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Morphology, composition, and structure of carbon deposits from diesel and biomass oil/diesel blends on a pintle-type fuel injector nozzle

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ABSTRACT

A biomass oil/diesel blend was prepared using an emulsion method and combusted in a diesel engine. An injector was then removed and the morphology, composition, and structure of the carbonaceous deposits on the pintle-type nozzle were characterized using a combination of HRTEM, SEM/EDAX, Raman and XRD. Results showed that the carbon deposition of the emulsified fuel with high crystallinity was greater than that of diesel. The agglomerated particulate diameters of the deposited carbon from diesel and emulsified fuel were approximately 10–30 μm and 50 μm, respectively. The carbon deposition mechanism from the emulsified fuel was attributed to the high oxygen content of the groups leading to increased polymerization and subsequent condensation on the nozzle surfaces that was then carbonised.

1. Introduction

There are two potential energy sources that are needed to sustain life and human development: renewable energy, such as that derived from solar, biomass, and wind energy, and non-renewable energy, such as coal, petroleum, and natural gas [1–3]. The rapid development of society and gradual reduction of non-renewable energy sources have negatively affected the energy supply of the world. Biomass, which is a renewable energy source, has received considerable research attention because of its wide distribution, large reserves, low cost, and ease of use. The exploitation and application of biomass energy has important economic and environmental benefits to society [4].

The liquefaction or gasification processes of biomass can be used to produce biomass oil or gas. Biomass oils are directly combusted to produce electricity and heat. The resulting substance can be used as an alternative fuel for diesel or gasoline engines and the use of biomass oil as an engine fuel has been gradually gaining acceptance [5–7]. Fast liquefaction biomass fuel has become one of the most important alternative fuels. Zhu et al. [8] utilized the fast liquefaction method to convert straw and rice husks into biomass crude oils, which are eco-friendly, renewable, and can be used as alternative fuels. However, the use of biomass crude oil produces soot, which can affect engine performance and emissions. Thus, biomass crude oil must be upgraded for modern engines. Emulsion is one of the most effective upgrading methods for obtaining an acceptable performance from alternative fuels [9,10]. Biomass crude oil also plays an important role in the wear and friction of engine parts through polymerization, oxidization, condensation, and corrosion reactions [11,12]. Hu et al. [13] investigated the wear and friction characteristics of biomass crude oil. Their results show that biomass derived fuels have a better lubrication performance compared with diesel. The lubrication performance of biomass crude oil was ascribed to the reaction of active functional groups with metals in forming boundary lubrication films.

One by-product of fuel combustion is carbon, the black soot that can collect and harden on critical engine components such as the cylinder head, cylinder wall, piston and valves. Carbon deposits in the combustion chamber can affect engine performance, including tribological properties, which results in higher oil consumption, engine knock and overheating. The morphology, composition, and structure of carbonaceous deposits should be considered for the wear and heat transfer of engine parts when biomass oils are used in engines [14]. Numerous studies have focused more on carbon deposits generated from a range of conventional and alternative engine fuels but less so with biodiesel derived deposits. Uy et. al. [15] characterized the nanostructure of gasoline soot. They determined and compared the degree of order of the graphitic planes of soot's primary particles extracted from the exhaust gas and from engine oil. Further, a recent study on soot agglomerates showed that centrifugation altered the distribution of size and shape of these particles [16]. Fuel additives can also effect the composition and formation of carbonaceous deposits. For example, Baker et al. in a series of papers performed engine tests using commercial and non-commercial low molecular weight polyisobutylenesuccinimide (PIBSI) as an engine fuel additive. They observed 'sticking' of needle valves within some

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injectors [17] and following spectroscopic analysis, postulate that formation is complex and multifaceted. Further tests using a commercial grade PIBSI detergent showed that sticking was eliminated. They describe the aromatic structure of internal diesel injector deposits (IDID) [18] and reviewed the development of diesel injector deposit theory as it has evolved with the engine technology in the light of their findings [19]. Mendiratta et al. [20] indicated that engine oils contribute significantly to the formation of carbon deposits. The basic parameters involved in deposit formation are surface temperature, engine operating conditions, and condensation and polymerization of engine oil components. Parsinejad et al. [21] investigated the characteristics of carbon deposits on different types of injector nozzle by using elemental and thermal analytical techniques; both fuel and engine lubricants contributed to the composition of deposits. The deposit composition on a direct-injection spark-ignition (DISI) intake valve consisted of 10 wt% or higher non-C (inorganic) elements wherein Ca, Mo, Zn, P, and S were dominant. The number of inorganic elements in the DISI intake valve deposit was at least one order of magnitude higher than that in the port fuel injection intake valve deposit. Analysis data showed that significant differences existed in the deposit volatility and inorganic component quantity between the combustion chamber deposits produced from Group III base oil (lower) and poly-alpha-olefin (PAO) base oil (higher). No correlation was observed between the sulfated ash value of the lubricating oil and elemental composition of the deposits.

