	602.5	2.50								
40	21	602.5	2.50	0.3230	4.4182 ± 0.738	6.2129 ± 0.1268	39.8005 ± 0.1225	0.3074	5.6654 ± 0.0966	10.6466 ± 0.2789	38.1508 ± 0.1304
50	21	602.5	2.50								
65	21	602.5	2.50	0.3077	7.2659 ± 0.0668	11.8352 ± 0.2117	39.0166 ± 0.1642	0.2719	12.2129 ± 0.1416	57.8712 ± 1.7465	35.3043 ± 0.1301
75	21	602.5	2.50	0.3005	11.1920 ± 0.2271	20.2087 ± 0.5163	38.4449 ± 0.1452	0.2639	31.8824 ± 0.7767	119.4245 ± 2.1172	34.3097 ± 0.1541
100	21	602.5	2.50	0.2850	51.8662 ± 0.6234	88.1821 ± 1.4783	38.1606 ± 0.1195	^b	^b	^b	^b
10	21	535.0	2.50	0.3150	8.5282 ± 0.1970	10.468 ± 0.2775		0.3120	8.9578 ± 0.1487	10.8891 ± 0.1919	
10	21	550.0	2.50	0.3208	6.1072 ± 0.1263	7.5832 ± 0.1848		0.3178	6.2749 ± 0.1510	7.8395 ± 0.2215	
10	21	570.0	2.50	0.3286	4.7904 ± 0.0766	5.9625 ± 0.1057		0.3255	4.8580 ± 0.0817	6.1251 ± 0.1320	
10	21	625.0	2.50	0.3501	2.4367 ± 0.0515	3.4523 ± 0.0752		0.3468	2.5667 ± 0.0399	3.6946 ± 0.0892	
10	21	650.0	2.50	0.3598	2.1500 ± 0.0235	3.1928 ± 0.0584		0.3564	2.1413 ± 0.0354	3.1900 ± 0.0689	
10	6	602.5	2.50	1.1946	4.2712 ± 0.0358	10.0645 ± 0.0881		1.2475	4.2300 ± 0.0386	10.9258 ± 0.0597	
10	9	602.5	2.50	0.7964	3.2031 ± 0.0249	5.8639 ± 0.0362		0.7889	3.3104 ± 0.0213	6.3398 ± 0.0538	
10	11	602.5	2.50	0.6516	3.3269 ± 0.0616	5.3614 ± 0.0705		0.6805	3.4043 ± 0.0364	5.7458 ± 0.0610	
10	16	602.5	2.50	0.4480	2.8324 ± 0.0324	4.2888 ± 0.0622		0.4437	2.9792 ± 0.0353	4.6936 ± 0.0355	
10	6	602.5	0.71	0.3413	3.7454 ± 0.0595	22.3129 ± 2.0397		0.3381	3.8470 ± 0.0457	26.6015 ± 1.8016	
10	9	602.5	1.07	0.3413	3.1873 ± 0.0328	7.4558 ± 0.5173		0.3381	3.2166 ± 0.0247	8.3689 ± 0.4020	
10	11	602.5	1.31	0.3413	3.0059 ± 0.0250	6.1669 ± 0.0958		0.3381	3.0882 ± 0.0432	6.7747 ± 0.1678	
10	16	602.5	1.91	0.3413	2.9117 ± 0.0190	4.0797 ± 0.0740		0.3381	2.9982 ± 0.0712	4.3610 ± 0.1053	

^a Limited by immiscibility of components.^b Autoignition delay exceeding acquisition time window.

