Available online at www.sciencedirect.com
ScienceDirect

Journal of Environmental Sciences 21(2009) 1208–1213

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Optimization of gasoline hydrocarbon compositions for reducing exhaust emissions

SHEN Yitao, SHUAI Shijin*, WANG Jianxin, XIAO Jianhua

State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China. E-mail: shenyt03@mails.tsinghua.edu.cn

Received 05 August 2008; revised 17 December 2008; accepted 26 February 2009

Abstract

Effects of hydrocarbon compositions on raw exhaust emissions and combustion processes were studied on an engine test bench. The optimization of gasoline hydrocarbon composition was discussed. As olefins content increased from 10.0% to 25.0% in volume, the combustion duration was shortened by about 2 degree crank angle (°CA), and the engine-out THC emission was reduced by about 15%. On the other hand, as aromatics content changed from 35.0% to 45.0%, the engine-out NOx emissions increased by 4%. An increment in olefins content resulted in a slight increase in engine-out CO emission, while the aromatics content had little effect on engine-out total hydrocarbon (THC) and CO emissions. Over the new European driving cycle (NEDC), the THC, NOx and CO emissions of fuel with 25.0% olefins and 35.0% aromatics were about 45%, 21% and 19% lower than those of fuel with 10.0% olefins and 40.0% aromatics, respectively. The optimized gasoline compositions for new engines and new vehicles have low aromatics and high olefins contents.

Key words: optimization; hydrocarbon composition; exhaust emissions; olefins; aromatics

DOI: 10.1016/S1001-0742(08)62405-5

Introduction

Exhaust emissions from vehicles are not dependent only on automotive technologies, but also on fuel qualities. With more stringent emission standards around the world, fuel quality is becoming a great concern for the automobile and oil industries. Gasoline is a mixture of hundreds or even thousands kinds of hydrocarbons, including paraffins, olefins and aromatics. These hydrocarbons have different physical and chemical characteristics that affect combustion processes and emissions in internal combustion engines.

Paraffins are saturated hydrocarbons, of which the octane numbers are generally lower than those of olefins and aromatics, that explains the limited paraffin content in high octane gasoline. During the combustion, thermal cracking of paraffins results in olefins exhaust emission, which has a strong ozone formation potential (OFP) (Kaiser *et al*., 1992).

Olefins are unsaturated hydrocarbons and have high anti-knock performance. They serve as proper blending components to increase the fuel octane number. Gasoline with high olefins content would release certain amounts of olefins emission that increases its OFP (Koehl *et al*., 1991). Olefins also have a modest tendency to form deposits on injectors and intake valves (Carlisle *et al*., 2001; Guo *et al*., 1999; Liu and Li, 2003; Nie *et al*., 2000). The effect of olefins on regulated exhaust emissions is unclear now. A reduction in olefins may or may not have a benefit on NOx emission (Diana *et al*., 1998; Kaiser *et al*., 1993; Kwon *et al*., 1999; Schifter *et al*., 2004). Bennett *et al*., (1996) found that there was no effect of olefins on hydrocarbon (HC) and CO emissions, but Schifter *et al*., (2004) showed lowering olefins decreased CO emissions. Liu and Xu (2004) and Thummadetsak *et al*., (1999) found that effects of olefins on exhaust emissions were different for different vehicles.

Aromatics are high octane-number unsaturated compounds with a ring structure. Lowering the aromatic or benzene content in fuel reduces benzene emissions (Diana *et al*., 1998; Thummadetsak *et al*., 1999). Aromatics have a strong deposit formation tendency. They promote injector deposit and combustion chamber deposit (CCD), which would deteriorate the mixture formation quality and in-cylinder combustion process (Ashida *et al*., 2001; Carlisle *et al*., 2001; Uehara *et al*., 1997). Aromatics have high peak flame temperatures. Decreasing the aromatic content could reduce engine-out NOx emission. A decrement of 1% in volume for aromatic content can lead to a decrease of NOx emissions 0.24–0.3 g/kWh (Diana *et al*., 1998; Pentikäinen *et al*., 1998). However, this effect may be attenuated or even reversed due to the reduction in NOx conversion rate of a three-way catalyst (TWC) for low aromatics fuel. Therefore, a reduction in aromatics may result in an increase in NOx emission on a vehicle with a catalyst system (McDonald *et al*., 1996; van den Brink and McDonald, 1995). The effects of aromatics on total hydrocarbon (THC) and CO emissions are not clear. Some

