Emissions from Using Viscous Agent-Treated Fishing Boat Fuel Oil: Tests with a Heavy-Duty Diesel Engine (HDDE) Dynamometer

Tser-Son Wu[1], Lien-Te Hsieh[2*], Sheng-Lun Lin[3], Yu-Cheng Chang[4], Chung-Bang Chen[5], Chung-Hsien Hung[6]

[1] Department of Mechanical Engineering, Kun Shan University, Tainan 71003, Taiwan
[2] Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, 1 Shuefu Fu Road, Pingtung 912, Taiwan
[3] Department of Environmental Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan
[4] Graduate Institute of Environmental Engineering, National Taiwan University, No. 1, Second 4, Roosevelt Road, Taipei, 10617 Taiwan
[5] Refining & Manufacturing Research Institute, No. 217, Min-Sheng Nan Road, Chiayi 600, Taiwan
[6] Department of Chemical and Materials Engineering, Cheng-Shiu University, No. 840, Cheng-Ching Road, Kaohsiung 833, Taiwan

ABSTRACT

In order to clamp down on the illegal use of fishing boat fuel A (FBFA) and to reduce exhaust emissions in Taiwan, the residue from a desulfurization unit (RDS) and pyrolysis fuel oil (PFO) were added into FBFA with the ratio of 0.5% to form two new blended fuels (RDS0.5 and PFO0.5). The appearances of fuels from dark to light are RDS0.5, PFO0.5, and FBFA. The two new fuels have higher viscosity than FBFA, which may damage engines and reduce the misuse. The exhaust emissions of CO, HC, NO_x, polycyclic aromatic hydrocarbons (PAHs), and carcinogenic potencies (BaP_{eq}) were analyzed by the heavy duty diesel engine (HDDE) transient cycle test. The results show that RDS0.5 has significantly lower particulate matter (PM) emissions, while the PM emissions of PFO0.5 are higher than those of FBFA. In addition, the total PAHs emissions concentration of all three of fishing boat fuels increase from premium (regular) diesel fuel. However, RDS0.5 has relatively lower BaP_{eq} emissions, which are usually considered as carcinogens, than the other fishing boat fuel.

Keywords: Viscous agent; FBFA; RDS0.5; Particulate matter; PAH.

A list of nomenclatures for the symbols used in this study

Symbols	Nomenclatures
AST	Automatic stack sampler
ASTM	American Society for Testing and Materials
BaP_{eq}	The toxicity equivalence of PAHs
CO	Carbon monoxide
CO_2	Carbon dioxide
CFCs	Chlorofluorocarbons
CPC	Chinese Petroleum Corporation
DL	Detection limit
ECD	Electro-chemical detector
EF_{CO}	Emission factor of CO, gram CO per brake horse power per hour
EF_{CO2}	Emission factor of CO_2, gram CO_2 per brake horse power per hour
$EF_{PMbhp\ h}$	Emission factor of PM, gram PM per brake horse power per hour
$EF_{PML\text{-}fuel}$	Emission factor of PM, gram PM per liter fuel
FBFA	Fishing boat fuel A
GC	Gas chromatography
HCB	hexachlorobenzene

A list of nomenclatures for the symbols used in this study (continued)

HDDEs	Heavy-duty diesel engines
LOQ	Limit of quantification
MSD	Mass spectrometer detector
NDIR	Non-dispersive infrared
NO_x	Nitrous oxides, NO and NO_2
·OH	Hydroxyl radical
PAHs	Polycyclic aromatic hydrocarbons
Acp	acenaphthene
AcPy	acenaphthylene
Ant	anthracene
BaA	benzo[a]anthracene
BaP	Benzo[a]pyrene
BbC	benzo[b]chrycene
BbF	benzo[b]fluoranthene
BeP	benzo[e]pyrene
Bghip	benzo[ghi]perylene
BkF	benzo[k]fluoranthene
CHR	chrysene
COR	coronene
CYC	cyclopenta[c,d]pyrene
DBA	dibenzo[a,h]anthracene
FL	fluoranthene
Flu	fluorine
IND	indeno[1,2,3,-cd]pyrene
Nap	naphthalene
PA	phenanthrene
PER	perylene
Pyr	pyrene
PDF	Premium diesel fuel
PFO	Pyrolysis fuel oil
PFO0.5	FBFA blended with 0.5% (v/v) pyrolysis fuel oil
PM	Particulate matter
PUF	Polyurethane Foam
RDS	Residue of desulfurization unit
RDS0.5	FBFA blended with 0.5% (v/v) residue of desulfurization unit
RSD	Relative standard deviation
SIM	Selective ion monitoring
SO_x	SO_2 and SO_3
T90	Distillation temperature when 90% fuel have been distilled
TDVs	Traveling diesel-vehicles
VOCs	Volatile organic compounds

INTRODUCTION

Fishery subsidies have recently been used to invigorate fisheries in many countries. In Taiwan, the premium price of fishing boat fuel A (FBFA) is set as NT$26–28, which

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* Corresponding author. Tel.: 886-8-774-0521;
  Fax: 886-8-774-0585
  E-mail address: Lthsieh@mail.npust.edu.tw

was NT$7 (26%) lower than the fixed price of petroleum diesel fuel (PDF) (Chinese Petroleum Corporation, 2008). In addition, FBFA is also exempt from commodity taxes, business taxes and air pollution control fees. This lower price leads to the illegal use of FBFA by traveling diesel-vehicles (TDVs) with heavy-duty diesel engines (HDDEs). In 2003, the estimated consumption of FBFA was significant less than real consumption (~33%). This difference was assumed to be illegally used in TDVs. According to statistics from Taiwan's government for 1988–2007, the power per fishing boat (hp/boats) increases

while the carrying capacity per boat (metric ton/boats) decreased. Consequently, there is an increase in fishing boat power per carrying capacity (hp/metric ton), which lead to even more FBFA being used illegally. This illegal use of FBFA not only wastes the subsidies and lowers competition in fishery industry, but increases the criteria gases and the emission of toxic pollutants.

