International Journal of Automotive Technology, Vol. 4, No. 2, pp. 95–100 (2003)

1229–9138/2003/012–05

EMISSION CHARACTERISTICS IN ULTRA LOW SULFUR DIESEL

S. K. OH, D. S. BAIK* and Y.-C. HAN

Graduate School of Automotive Engineering, Kookmin University, Seoul 136-100, Korea

(Received 11 March 2002; Revised 28 April 2003)

ABSTRACT–Automobile industry has been developed rapidly as a key manufacturing industry in Korea. Meanwhile, air pollution is getting worse noticeably than ever. In the diesel emission, PM (Particulate Matter) and NOx (Nitrogen Oxides) have been exhausted with a great amount and the corresponding emission regulations are getting stringent. In order to develop low emission engines, it is necessary to research on better qualified fuels. Sulfur contained in fuel is transformed to sulfur compound by DOC (Diesel Oxidation Catalyst) and then it causes to the increase of sulfate-laden PM on the surface of catalyst. In this research, ULSD (Ultra Low Sulfur Diesel) is used as a fuel and some experimental results are investigated. ULSD can reduce not only PM but also gas materials because cetane value, flash point, distillation 90%, pour point and viscosity are improved in the process of desulfurization. However, excessively reduced sulfur may cause to decrease lubricity of fuel and engine performance in fuel injection system. Therefore, it requires only modest adjusted amount of sulfur can improve engine performance and DOC, as well as decrease of emission.

KEY WORDS : Sulfur, ULSD(Ultra Low Sulfur Diesel), SOF(Soluble Organic Fraction), Sulfate, PM(Particulate Matter), DOC(Diesel Oxidation catalyst), Cetane index, distillation 90%, Pour point, Viscosity

1. INTRODUCTION

Recent diesel-automobile industries are focused on the development of reduction techniques on PM (particulate matter) by modifying combustion chambers and by repressing sulfates formed by reducing concentration of sulfur in fuel and removing dry carbon. The stringent emission regulation and development on low emission vehicles strongly requires superior fuels. In particular, the content of sulfur compound in diesel fuel causes to increase not only PM emission directly but also pollution materials, which reduce significantly life of engine and any auxiliary parts. Also, SO_2 and SO_3 resulted from sulfur compound cause acid rain in atmosphere and respiratory diseases (Han and Kim, 1998; Jung, 1998; Arai, 1992).

2. THEORETICAL REVIEW

2.1. Desulfurization

Desulfurization has been processed by hydrogen added to fuel as a catalyst and then a form of sulfur-hydrogen is eliminated. 4.6-dibenzothiphene existing in fuel is very difficult structurally in desulfurization treatment. However, it has been investigated that sulfur compound which is very difficult in desulfurization can be affected by a small amount of natural polar compound. In addition, the techniques of pre-adsorption have been studied to obtain ULSD under 50 ppm. However, severe desulfurization treatment had greatly reduced the capability of fuel injection because of its viscosity. Thus, it requires modest desulfurization and certain ranges of viscosity (Stephen, 1999).

**Corresponding author.* e-mail: dsbaik@kookmin.ac.kr

2.2. Characteristics of Low Sulfur Fuel

In diesel, sulfur exists in very complex forms. Also improved technique on desulfurization enables to eliminate aromatics and high boiling point components and then changes fuel characteristics such as the cetane value, distillation 90%, pour point, viscosity, aromatics and flash point in Table 2 (Port, 1991, Stephen, 1999).

2.2.1. Cetane index

In general, the higher is the cetane value, the shorter ignition timing is expected. When cetane value is reduced from 53 to 41, the ignition timing are delayed and combustion pressure ratio is increased because of increased crank angle, about 2°. Thus, in case of lower centane values, there are difficulties in cold starting accompanying with increase in a maximum cylinder pressure, engine noise, and HC.

2.2.2. Distillation 90% and aromatics

Aromatics and distillation 90% affect emission of PM.

Particulate Matter can be divided into soluble organic fraction and dry soot particularly. Increasing Distillation 90% gives an advantage on engine power because of high boiling point components containing a lot of heavy hydrocarbons and high heat releasing rate, but delayed combustion can result from soluble organic fraction. Increasing aromatics can cause an increase of carbon and hydrogen and high distillation latent heat easily due to imperfect burning leaving dry soot (Kim *et al*., 1999; John *et al*., 1995).