* Corresponding author. E-mail: sjshuai@mail.tsinghua.edu.cn

results showed aromatics increased THC emission (Goodfellow *et al*., 1996; Hamasaki *et al*., 2000; Liu and Xu, 2004) and CO emission (Kwon *et al*., 1999), but some results showed aromatics had no effect on THC emission (Bennett *et al*., 1996; Kwon *et al*., 1999) and CO emission (Diana *et al*., 1998). The effect of aromatics on emissions may be closely related to the test conditions (Hamasaki *et al*., 2000).

From previous publications it was clear that olefins had some effects on the OFP of engine emissions and increased deposits in injection or intake systems, while aromatics increased benzene emission and deposits in combustion chambers and injectors. The effect of hydrocarbon composition on engine-out regulated emissions was not clear enough. Since the previous studies were mostly conducted on vehicles under different emission test conditions, the test results showed the combined effects of complicated factors, such as fuel composition, engine technologies, emissions control systems and operation conditions. This study was designed to find out the effects of hydrocarbon compositions on combustion and regulated exhaust emissions of new engines, from which optimized hydrocarbon compositions of gasoline can be acquired. The optimized compositions were then tested on new vehicles to verify the engine-test results.

1 Experimental setup

1.1 Test engine and vehicle

A new port fuel injection gasoline engine (Touran 2.0, Shanghai Volkswagen Company, China) and a gasoline passenger vehicle (Sylphy, Dongfeng Nissan Passenger Vehicle Company, China, 2006) with mileage 10600 km were selected for tests. The specifications are shown in Table 1.

1.2 Test fuels

Five gasoline samples with similar octane number were supplied by Liaoning Fangyuan National Reference Petrol Co., Ltd., China. Specifications of these fuels are shown in Table 2. No. 1–No. 3 samples with olefins content range 10.0%–25.0% in volume and almost constant aromatics contents were used to test on olefins. The samples No. 2, 4, and 5 with almost same olefins contents were used for tests on aromatics.

Table 1 Specifications of the test engine and vehicle

	Parameter	Value
Engine	Type	Straight line, four-stroke, water cooling, naturally aspirated
	Number of cylinders	4
	Bore × stroke (mm× mm)	82.5 × 92.8
	Displacement (L)	1.984
	Rated power/engine speed (kW/(r/min))	85/5200
	Maximum torque/engine speed ((N·m)/(r/min))	170/4000
	Compression ratio	10.3:1
Vehicle	Displacement (L)	2.0
	Fuel injection	Multi point injection
	O_2 sensor	With
	Transmission	Automatic transmission
	Catalyst	Three way catalyst

1.3 Test procedure

The schematic diagram of the engine test bench is shown in Fig. 1 and operation conditions are shown in Table 3. The fuel supply system was designed to save test fuels and ensure the accuracy of experiments, which could switch quickly between different test fuels on board. Engine-out NO*x*, THC and CO emissions were measured by an exhaust gas analyzer (AVL CEB II, Austria). THC was measured via a flame ionization detector (FID), CO measured via a non-dispersive infrared analyzer (NDIR), and NO*x* measured via chemiluminescence. Cylinder pressures were measured by a Kistler 6125B pressure sensor (Kistler, Switzerland). For vehicle tests, experiments were conducted on a chassis dynamometer bench (Burke E. Porter Machinery Company, USA) under new European driving cycle (NEDC) cycle. Vehicle tailpipe emissions were measured by MEXA-7000 and CVS-7000 (Horiba Company, Japan). All tests were repeated two times.

