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Effect of biodiesel saturation on soot formation in diesel engines

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HIGHLIGHTS

- Numerical study on soot formation of biodiesel from different feedstocks.
- The acetylene production is proportional to the content of unsaturated FAME.
- The biodiesel with less C═C result in the lower formation of soot emissions.
- Reduced soot formation and improved soot oxidation were achieved for biodiesel.

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ABSTRACT

To understand soot formation in a diesel engine fueled with different biodiesels, a numerical study was performed using the KIVA-3V code, combined with a multi-step phenomenological soot model. The simulations were used to predict differences in soot formation for three various biodiesel feedstock types. Good agreements on soot emissions were achieved in comparisons of engine experiments and simulations at various engine operating conditions. The experimental data and simulated results showed that the degree of saturation and the oxygen content of biodiesel fuels are the major factors responsible for biodiesel soot production. The reduction of soot mass concentration for biodiesel is achieved due to the suppressed soot formation process and improved oxidation rate compared with diesel. It is observed that the acetylene generated in the pyrolysis of biodiesel is proportional to the content of unsaturated fatty acid methyl ester (the number of C—C double bonds). Among the three different biodiesel fuels, the lowest soot tendency was found for the Jatropha Methyl Ester because of its lowest amount of unsaturated alkyl esters through both numerical modeling and diesel engine experiments.

1. Introduction

Nowadays, conventional diesel engines and gasoline engines face challenge of soot emissions and super-knock [1,2]. Increasingly stringent environmental regulations and energy consumption have put forward a strong demand on seeking alternative solutions to reduce dependence on conventional fossil fuels. Biodiesel, as an attractive renewable fuel, can be used directly in compression ignition engines which need almost no modification [3–5]. Usually, biodiesel refers to a mixture of alkyl esters that are produced from various biological feedstocks. Methyl biodiesel is comprised primarily of methyl palmitate ($C_{17}H_{34}O_2$), methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), and methyl linoleate ($C_{19}H_{32}O_2$) [6]. Biodiesel is an alternative fuel with oxygen content of approximately 10% by weight, and therefore reduce exhaust emissions. Most researchers have reported that a decrease in particular matter (PM) was observed when using neat biodiesel or the biodiesel/diesel blends [7–10]. As well, the fuel composition has an important effect on the formation of soot emissions in diesel combustion. Recently numerical modeling has shown that oxygen in the fuel is beneficial for suppressing the soot precursor formation in fuel-rich regions, thus reducing soot production [11–14].

Biodiesel comprised of a variety of long-chain fatty acid alkyl esters including saturated and unsaturated compounds. The presence of carbon–carbon double bonds in unsaturated mono-alkyl esters appears to influence sooting tendency significantly. Sarathy et al. [15] and Gaïl et al. [16] conducted experimental and computational studies of methyl butanoate (MB) and methyl crotonate (MC) combustion using a jet stirred reactor (JSR) and an opposed-flow diffusion flame. They found that the unsaturated C_4 FAME (i.e., MC) shows higher sooting tendency than the saturated C_4 FAME (i.e., MB) due to the presence of C═C bond in MC. Garner

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et al. [17] experimentally investigated the combustion characteristic of methyl octenoate and methyl octanoate in shock tube. The positive correlation was found between the increased tendency of acetylene formation and the number of C=C bonds in the ester structure or the degree of unsaturation. Feng et al. [18] also observed that the higher amount of the C—C double bond in methyl esters results in greater soot propensity.

Still much work needs to be conducted to gain a deep insight into the effect of fuel composition on the soot emissions both experimentally and numerically. Especially, it is essential to understand how the saturation of biodiesel affects soot formation so as to find the difference in soot emissions for different biodiesels. Kinetic modeling provides an effective method to obtain thorough understanding of the combustion features of fuel in internal combustion engines [19]. Considering the complexity of real biodiesel, simpler esters were usually used as surrogates of large methyl esters during the combustion simulation. A detailed chemical kinetic model for the methyl butanoate ($C_5H_{10}O_2$) was proposed by Fisher et al. [20] to represent the characteristic of biodiesel. However, the simpler species do not adequately represent the combustion features of biodiesel due to the insufficient length of the carbon chain of the surrogate molecule. Therefore, Herbinet et al. [21] developed a combined oxidation model using a three component blends of methyl decanoate (MD), methyl-9-decenoate (MD9D), and n-heptane, which is capable of matching the C/H/O ratio for the real fuels. Moreover, this detailed chemical kinetic mechanism was validated against the jet stirred reactor (JSR) results by Dagaut and coworkers [22], and well reproduced the reactivity properties of rapeseed methyl ester. Later, Brakora and Reitz [23] reduced the MD/MD9D detailed mechanism of Herbinet, and applied it in multi-dimensional engine simulations. The reduced model was validated against experimental results of spray and combustion at conventional diesel operating conditions.