2.2.3. Viscosity

Viscosity of diesel fuel is a very important parameter in consideration of spraying characteristics. Burning starts with atomization but it requires lower viscosity. Lower viscosity forms better distribution of an injected fuel. Thus, atomization and distribution enable to accelerate heating evaporation and shorten ignition delay. However, excessively lower viscosity may cause depression of lubricity and distribution inside cylinder and results in unstable combustion condition. Thus, it requires certain ranges of viscosity in fuel (Yoon and Cho, 1999).

2.2.4. Density

Fuel density indicates characteristics of ignition timing, power, fuel and air ratio and PM. The change of fuel density affects engine power by changing mass of a sprayed fuel because fuel injection system is operated by a technique of volume measurement. When fuel density is increased, PM is increased instead of increasing engine power. Fuel density affects local fuel air ratio and when density is increased, fuel air ratio is decreased temporarily and results in accelerating increment of PM (Daniels *et al*., 1996; Clark, 2000).

2.3. Effects of Sulfur

2.3.1. Emission

Sulfur in diesel is organic and is transformed to SO_2 during combustion process. In most SO_2 exhausted to atmosphere, chemical reactions occurr additionally and cause air pollution. And rest of SO_2 are exhausted to air in the form of SO_3. SO_3 reacts with vapor contained in exhausted gases and becomes molecules of H_2SO_4 and are adsorbed on the surface of PM and exhausted. In addition, H_2SO_4 is neutralized by ammonia or other alkali metal and transformed to sulfate. These H_2SO_4 and sulfate can be adsorbed easily and form H_2SO_4 aerosol when they contact wet air and H_2SO_4 is exhausted in the form of PM (Batt *et al*., 1996; Barris, 1992).

2.3.2. DOC

Sulfur in diesel fuel affects DOC efficiency directly, and degrades seriously catalyst's ability after operation of some period giving poison effects on the surface of catalysts. Accordingly, sulfur laden on surface of catalysts is exhausted and may cause an increase of PM. Also, these poison phenomena degrade the ability of catalyst for oxidization of CO and HC, particularly at a low temperature.

In DOC application, there are more differences in converting HC or CO into CO_2 and H_2O in accordance with sulfur concentration. At lower temperatures of exhaust emission, it is possible to suppress oxidation of sulfur in order to avoid degradation of performance, but at higher temperatures SO_2 converts SO_3 leaving sulfates. Therefore, some counter-measurements are required and quantity of sulfur contained in fuel should be restricted particularly in an engine driving at higher temperature (Michael *et al*., 1995; Kim *et al.*, 1999).

Table 1. Standards for sulfur contents.

Country	Application year	Emission standard (ppm)	Note
Korea	1996	500	
	2000	500	
U.S.A	1993	500	ULSD
	2006	15	
EU	2000	350	
	2005	50	
	2011	10	
Japan	1996	500	
	2003	50	

2.4. Sulfur Regulation

EPA in USA established regulations on sulfur and has been on the way of legislation to 15 ppm sulfur in 2006 year. Similarly in Japan and Europe, a regulation on sulfur of less than 50 ppm is going on. In Korea also, there has been discussed on this regulation and development of ULSD. In fact, it has been reported that performance and durability of DOC are improved and also SOF, sulfate and NOx are decreased.

3. EXPERIMENTAL APPARATUS

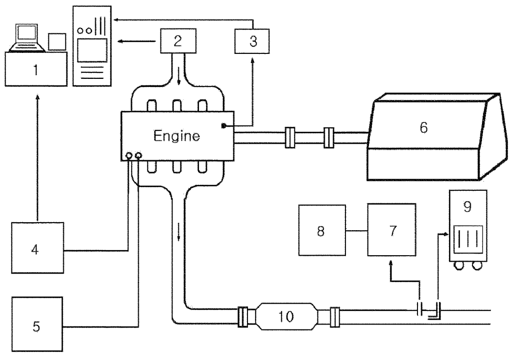
3.1. Experimental Apparatus

3.1.1. Test engine

Test engine is a heavy-duty diesel engine which is manufactured by a Korean motor company and onboard in city buses and heavy trucks.

Table 2. Specifications of test engine.

Items	Specifications
Model	D6AU
Type	6 Cylinder
Fuel injection type	DI
Displacement (cc)	11,149
Compression ratio	17.1:1
Max.Power (PS/rpm)	225/2200
Max.Torque (kgf.m/rpm)	78/1400



1. Dynamometer control desk
2. air consumption meter
3. Throttle actuator
4. Fuel-temperature controller
5. Oil temperature controller
6. Engine dynamometer
7. Exhaust gas analyzer
8. Pen recorder
9. Mini dilution tunnel
10. Diesel oxidation catalyst

Figure 1. Schematic diagram of emission measuring apparatus.

