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Synthesis of carbon nanotubes from biofuel as a carbon source through a diesel engine

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ABSTRACT

Carbon nanotube (CNT) was synthesized during combustion in a diesel engine by using biodiesel, fatty-acid methyl ester (FAME), as main fuel. Ethanol which is also known as biomass-derived material was blended with main fuel. These mixed fuel acted as a carbon and heat source. Ferrocene as a catalyst source for CNT growth and molybdenum/sulfur as a promoter were added into mixed fuel. CNTs produced in each experimental condition were assessed mainly by scanning electron microscope and transmission electron microscope whether CNT was really synthesized or not. Gas compositions of an exhaust from an engine were examined by two types of gas chromatograph, thermal conductivity detector for O_2, CO, CO_2 and flame ionization detector for C1–C3 low molecular hydrocarbons. As a comparative study, experiments using 1-decanol and n-dodecane as main fuel were carried out. The former is an emerging material which has been applied for a diesel engine operation in recent years. The latter has been utilized as surrogate fuel of commercial transport fuel in order to mimic several properties of real fuel. Obtained results indicated that FAME and 1-decanol had a propensity to produce larger CO amount which led to CNT formation than that produced from n-dodecane based fuel even at a low ethanol fraction in fuel. We believe that our outcomes will provide fruitful information that high-valued material like CNT can be produced from biomass-derived materials through a diesel engine which generates electrical power in addition to CNT production.

1. Introduction

The applications of alternative fuels such as fatty-acid methyl ester (FAME) instead of conventional diesel fuel for a diesel engine operation were studied in recent years because of its renewable ability or the necessity for preventing global warming [1,2,3,4,5]. Originally, a diesel engine was developed for running by means of vegetable oils more than a century ago. Merits of employing vegetable oils are, for examples, cleaner emissions from its combustion, reduction of CO_2 by carbon-neutral through combining water and CO_2 by photosynthesis and consuming by combustion, similar properties with diesel fuel such as cetane number, and so on [6]. Since raw vegetable oils cannot be utilized for a present diesel engine, they have to be converted to FAME which is regarded as biodiesel. FAME can be produced from not only a wide variety of vegetable oils, but also diverse animal fats and waste grease by means of a transesterification reaction usually with methanol. Depending on the area and oil feedstock, typical compositions of biodiesel are different with respect to one another [6,7,8]. For instance, methyl linoleate is a dominant compound from soybean oils in USA, methyl oleate is most included in case of rapeseed oils in Europe, methyl palmitate and methyl oleate are primary constituents from palm oils in Southeast Asia, and methyl laurate consists mainly of biodiesel when coconut oils are used as a feedstock in Philippines. In any case, due to its simple production process and an intensive expectation as an alternative fuel, emission properties or oxidation pathways when FAME was employed as fuel have been explored by a lot of research groups with the application for an actual engine in mind [8,9,10].

In addition to FAME, ethanol was mixed with FAME in this study for the use of a diesel engine operation. Ethanol is attracting many attentions since it can be produced from sugar cane or corn and regarded as a clean alternative fuel. Actually, ethanol is mainly used as additives to gasoline for increasing octane number in many countries such as USA, Brazil, India, and others [6]. Although ethanol has ever been utilized for spark-ignition engines, attempts for applying it to a diesel engine have been carried out because a low percentage mixing of ethanol with diesel fuel does not require any modification in a conventional diesel system. In practice, ethanol blending up to several tens of volume percentage did not affect an operation stability [11,12]. In our

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preceding report, carbon nanotube (CNT) growth in a diesel engine was found when ethanol blended fuel was used [13,14]. Moreover, ethanol has been employed as a carbon sources for CNT synthesis in chemical vapor deposition (CVD) process, and high-quality CNT can be successfully produced [15,16]. Also, even in the flame process using a burner, CNTs were synthesized as well by supplying ethanol as feed gas [17]. Furthermore, it has been reported in some preceding literatures that soot formation was reduced by employing alcohol blended fuel in a diesel engine [12,18]. Because the reduction of soot formation is preferable for CNT synthesis owing to the suppression of catalyst deactivation by soot, we can expect that CNT growth would be increased accordingly. Therefore, ethanol can be regarded as a promising material for intentional CNT synthesis through a diesel engine.

The synthesis of carbon nanomaterials like CNT and graphene from natural or wasted hydrocarbons as a carbon source is one of the hot topics in recent years. Instead of conventional carbon feedstock such as methane, ethylene, toluene, etc. which are produced from fossil fuel, many processes utilizing alternative materials like natural hydrocarbon or industrial carbonaceous waste has been proposed to date [19]. For examples of CNT synthesis, camphor [20,21,22], turpentine oil [23], eucalyptus oil [24], palm oil [25], jatropha derived biodiesel [26], castor oil [27], sesame oil [28] and others were studied in laboratory stage. In this report, we propose a new CNT synthesis process to use biofuel as a carbon source. Although the technique to date was mainly CVD process with CNT growth on substrates, we utilized combustion reactions and floating catalysts for CNT formation. Our group regards a diesel engine as a combustion reactor to form nanomaterials, and actually could successfully synthesize CNT using diesel fuel or n-dodecane blended with ethanol as fuel in preceding articles [13,14]. The advantages of a diesel engine as a reactor are to provide not only power generation which is well recognized as a conventional function of an engine, but also simultaneous synthesis of high-valued materials such as CNT that is new aspect of a diesel engine offered by us.