A series of complicated physical and chemical processes are involved with the soot formation in compression ignition engines. Thus, a good soot model is essential to better understand soot formation in diesel engines fueled with biodiesel. The most widely used two-step soot model includes the soot formation expression by Hiroyasu and Kadota [24] and the oxidation expression by Nagel and Strickland Constable [25]. Since the formation process of the empirical soot model is simplified and couldn't reflect the effect of fuel composition on soot production. Further, it provides no knowledge about soot number density and agglomeration. Consequently some more detailed multi-step phenomenological soot models have been proposed [26–28]. Tao et al. [28] developed a phenomenological soot model. In this model, acetylene is involved during precursor formation after fuel pyrolysis. Then precursor species formation, particle inception and coagulation, surface growth, and oxidation are considered as subsequent steps. Validations of this model over wide ranges of engine conditions were presented in [29–31]. Moreover, this soot model can be implemented in CFD codes for three-dimensional simulations where detailed soot mechanisms may be too computationally expensive.

McEnally and Pfefferle [32] found that the structure of biodiesel fuel affects sooting tendencies in laboratory-scale flames. Previous experimental investigations have proved that different FAME fuels produce different levels of soot emissions in engine tests [33,34]. Few modeling studies capture biodiesel composition effects on soot formation. Therefore, it is necessary to study the combustion of different FAME fuels to account for the effect of fuel structure on soot formation.

The purpose of this work was to investigate the influence of biodiesel composition on soot formation and oxidation. Three FAMEs with different levels of saturation were tested using a diesel engine and the results were compared with CFD modeling results using a multi-component biodiesel mechanism coupled with a multi-step phenomenological soot model. The combustion process and spatial distributions of soot-relevant intermediate species for different biodiesel fuels were studied in detail.

2. Methodology

2.1. Experimental approach

The experiments were conducted using a Cummins ISDe4 diesel engine equipped with a common rail fuel injection system. Table 1 lists the specifications of the engine, and the detailed operating conditions are shown in Table 2. An AVLSPC-472 partial flow dilution smart sampler was used to collect soot samples on filters. Before and after sampling, the filters are weighed using an electronic scale with 10 μg sensitivity, which were kept under constant temperature (22 ± 3 °C) and relative humidity (45% ± 8%) conditions. The total PM was separated into the dry soot and non-soot fractions by extraction in dichloromethane (CH_2Cl_2) and then in de-ionized water.

The three different biodiesels studied were: Jatropha Methyl Ester (JME), Cottonseed Methyl Ester (CME), and Rubber seed oil Methyl Ester (RME). Table 3 gives the properties of the reference diesel fuel and the biodiesels. Compared with the diesel fuel, the biodiesels have lower heating values, higher densities and viscosities. Moreover, the cetane number of JME is the highest while RME has the lowest.

2.2. Numerical methodology

2.2.1. Biodiesel reaction mechanism

The multi-dimensional computations were performed using the KIVA-3V code coupled with CHEMKIN II. The original biodiesel combustion mechanism was developed by combining the mechanisms of MD ($C_{11}H_{22}O_2$) and MD9D ($C_{11}H_{20}O_2$) from LLNL [6,21]. The biodiesel mechanisms used in this study was developed by Brakora et al. [35], which was reduced from a combined mechanism of MD, MD9D and n-heptane. Various biofuel compositions in biodiesels were represented by adjusting the mole fractions of MD, MD9D, and n-heptane. As discussed above, biodiesel fuels derived from different feedstocks mainly contain five long-chain methyl esters: methyl palmitate (MP; C16:0), methyl stearate (MS; C18:0), methyl oleate (MO; C18:1), methyl linoleate (MLO; C18:2), and methyl linolenate (MLN; C18:3). The first two species (MP and MS) are saturated methyl esters, while the last three components contain one (MO), two (MLO), and three (MLN) double bonds, respectively. The physical properties of real biodiesel fuels are represented by those of the five methyl esters. While in terms of chemistry, the two saturated species was represented by MD and the other unsaturated species was represented by MD9D. The fractions of these five components in JME, CME and RME are listed in Fig. 1. The five components are listed (left to right) in the order of decreasing saturation. This composition for the different biodiesel fuels was also applied in the simulations. For exam-

Table 1
Engine specifications.

Engine type	Four cylinder DI
Bore × stroke	107 × 124 mm
Connecting rod	192 mm
Displacement	4.5 L
Compression ratio	17.5
Injection pressure	160 MPa
Nozzle diameter	0.168 m
Nozzle number	8 holes
Intake valve close timing	155 °CA BTDC
Exhaust valve open timing	120 °CA ATDC