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Author(s)	Takenaka, N; Kameda, T; Nakao, T et al.
Citation	Annual Report of FY 2007, The Core University Program between Japan Society for the Promotion of Science (JSPS) and Vietnamese Academy of Science and Technology (VAST). 2008, p. 125-128
Version Type	VoR
URL	https://hdl.handle.net/11094/13084
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### EVALUATION OF EXHAUST GAS FROM BIO-DIESEL FUEL ENGINE

N. Takenaka\*, T. Kameda\*\*, T. Nakao\*, K. Okitsu\*, H. Bandow\* and Y. Maeda\*

#### ABSTRACT

The biodiesel fuel (BDF) derived from canola oil was tested as an alternative fuel for diesel engines in this study. Diesel-engine exhaust particles (DEP) were collected by using hi-volume air sampler. Eight kinds of polycyclic aromatic hydrocarbons (PAHs) and two kinds of nitrated polycyclic aromatic hydrocarbons (NPAHs) in DEP from BDF and petroleum diesel fuel (PDF) were measured. Since BDF contains oxygen, it can promote combustion and strongly influence chemical components in the exhaust gas and particles. The use of BDF brought lower emissions of carbon monoxide, particulate matters, and slight increase in nitrogen oxides emissions. All PAHs and NPAHs in the DEP decreased with increasing the content of BDF in diesel fuel. However, aromatic compounds such as PAHs and NPAHs were also found in the exhaust gas from BDF despite the fact that BDF did not include aromatic compound. PAHs are produced by the cyclization and/or polymerization of hydrocarbons when fuel burns incompletely. The mutagenic activity of soluble organic fraction of the DEP also remarkably decreased with increasing BDF contents in the fuel. It is concluded that BDF will be a quite effective alternative fuel to reduce the genotoxic potential of DEP.

#### **KEYWORDS**

Polycyclic aromatic hydrocarbons, Nitrated Polycyclic aromatic hydrocarbons, Bio-diesel fuel, Diesel exhaust particles, Mutagenicity.

# INTRODUCTION

Drain of oil resources will become a real possibility. Development of alternative energy is required to permanent development of human civilization. Furthermore, reductions of greenhouse gases such as carbon dioxide have been a big problem in the world. To use biomass is one of the best ways to solve these problems. The energy we can use permanently is only solar energy. Only plants can directly use solar energy, and therefore, BDF is hopeful energy of alternative energy of PDF [Bűnger et al., 1998; Durbin and Norbeck, 2002; Shi et al., 2006].

Recently BDF has been used worldwide. Many measurements of diesel exhaust gases and particles have been performed. Are the exhaust gases and particle emitted from BDF engine safety for our health and other animals and also the environment? Since BDF contains oxygen, it can promote combustion and strongly influence chemical components in the exhaust gas and particles. It is reported that CO and particles decrease due to the promotion of combustion, while NOx increases [Durbin et al., 2000; Wang et al., 2000; Durbin and Norbeck, 2002; Krahl et al., 2002; Shi et al.,

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2006, Pang *et al.*, 2006]. It is not clear that the products of combustion of BDF are less toxic or not than those of PDF. Therefore, it is required to measure toxic compounds such as PAHs and NPAHs. Also, mutagenicty could be one of the best indicators to evaluate the toxicity. In this study, we report the measurements results of CO and NOx in exhaust gas and PAHs and NPAHs in particles from diesel engine with BDF and normal PDF. Furthermore, we report the mutagenicity of DEP.

#### MATERIALS AND METHODS

#### **BDF Production** [Stavarache *et al.* 2005]

Canola oil and methanol, which contain 0.75 %(w/w of oil) of KOH, were pumped and introduced to the Dr. Hielscher type flow reactor. The flow rates of methanol and the oil were 48 ml/minute and 187 ml/minute, respectively. The reaction was performed for 60 minutes.

#### Generation and Collection of Diesel Exhaust Particles

The exhaust emission of a diesel-powered vehicle (a 1998 Nissan Civilian with a diesel engine of model U-BW40, 3465 cc displacement volume) were collected under idling conditions controlled the engine speed. The fresh exhaust was vigorously mixed with ambient air, which was negligibly polluted, in 25 m³ dark dilution chamber using a large fan. Concentrations of NOx and CO were monitored throughout DEP sampling by chemiluminescence NOx analyzer and NDIR CO monitor, respectively. The generated DEP were immediately collected by using a high volume air sampler at a flow rate of 900 L / minute.

#### Measurement of PAHs and NPAHs

According to the literature, PAHs and NPAHs on the filters were extracted with benzene / ethanol (3 / 1 v/v) by sonication [Kameda *et al.* 2004; Hien *et al.*, 2005]. The extracted solution was washed with NaOH,  $H_2SO_4$  and water. Then, the solution was dried under reduced pressure with rotary evaporator. The residue was dissolved in 3 ml of methanol, and PAHs and NPAHs were determined by HPLC-fluorescence detection and HPLC-chemiluminescence detection. Mutagenicity was investigated by Ames Test with TA98 and TA100 with and without S9 mix.