Diesel engines (DEs) are known for their high fuel efficiency, power output, and fuel economy. In recent years, increasing attention has been paid to the emissions from diesel engines, which like gasoline engine emissions, including carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) (Williams *et al.*, 1989; Schinder, 1992). Diesel engines also produce significant levels of particulate matter (PM), which consists mostly of carbonaceous soot and a soluble organic fraction (SOF) of hydrocarbons that condense on the soot (Lin, 2005; Fino, 2007), and high-duty diesel engines (HDDEs) produce more PM than light-duty diesel ones (Neeft *et al.*, 1996). Moreover, in addition to those traditional pollutants, some unregulated toxins, such as polycyclic aromatic hydrocarbons (PAHs), have also been found by recent research (Xu *et al.*, 2008; Chien *et al.*, 2009). Yang indicated that the contribution of total-PAH concentration is 91.8% from vehicles to the environment at the traffic crossroads (Yang *et al.*, 1999), with total-PAH concentrations in the ambient air at such locations approximately 5.3 and 8.3 times higher than average values in the urban and rural atmosphere, respectively (Lee *et al.*, 1995). Lin *et al.* reported that PM emission had a significant effect on particulate PHA emissions. The average particulate total-PAHs in five samplings displayed a trimodal distribution with a major peak in the Aitken mode (0.032–0.056 μm). About half of the particulate total-PAHs were in the ultrafine size range (Lin *et al.*, 2008).

Furthermore, Barfknecht indicates that the total-PAH emission factor of diesel engines was 10 times higher than that of gasoline ones (Barfknecht, 1983). Recently, several studies have also investigated such the topic (Shah *et al.*, 2005; De Kok *et al.*, 2006; Ballesteros *et al.*, 2009; Moldanová *et al.*, 2009). Many studies have suggested the exhaust of pollutants from HDDE is directly related to some properties and indexes of diesel fuel, such as the cetane index, dynamic viscosity, density, distillation temperature at 90% (T90), total aromatic content, sulfur content, and operation parameters (Westerholm, 1994; Collier, 1995 *et al.*; Sjögren *et al.*, 1995; Hori *et al.*, 1997; Yang *et al.*, 1998; Mi *et al.*, 2000). In other words, fuel properties and contents will dominate the emission of pollutants if a given type of HDDE is operated in controlled conditions. For evidence, Lin indicates that the mean sulfur and aromatic contents in FBFA are 43.0 and 1.04 times higher than those of petroleum diesel fuel (PDF), respectively, while the emission factors of total-PAHs and total-BaP$_{eq}$ obtained by utilizing FBFA are 3.41 and 5.82 times higher than those obtained by PDF, respectively, in an HDDE dynamometer test (Lin *et al.*, 2006).

However, the existing studies focuses only on the emission detection and environmental impact assessment, and lacks of any suggestions to improve the situation. In this study, the feasibility of reducing the amount of FBFA used by TDVs is a major topic, along with ways to reduce the emission of pollutants, and thus the viscosity and color of FBFA are the focus of this study.

The structure of this study is as follows: (1) Establishment of two new ingredients of FBFA (RDS0.5 and PFO0.5). (2) Observing the color of PDF, FBFA, RDS0.5 and PFO0.5. (3) Measurements of the sulfur and total-aromatic contents, dynamic viscosity and 90% distilled temperature (T90) of PDF, FBFA, RDS and PFO. (4) Tests of mechanical performance and pollutant emissions for PDF, FBFA, RDS0.5 and PFO0.5 in a diesel-engine dynamometer. Finally, the feasibility of using FBFA with the new ingredients in TDVs will be assessed, as well as the emission impact.

METHODS

Test Fuels

There were four test fuels used in this study: (1) Petroleum diesel fuel (PDF), (2) fishing boat fuel A (FBFA), (3) FBFA blended with 0.5 vol. % residue of desulfurization unit (RDS0.5), and (4) FBFA blended with 0.5 vol. % pyrolysis fuel oil (PFO0.5). Both PDF and FBFA were bought from Chinese Petroleum Corporation (CPC) gas stations. RDS is the residue from an atmospheric distillation and desulfurization unit used in the refinery process, while PFO is a byproduct from polymerization in the naphtha cracking process. In order to prepare enough and accurate amount of PFO0.5 and RDS0.5, a 20 L container was first quantitatively determined by a 1 L flask. Utilizing the similar procedure, 200 L barrel was determined by the 20 L container. One liter of neat PFO or RDS was first added into this 200 L barrel which already had been filled with approximately 190 L FBFA. Then, this barrel was eventually filled to 200 L with FBFA. PFO0.5 and RDS0.5 were thus produced. Stirring was conducted with an 850 rpm cement mixer for 10 min each barrel.

Diesel Engine and Dynamometer System

In this study, the heavy-duty diesel engine (without catalyst) was a Cummins B5.9-160, as shown in Fig. 1, six-cylinders, four strokes, a direct injector, 1-5-3-6-2-4 fuel injection sequence, 102 mm bore, 120 mm stroke, 5880 ml total displacement, 17.9:1 compression ratio, 118 kW maximum horsepower (at 2500 rpm), and 534 Nm maximum torque (at 1600 rpm). A dilution tunnel and monitoring system were both installed downstream of the diesel engine exhaust, with the former supplying air in an appropriate ratio, and the latter continuously sampling smoke, particulate matter (PM) and gas-phase pollutants.

