Relations Research between Diesel Exhaust Temperature and Particulate Fractions

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Abstract. Particulate emission of diesel engines which seriously affects environment and human health is a hot topic in recent diesel engine researches. In this article, a diesel engine particulate sampling devise was designed, particulate sampling experiments were done in different positions with different exhaust temperatures of a diesel engine exhaust pipe. The temperature difference was expected to preliminarily simulate the exhaust cooling process in some exhaust after-treatment apparatus. For each particulate sample, the insoluble organic fraction (IOF) and soluble organic fraction (SOF) was separated. With GC/MS technique, the fractions of SOF were analyzed. The experimental results showed that under rated speed or maximum torque speed with medium or small load, IOF is the main fraction of particulate. For a changeless mode, with the decreasing of sampling temperature, SOF mass content in particulate increased, at the same time, more kinds of fractions, more alkanes content and less aromatic hydrocarbons content were detected.

1. Introduction

Diesel engine is an important mechanical power in modern daily life which has a wide variety of application. High-power diesel engines, particularly, applied to fields such as trucks, passenger cars, power generation and ship propulsion, brought much convenience to industry production and our life. However, as environmental pollution deteriorating worldwide, vehicle population progressively increasing year by year, and substances like PM and NOx within diesel exhaust are all major pollutant source, emission regulations of diesel engines is increasingly stringent. Heavy-Duty diesel vehicles, for instance, imminent Euro VI Standard limited PM emission to 0.01g/kWh, reducing over 97% PM emission compared to 0.36g/kWh of Euro I Standard in 1992, and the standard would still be more strict in predictable future. As diesel oil is difficult to evaporate, diesel engine combustion is diffusion combustion, mixing and burning simultaneously, insufficiently mixed partially, soot inevitably generates within combustion progress, which is an emphasis and difficulty of diesel engine harmful emission controlling, increasingly concerned in the industry. Quite a few control measures have emerged hitherto, these measures could be divided into in-engine purification and off-engine purification. In-engine purification measures focus on reducing PM production from its source, such as optimizing combustion system, turbocharging and turbocharger inter-cooling, reducing oil consumption, and improving fuel and lubricant quality[1-3].Off-engine purification measures focus on eliminating PM generated, using particulate filtration units with various filters and its regeneration device, catalytic converters, and electrostatic particulate traps. Through in-engine purification and off-engine purification, diesel engine particulate emissions could be reduced effectively and reach the current emission standard[4,5].

From recent research, domestic and foreign researchers have basically reached a consensus about particulate fractions, which mainly consists insoluble organic fraction (IOF) and soluble organic fraction (SOF), the major component of IOF is dry soot, while components of SOF is relatively complicated[6,7]. Much more remains to be done for further examination of particle generation mechanism and influencing factors. Nowadays, some aftertreatment device to reduce particulate emission works directly under exhaust temperature, while the majority of aftertreatment device to reduce particulate emission could not work under high temperature, these devises need additional cooler to pre-cool the exhaust gas. So what would these devise collect under different temperature? And how exhaust gas pre-cooling affect particulate fractions? Research in this area is quite necessary, for if the mechanism is fully investigated, could be helpful for design, usage and evaluation of aftertreatment devices for PM. So this article picked one diesel engine, conducted preliminary tests and analyses of cases with different exhaust temperature.