Several studies have also been conducted to classify deposit structures [22–24]. Researchers found that generally carbon material was amorphous, porous, and characterized by a heterogeneous granular structure. Studies have been conducted by using transmission electron microscopy [13], C solid-state nuclear magnetic resonance, Fourier transform infrared spectroscopy, gas chromatography–mass spectrometry, and other techniques. The heterogeneity of the deposit structures, which were composed of unburned hydrocarbon chains and varying amounts of O, C, K, and Ca, made the analysis complex. Substantial variations existed in the composition of deposits from different parts of the combustion chamber.

No reports have been made on C deposits in engine nozzles when emulsified biomass oil is used with diesel, blended as alternative fuel. The present paper studied the morphology, composition, and structure of C deposits formed as a result of the combustion of an emulsified biomass oil/diesel blend, on a pintle-type nozzle. This study aimed to understand the performance of C deposition and the formation mechanism of emulsified biomass oil derived deposits.

2. Materials and methods

2.1. Materials

The Key Laboratory for Biomass Clean Energy of Anhui Province in China produced liquid biomass oil using the fast pyrolysis of rice husks. A commercial diesel fuel (0#) was purchased from China Sinopec Corporation for reference. Distilled–refined biomass oils were obtained by the reduced-pressure method with a vacuum value of −0.1 MPa at 78 °C. All other chemical reagents were of analytical grade.

The biomass oil/diesel blend was prepared by mixing the diesel with distilled–refined biomass oils, using a high shear emulsion machine (model SG × 400). The detailed preparation procedure for the blend was as follows: 1.02 g emulsifier (Span-80) was added into 1.0 g biomass oil. Thereafter, a 0.98 g emulsifier (OP-10) was added into 97 g of $0^{\#}$ diesel fuel. The mixture was stirred until the liquid was uniform. The former mixture was slowly added into the latter mixture with a shear speed of 1500 rpm at 30 °C for 20 min. The physical and chemical properties of diesel and emulsified fuel are listed in Table 1.

Table 1
Physical and chemical properties of diesel and emulsified fuel.

Items	$0^{\#}$ Diesel	Emulsified fuel	Test standards
Flash point (°C)	55	50	ASTMD93
Kinematical viscosity (40 °C, mm^2/s)	2.92	3.09	ASTMD445
Acid number(mgKOH/g)	0.12	1.52	ASTMD664
Sulfur content (wt%)	0.25	ND	ASTMD4294
Density (20 °C, kg/mm^3)	817	743	ASTMD4052
Water content (V/V%)	Trace	Trace	ASTMD6304
Gross heat value (MJ/kg)	42.2	41.7	ASTM D240

ND: No detected

2.2. Engine tests

Engine tests were conducted using a mode S195 diesel engine test bench (Anhui Quanjiao Diesel Engine Co.), running with an emulsified biomass oil/diesel blend and $0^{\#}$ diesel under idle load condition for 10 h respectively. The specification of the engine is given in Table 2. After running for 10 h, the injector nozzle was removed and the deposit analyzed. In addition to this, at the end of each test, a new injector nozzle was selected and installed. The engine was then flushed and a new lubricant was added for each test.

Soot particles extracted from the engine oil were prepared using a solvent extraction process as outlined in [25] for each fuel combination. This entailed diluting the oil at a ratio of 1:60 in heptane, producing a solution containing much lower oil content, and also at a suitable low viscosity to allow deposition onto a carbon coated transmission electron microscope grid. During the sample preparation and following deposition, the solvent evaporates rapidly to leave soot particles of varying sizes and aggregations.

2.3. Characterization

Morphology, composition, and structural analyses were performed on the removed pintle nozzles by scanning electron microscopy/energy dispersion spectroscopy (SEM/EDS; JEOL Model JSM-6490), optical microscopy (OM; LY-WN-HPCCD), high resolution transmission electron microscope (HRTEM, JEOL JEM-2010 at an acceleration voltage of 200 kV), X-ray diffraction (XRD, Rigaku D/max-γB X-ray diffractometer with Cu-Kα radiation). Finally a Raman spectrometer (Raman, LabRAM-HR; resolution = 0.6 cm^{-1}, scanning repeatability = ±0.2 cm^{-1}) which consisted of a light microscope (Leica DL-LM; Olympus BX) with three different excitation lasers. Finally, the

Table 2
Main technical specifications of Model S195 diesel engine.

MODEL	S195
Type	Single cylinder, horizontal, 4-stroke
Cylinder diameter*piston stroke	95*115
Piston exhaust volume	0.815 L
Rated output Power/rmp	9.7 kw/2000 r/min
Cooling method	Water
Starting method	Hand
Net weight (kg)	145
Size (mm)	866*412*639
Compression ratio	20:1
Lubrication system	Combined pressure and splash
Combustion system	Swirl
Output (HP/rpm)	12/2000
Piston total displacement (L)	0.815
Specific fuel consumption(g/kW h)	≤ 287
Injection pressure (MPa)	12.6