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Effects of six-carbon alcohols, ethers and ketones with chain or ring molecular structures on diesel low temperature combustion

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ABSTRACT

The effect of oxygenated additives with different oxygen functional groups and different carbon chain structures on the combustion and emissions was investigated on a single-cylinder diesel engine. Three different oxygenated hydrocarbons with ring molecular structure including cyclohexanone, cyclohexanol and 2,5-dimethylfuran and other three oxygenated hydrocarbons with chain molecular structure including 2-hexanone, *n*-hexanol, and isopropyl ether were blended with diesel fuel separately to formulate 6 blended fuels with the same oxygen content (4 wt%). A wide range of exhaust gas recirculation rates (from 0 to misfire) were employed to cover both conventional diesel combustion and low temperature combustion. The results indicate that the effect of oxygenated fuels on combustion and emission get larger at high rates of exhaust gas recirculation. For chain structure oxygenated additives, although *n*-hexanol presents much longer ignition delay at high rates of exhaust gas recirculation, it exhibits the highest soot peak due to its high boiling point. And isopropyl ether has the lowest soot emission attributing to its better volatility. The ring structure oxygenated additives present more significant difference in combustion than chain structure ones, and the sequence of ignition delay is 2,5-dimethylfuran > cyclohexanol > cyclohexanone > diesel. The soot emissions show a close relation with the ignition delay of the fuel, i.e., the fuel with longer ignition delay always exhibits lower soot emissions. And the lowest soot emission can be obtained with 2,5-dimethylfuran companied with apparent improvement in combustion efficiency and thermal efficiency. For the soot reduction ability of different oxygen functional groups, the sequence is alcohols < ketones < ethers. The oxygenated fuels with ring molecular structure tend to produce more soot compared with the ones with chain structure if only the oxygenated effect is considered, while the soot emissions is also influenced by the position of oxygen functional group. Taking all the effects together, 2,5-dimethylfuran is more effective in realizing high efficiency and clean low temperature combustion.

1. Introduction

Recently, with the fast development of biotechnology, more and more oxygenated biofuels can be produced at an acceptable cost gradually, which provides a feasible way to alleviate the pressure of energy crisis and remarkably reduce CO_2 emissions [1]. Besides the widely researched chain-like biofuels such as ethanol, butanol [2], biofuels with ring molecular structure such as 2,5-dimethylfuran (DMF), cyclohexanol and cyclohexanone also gradually attract attention of researchers. These ring structures form a new class of second generation biofuels which can be derived from lingo-cellulosic biomass that is abundant in nature and available at low cost [3]. And some relevant studies have reported how to produce these ring-structure biofuels by biomass resources, such as the production of furan studied by Zhao et al. [4] who reported the catalytic conversion of sugars giving high yield to 5-hydroxymethylfurfural (HMF), a versatile intermediate. Meantime, Mascal and Nikitin [5] reported cellulose can be converted into furanic biofuels in unprecedented yields using an inexpensive, simple process involving concurrent hydrolysis, dehydration, and chlorine substitution reactions coupled with continuous extraction into an organic phase. Long et al. [6] reported the selective cyclohexanol production from the renewable lignin derived phenolic, and 97.74% guaiacol conversion with 100% cyclohexanol selectivity was achieved. Yi et al. [7] proposed the hydrogenation of phenols to cyclohexanols under mild conditions in aqueous solution by using Pd/γ-Al_2O_3 as catalyst. Song et al. [8] found that cyclohexanone is a significant by-product in the degradation process of lignocelluloses which makes up a high proportion of biomass, and the production of cyclohexanol can be derived from biomass-derived cyclohexanone over Cu catalyst.

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DMF is a kind of ethers with 6-carbon ring structure and its energy density is 40% higher than ethanol [9]. In the last several years, some investigations of DMF on engines have shown its feasibility as an engine fuel [10]. By blending DMF into diesel fuel, Liu et al. [11] conducted experimental investigation on a diesel engine, and showed that DMF had great potential in reducing soot emission mainly due to the extended ignition delay. Cyclohexanone and cyclohexanol are 6-carbon ring-structure oxygenated ketone and alcohol fuels respectively. Compared with DMF, there are less study works on both of these ring-structure oxygenated fuels. Klein-Douwel et al. [12] conducted the first diesel combustion study of cyclohexanone and the results indicated that the keto-on the molecular restrained the generation of soot, which was the mechanism of reducing soot emission by cyclohexanone. Herreros et al. [13] investigated the effects of cyclohexanol on combustion and emissions on a diesel engine and showed a reduction in soot and NOx in comparison to conventional diesel fuel. In general, these new kind of biofuels usually have properties of low cetane number, oxygen-containing, low boiling point, and so on. More importantly, they can be made from no-food biomass materials which extensively exist in the world and are conducive to achieve carbon neutral. So these biofuels present great prospect for future application.

Meanwhile, the increasingly stringent emission regulations bring more severe challenges for internal combustion engines. And it is also the main driving force for the development of engine technologies, especially to promote the progress in combustion theory and technology. The new combustion mode represented by homogeneous charge compression ignition (HCCI) and low temperature combustion (LTC) is considered as the key technology to realize efficient clean combustion and meet the future emission regulations. Employing exhaust gas recirculation (EGR) is an effective way to reduce NOx and achieve low temperature combustion [14], however there is a soot-bump in high EGR rate region, and the soot emission is very sensitive to the change of EGR at this area. Blending oxygenated biofuels with diesel fuel can effectively improve the low temperature combustion and emissions.