2. Particulate sampling test and analysis

2.1 Devices.

Particulate sampling test is conducted on a modified turbocharged diesel engine platform, using a inline 4-stroke six-cylinder diesel engine, rated condition at 2 400r/min(206kW), maximum torque working condition at 1 500r/min(1 070Nm). To reduce the affection to engine performance due to higher backpressure, exhaust out of turbocharger was divided into two parts, the larger part discards directly into atmosphere, the smaller part was directed to particulate sampling tube. Of the two sampler installed on the sampling tube, Sampler A is closer to turbocharger, with higher sampling temperature than Sampler B, the temperature difference of two samplers can be used for a simplified simulation of the exhaust cooling effect affected by the cooler. To enlarge the sample area for more complete PM collection, samplers adopted cylindrical structure, inner and outer layers of glass fiber filter papers were both circumferentially fixed by two layers of stainless steel protective screen, all exhaust inside sampling tube flow through filter papers. All other main test instruments, devices and reagents includes HP5890 GC and HP5970 MS, SE-50 30m×0.2mm×0.2μm chromatographic column, KQ218 ultrasonic cleaner, dichloromethane, electronic analytical balance with a precision of 0.1 mg, etc. Also, a gas flowmeter was added on diesel engine exhaust pipe to measure the quantitative result of particulate emission.

2.2 Contents.

Select one certain working mode of the diesel engine, according to engine intake air flow, adjust the opening size of flow control valve on main exhaust pipe, after a period of stable operation, add preconditioned glass fiber filter papers to collect particulate sample and record sampling time. After the sampling of all working mode were collected, process remove moisture baking of particulate samples, then use precise electronic analytical balance to weigh baked particulate samples in a constant temperature and humidity cleanroom. Repeat the same process of baking and weighing till the mass of particulate samples remain constant, then store the samples in dry bottles away from light for further analysis.

Put crushed particulate samples of each working mode into clean flasks, add 100mL dichloromethane respectively as solvent, soak samples completely into solvents. Use ultrasonic cleaner to give flasks a 10 minute ultrasonic elution. Filter solid-liquid mixtures inside flasks with quantitative filter paper, pour soild remains(sample filter paper and IOF) into another clean container which was already weighed, bake the container inside an oven with constant temperature of 500℃ to volatilize the solvent, after the oven naturally cooled to room temperature, take out the container for weighing. Repeat the same process of baking and weighing till the mass remain constant.

Respectively concentrate soluble organic fraction filtrate of each working mode naturally into 1mL for GC analysis. Working condition of gas chromatograph were as follows: temperature programming, initial temperature is 100℃, maintain for 2.0min, heat to 160℃ at heating rate of 4.0℃/min, then heat to 250℃ at heating rate of 8℃/min, maintain the temperature for 31.75min; temperature of boil room is 260℃, with helium gas as carrier; chapiter pressure 45 kPa.Working condition of mass spectrometry were as follows: electron impact energy of mass spectrometer is 70 eV; multiplier voltage is 1 800 V; mass range 300~500amu, with precision of 1amu, sample size of 1μL.

3. Test Result and Analysis

3.1 Test Result.

Four working modes was selected for particle component analysis, namely under the rated speed or the maximum torque speed with medium or small load respectively, engine parameters of each working modes were listed in Tab.1.

Table 1 GC/MS engine parameters of each working modes

Mode	Speed / r·min^{-1}	Power / kW	Torque /N·m	Sample Temperature / ℃	Particulate emission mass flow / g·h^{-1}
1	1501	45	286.5	140	7.28
2	1501	45	286.5	284	8.92
3	1499	85.3	544.4	185	14.72
4	1499	85.3	544.4	410	18.62
5	2402	103.2	410.7	191	13.16
6	2402	103.2	410.7	416	16.88
7	2390	55.0	219.7	161	7.15
8	2390	54.9	219.7	326	8.87

GC/MS experimental result and mass content of fractions in particulate SOF under test conditions are listed in Tab.2.

Table 2 GC/MS experimental result and mass content of fractions in particulate SOF