3.1.2. Test fuel

For experimental study, standard fuel contained sulfur less than 500 ppm and Ultra Low Sulfur Diesel (50 ppm, less than 15 ppm) are applied.

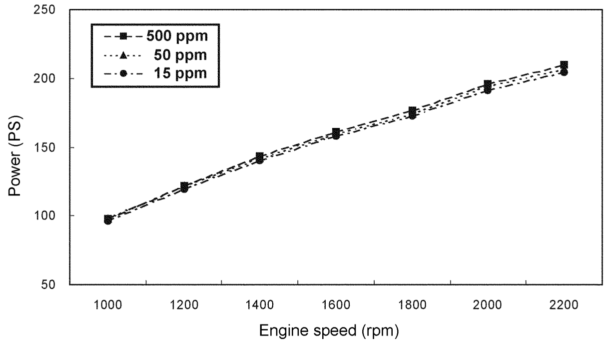


Figure 2. Engine performance test results (Power).

3.2. Experimental Details

3.2.1. Engine performance

Engine performance test was conducted by increasing engine speed from 1000 rpm to 2200 rpm at 200 rpm interval and measured fuel consumptions, engine powers and torques and took an arithmetic average for 3 seconds after stabilizing fuel consumptions, engine powers and torques for three minutes at a full engine load.

3.2.2. Emission test

Emission test was done by measuring CO, THC and NOx in D-13 mode. Exhaust pressure is maintained at less than ± 650Pa.

4. RESULTS AND DISCUSSION

4.1. Engine Performance Test Results

4.1.1. Engine power and torque

Figure 2, 3 illustrated engine powers and torques. In comparison with the standard fuel contained 500 ppm

Table 3. Specifications of test fuel.

Item of test	Standard	Result of test		
		500 ppm below	50 ppm below	15 ppm below
Flash point (PM, °C)	40 above	59	63	65
Pour point (°C)	0.0 below	-7.5	-22.5	-25.0
Distillation 90% (°C)	360 below	350	334	336
Carbon residue on 10% residue (%)	0.15 below	0.01	0.01	0.01
Ash (%)	0.02 below	under 0.01	under 0.01	under 0.01
Viscosity (40°C, cst)	1.95.5	2.9	2.6	2.8
sulfur content (weigh)	0.05 below	390 ppm	47 ppm	13 ppm
cetane index	45, above	51	54	57

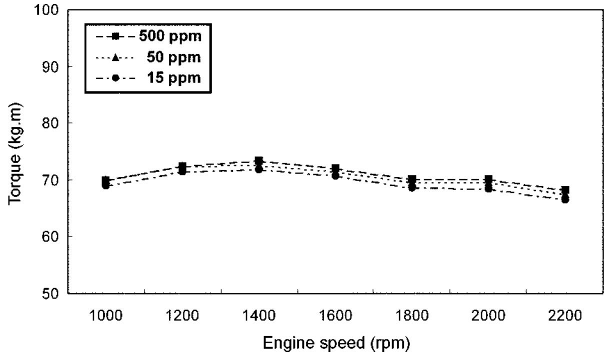


Figure 3. Engine performance test results (Torque).

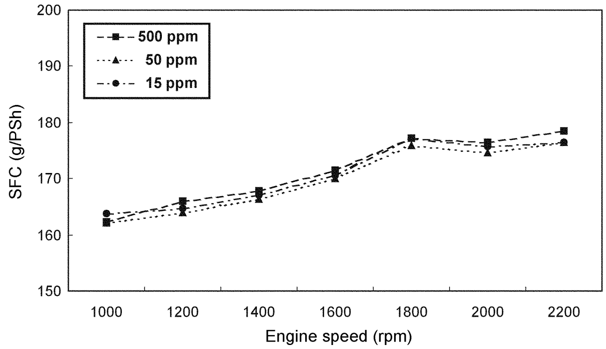


Figure 4. Engine performance test results (SFC).

sulfur, big differences in engine powers and torques in general were not found.

4.1.2. Fuel consumption rate

Figure 4 shows changes of fuel consumption rates under different sulfur contents. In comparison with a fuel containing 500 ppm sulfur, there were about 0.1~1.0% reduction of fuel consumption rate in case of 50 ppm sulfur and about 1% reduction in case of 15 ppm. This may be due to atomization of sprayed fuel, somehow.