The testing procedures were classified into two parts: (1) The engine performance tests of each fuel were conducted according to the Wide-Open Throttle (WOT) rule and by measuring the horsepower (hp), torque, and fuel
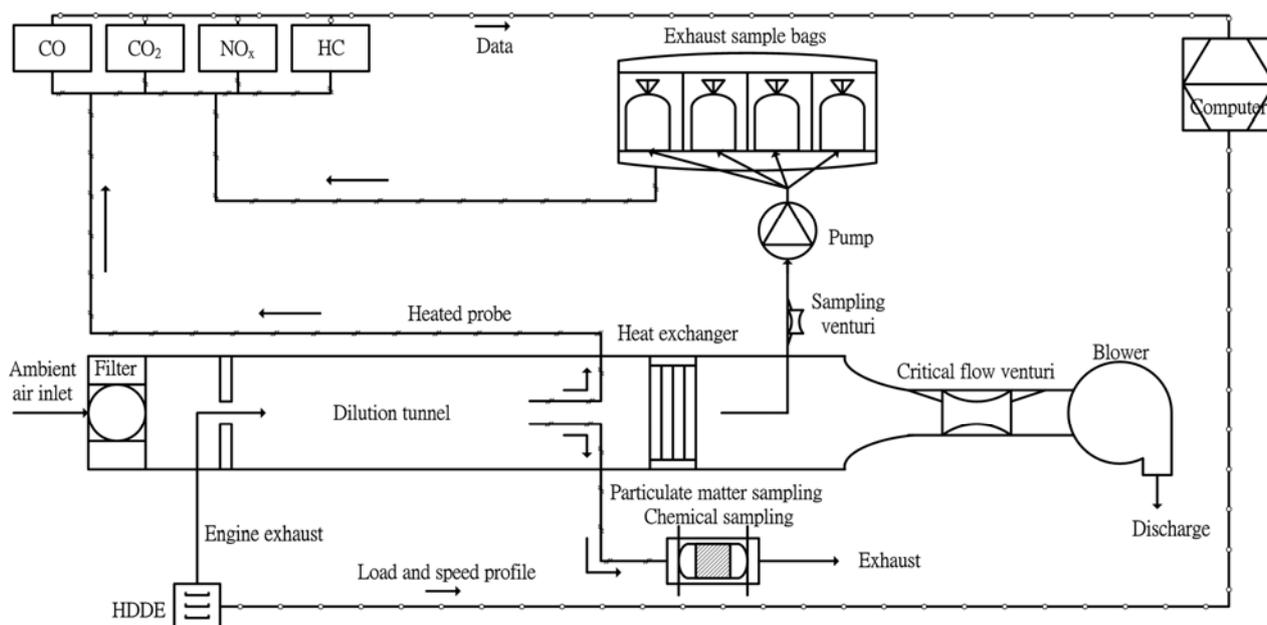
Fig. 1. Dynamometer sampling system.

consumption of the engine. (2) The emission tests followed the USHDD Transient Cycle (Code of Federal Regulations 40, Part 86, Subpart N), which included various speeds (rpm) and loads (%) to simulate real traffic on an express way and in congested-urban and uncongested-urban environments. Cold start and hot start emissions were measured to derive a multiple emission index $E_i = 1/7$ cold start + 6/7 hot start. This cycle is used in Taiwan as a regulatory test of pollutant emissions from vehicles.

Criteria Pollutant Sampling

Criteria gaseous emissions were measured in three ways: Repeat dilution sampling, measured on line, or constant volume exhaust bag sampling with different analyzers for CO, THC and NO_x emissions. Specifically, CO was analyzed with a non-dispersive infrared (NDIR) analyzer, NO_x with a chemiluminescent detector (CLD) and THC with a flame ionization detector (FID). The relative standard deviation (RSD) was less than 2% for all CO, total hydrocarbon (THC) and NO_x emissions. Exhaust smoke was analyzed with AVL415 and AVL439 smoke analyzers, with the results given in the form of absorption ratios (A, %). An AVL 472 dilution sampling system was used to harvest particulate matter (PM) on two 70-mm filters, and the temperature of the diluted mixture was maintained below 52°C. The PM mass on each filter was determined gravimetrically by the difference in mass before and after each test using an electronic analytical microbalance (Sartorius ME 5-F) with an accuracy of 0.01 mg.

PAHs Sampling

In this study, the PAH sampling and analyzing methods refer to the standard process of National Institute of Environmental Analysis (NIEA A730.70C). Both the particulate and gaseous PAH were collected by using a PAH sampling system at a temperature below 52°C. Particulate-phase PAHs were collected on a glass fiber filter which was placed in an oven at 450°C for 8 h before sampling to burn off all organic compounds that might be present. The cleaned filters were then stored in a desiccator for at least 8 h to reach the moisture equilibrium before weighing. After sampling, the filters were brought back to the laboratory and put into a desiccator for another 8 h to remove moisture. They were then weighed again to determine the net mass of particles collected. Gas-phase PAHs were collected on a two-stage glass cartridge packed with 5.0 cm of XAD-16 resin sandwiched between a 2.5-cm upper PUF plug and a 2.5-cm bottom PUF plug. Silicone glue was used to seal and hold these two pieces of PUF to prevent resin from leaking out during the sampling and extraction processes. After 8 h of adherence, the new PUF/resin cartridges were cleaned in a Soxhlet extractor for 24 h each with distilled water, methanol, dichloromethane and finally n-hexane for a total of four days, and then the PUF/resin cartridges were placed in a vacuum oven at 60°C for 2 h to dry and to evaporate the residual solvent. After drying, each PUF/resin cartridge was individually wrapped in hexane-washed aluminum foil, stored in a refrigerator at 4°C, and transported in clean screw-capped jars with Teflon cap liners before sampling. Each glass fiber filter was transported to and from the field in a glass box, which was also wrapped with aluminum foil.