The effects of oxygenated biofuels on combustion and emissions are mainly resulting from two factors. One is the function of cetane number. As mentioned above, oxygenated biofuels usually have low cetane number compared to diesel as shown the study by Imtenan et al. [15] who reported that *n*-butanol was added into diesel–jatropha biodiesel blend. When these oxygenated biofuels are blended into diesel fuel, the ignition delay can be further prolonged under high EGR rate as studied by Kalghatgi et al. [16]. Meanwhile, a longer flame lift-off length can be achieved by using the blends of diesel-biofuel as studied by Jing et al. [17]. All of these result in a better mixing process and consequent lower soot emissions. And the other is the function of oxygenated feature, including the amount of oxygen and the molecular structure of the oxygenated hydrocarbons. Molecular structure includes different types and position of oxygen functional groups and the structure of carbon chain. It is widely accepted that soot emission decreases with oxygen concentration increasing in blending fuel, especially at high load [18]. Musculus et al. [19] measured in-cylinder soot on a heavy-duty diesel engine using two commercial diesel fuels and oxygenated paraffinic fuel blends. They found that for oxygenated paraffinic fuels, no soot would form when the fuel atomic O/C ratio exceeds 0.4 or the oxygen content exceeds about 30 wt%. And some earlier studies also indicated that the reduction in soot emission is mainly related to the oxygen concentration of the fuels, and not sensitive to the different molecular structures of oxygenated fuels such as Miyamoto et al. [20,21] who found that smoke emission decreased sharply and linearly with an increase in oxygen content and disappeared entirely at an oxygen content above 38 wt%, even at stoichiometric conditions. Choi et al. [22] also founded that chemical inhibition is not a major factor in the reduction of soot when the ether and ester oxygenate was utilized. In fact, the fuel-bound oxygen concentration was the best indicator in determining the amount of soot reduction.

However, some studies have demonstrated that the ability on soot reduction is also influenced by the oxygenated structure of fuels [23–26]. Westbrook et al. [23] adopted detailed chemical kinetic model to investigate the effect of oxygenated additives on soot emission in diesel engines. The results showed that different kinds of oxygenated molecules presented different efficiency to reduce soot precursors, among which esters showed the weakest reduction ability. The reason is that the two oxygen atoms on ester group are tied to the same carbon atom, so that the oxygen atoms are more inclined to generate CO_2 instead of preventing the carbon atoms generating soot precursors. Barrientos et al. [24] conducted combustion experiments using different C-5 oxygenated hydrocarbon fuels and put forward the evaluation standard of soot formation ability. They pointed out that among the C-5 mono-oxygenated compounds, the sooting tendency was in this order: aldehydes < alcohols < ketones < ethers < *n*-alkanes, and both unsaturated and branched compounds showed slight increases in sooting tendency as compared with their saturated and linear counterparts. Liu et al. [25] found that *n*-butanol has larger soot reduction ability than that of methyl octynoate addition to diesel fuel under the same oxygen content at both conventional and low-temperature diesel combustion conditions. Furthermore, the soot suppression efficiency of various oxygenated structures also depended on the ambient temperature [26]. Tree and Svensson [27] compared the soot emission of C-6 hydrocarbons and concluded the order is: *n*-hexane < cyclohexane < benzene, which means that ring and unsaturated molecular structure tends to form more soot. Compared with straight chain hydrocarbons, soot production of fuels with aromatic rings and triple-bonded carbon-carbon are relatively higher. In addition, Pepiot-Desjardins et al. [28] found that the position of the oxygen functional group has remarkable influence on soot reduction. They pointed out that oxygen groups at the center of the molecule presents much better effect on soot reduction than oxygen groups on the side of the molecule.

In summary, with the significant progress in biotechnology, it is possible to produce biofuels in large scale and low cost in the near future. Meanwhile, some oxygenated biofuels show advantages in improving combustion and emissions, especially soot emissions under low temperature combustion conditions of diesel engines, and have attracted more and more attention all over the world. Among these biofuels, there are two kinds of typical structures, i.e., chain and ring molecular structures. However, up to now, the investigations on effects of oxygenated fuels on combustion and soot emission of diesel engines were mainly focused on oxygenated hydrocarbons with chain molecular structures. And there are few reports on oxygenated hydrocarbons with ring molecular structures. The systematic comparison between ring and chain structure hydrocarbons with the same oxygen functional group has been scarcely reported. Therefore, in the current study, six-carbon ring-structure oxygenated biofuels were selected, including cyclohexanone, cyclohexanol and DMF. Meanwhile, to compare the effects of ring and chain oxygenated structures on diesel combustion and emissions, three chain-like biofuels including 2-hexanone, *n*-hexanol, and isopropyl ether were selected to represent the same oxygen functional group. Meantime, 2-ethyl hexyl nitrate ester (EHN) was added into tested fuels to isolate the effect of cetane number. By blending these six oxygenated fuels into diesel, the effects of molecular structure (ring or chain) and oxygen functional group (ketone, alcohol, ether) on low temperature combustion and emissions were clarified in the current paper. And this study