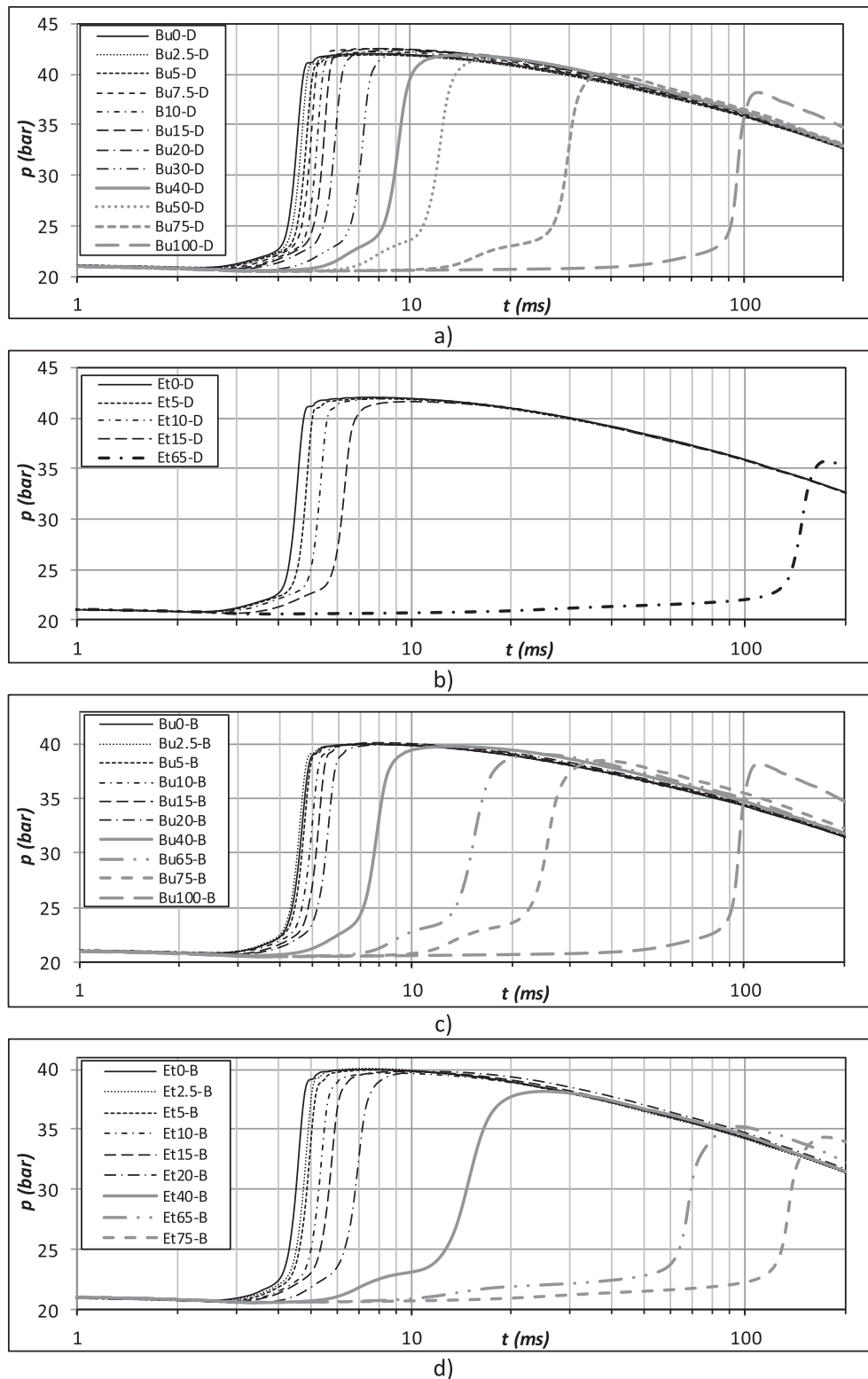


Fig. 1. Pressure signals recorded during the combustion process for (a) butanol-diesel, (b) ethanol-diesel, (c) butanol-biodiesel and (d) ethanol-biodiesel blends at $p_0 = 21$ bar, $T_0 = 602.5$ °C.

in ID_M . It is also noticeable that, from a certain alcohol content onwards, the differences between ethanol and butanol blends were magnified when alcohols were blended with diesel fuel, whereas they were minimized when they were blended with biodiesel fuel. Another interesting observation is that, despite the similar cetane

numbers of diesel and biodiesel fuels, alcohols (but especially ethanol) enlarge the delay time more when blended with diesel than when blended with biodiesel fuel. This cannot be explained based on the equivalence ratio, since it is higher in the case of diesel blends. Some divergence with respect to the cetane number trend