PAH Analysis

Each collected sample (including particulate and gaseous PAH samples) was extracted in a Soxhlet extractor with a mixed solvent for 24 h (volume ratio of n-hexane:dichloromethane was 1:1 with totals of 250 mL and 700 mL for particulate and gaseous samples, respectively). The extract was then concentrated by

purging with ultra-pure nitrogen to 2 mL for the later cleanup process. The eluent from the cleanup process was then reconcentrated to exactly 1.0 mL. The PAH contents were determined with a gas chromatograph (GC) (HP 5890A; Hewlett-Packard, Wilmington, DE, USA), a mass selective detector (MSD) (HP 5972), and a computer workstation (Aspire C500; Acer, Taipei, Taiwan). This GC/ MSD was equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17   m) and an automatic sampler (HP-7673A), and operated under the following conditions: injection volume of 1 μL; splitless injection at 310°C; ion source temperature at 310°C; oven temperature from 50 to100°C at 20°C/min, 100 to 290°C at 3°C/min, and held at 290°C for 40 min. The mass of primary and secondary PAHs ions was determined by using the scan mode for pure PAH standards. The PAHs were qualified by using the selected ion monitoring (SIM) mode. PAH homologues grouped by the number of rings are as follows: naphthalene (Nap) for two-ring; acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA), and anthracene (Ant) for three-ring; fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (CHR) for four-ring; cyclopenta[c,d]pyrene (CYC), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), dibenzo[a,h]anthracene (DBA), benzo[b]chrycene (BbC) for five-ring; indeno[1,2,3,-cd]pyrene (IND), benzo[ghi]perylene (Bghip) for six-ring; and, coronene (COR) for seven-ring. According to the molecular weight, these 21 individual PAHs are divided into three categories: low molecular weights (LM-PAHs containing two- and three-ring PAHs); middle molecular weights (MM-PAHs containing four-ring PAHs); and, high molecular weights (HM-PAHs containing five- to seven-ring PAHs). The total-PAH data for the heavy-duty diesel engine (HDDE) exhaust was the sum of the 21 individual PAHs. The GC/MSD was calibrated with a diluted standard solution of 16 PAH compounds (PAH mixture-610M; Supelco, Bellefonte, PA, USA), plus five additional individual PAHs obtained from Merck (Darmstadt, Germany). Analysis of serial dilutions of PAHs standards showed the detection limit (DL) for GC/MSD was between 25 and 321 pg for the 21 PAH compounds. The limit of quantification (LOQ) is defined as DL divided by the sampling volume or sampling time. The LOQ for individual PAHs was between 22 and 284 pg/m^3, while values for sampling time were between 75 and 963 pg/h. Ten consecutive injections of a PAH 610-M standard yielded an average relative standard deviation of the GC/MSD integration area of 6.86%, within a range of 4.29–9.67%. Following the same experimental procedures used for sample treatment, recovery efficiencies were determined by processing a solution containing known PAH concentrations. The results showed that the recovery efficiencies for the 21 PAH compounds ranged from 0.799 to 0.901, with an average value of 0.842. Analyses of field blanks, including aluminum foil, glass-fiber filters, and PUF/XAD-16 cartridges, revealed no significant contamination (GC/MSD integrated area < detection limit).

RESULTS AND DISCUSSION

Appearance and Properties of Test Fuels

The difficulty of telling pale yellow FBFA from pale green petroleum diesel fuel (PDF) is one of the major problems in the investigation of illegal use. The additives in this study (RDS, PFO) are both dark brown in color, and cause the resulting fuel to appear as brown. Although the fuels are still hard to distinguish in barrels, they are obviously different in test tube samples. According to Lambert's Law, the shorter optical path causes the smaller absorption coefficient which causes the lighter color of fuels. The order of fuels from dark to light is as follows: RDS0.5, PFO0.5, FBFA, and PDF.