# PAHs and NPAHs investigated in this study

Eight kinds of PAHs and two kinds of NPAHs measured in this study were as follows. Fluoranthene(Fl), Pyrene(Py), Chrysene(Chry), Benz[a]anthracene(BaA), Benzo[e]pyrene(BeP), Benzo[b]fluoranthene(BbF), Benzo[k]fluoranhene(BkF), Benzo[a]pyrene(BaP), 1-Nitropyrene(1-NP), 3-nitrobenzanthrone(3-NBA).

# RESULTS AND DISCUSSION

Change in CO, NOx and particulate matter concentrations by changing mixing ratios of BDF in diesel fuel are shown in Fig. 1. The concentration of carbon monoxide decreased with increasing BDF content. This is due to preceding oxidation of organics at higher temperature in engine because of effective combustion due to the fact that BDF contains oxygen. From the same reason, the NOx concentrations increased with increasing BDF content. However, the concentration of particulate matter did not change vary much. It is reported that the concentration of soot decreases by using BDF [Wang *et al.*, 2000]. It is also reported that when BDF is used, unburned ester is emitted to cause increase in the concentration of particulate matter [Noda et al., 2004]. However, in this study, both tendencies were not observed. The reason is not clear so far.

Fig. 2 shows change in concentrations of NPAHs and PAHs in particles due to change in BDF content. The concentrations of NPAHs and PAHs in the particle of BDF containing fuel were much lower than those 100% PDF. However, the ratios of depression were different in kinds compounds. Furthermore, BDF does not contain any aromatic compound. This means that PAHs are produced by the cyclization and/or polymerization of hydrocarbons when fuel burns incompletely but not only by the reactions of aromatic compounds of the fuel. Actually, we investigated the NOx, CO and PM concentrations in the exhaust from the fuels in which benzene was added to BDF (5 and 20 % v/v of BDF). The concentrations of NOx were the almost the same in 0, 5, 20 % benzene/BDF exhaust gas. The concentration of CO increased slightly with increasing benzene content. The concentration of PAHs

in 20% benzene including fuel-exhaust 'p gas was slightly lower than that of 0 % benzene. This result indicates that PAHs were produced by the incomplete combustion. It Is apparent that the production of NPAHs and PAHS are due to incomplete combustion, but the use of BDF decreases production of NPAHs and PAHs. In Fig. 2, 2-NBA, the reduction was not observed for 3-NBA. This is probably due to the fact that 3-NBA produces secondary reaction in the atmosphere.

Fig. 3 shows the mutagenic acitivy of DEP from BDF and PDF. By using BDF, the mutagenicity decreased very much. BDF contains oxygen, and the

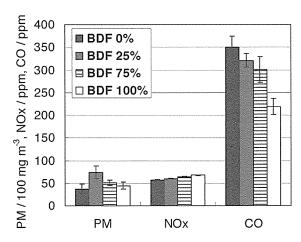


Fig. 1 Concentrations of particulate matters, NOx and CO emitted from the combustion of BDF, PDF and their mixtures.

Black bars: BDF 0 %, Gray bars: BDF 25%, Striped bars: BDF 75%, White Bars: BDF 100%. Error bars indicate one standard deviations of the average (n=3).

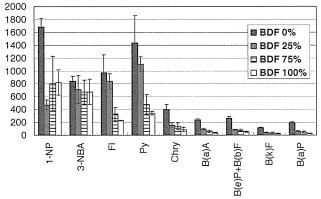


Fig. 2 Concentration of NPAHs and PAHs in the particulate matter emitted from the combustion of BDF, PDF and their mixtures.

Black bars: BDF 0 %, Gray bars: BDF 25%, Striped bars: BDF 75%, White Bars: BDF 100%. Error bars indicate one standard deviations of the average (n=3).

combustion condition of BDF is more oxidative than that of PDF. However, the results show the particulate products from BDF are much less toxic than the products from PDF. As a result, it is concluded that BDF is a quite effective alternative fuel to reduce the concentration of NPAHs and PAHs and the genotoxic potential of DEP.

#### **CONCLUSIONS**

From this study it is confirmed that the concentration of CO in the exhaust gas from BDF-using engine decreases but that of NOx increases because of more oxidative combustion condition of BDF-using engine. The concentrations of NPAHs and PAHs except the secondary product, 3-NBA

also decreased very much by using BDF. Furthermore, it is found that the mutagenicity also decreased. From the above results, it is concluded that the use of BDF is very effective to reduce pollutants and toxicity of the atmosphere.

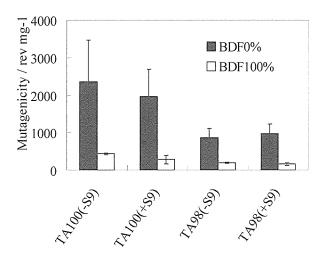


Fig. 3 Mutagenic acitivy of DEP from BDF and PDF.

Black bars: BDF 0 %, White Bars: BDF 100%. Error bars indicate one standard deviations of the average (n=3).

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