		Mass percentage							
Compound	Molecular formula	Mode 1H	Mode 1L	Mode 2H	Mode 2L	Mode 3H	Mode 3L	Mode 4H	Mode 4L
Naphthalene	$C_{10}H_8$			0.13					
n-Nonane	C_9H_{20}			0.37					
n-Tridecane	$C_{13}H_{28}$			1.85					
Methylnaphthalene	$C_{11}H_{10}$			0.56					
Side Chain Tridecane	$C_{13}H_{28}$					4.73			
n-Tetradecane	$C_{14}H_{30}$			2.86	0.70	4.79	0.86	0.16	
Dimethylnaphthalene	$C_{12}H_{12}$			2.62		1.37		0.31	
Side Chain Tetradecane	$C_{14}H_{30}$			1.32	1.29		0.84		
n-Pentadecane	$C_{15}H_{32}$	0.49		5.86	4.39	10.73	4.56	1.02	0.26
Trimethylnaphthalene	$C_{13}H_{14}$	0.65		6.65	3.42	6.57	3.56	3.53	
Side Chain Pentadecane	$C_{15}H_{32}$	1.76		7.16	11.71	3.51	6.12	0.50	5.61
9-H Fluorene	$C_{13}H_{10}$			0.95				0.90	
n-Hexadecane	$C_{16}H_{34}$	2.10	0.29	9.47	10.85	11.36	13.4	6.20	2.68
1-(1, 1-dimethylethyl) naphthalene	$C_{16}H_{14}$	0.38		0.99					
Hexadecylene	$C_{16}H_{32}$					1.98	2.33	2.07	
Hexadecylene-1	$C_{16}H_{32}$			1.96	2.14				
Side Chain Hexadecane	$C_{16}H_{34}$	0.73	0.25	4.17	4.81	32.19	10.87	14.65	
Tetramethylnaphthalene	$C_{14}H_{16}$	0.72		3.81	4.78	1.92	4.17	6.15	
Tetramethyl Dibenzofuran	$C_{13}H_{10}O$							1.13	
n-Heptadecane	$C_{17}H_{36}$	4.24	0.85	8.07	11.61	6.06	12.85	10.00	9.35
9-Methyl 9H-Fluorene	$C_{14}H_{12}$	1.78							
Side Chain Heptadecane	$C_{17}H_{36}$	10.84	0.69	14.07	12.49	4.17	13.48	13.2	9.8
9-Methyl Fluorene	$C_{14}H_{12}$				1.99				
Phenanthrene	$C_{14}H_{10}$	3.77		2.29	3.04		2.49	5.58	4.65
n-Octadecane	$C_{18}H_{38}$	5.83	1.48	5.31	6.29	2.71	6.57	7.43	11.75
Dimethyl Fluorene	$C_{15}H_{14}$				2.41				
Side Chain Octadecane	$C_{18}H_{38}$	13.8	1.47	5.65	8.27	3.04	7.73	12.14	21.51
DIBP	$C_{16}H_{22}O_4$	2.97		1.73	1.74	0.77	1.51	2.63	3.91
n-Nonadecane	$C_{19}H_{40}$	6.10	2.16	2.92	2.23	1.02	2.32	3.04	6.79
Methylphenanthrene	$C_{15}H_{12}$	8.34		1.67				2.24	6.32

4-Methylphenanthrene	$C_{15}H_{12}$				1.41			1.77	
DEHP	$C_{16}H_{22}O_4$	7.31	1.39	2.58	2.36	1.71	3.26	3.45	7.95
Side Chain Nonadecane	$C_{19}H_{40}$	1.76							
n-Eicosane	$C_{20}H_{42}$	5.82	4.27	1.87	0.81	0.52	1.27	1.46	3.87
Side Chain Eicosane	$C_{20}H_{42}$	3.82	4.14						
Dimethylphenanthrene	$C_{16}H_{14}$	5.67							
n-Heneicosane	$C_{21}H_{44}$	4.28	7.47	1.30	0.35	0.27	0.65	0.25	2.07
Side Chain Heneicosane	$C_{21}H_{44}$	1.11	4.96						
n-Docosane	$C_{22}H_{46}$	3.44	10.47	1.08	0.33	0.35	0.65	0.17	1.26
Side Chain Docosane	$C_{22}H_{46}$		8.36						
n-Tricosane	$C_{23}H_{48}$	1.35	11.44	0.44	0.29	0.23	0.49		0.87
Side Chain Tricosane	$C_{23}H_{48}$		7.15						
n-Tetracosane	$C_{24}H_{50}$	0.53	8.55	0.14	0.29				0.78
DOP	$C_{24}H_{38}O_4$								0.55
Side Chain Tetracosane	$C_{24}H_{50}$		2.50	0.16					
n-Pentacosane	$C_{25}H_{52}$	0.42	8.71						
Side Chain Pentacosane	$C_{25}H_{52}$		2.55						
n-Hexacosane	$C_{26}H_{54}$		5.60						
Side Chain Hexacosane	$C_{26}H_{54}$		2.28						
n-Heptacosane	$C_{27}H_{56}$		1.95						
n-Octacosane	$C_{28}H_{58}$		1.04						