PFO and RDS, with kinetic viscosities of 5.351 and 7.863 cSt, were added into FBFA (4.078 cSt) and raised the viscosities to 4.136 (PFO0.5) and 4.674 (RDS0.5). The kinetic viscosities of FBFA, RDS0.5, and PFO0.5 are about 1.36, 1.55, and 1.38 times that of PDF, respectively. Generally, high viscosity leads to high carbon deposit formation, injector coking, piston ring sticking, lubrication oil dilution and oil degradation (Avinash, 2007). Furthermore, the two new blended fuels have higher viscosities than FBFA, especially RDS0.5, which is 14.5% higher. T90 is the temperature at which 90% of fuel is distilled, and this usually has the same trend as kinetic viscosity. However, those T90 of PFO0.5 and RDS0.5 (352.2 and 351.8°C) were still very close to that of FBFA as shown in Fig. 2 in this study even T90s of PFO and RDS (405.2 and 377.4°C) are obviously higher than that of FBFA (353.8°C). The T90 of fishing boat fuels was all higher than PDF. The cetane index is usually used to indicate the flammability of diesel fuel. With regard to the influence of the addition of additives on FBFA, cetane index had the same effect with T90. Fig. 3 shows the three fishing boat fuels have similar cetane index values, with all about 16.5% lower than that of PDF. This might cause incomplete combustion, greater fuel consumption, and emission of more emission of air pollutants. Nevertheless, the flash point of FBFA is higher than that of PDF, while those of RDS0.5 and PFO0.5 are lower than that of PDF (Fig. 4). The lower flash points of blended fuels are caused by the addition of RDS and PFO with lower flash point, 81 and 80°C, respectively. This property indicates that the new blended fuels will easily ignite and be well combusted, which conflicts with the results of T90 and cetane index. In addition, the order of heating value, which is usually considered the major factor to affect the fuel consumption rate, is as follows: PDF > FBFA > RDS0.5 > PFO0.5. Moreover, the fuel consumption rates of PDF, FBFA, RDS0.5, and PFO0.5 are 27.7, 29.5, 29.2, and 29.3 L/hr, respectively. Consequently, the fuel consumption rate is obviously not dominated by one factor (e.g. heating value), but results from the competition between each factor analyzed in this study. Briefly, kinetic viscosity, T90, cetane index, flash point, and heating value are all factors that might dominate the engine performance and emission of air pollutants.
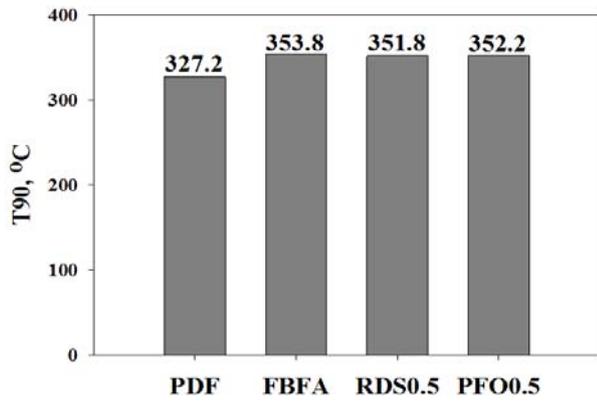
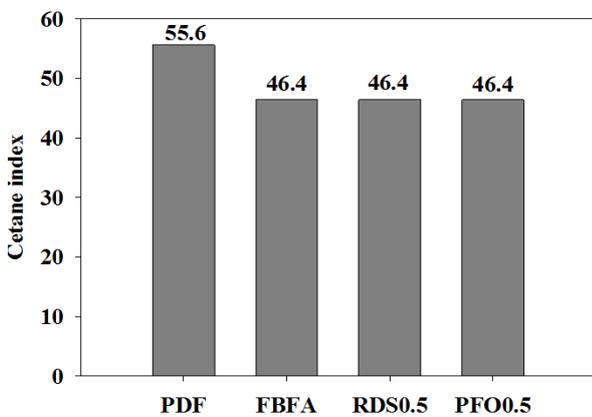**Fig. 2.** T90 of PDF, FBFA, RDS0.5, and PFO0.5.

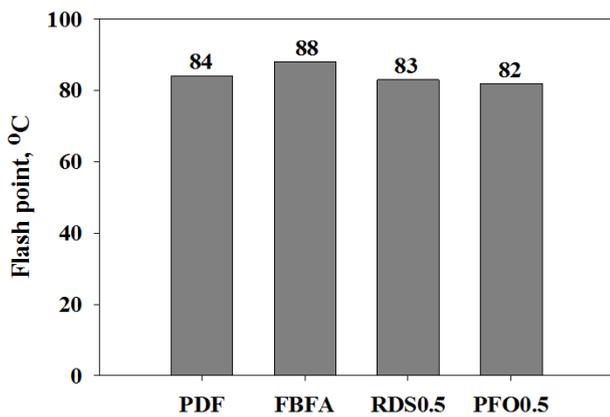**Fig. 3.** Cetane indexes of PDF, FBFA, RDS0.5, and PFO0.5.

Fig. 4. Flash points of PDF, FBFA, RDS0.5, and PFO0.5.

Sulfur and Total Aromatic Contents

The sulfur and total aromatic contents of each test fuel. The sulfur content of RDS0.5 (4720 ppm_w) is significantly lower than that of FBFA (5600 ppm_w) after neat RDS (180 ppm_w) was added (Fig. 5A). However, RDS0.5 and PFO0.5 also have much higher sulfur content (4720 and 5050 ppmw) than PDF, but 15.7% and 9.82% lower than FBFA, respectively. In addition, the total aromatic contents of FBFA, RDS0.5, and PFO0.5 were significantly

higher than that of PDF, by about 1.51, 1.64, and 1.67 times (Fig. 5B). These increases are according to the higher aromatic contents in RDS and PFO with 59.0 and 63.1 vol. %, respectively. The sulfur and total aromatic contents of FBFA, RDS0.5, and PFO0.5 all exceed the regulations of vehicle-used diesel contents in Taiwan (Taiwan EPA, 2005) and this might cause more environmental impact from sulfur dioxide (SO_2), PM, and PAHs emission when FBFA is illegally used by TDVs.

Criteria Pollutant Emissions

In this study, five regulated pollutants are considered, namely: carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbon (HC), nitrous oxides (NO_x), and particulate matter (PM). CO is not only a regulated pollutant, but also the most common index to determine the combustion condition. Fig. 6A shows the mean CO emission factors (EF_{CO}) of each test fuels from three replications and the regulation standard (10 g/bhp-hr). The EF_{CO} of FBFA is about 33% higher than that of PDF. The addition of RDS decreased the EF_{CO} when RDS0.5 had a slightly lower EF_{CO} (7.34%) than that of FBFA. Because HDDEs are usually operated at a lean fuel condition to avoid CO and HC production, the EF_{CO} of test fuels are all under the regulated level (10 g/bhp-hr). Consequently,
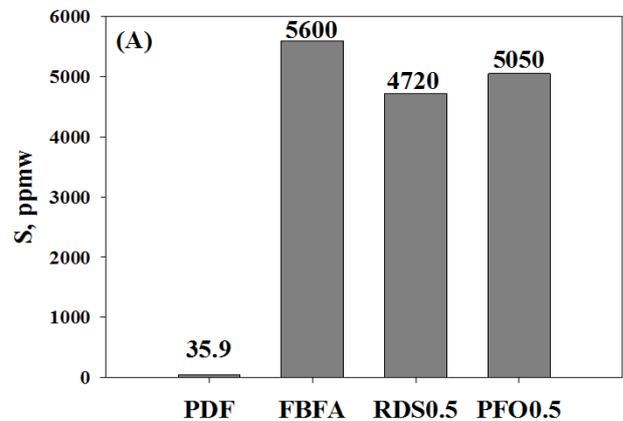

