Fuel Processing Technology 140 (2015) 113–118

Contents lists available at ScienceDirect

Fuel Processing Technology

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

NO_x emissions from low-temperature combustion of biodiesel made of various feedstocks and blends

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ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form 13 August 2015
Accepted 25 August 2015
Available online 12 September 2015

Keywords:
Biodiesel NO_x emissions
Unsaturation degree
Ignition delay
Ignition temperature
Low-temperature combustion
Paired t-test analysis

ABSTRACT

Nitrogen oxides (NO_x) are one of the major hazardous emissions from biodiesel-fueled engines that need to be regulated stringently. In this paper, NO_x emissions from different types of biodiesel were studied using a laboratory combustion chamber. Biodiesel fuels with various portion of fatty acid methyl esters (FAMEs) from soybean methyl ester (SME), tallow oil (TO), and waste cooking oil (WCO) were combusted at 330–420 °C simulating low-temperature combustion (LTC). Combustion analysis results show that neat biodiesel fuels had longer ignition delay and lower ignition temperatures compared to ultra-low sulfur diesel (ULSD). The unsaturation of biodiesel samples and their blends with ULSD was analyzed for its effects on NO_x emissions. The results showed that biodiesel with more unsaturated fatty acids emitted more NO_x compared to biodiesel with more saturated fatty acids. A paired t-test showed that neat TO, WCO, and WCO B50 had significant reduction in the formation of NO_x compared with ULSD and SME B20. It is concluded that less unsaturated FAME fuels would be preferable when reduction of NO_x emissions is a critical issue.

1. Introduction

Biodiesel and its blends in general are known to produce lower carbon monoxide (CO), soot, hydrocarbon (HC) emissions, and higher NO_x emissions compared with regular diesel [1–10]. Because of the lower heating value of biodiesel, more biodiesel should be burned to produce the equivalent energy of ULSD. Also, due to the presence of high oxygen content in biodiesel fuels, generally biodiesel fuels emit more NO_x than regular diesel for the same heat generation. The reduction of NO_x emissions is one of the most important technical challenges facing biodiesel, especially in light of the increasingly stringent exhaust emission regulations on diesel engines [11]. NO_x formation during biodiesel combustion is associated with a number of factors such as the property of biodiesel and combustion conditions. Combustion temperature influencesthermal NO_x emissions [2,4,12]. Low-temperature may help thermal NO_x reduce during combustion, leading to LTC technology [13,14]. All the experiments in this study were performed at low-temperatures to simulate LTC conditions.

Biodiesel defined by ASTM D6571 is a non-petroleum-based diesel fuel which is made by transesterification of mono-alkyl esters of fatty acids from vegetable oils and animal fats. Therefore an essential characteristic of biodiesel fuels is that its fatty acid profile corresponds to its principal oil or fat. The main structural features of fatty acids are their chain length and the number of double bonds. Most commercial biodiesel fuels are mainly composed of medium to long-chain FAMEs. The major fatty acid structures and compositions for neat biodiesel samples used in this study are presented in Table 1 and plotted in Fig. 1. As shown in Fig. 1, oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) have 18 carbon atoms and 1, 2, or 3 double bonds in their structure, respectively.

The degree of unsaturation of a FAME molecule depends on the number of double bonds present in its fatty acid chain. The high numbers of double bonds represent high degrees of unsaturation [15]. As shown in Table 1, SME is the most unsaturated fuel with significant contents of mono-unsaturated (22.8% C18:1), di-unsaturated (53.7% C18:2) and tri-unsaturated (8.6% C18:3) fatty acids. Compared with SME, WCO is medium unsaturated with 52.9% of mono-unsaturated and 13.5% of di-unsaturated fatty acid. TO is the least unsaturated with only 42.4% of mono-unsaturated fatty acid. The unsaturation of biodiesel fuel may be estimated by iodine value (IV), which corresponds to the gram of iodine consumed per 100 g of substance. Due to the presence of mostly 18-carbon saturated and unsaturated chains in FAMEs, the effects of chain lengths on combustion parameters and NO_x emissions are considered insignificant compared to the degree of unsaturation.

Although no single theory provides an adequate explanation on the relations between biodiesel properties and NO_x emissions under various conditions, it has been suggested that the degree of unsaturation of biodiesel plays an important role in NO_x formation during combustion [15,20]. The main goal of the present study is to better understand the effect of unsaturation on the combustion parameters including ignition temperature/delay and NO_x emissions from LTC of biodiesel.

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http://dx.doi.org/10.1016/j.fuproc.2015.08.031
0378-3820/

Table 1
Major fatty acid composition of the feedstocks in mass percent [16–19].

Fatty acids	Chemical formula	Chemical structure*	SME	TO	WCO
Lauric	$C_{12}H_{24}O_2$	C12:0	0.1	0.1	0.0
Myristic	$C_{14}H_{28}O_2$	C14:0	0.1	2.8	0.9
Palmitic	$C_{16}H_{34}O_2$	C16:0	10.2	23.3	20.4
Stearic	$C_{18}H_{38}O_2$	C18:0	3.7	19.4	4.8
Oleic	$C_{18}H_{36}O_2$	C18:1	22.8	42.4	52.9
Linoleic	$C_{18}H_{34}O_2$	C18:2	53.7	2.9	13.5
Linolenic	$C_{18}H_{32}O_2$	C18:3	8.6	0.9	0.8
Total saturated			14.1	45.6	26.1
Total unsaturated			85.1	46.2	67.2
Cetane number (ASTM D 613)			47.0	NR**	49.3
IV (gr I_2/100 g oil)			125–144	~100	46.9

Note:
* C18:2 describes a molecule with a HC chain of 18 carbon atoms and 2 double bonds.
** NR: not reported by the supplier.