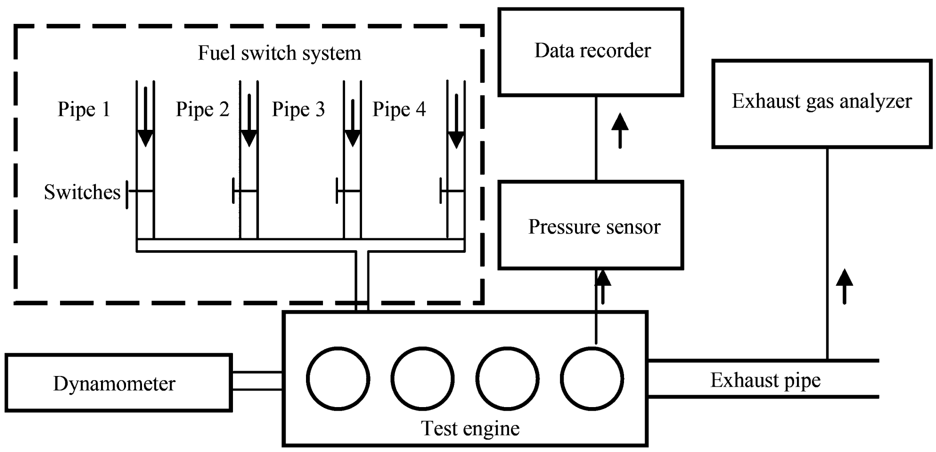

Fig. 1 Schematic of the engine test bench.

Table 2 Specifications of the test fuels

Sample	RON	Density (kg/m^3)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	EP (°C)	RVP (kPa)	Sulfur ($\times10^{-6}$, *m/m*)	Oxygen (%, *m/m*)	Aromatic (%, *V/V*)	Olefins (%, *V/V*)	C/H (*m/m*)
No. 1	93.3	779.1	70.0	109.0	161.0	195.0	52.2	320	0.0	40.0	10.0	7.72
No. 2	93.1	775.1	70.0	110.0	163.0	195.0	50.0	210	0.0	39.5	16.4	7.42
No. 3	93.5	742.2	55.0	96.0	162.0	191.0	64.0	500	0.6	35.0	25.0	6.65
No. 4	93.1	788.9	69.0	109.0	163.0	198.0	60.2	180	0.0	35.2	16.4	7.41
No. 5	93.3	787.3	70.0	111.0	163.0	199.0	54.2	250	0.0	45.0	16.9	6.74

RON is research octane number; T_{10}, T_{50} and T_{90} are the temperatures related to 10%, 50% or 90% in the distillation curve; EP is the end point in distillation curve; RVP is Reid vapor pressure; C/H is the mass ratio of carbon to hydrogen. Density was conducted at 20°C. "*m/m*" means mass ratio; "*V/V*" means volume ratio.

Table 3 Operation conditions

Operation condition	Engine speed (r/min)	BMEP (MPa)	Excess air coefficient (Φa)
1	2000	0.19	1
2	2000	0.44	1
3	2000	0.88	1
4	3500	0.19	1
5	3500	0.44	1
6	3500	0.95	0.97

BMEP means brake mean effective pressure.

2 Results and discussion

2.1 Effect of olefins and aromatics on engine-out emissions

For THC emission, as shown in Fig. 2a, engine-out THC emissions are decreased significantly as olefins content increases (No. 1–No. 3). At high load conditions, such as BMEP 0.88 or 0.95 MPa, THC emissions are decreased by about 18% as olefins content increases from 10.0% to 25.0%. At low load condition (BMEP 0.19 MPa), they are decreased by nearly 10%. For gasoline with higher olefins, the released HC from crevice storage, oil absorption and wall-film contain more olefins and can be easily burnt up during post combustion process, and thus reduce THC emissions. The reduction of THC is greater at high load conditions than at low load conditions, because high load operations have higher combustion temperature and exhaust temperature which can promote olefins burnt up. It should be noted that the fuel with olefins 25.0% has lower T_{10}, T_{50} and contains some oxygen. High volatility reduces THC emissions by improving homogeneity of air/fuel mixture and reducing the amount of wall wetting. Oxygen in fuel also shows some benefits in reducing THC emissions (Koehl *et al*., 1991). On average, 1% reduction in olefins content results in a 1% reduction in THC emission.