In this report, we employed three types of fuel for a diesel engine operation: mixture of methyl laurate as FAME and ethanol, mixture of 1-decanol as long chain alcohol and ethanol, and mixture of n-dodecane as normal alkane and ethanol for comparison. N-dodecane is a popular hydrocarbon which has been widely utilized as model fuel of actual transport fuel. We used n-dodecane/ethanol mixing fuel for synthesizing CNT in our previous report [14]. Long chain alcohol could be synthesized from a biomass-derived material [29] and utilized as a fuel for a diesel engine [30]. However, in this work, 1-decanol was employed mainly as a comparative material in this study because it includes oxygen atom in their chemical structure. Gas compositions of an exhaust gas from an engine were examined and whether CNT was grown or not was evaluated by means of microscopes, then we confirmed that CNTs were successfully synthesized in proper conditions. Moreover, results obtained here suggested that CO might play a key role for CNT growth in our system.

2. Experimental

The diesel engine used in this study was a direct injection, 4-stroke cycle engine (KIPOR KDE.2.0E). Main specifications of this engine are shown in Table 1. Methyl laurate (Wako Pure Chemical Industries, Ltd.), 1-decanol (Tokyo Chemical Industry Co., Ltd.) and n-dodecane (Wako Pure Chemical Industries, Ltd.) were employed as main fuel. The chemical structure used in this study is shown in Fig. 1. Super dehydrated ethanol (Wako Pure Chemical Industries, Ltd.) was mixed with main fuel and an ethanol fraction was changed from 0 vol% to 40 vol% for methyl laurate and 1-decanol and from 0 vol% to 50 vol% for n-dodecane. In order to prevent a phase separation, 4 vol% of 1-octanol (Wako Pure Chemical Industries, Ltd.) was added in case of n-dodecane/ethanol mixing fuel. As a catalyst source, 5000 ppm by mass of ferrocene (Wako Pure Chemical Industries, Ltd.) was dissolved into mixing fuel. During combustion, ferrocene is decomposed to form iron nanoparticles and those nanoparticles behave as floating catalysts to grow CNT in a diesel engine. Additionally, molybdenum acetate dimer (Sigma-Aldrich) and sulfur powder (Wako Pure Chemical Industries, Ltd.) which played as a promoter for CNT synthesis were dissolved into fuel so that an atomic ratio of Mo/Fe and S/Fe to be 0.01 and 2.2, respectively. Although Mo did not promote CNT synthesis so much, sulfur addition was crucial for the successful growth of CNTs in a diesel system shown in our previous work [13]. An engine load was provided by an external heater and its load was varied from 0 kW to 1.65 kW. A summary of experimental conditions in this research appears in Table 2. A portion of an exhaust gas from an engine was introduced to a sampling holder and gas chromatograph. A membrane filter with mean pore size of 200 nm (K020A052A ADVANTEC) or TEM grid (Tokyo Ohka Kogyo Co., Ltd.) was placed on a sampling holder and CNTs in addition to carbonaceous materials like soot were directly caught on them. Sampling time was 20 s for all measurements. A photograph of an experimental setup and a sampling system in this study can be referred to our previous paper [14]. The impacts of differences of fuel chemical structure were evaluated by means of field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) and transmission electron microscopy (TEM, Hitachi H-7650 Zero. A). For analyzing CNT structure in detail, high-resolution transmission electron microscopy (HR-TEM, JEOL JEM2010F) was used. An elemental analysis of our samples was performed using energy dispersive X-ray analysis (EDX) equipped with HR-TEM. Two types of gas chromatograph (GC-8A Shimadzu) were adopted to detect compositions of an exhaust gas. One is thermal conductivity detector (TCD) equipped with SHINCARBON ST (Shimadzu) as a packed column for detecting O_2, CO, CO_2 in an exhaust gas. The other is flame ionization detector (FID) equipped with Unipak S (GL Sciences Inc.) as a packed column for detecting C1–C3 hydrocarbons, namely CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8. Mean adiabatic combustion temperatures inside an engine chamber were estimated in

Table 1
Specifications of diesel engine used in this study.

Model	KIPOR KDE.2.0E
Number of cylinder	1
Fuel injection	Direct injection
Number of stroke	4
Diameter (mm) × stroke (mm)	70 × 55
Cylinder volume (cm^3)	211
Compression ratio	20
Rated power	2.5 kW at 3000 rpm

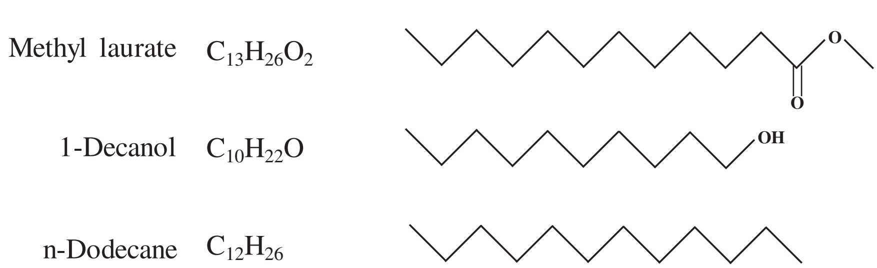

Fig. 1. Chemical structure of main fuel used in this study.