Experiments were conducted on a laboratory combustion chamber fueled with three different types of biodiesel and their blends with ULSD. The physical and chemical characteristics of biodiesel samples were discussed and compared with those of ULSD. Molecular structures of various biodiesel feedstocks were analyzed using Fourier transform infrared spectroscopy (FTIR) mainly for their unsaturation. Then, the effects of defined combustion parameters were discussed. NO_x emissions from the blends of the biodiesel samples were compared to each other to determine the samples that most significantly reduced NO_x emissions. Paired t-test was used to statistically assess the difference in the effects of NO_x emissions from the pair of fuels [21–24].

2. Experimental setup and procedure

2.1. Experimental setup

Combustion tests were carried out in a laboratory reactor (300 ml) purchased from Parr Instrument Company. The device included a stainless steel reactor (2.5″ inside diameter with 4.0″ inside depth) placed in an electrically heated chamber. A J type thermocouple was placed inside the reactor for temperature recording, and a temperature controller was installed to preserve the reaction conditions at the predetermined values. With this arrangement, the reaction temperature could be controlled and monitored with a precision of 0.1 °C. A compressed air tank was used to maintain the combustion condition. A schematic diagram of the entire experimental setup is shown in Fig. 2.

2.2. Fuels specification

In the first step, the test samples were grouped into three blends (B20 (it means 20 vol% biodiesel and 80 vol% ULSD), B50, and B100) of three different biodiesel feedstocks (SME, TO, WCO). ULSD (as a control fuel) and SME were obtained from Toledo area regional transit authority (TARTA) company (purchased from Peter Cremer), TO was obtained from United Oil Inc., and WCO was obtained from White Mountain Biodiesel. These fuels and their blends with ULSD were tested for combustion and emission analysis in a laboratory combustion chamber with particular emphasis upon NO_x emissions.

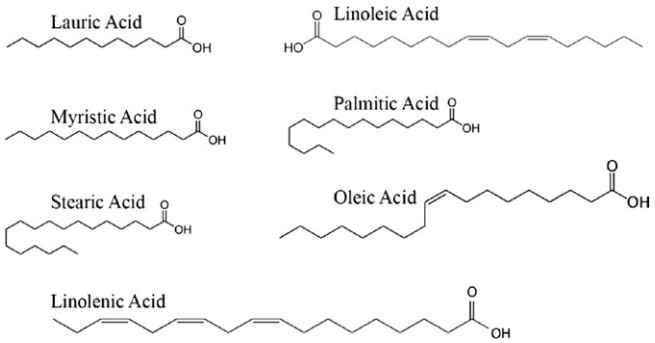

Fig. 1. Seven fatty acid molecules commonly found in biodiesel [16,17].

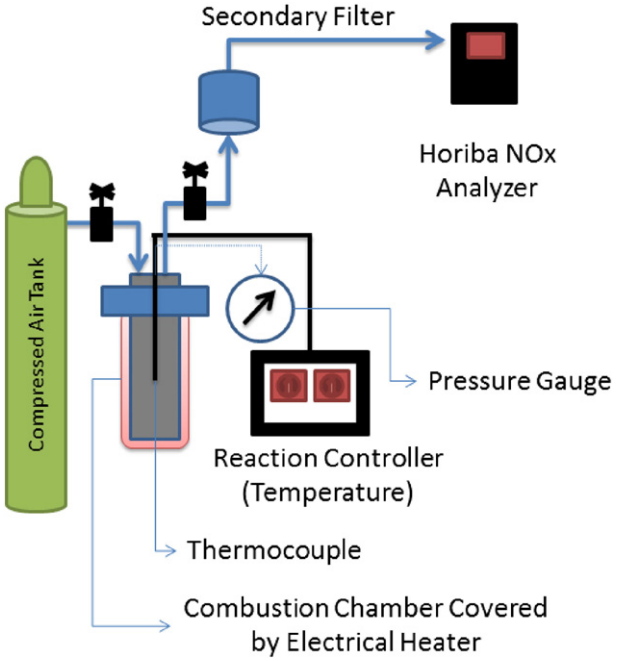

Fig. 2. Schematic diagram of experimental set-up.

2.3. Experimental procedure

Experiments were conducted in a combustion chamber as a single cycle of combustion in an engine cylinder. The amounts of fuel and air were determined to keep the equivalence ratio as one. To estimate the equivalence ratio, λ, stoichiometric conditions were calculated from a mixture of various esters as a representative for a biodiesel fuel as shown in Table 1 [16–19]. Stoichiometric combustion occurs when all the oxygen is consumed in the reaction, and there is no molecular oxygen in the products. The equivalence ratio is obtained from a dimensionless formula as follows:

$$\lambda = \frac{\left(\text{Fuel}/\text{Oxygen}\right)_{\text{actual}}}{\left(\text{Fuel}/\text{Oxygen}\right)_{\text{stoichiometric}}}$$

Fuel was placed inside the reactor at room temperature and air was injected from a high pressure air tank (dried air purchased from Airgas®) into the chamber while the pressure was monitored. The combustion process can be called premixed combustion because the oxygen came into contact with the fuel before combustion. Then the heater was turned on to elevate the temperature until the fuel ignited. The ignition point of combustion was determined by observing the combustion peak for temperature and pressure via a computer software program and pressure gauge provided by Parr Instrument. The elapsed time to observe an ignition temperature peak was named ignition delay and the value of temperature was named ignition temperature as shown in Fig. 3. After ignition terminated, the combustion gases were released and allowed to pass through a PTFE membrane filter capsule with 0.2 μm pore size that was placed before the NO_x analyzer. NO_x data were recorded as the gases passed through the detector until the reactor depressurized. Each experiment was repeated at least five times and