No. 5 fuel with the highest aromatic content has the lowest THC emission, and No. 2 and No. 4 fuels have similar THC emissions, among them the difference of THC emissions is below 5%. This is contrary to the finding of some researchers that aromatics increase THC emissions (Goodfellow *et al*., 1996; Hamasaki *et al*., 2000; Liu and Xu, 2004). There are two reasons for the lowest THC emissions of No. 5 fuel. One is that No. 5 fuel has a shorter combustion duration than No. 2 and No. 4 fuels (Fig. 3a), and the improvement in combustion will result in the reduction of THC emission. The other one is that

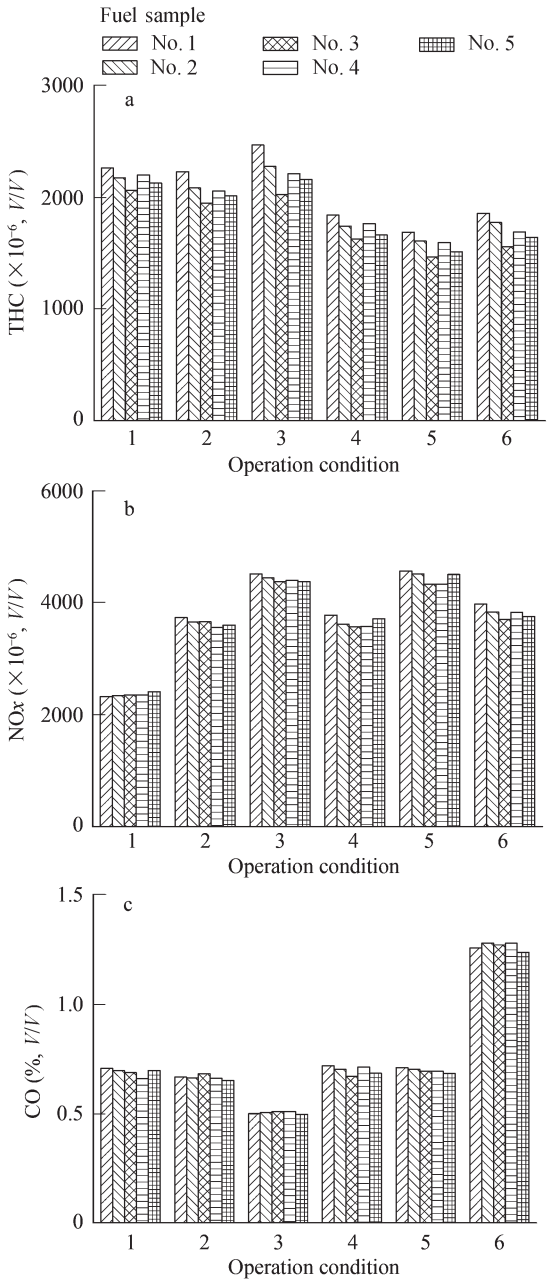

Fig. 2 Effect of hydrocarbon compositions on engine-out THC (a), NO*x* (b) and CO (c) emissions.

No. 5 fuel has the lowest C/H ratio which reduces THC emission. Comparing the THC emissions of No. 2 and No. 4 fuels, it can be considered that the effect of aromatics content on THC emissions is indistinctive. If the influence