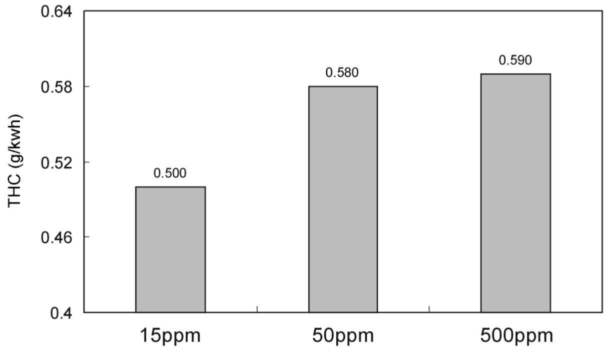


Figure 6. Result of exhaust gas test according to sulfur content (THC).

4.2. Results of Exhaust Gas

4.2.1. CO

Figure 5 shows that CO emission decreases a little bit when sulfur concentration in fuel decreases. In case of fuels of 15 ppm and 50 ppm, CO decreass to about 6.0% in comparison with a standard fuel.

4.2.2. HC

Figure 6 illustrates that hydrogen carbon concentration decreases when fuel sulfur level is low. In a fuel contained sulfur 15 ppm, reduction rate is about 15.3% and in a fuel contained sulfur 50 ppm, reduction rate is about 1.7%. This may be due to the improved fuel quality, cetane value and atomization.

4.2.3. NOx

In Figure 7, NOx in a fuel containing sulfur 15 ppm was

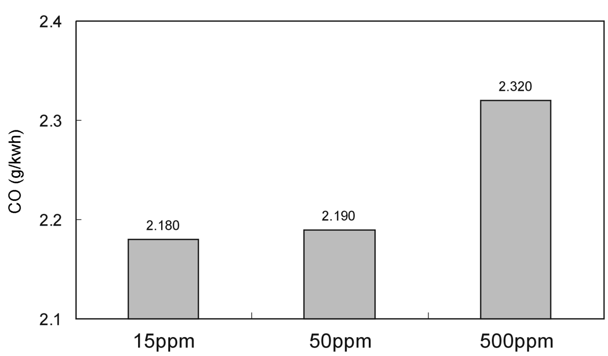


Figure 5. Result of exhaust gas test according to sulfur content (CO).

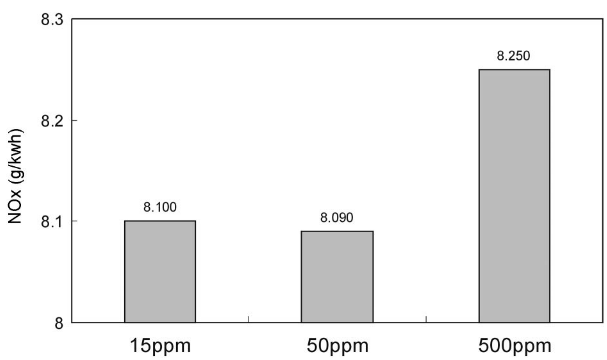


Figure 7. Result of exhaust gas test according to sulfur content (NOx).

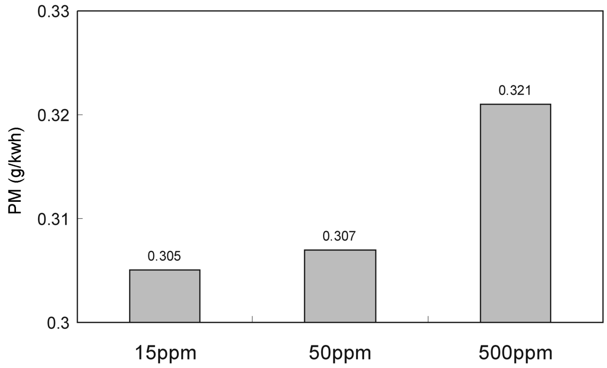


Figure 8. Result of exhaust gas test according to sulfur content (PM).

decreased to about 1.8%, and NOx in case of sulfur 50 ppm was decreased when compared with standard one. During desulfurization, aromatic compound was related with engine combustion temperature closely and this reduced aromatic compound caused a decrease of cylinder temperature (Schroder, *et al*., 1999).

4.2.4. PM

PM in fuel containing sulfur 15 ppm decreased 5.0% in comparison with standard one. PM in sulfur 50 ppm was decreased 4.4% similarly. This is due to the reduction of sulfate or aromatics (See Figure 8).

4.2.5. Unidentified emission material

In general, composition of PM in diesel engine consists of dry carbons 50~60%, about soluble organic fraction 20%, sulfate and heavy metal.