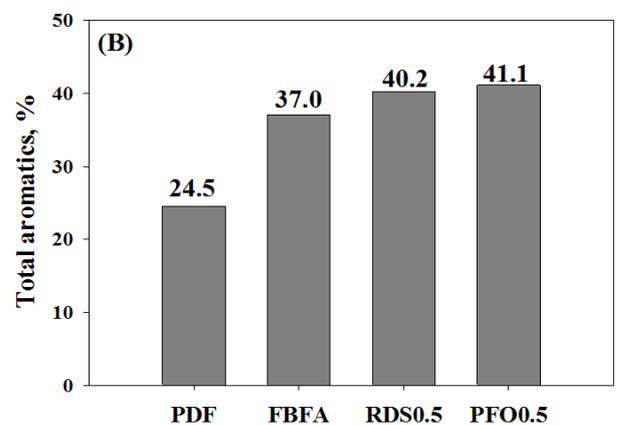**Fig. 5A.** Sulfur contents of PDF, FBFA, RDS0.5, PFO0.5.

Fig. 5B. Total aromatic contents of PDF, FBFA, RDS0.5, PFO0.5.

there might be no significant impact with regard to CO emission, even if FBFA is misused by TDVs. The combustion efficiency could be rechecked by the CO_2 and HC emissions. PDF has better combustion efficiency than FBFA, as suggested by the obviously lower EF_{CO} and higher emission factor of CO_2 (EF_{CO2}). RDS0.5 has the highest EF_{CO2} of the three kinds of fishing boat fuel, and thus could be considered more efficient among three fishing boat fuels for engine performance, although it is still much lower than that of PDF. In addition, the emission factor of HC (EF_{HC}) indicated a different trend to the above results (Fig. 6B). Originally, the EF_{HC} of FBFA and PDF were not significantly different (0.26 and 0.25, respectively), while RDS0.5 had the highest HC emission of all the test fuels. This result is in contrast with the CO and CO_2 emissions, which show that RDS0.5 approached more complete combustion than the other fishing boat fuels in HDDE. Incomplete combustion might be caused by the high viscosity of RDS0.5 (4.674cSt), which makes it hard to nebulize. NO_x are the precursors of some harmful pollutants, such as O_3 and smog. The NO_x emission factors of PDF, FBFA, RDS0.5, and PFO0.5 are much higher than the regulated standards in untreated exhaust gas and it is thus essential to install a catalyst system at the end of the exhaust.
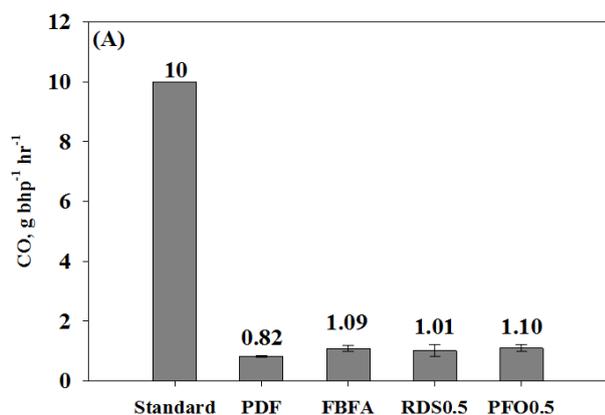

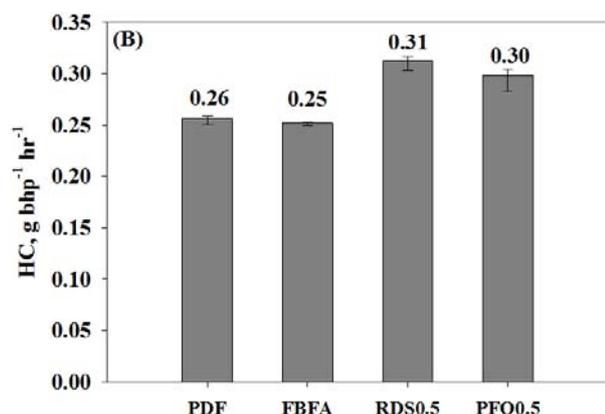**Fig. 6A.** CO emission factors of PDF, FBFA, RDS0.5, and PFO0.5.

Fig. 6B. HC emission factors of PDF, FBFA, RDS0.5, and PFO0.5.

PM Emissions

In many studies, PM has been shown to be harmful to the human respiratory system, especially in the form of fine particles. The accumulation/condensation mode is the major pathway to form fine particles in diesel engines (Maricq *et al.*, 2002; Vogt *et al.*, 2003), and can occur with incomplete combustion. As illustrated in Fig. 7, the PM emission factor (EF_{PM}) of PDF without any treatment is 1.8 times higher than the regulated standard (1 g/bhp-hr). In addition, the EF_{PM} of FBFA, RDS0.5, and PFO0.5 are 1.78, 1.67, and 1.89 times that of PDF, respectively which are thus more PM that have to be removed by using a diesel particulate filter (DPF). However, addition of 0.5% RDS decreases the PM emission by about 6.25% that of FBFA. Lyyränen et al. have reported that the presence of sulfur in diesel fuels leads to the formation of sulfuric acid in the exhaust gases at a temperature that is lower than that in the engine. The sulfuric acid could then form PM by accumulation or condensation on the soot and metallic ash (Lyyränen *et al.*, 2002). Thus, the lower sulfur content in RDS than that in PFO and FBFA causes the lower sulfuric acid formation, which further forms accumulation/condensation mode PM.