Fig.1 showed total ion chromatogram of SOF samples in exhaust particulate matters of two working modes, horizontal coordinate is retention time, vertical coordinate is abundance, or intensity of ion current.

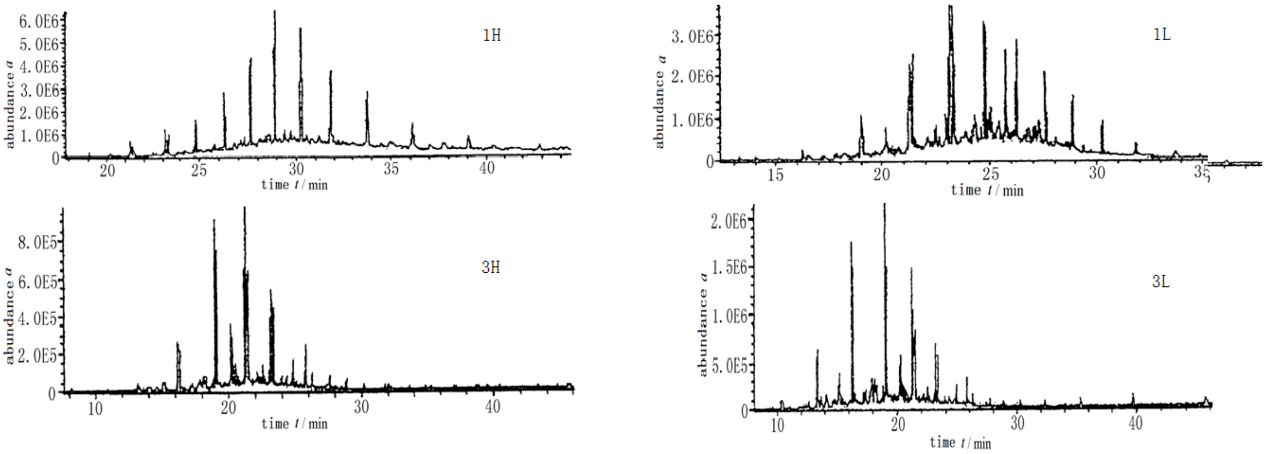

Fig.1 Total ionic chromatogram of SOF in diesel particulate of some testing modes

3. 2 Analysis.

Tab.3 showed the calculations of mass content percentage of fractions in particulate matters, according to the weighing results of particulate samples and figures in Tab.2.

Compare test results of samplers in high and low temperature with same working mode in Tab.2 and Tab.3, it showed: in all four testing working mode, the mass content of SOF is smaller, at 8%～18%, with an average content of 12.12％; the mass content of IOF is larger, at 82%～92%, with an average content of 87.88%. As the results showed, under the rated speed or the maximum torque speed with medium or small load working mode of this test, the main fraction of particulate was IOF. Also, within the same working mode, the kinds of SOF in the particulates and the mass fraction of SOF increases with sample temperature decrease, the mass increment of four working modes were 4.79%, 1.93%, 1.89%, 3.71%. Though the temperature difference of the high temperature sampler and the low temperature sampler in each working mode is different, the regularity is still obvious.