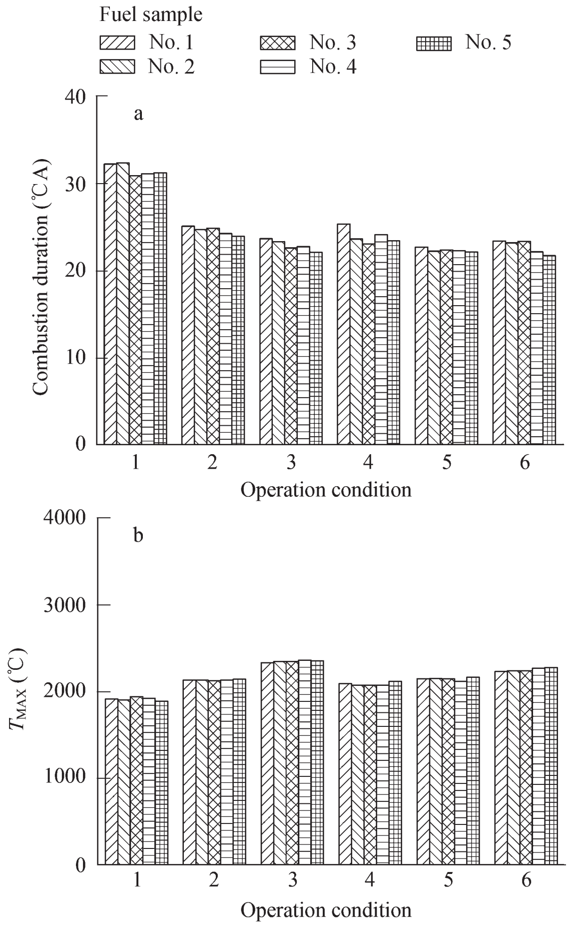

Fig. 3 Effect of hydrocarbon compositions on combustion duration (a) and T_{MAX} (b).

of C/H ratio was excluded from No. 5 fuel, the difference between THC emissions of these three fuels would be small. Therefore, aromatics content has little effect on THC emission.

As shown in Fig. 2b, NO*x* emissions are decreased by about 4% as olefins content increases from 10.0% – 25.0%. This phenomenon is different from the results of some research works (Bennett *et al*., 1996; Diana *et al*., 1998; Kaiser *et al*., 1993). The fuel with high olefin content has a lower C/H ratio which lowers adiabatic flame temperature and reduces NO*x* emission. Although NO*x* emission should be increased due to the improved combustion with high olefins content, C/H ratio dominates the behavior of NO*x* emission. The influence of olefins content on NO*x* emission is small.

Engine-out NO*x* emission was increased by about 4% as aromatics content increases from 35.0% to 45.0%. The result agrees with previous studies (Diana *et al*., 1998; McDonald *et al*., 1996; Pentikäinen *et al*., 1998). Therefore, aromatics only have a small effect on NO*x* emission.

As presented in Fig. 2c, CO emission is decreased at low load condition (BMEP 0.19 MPa) and increased at high load conditions (BMEP 0.88 or 0.9 MPa) as olefins content increases. There are two factors. One is post combustion of olefins, in which olefins are easier to be oxidized to CO and thus increase engine-out CO emission than paraffin. The other one is C/H ratio. CO emission is decreased as C/H ratio decreases from 7.72 to 6.65 for No. 1, 2 and 3 fuels. At low load conditions, C/H ratio dominates the amount of CO emission. As load increases, CO emission formed during post combustion increases gradually and plays a dominant role. Due to those reasons, the variation of CO emission is below 5% when olefins content changes in the range of 10.0%–25.0%. There is no trend for CO emission as aromatics content changes from 35.0% to 45.0%.

It can be concluded that olefins show a great benefit in reducing engine-out THC emission, a little negative effect on engine-out CO emission and little effect on engine-out NO*x* emission. Whereas aromatics have little effect on engine-out THC and CO emission and a little negative effect on engine-out NO*x* emission. Therefore, using gasoline with high olefins and low aromatics is an effective way to reduce engine-out exhaust emissions of the new engine. For this reason, engine-out THC and NO*x* emissions of No. 3 are 15% and 4% lower than those of No. 1, respectively.