In addition, Scheer indicates that the particles which are formed by the nucleation mode are completely volatile (Scheer *et al.*, 2005). Tobias indicates that the nucleation particles are dominated by hydrocarbon (Tobias, 2001), which comes from the lube oil and heavy fuel components (such as RDS). The highest HC emission of RDS0.5 is considered to cause the highest nucleation mode PM. After the competition of sulfur content and HC emission effects, the total PM emission of RDS0.5 is dominated by the accumulation/condensation mode in this study.

PAH Emissions

Each filter and three-stage cartridge was analyzed for PAH concentration in preliminary sampling. The total PAH concentration adsorbed in the third stage cartridge was less than 3% of the total three-stage content, which means that the breakthrough effect can be ignored. Thus, the two-stage cartridge was used to adsorb gaseous PAH in this study. Additionally, the PAH emissions of cold and
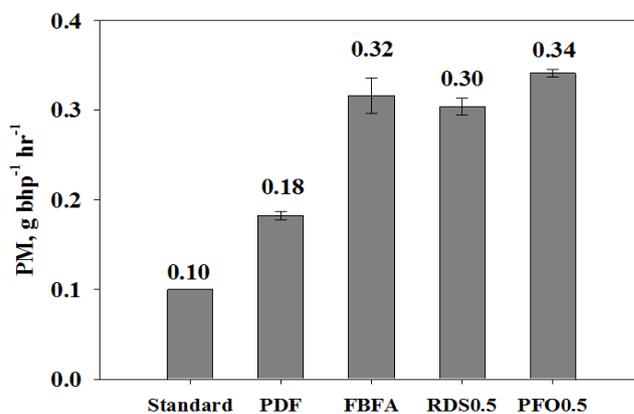

Fig. 7. PM emission factors of PDF, FBFA, RDS0.5, and PFO0.5.

hot starts in the dynamometer tests were only slightly different (< 5%), small enough to be ignored in this study.

Table 1 illustrates the total PAH emission concentrations (i.e. gaseous- + particulate-phase) of four test fuels (PDF, FBFA, RDS0.5, and PFO0.5) in the HDDE dynamometer system. First, we found that all three of the fishing boat fuels had much higher total PAH concentrations (FBFA: 1923 μg/m^3, RDS0.5: 2062 μg/m^3, PFO: 2011 μμg/m^3) than PDF (1207 μg/m^3), which would cause serious levels of extra emissions in their illegal use by TDVs (Lin *et al.*, 2006). The aromatics content of the fuel is the major factor that directly effects the total PAH concentration in exhaust gas and this might be due to one of the major PAH forming mechanisms that direct the emissions of unburned aromatics containing-fuels (Williams *et al.*, 1989).

Regarding the measured total BaP$_{eq}$ concentrations (i.e. gas- + particulate-phase), the concentration found in the FBFA (12.8 μg/m^3) is almost 30% higher than that found in PDF (9.9 μg/m^3) when RDS0.5 and PFO0.5 are 9.21 and 12.5 μg/m^3, respectively. The blended fuel RDS0.5 shows a critical low value of BaP$_{eq}$ emission concentration, while it has a relatively high total aromatics content compared to FBFA. However, the sum of the concentrations from the two most toxic PAH homologues (BaP + DBA) of PDF, FBFA, RDS0.5, and PFO0.5 are 7.38, 9.11, 5.83, and 8.75 μg/m^3, respectively. This result can explain why RDS0.5 has relatively lower emissions of BaP$_{eq}$ compared to FBFA, while PFO0.5 has relatively higher ones.

Table 1 also shows the PAH homologue distributions of different test fuels. The fractions of ∑LM-PAHs, ∑MM-PAHs, and ∑HM-PAHs in the total PAHs are different among PDF (95.0%, 1.85%, and 3.15%, respectively), FBFA (92.5%, 2.02%, 2.48%, respectively), RDS0.5 (96.3%, 2.15%, 1.55%, respectively), and PFO0.5 (95.7%, 1.97%, and 2.33%, respectively). The result shows that the fraction of LM-PAHs is the major group in total PAH emissions from HDDE, especially naphthalene (Nap). RDS0.5 has a much lower fraction of HM-PAHs in total PAH emissions than other three kinds of fuel, because RDS0.5 has a much lower PM emission concentration, which is considered as an adsorbent of low volatile HM-PAHs. In addition, the HM-PAH compounds have higher toxicity (Bap$_{eq}$), and the lowest ∑HMW-PAHs emission fraction of RDS0.5 thus causes the lowest BaP$_{eq}$ emissions.

PAH emission factors (mg/L-fuel or mg/bhp-h) on both total-PAHs and total-BaP$_{eq}$ (denoted EF$_{total-PAHs}$ and

Table 1. PAH emission concentrations.