Figure 9, 10 illustrates exhausted SOF and sulfates in accordance with change of sulfur. Rates of SOF contained in PM are 19.4% at 500 ppm of sulfur concentration and 18.2% at 50 ppm and 17.2% at 15 ppm. The rates of sulfate are 1.4% at 500 ppm of sulfur concentration, 0.5%

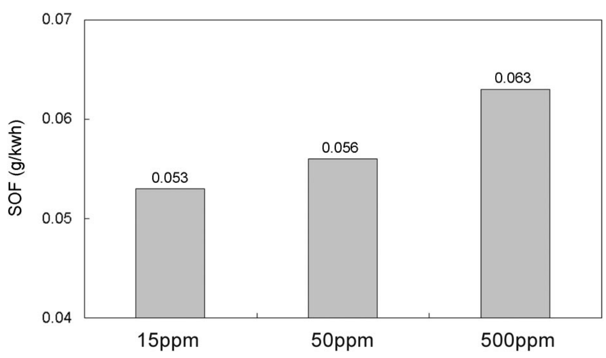


Figure 9. The result of exhaust gas test (SOF).

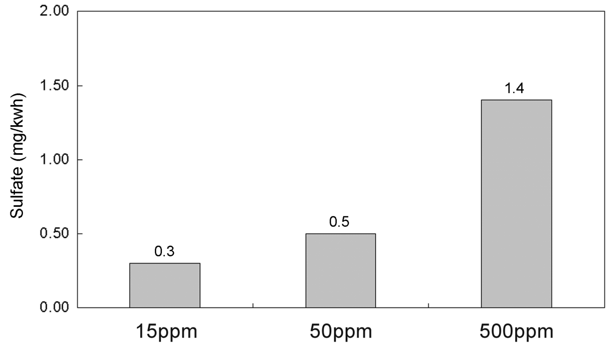


Figure 10. The result of exhaust gas test (Sulfate).

at 50 ppm, and 0.3% at 15 ppm.

Both SOF and sulfate decreased when concentration of sulfur decreased simultaneously. It indicates that decreased sulfur oxide causes a decrease of sulfates.

5. CONCLUSIONS

This research was focused on the engine performance, gas materials based on experiment and following conclusions were made.

(1) The effect of engine power and fuel consumption is negligible in ULSD when compared with one of standard fuel.

(2) PM and CO decreased about 5% and HC decreased about 215%. NOx decreased about 2% and SOF and sulfate in PM tend to decrease.

REFERENCES

Arai, M. (1992). Impact of changes in fuel properties and lubrication oil particulate emission and SOF, *SAE Paper No. 920556*.

Batt, R. J., Mcmillan, J. A. and Bradbury, I. P. (1996). Lubricity additives- performance and NO effects in low sulfur fuels", *SAE Paper No. 961943*.

Clark, W. and Sverdrup, G. M. (2000). Overview of diesel emission control-sulfur effects program, *SAE Paper No. 2000-01-1879*.

Daniels, T. L. and Carlson, P. N. (1996). The effect of diesel sulfur content and oxidation catalysts on transient emissions, *SAE Paper No. 961974*.

Han, Y. C. and Kim, D. J. (2000). *New Edition Internal Combustion Engine*, Moonwoon Publishing, 179–203. Seoul, Korea.

John, J. C. and Andrew, J. Y. (1995). Three dimensional computer modeling of the internal flow within a swirl atomizer, *ILASS-Europe*, 191. England.

Jung, Y. I. (1998). *Automotive and Environment*, Hansung Univ. Publishing, 16–23. Seoul, Korea.

Kim, J. H., Lee, B. S. and Koo, J. Y. (1999). The effect of ambient gas density on the development of impinging diesel spray, *ILASS- KOREA* **4**, **2**, 40. Seoul, Korea.

Martiy, A. Barris, (1992). Development of diesel exhaust catalystic converter mufflers, *SAE Paper No. 920369*.

Michael, G. Campbell and Edward P. Martin, (1995). Substrate selection for a diesel catalyst, *SAE Paper No. 950372*.

Port, B. (1991). Engine and catalyst strategies for 1994, *SAE Paper No. 910604*.

Schroder, O., Krahl, J. and Munack, A. (1999). Environmental and health effects caused by the use of biodiesel, *SAE Paper No. 1999-01-3561*.

Stephen, R. Turns, (1999). *An Introduction to Combustion*, Concepts and Applications, McGraw-Hill, 240. New York.

Stephen, R. Turns, (1999). *An Introduction to Combustion*, Concepts and Applications, McGraw-Hill, 337. New York.

Yoon, S. J. and Cho, D. J. (1999). The effect of viscosity on the spray characteristics of pressure swirl atomizer, *ILASS-KOREA* **4**, **4**, 24. Seoul, Korea.