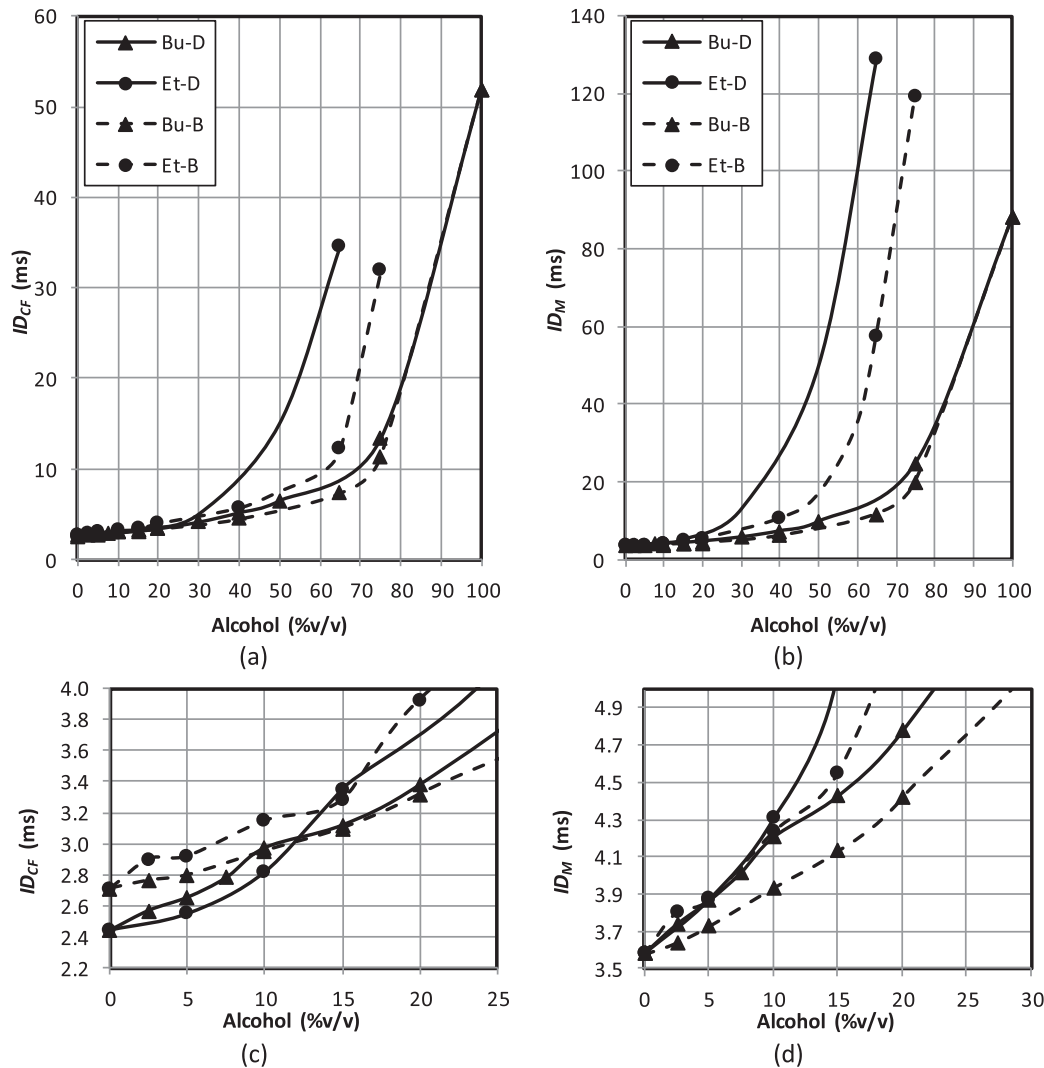


Fig. 2. Variation of ignition delay time for cool-flame combustion, ID_{CF} and main combustion, ID_M , with the alcohol content (butanol \blacktriangle or ethanol \bullet) in the blends ($p_0 = 21$ bar, $T_0 = 602.5$ °C).

was also observed in diesel engines when 15% alcohol was blended with diesel and biodiesel fuels [32].

In general, similar trends can be observed for both ID_{CF} and ID_M and thus, the former will not be presented in the following sections.