2.2 Effect of olefins and aromatics on combustion

Combustion duration (5%–90% mass-burning period) and peak mean temperature (T_{MAX}) during combustion are analyzed through cylinder pressures. As shown in Fig. 3a, combustion durations are shorten as olefins content increases at some operation points (1, 3–5). The maximum reduction in combustion duration is about 2°CA. This means olefins can improve combustion process and reduce unburned THC emissions. The combustion duration of No. 5 fuel is shorter than those of No. 2 and 4 fuels. The shorter the combustion duration is, the higher the combustion temperature is. Therefore, the NO*x* emission of No. 5 fuel is higher than those of No. 2 and 4 fuels. Different combustion durations of No. 2, 4, and 5 fuels may due to their difference in both aromatics species and aromatics content, which needs to be further studied.

T_{MAX} has strong influence on NO*x* emission. Because T_{MAX} of all fuels is close (Fig. 3b), the difference between NO*x* emissions of these fuels is below 5%.

2.3 Optimization of hydrocarbons to reduce vehicle emissions

Because olefins have a significant benefit in reducing engine-out THC emission and aromatics have a little negative effect on engine-out NO*x* emission, No. 3 fuel with the highest olefins and lowest aromatics is expected to reduce vehicle emissions. No. 1 fuel is used for comparison.

Figure 4a shows the tailpipe emissions during urban driving cycle (UDC) test cycle, including cold start process and low vehicle speed process. THC, NO*x* and CO emissions of No. 3 fuel are lowered by about 46%, 26% and 25%, respectively, compared to those of No. 1 fuel. It can be found from Fig. 5 that the reduction in THC and CO emissions of No. 3 fuel mainly comes from initial 100 s during which catalyst does not light off and THC, CO emissions are exhausted without conversion. This phenomenon also supports the previous conclusion that olefins can reduce engine-out THC emissions. The difference in

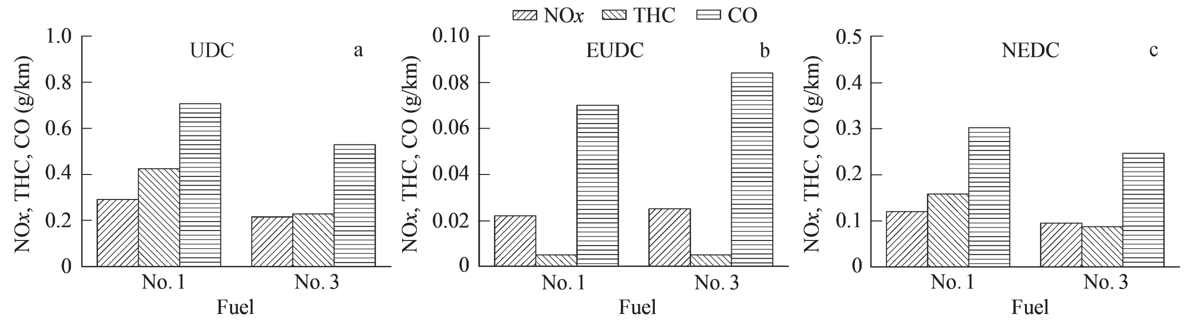

Fig. 4 Effect of hydrocarbon compositions on tailpipe emissions over UDC (a), EUDC (b), and new European driving cycle (NEDC) (c) cycles.

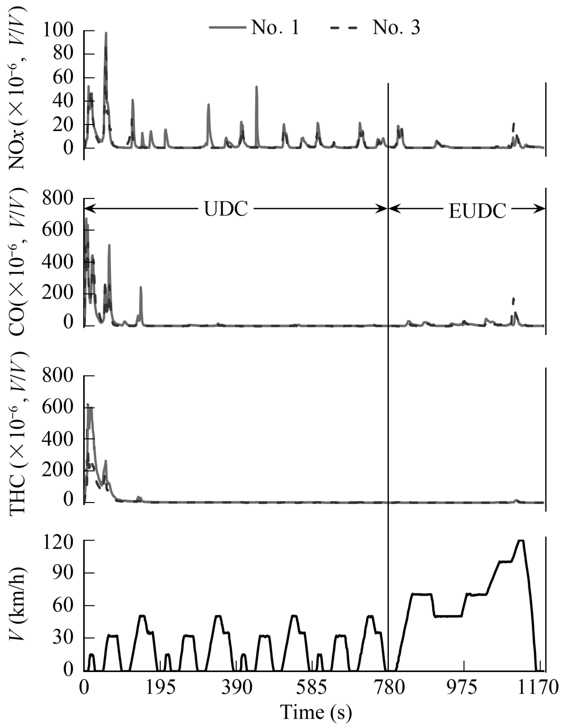

Fig. 5 Real time tailpipe emissions over NEDC cycle.