Fore mentioned phenomenon could be explained by two factors: first, after exhaust has been pushed combustion chamber, when in higher temperature (among four working modes, the lowest sample temperature is 185℃, the highest is 326℃) , some fractions of SOF reached or exceed its boiling point, were partially or completely exist in gaseous form and could pass through filter papers, causing a decrease of SOF in collected particulate samples while the mass fraction of IOF was relatively higher; second, at higher temperature, subsequent reactions inside exhaust pipe still exist, and consumed some particulate fractions, especially among SOF in these reactions in exhaust pipe. Studies showed: particulate matters generated in in-cylinder combustion were extremely unstable, “secondary generation” could occur in exhaust process, test results above match with this theory. Further more, with temperature decrease, the SOF increase will increase the total particulate matters amount in exhaust, which proved by the test results of particulate mass flow in Tab.1. Also, in existing test figures, higher temperature difference of two samplers resulted in higher particulate mass flow difference, yet no obvious proportional relation between the two has yet shown.

Figures in Tab.2 and Tab.3 also showed that in each working modes, main fractions of SOF are n-alkanes or side chain alkanes among C9 to C28, exact fractions varies in different working modes, alkanes consisted an average 80％ of SOF. In same working modes, the mass fraction of alkanes in SOF generally increases with sample temperature decrease, while aromatic hydrocarbon content and naphthalene aromatic hydrocarbon content decreases at the same time. This showed that in subsequent reactions inside exhaust pipe, SOF could generate alkanes in subsequent reactions. However, except working mode 1H and 1L, exhaust temperature decrease resulted in modest increase of mass fraction of alkanes, with an average absolute value of only 4.31%, thus, it is safe to assume that content of fractions in particulate matters mainly depends on in-cylinder combustion status.

Table 3 Mass content percentage of fractions in particulate matters

Mode	Sample temperature /℃	SOF mass content in particulate	IOF mass content in particulate	Alkanes mass content in SOF	Aromatic hydrocarbons mass content in SOF	Naphthalene aromatic hydrocarbon mass content in SOF	Phenanthrene aromatic hydrocarbon mass content in SOF	Other organic fractions mass content in SOF
1H	284	13.38	86.62	68.42	21.31	1.75	17.78	10.28
1L	140	18.17	81.83	98.63	0	0	0	1.39
2H	410	8.58	91.42	74.07	19.67	14.76	3.96	6.27
2L	185	10.51	89.49	76.71	17.05	8.2	4.45	6.24
3H	416	8.01	91.99	85.68	9.86	9.86	0	4.46
3L	191	9.90	90.10	82.66	10.22	7.73	2.49	7.10
4H	326	12.33	87.67	70.22	21.61	9.99	9.59	8.15
4L	161	16.04	83.96	76.6	10.97	0	10.97	12.41

PS: Aromatic hydrocarbons were homologues of indene, fluorene, phenanthrene, naphthalene, etc; other organic fraction include diisobutyl phthalate(DIBP), di (2-ethylhexyl) phthalate(DEHP), dioctyl phthalate(DOP), etc.

GC analysis also detected other organic fraction in particulate SOF, include diisobutyl phthalate(DIBP), di (2-ethylhexyl) phthalate(DEHP), dioctyl phthalate(DOP), the average percentage of which in each working mode is 7.04%, yet the effect of exhaust temperature on impurity generation showed no obvious regularity

4. Summary

Developed diesel engine particulate sampling device, collected exhaust particulate sample at various sample spots with different temperature inside exhaust pipe of the same diesel engine, acquired diesel engine exhaust particulate sample at different exhaust temperature. GC/MS analysis showed that under the rated speed or the maximum torque speed with medium or small load, the main fraction of particulate was IOF, consisted 87.88% of average mass fraction, while SOF consisted 12.12％; within the same working modes, the kinds of SOF in the particulates, the mass fraction of SOF and the mass flow of the particulates increases with sample temperature decrease; at testing modes, alkane consisted about 80% of particulate SOF. Within the same working mode, with sample temperature decrease, alkane content of SOF increases, aromatic hydrocarbon content and naphthalene aromatic hydrocarbon content decreases.

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