As shown in Fig. 3, the pressure peaks in the combustion chamber were observed to decrease as the alcohol content increased. This decrease can be explained by a three-fold effect. First, the heat release is reduced as the alcohol content is increased due to the reduced heating value (energy effect). This effect also includes the cooling effect from evaporation, which is higher for higher alcohol contents, due to their higher enthalpy of vaporization (see Table 1). Second, the blend is burned under leaner conditions since it requires less air-oxygen to react with the mass of fuel injected due to its increased bond-oxygen content (chemical effect). Third, the gaseous fuel is more and more diluted because the autoignition time is larger (dilution effect), thus reducing the local equivalence ratio and making the combustion leaner. Both chemical and dilution effects contribute to reduce the flame velocity, and thus to enhance the heat transfer to the chamber walls during combustion. All three effects (energy effect, chemical effect and dilution effect) are more important in the case of ethanol

blends than in the case of butanol blends. However, for low ethanol and butanol contents, some increases in the pressure peaks were observed (up to 15% butanol content and up to 5% ethanol content). These increases can be explained because the increase in the amount of premixed gaseous fuel-air mixture before combustion and the increase of the flame speed derived from the presence of alcohols in the blends (as proved in Ref. [33]) are more significant than the reduction in the heating value when the alcohol is added. Further alcohol concentrations led to progressive reductions of the pressure peaks, as a consequence of the above mentioned energy, chemical and dilution effects.

With respect to the pressure peaks observed for pure diesel and biodiesel fuels, the above described increase in pressure peaks is more relevant for butanol than for ethanol blends probably due to the higher heat of vaporization of ethanol (see Table 1), which reduces slightly the initial temperature and pressure. However, this is contrary to the higher increase in pressure peaks found with ethanol/biodiesel blends with respect to butanol/biodiesel blends [23]. In the present study, the highest increases in peak pressure are observed for *n*-butanol/diesel blends. For these blends, the range of butanol contents leading to some increases in the pressure peaks is

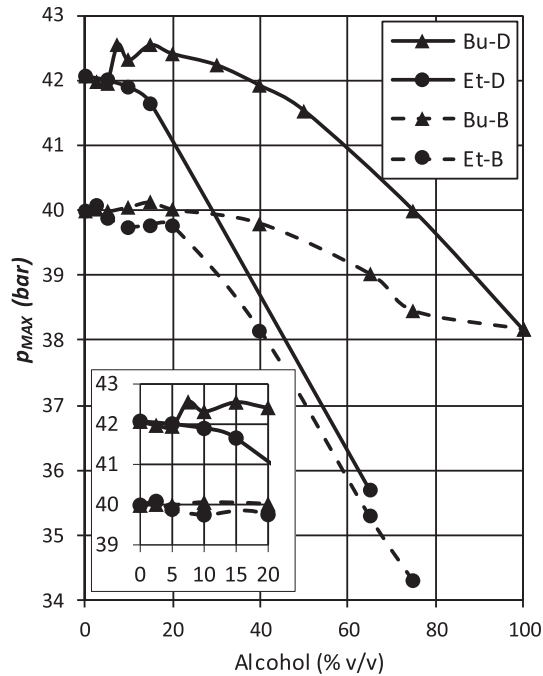


Fig. 3. Pressure peaks measured during the combustion process of each blend vs alcohol content (butanol ▲ or ethanol ●) in the blends ($p_0 = 21$ bar, $T_0 = 602.5$ °C).

extended to around 38% in volume. This effect can be confirmed in diesel engine tests, such as those carried out by Huang et al., who tested blends of 30% butanol with diesel fuel with no biodiesel content [34].

3.2. Effect of initial temperature

A comparison between the ignition delay times of blends Bu10-D, Et10-D, Bu10-B and Et10-B is shown in Fig. 4. Trends for ignition