PAH (μg/m^3)	PDF (n = 3)		FBFA (n = 3)		RDS 0.5 (n = 3)		PFO0.5 (n = 3)		TEF
	Mean	RSD%	Mean	RSD%	Mean	RSD%	Mean	RSD%	
NaP	682	11.5	1162	22.1	1267	19.9	1232	18.4	0.001
AcPy	132	20.4	198	13.0	209	10.1	211	12.9	0.001
Acp	102	17.7	138	15.5	149	18.2	139	15.8	0.001
Flu	96.5	12.3	132	17.2	146	15.2	134	13.0	0.001
PA	119	15.9	187	13.5	189	12.1	183	16.5	0.001
Ant	15.2	19.9	19.5	16.1	26.9	17.6	26.3	15.5	0.01
FL	8.74	14.9	13.1	17.3	18.3	21.7	14.2	14.9	0.001
Pyr	8.80	10.5	18.3	12.9	20.4	13.4	18.9	19.1	0.001
CHR	0.70	6.68	1.74	8.94	1.48	5.61	1.31	15.6	0.01
BaA	3.19	1.75	4.51	8.44	2.92	7.29	4.13	4.41	0.1
CYC	0.71	9.01	1.08	2.04	1.30	13.4	1.18	10.1	[a]
BbF	3.85	3.34	5.15	3.97	3.25	4.39	4.68	3.06	0.1
BkF	0.76	4.53	1.00	9.29	1.24	3.01	1.30	4.67	0.1
BeP	2.51	4.50	2.69	3.22	2.16	7.04	2.96	3.85	[a]
BaP	4.73	0.90	5.93	1.38	3.81	1.93	5.64	2.47	1.0
PER	2.99	0.69	3.58	4.40	2.28	4.45	3.51	2.85	[a]
IND	4.24	0.63	5.29	0.91	3.40	2.03	5.06	2.51	0.1
DBA	2.65	0.54	3.18	4.63	2.02	4.94	3.11	2.88	1.0
BbC	9.38	0.39	11.2	4.33	7.15	4.97	11.0	2.90	[a]
BghiP	1.07	1.17	1.41	9.03	1.15	16.9	1.38	4.17	0.01
COR	5.87	0.76	8.12	9.17	4.61	2.74	6.92	2.56	[a]
∑LM-PAHs	1147	13.7	1837	18.6	1987	16.8	1925	15.6	
∑MM-PAHs	21.43	10.7	37.65	11.4	43.10	15.4	38.54	13.6	
∑HM-PAHs	38.76	1.05	48.63	1.08	32.37	1.77	46.74	2.51	
Total PAHs	1207	13.2	1923	17.9	2062	16.5	2011		15.2
Total BaP$_{eq}$	9.90	2.66	12.8	1.97	9.21	3.01	12.5		2.48

[a] No TEF has been suggested.

Table 2. PAH emission factors of different fuels in exhaust gas.

Emission factors	PDF (n = 3)	FBFA (n = 3)	RDS0.5 (n = 3)	PFO0.5 (n = 3)
$EF_{Total\ PAHs}$ (mg/L-fuel)	5.75	7.28	10.71	7.20
$EF_{Total\ BaPeq}$ (mg/L-fuel)	0.024	0.083	0.074	0.074
$EF_{Total\ PAHs}$ (mg/bhp-h)	2.52	3.2	4.67	3.15
$EF_{Total\ BaPeq}$ (mg/bhp-h)	0.021	0.021	0.021	0.02

$EF_{total\text{-}BaPeq}$, respectively) were calculated in this study. As shown in Table 2, the value of $EF_{total\text{-}PAHs}$ and $EF_{total\text{-}BaPeq}$ in mg/L-fuel finds RDS0.5 (10.71 mg/L-fuel) > FBFA (7.28 mg/L-fuel)~PFO0.5 (7.20 mg/L-fuel) > PDF (5.75 mg L^{-1}-fuel) and FBFA (0.083 mg/L-fuel) > PFO0.5 (0.074 mg/L-fuel)~RDS0.5 (0.074 mg/L-fuel) > PDF (0.024 mg/L-fuel), respectively. This total PAH emission factor might be caused by the density and aromatics content of the fuels. In addition, the total BaP_{eq} emission factor had the same trend as the $\sum$HMW-PAHs and BaP + DBA concentrations. A similar trend is found with another kind of emission factor, $EF_{total\text{-}PAHs}$: RDS0.5 (4.67 mg/bhp-h) > FBFA (3.20 mg/bhp-h)~PFO0.5 (3.15 mg/bhp-h) > PDF (2.52 mg/bhp-h), and about 0.021 mg/bhp-h of all four test fuels. The above results indicate that in the real HDDE operating case, the order of the total mass of PAH emission per energy output is RDS0.5 > FBFA > PFO0.5 > PDF. However, PAHs with a higher molecular weight (HW-PAHs) are considered as having greater carcinogenic potencies. RDS0.5 has relatively lower HW-PAH emissions which cause lower $EF_{total\text{-}BaPeq}$ emission even it has the highest $EF_{total\text{-}PAHs}$.

CONCLUSIONS

The study shows that the FBFA has more CO, HC, PM, and PAHs emissions compared to PDF in HDDE, as suggested by Lin et al.'s research (Lin *et al.*, 2006). In the comparison of FBFA and the two new blended fuels, RDS0.5 has significantly lower PM but has higher HC emissions compared to FBFA. In addition, both the PM and HC emissions of PFO0.5, are higher than those of FBFA. The results for the CO and NO_x emissions show that there are no significant differences between the three kinds of blended fishing boat fuel. In addition, the different appearances of RDS0.5, FBFA, PDF, and PFO0.5 make easier to clamp down on the illegal use of fishing boat fuels in TDVs. The emission result shows that the total PAHs emission concentration will increase along with the misuse of all three of fishing boat fuels on-road. However, RDS0.5 has relatively low BaP_{eq} and HW-PAHs emissions, and these are usually considered as carcinogens. Consequently, if RDS0.5 is used as an alternative fuel to replace FBFA, it would be easier to identify if investigating possible misuse, as well as produce lower PM and BaP_{eq} emissions.

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