NO*x* emissions is large at transitional driving conditions. For example, the NO*x* emissions of No. 1 fuel are higher than those of No. 3 fuel during acceleration processes. This is caused by leaner air/fuel ratio when No. 1 fuel is used. Fig. 4b shows the tailpipe emissions during extra urban driving cycle (EUDC) test cycle. THC, NO*x* and CO emissions are very low for both fuels during EUDC cycle. The variation in regulated emissions is also mainly caused by the drift in air/fuel ratio during transitional conditions. Over the composite NEDC cycle, THC, NO*x* and CO emissions of No. 3 fuel are about 45%, 21% and 19% lower than those of No. 1 fuel, respectively (Fig. 4c).

Vehicle THC emission is significantly reduced by using gasoline with highest olefins content. This agrees well with engine tests. Reduction in NO*x* and CO emissions of No. 3 fuel may be caused by other fuel qualities such as volatility.

2.4 Discussion

Olefins in gasoline may increase olefins emissions, including evaporation emissions and exhaust emissions. It should be noted that light olefins contribute almost all of the OFP of exhaust emissions and olefins in exhaust emissions have weak relationship with the olefins content in gasoline. Therefore, no real environmental benefit is expected if only the total content of olefins is limited (Pentikäinen *et al*., 2004; Renner *et al*., 1993). The amount of light olefins should be limited. Olefins are thermally unstable and increase deposit in intake and injection systems. Adding deposit control additives is one way to solve this problem. Petro-China Lubricating Oil Research and Development Center found that a detergent additive could reduce intake valve deposit (IVD) about 80%, but this inhibition effect of detergent on IVD decreased with the increase of olefins content (Liu and Li, 2003). As olefins with high octane number components have attractive advantages, such as are able to improve combustion process and shorten combustion duration, they have a great benefit in reducing engine-out THC emission.

Aromatics increase CO_2 (Kwon *et al*., 1999), NO*x* and benzene emissions and have a trend to increase CCD and injector deposits which increase engine emissions, therefore, aromatics should be restricted.

Both olefins and aromatics have some negative effects on emissions or engine performance. Compared to aromatics, olefins have a benefit in reducing THC emission. Since it is impossible to produce high octane gasoline just with paraffin, it can be a solution that the upper limit of olefins content is moderated at 18.0 V% and light olefins is stringently restricted; or aromatics content is as low as possible and benzene content is strictly controlled; or the content of paraffin with high octane number is increase. From this study and previous research, it seems that it is also necessary to control the content of some special kinds of hydrocarbons besides the total content of olefins or aromatics. Other parameters such as C/H also have some effects on exhaust emissions. Therefore, the further study is needed.

3 Conclusions

Optimizing gasoline hydrocarbon compositions was an effective way to reduce engines and vehicles exhaust emissions. Olefins were able to improve combustion process and had a great benefit in reducing engine-out THC emission for the new engine, while aromatics had a little negative effect on engine-out NO*x* emission. Olefins 25.0% and aromatics 35.0% was one of the optimized gasoline compositions. Engine-out THC and NO*x* emissions were decreased about 15% and 4% by the optimized hydrocarbon compositions. Over the composite NEDC cycle, tailpipe THC, NO*x* and CO emissions were decreased about 45%, 21% and 19%, respectively, by the optimized hydrocarbon composition.