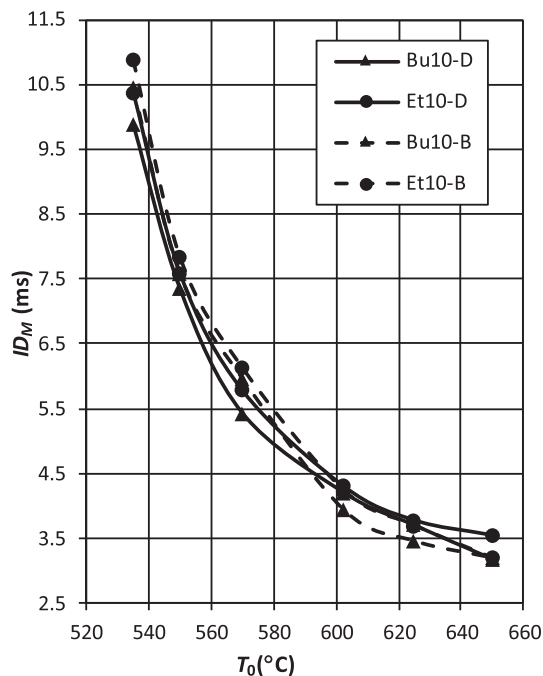


Fig. 4. Variation of ID_M with initial temperature of chamber for 10% alcohol (butanol ▲ or ethanol ●) blends ($p_0 = 21$ bar).

delay times are very similar for the four blends. In all cases, the delay times decreased as the initial temperature was increased, thus proving that there is no negative temperature coefficient in this range of temperature at this initial pressure. Again in this case increasing the initial temperature reduces the mass of air enclosed in the combustion chamber thus increasing slightly the equivalence ratio (see Table 3), which may have some contribution to the decreases in delay time. However, it can be noticed that for biodiesel blends (whose ID were initially slightly higher than those for diesel blends), when the initial temperature was increased, the reduction of ID_M was higher. This effect can be explained because at low temperatures, the physical properties of biodiesel (higher density, viscosity and boiling point) slow down the atomization and evaporation processes, which affect the mixing of the air and fuel vapors. This makes the contribution of the physical processes to the autoignition delay (which is basically associated with the chemical kinetics) more important than in the case of diesel blends. Furthermore, as the temperature increases, the contribution of the physical processes becomes negligible in front of the reaction mechanisms regardless the base fuel used.

3.3. Effect of initial pressure

Fig. 5 shows (in black lines) that autoignition delay times increase with decreasing initial pressure, for the same 10% blends as in the previous study, as expected. The same trend can be observed for all four blends, and no differences in increasing rates can be clearly distinguished between them. In this case, differently to the previous studies with varying alcohol content and initial temperature, initial pressure variations involve significant changes in equivalence ratios (see Table 3). Tests at 21, 16, 11 and 9 bar implied lean mixtures, with equivalence ratios around 0.35, 0.46, 0.7 and 0.83 respectively, whereas tests at 6 bar led to rich mixtures with equivalence ratios around 1.25. For this reason, additional tests were made at 6, 9, 11 and 16 bar (with results shown in gray lines) reducing the injection duration (and thus the injected fuel mass) to

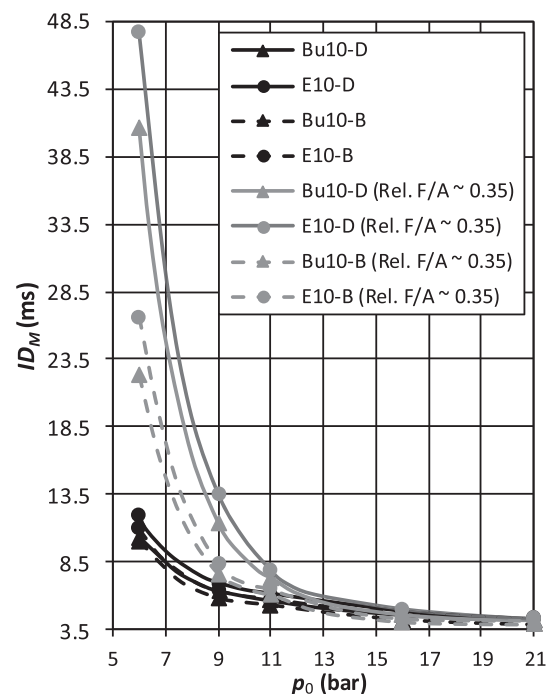


Fig. 5. Variation of ID_M with initial pressure of chamber for 10% alcohol (butanol ▲ or ethanol ●) blends ($T_0 = 602.5$ °C).

ensure that the equivalence ratios remained equal to those of tests made at 21 bar (around 0.35). These additional results (see also Table 3) permitted to evaluate the effect of the initial pressure independently of the equivalence ratio. Ignition delay times for equal equivalence ratios increase exponentially with decreasing pressure, with exponents around -1.84 in the case of diesel blends, and around -1.39 in the case of biodiesel blends, with minor effect of the alcohol blended. These pressure exponents are not far from other pressure exponents proposed in the literature for diesel [35] and biodiesel [36] fuels.

Since the initial temperature in these tests was $602.5\text{ }^{\circ}\text{C}$, biodiesel blends showed shorter delay times than diesel blends, consistently with the results discussed in the previous subsection. In all cases (diesel and biodiesel blends with ethanol or butanol), when the excess air (which acts as a heat absorber) is reduced or even eliminated (black lines) ignition delays become shorter, compensating partially the effect of the decreasing pressure.

These results, together with the above described effect of the initial temperature imply that the initial thermodynamic conditions affect differently the chemical kinetics of diesel fuels (typically composed of paraffins, naphthenes and aromatics) and biodiesel fuels (methyl esters), despite their similar cetane numbers. However, they have only minor effects on the kinetics of alcohols with different carbon numbers, despite their different cetane numbers.

4. Conclusions

The following conclusions can be drawn from the present study:

- The increase in alcohol content in diesel or biodiesel fuels always led to an increase in both ID_{CF} and ID_M . Such an increase was sharper at high alcohol contents. This implies that weight or volume averaging of autoignition parameters (such as cetane number) is not an accurate method to predict the autoignition behaviour of alcohol blends.
- The increase in the delay time with the ethanol content is more prominent than for butanol, consistently with its lower cetane number. However, the differences in autoignition time become more visible when these alcohols are blended with diesel fuel whereas they become less significant when they are blended with biodiesel fuel (at least for high alcohol contents).
- For butanol blends, the increase in autoignition delay time is very similar when diesel or biodiesel (with similar cetane numbers) were used in the blends. However, some differences appear when ethanol is blended with diesel or biodiesel fuels, with larger delay times in the former case.
- The maximum pressure in the combustion chamber was observed to decrease as the alcohol content was increased, especially in the case of ethanol, as a consequence of the reduced heating value, of the reduced equivalence ratio and of the over-dilution caused by their large delay times.
- Some increases in the pressure peaks were observed in a narrow range of low ethanol and butanol contents (especially in butanol blends), probably due to a combination of effects which compensate the above mentioned effects: increase in the amount of premixed combustion and increase in the flame speed derived from the presence of alcohols in the blends.
- For blends with 10% v/v alcohol and 90% diesel (or biodiesel), the autoignition delay times decrease as the temperature increases. This effect is slightly more prominent for biodiesel than for diesel fuel, as a consequence of the physical properties of biodiesel (mainly higher viscosity and higher boiling point) which lead to some contribution of the physical delay especially at moderate temperatures.

- For blends with 10% v/v alcohol, the autoignition delay times increase exponentially as the pressure is decreased (for equal equivalence ratio). The fitting exponents are similar for both alcohols, but higher for diesel blends than for biodiesel ones. However, such increase is partly compensated by the increase in equivalence ratio.

Acknowledgements

The research leading to these results was co-funded by the European Union Horizon 2020 Research and Innovation Programme under grant agreement n° 640462 (ButaNexT project). Repsol, Bio Oils, Green Biologics and Abengoa Bioenergy are gratefully acknowledged for the donation of diesel, biodiesel, *n*-butanol and ethanol fuels respectively.

Nomenclature

<i>v</i>	Volume
ABE	Acetone-butanol-ethanol
<i>ID</i>	Ignition delay time
Bu	Butanol
Et	Ethanol
D	Diesel
B	Biodiesel
<i>n</i>	Number of carbon atoms
<i>db</i>	Number of double bonds
Relative <i>F/A</i>	Equivalence ratio
<i>p</i>	Pressure
<i>t</i>	Time, duration
<i>T</i>	Temperature
CFPP	Cold Filter Plugging Point

Subscripts

CF	Cool Flame stage
<i>M</i>	Main combustion stage
0	Initial conditions
MAX	Maximum

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