Acknowledgments

This research was supported by the Beijing Municipal Science & Technology Commission (No. D0405002040221). The authors also would like to express sincere thanks for the support of Shanghai Volkswagen Company and Dongfeng Nissan Passenger Vehicle Company.

References

Ashida T, Takei Y, Hosi H, 2001. Effects of fuel properties on SIDI fuel injector deposit. SAE paper, No. 2001-01-3694.

Bennett P J, Beckwith P, Bjordal S D, Goodfellow C L, 1996. Relative effects of vehicle technology and fuel formulation on gasoline vehicle exhaust emissions. SAE paper, No. 961901.

Carlisle H W, Frew R W, Mills J R, Aradi A A, Avery N L, 2001. The effect of fuel composition and additive content on injector deposits and performance of an air-assisted direct injection spark ignition (DISI) research engine. SAE paper, No. 2001-01-2030.

Diana S, Giglio V, Lorio B, Police G, 1998. The influence of fuel composition on pollutant emission of premixed spark ignition engines in presence of EGR. SAE paper, No. 982621.

Goodfellow C L, Gorse R A, Hawkins M J, McArragher J S, 1996. European programme on emissions, fuels and engine technologies (EPEFE)-gasoline aromatics/E100 study. SAE paper, No. 961072.

Guo H J, Guo X C, Liu Z Z, 1999. The effect of petroproduct quality on deposit formation of PFI gasoline engine. *Petroleum Products Application Research*, (6): 18–20.

Hamasaki M, Yamaguchi M, Hirose K, 2000. Japan clean air program (JCAP)-step I study of gasoline vehicle and fuel influence on emissions. SAE paper, No. 2000-01-1972.

Kaiser E W, Siegl W O, Cotton D F, Anderson R W, 1992. Effect of fuel structure on emissions from a spark-ignited engine. 2. naphthene and aromatic fuels. *Environmental Science and Technology*, 26(8): 1581–1586.

Kaiser E W, Siegl W O, Cotton D F, Anderson R W, 1993. Effect of fuel structure on emissions from a spark-ignited engine. 3. olefinic fuels. *Environmental Science and Technology*, 27(7): 1440–1447.

Koehl W J, Benson J D, Burns V, Gorse R A, Hochhauster A M, Reuter R M, 1991. Effects of gasoline composition and properties on vehicles emissions: A review of prior studies-auto/oil air quality improvement research program. SAE paper, No. 912321.

Kwon Y K, Esmilaire O, Morgan T D B, Broeckx W, Liiva P, Bazzani R *et al*., 1999. Direct-injection gasoline vehicle to a fuels matrix incorporating independent variations in both compositional and distillation parameters. SAE paper, No. 1999-01-3663.

Liu Q S, Xu X H, 2004. A study on hydrocarbon composition of gasoline and exhaustion pollution. *Petroleum Products Application Research*, (5): 14–19.

Liu W J, Li W H, 2003. The effect of gasoline on engine intake system deposits. *Automobile Technology and Material*, (11): 27–30.

McDonald C R, Morgan T D B, Graupner O, Wilkinson E, 1996. The independent effects of fuel aromatic content and mid-range volatility on tailpipe emissions from current technology European vehicle fleets. SAE paper, No. 962026.

Nie G, Liu W J, Niu C J, Wang Q M, 2000. An investigation on effect of olefin on clean performance of gasoline and detergent additives. *Automobile Technology and Material*, (10): 17–18.

Pentikäinen J, Rantanen L, Aakko P, 2004. The effect of heavy olefins and ethanol on gasoline emissions. SAE paper, No. 2004-01-2003.

Pentikäinen J, Wensing M, Juutinen S, Mnch K U, Leipertz A, 1998. Gasoline: influence of fuel-oxygen on NO*x*-emissions. SAE paper, No. 981366.

Renner T A, Knepper J C, Huff G A, Hargreaves J T, 1993. Effect of olefin carbon number on reactivity of automotive hydrocarbon emissions. SAE paper, No. 930371.

Schifter I, Díaz L, Vera M, Guzmán E, López-Salinas E, 2004. Fuel formulation and vehicle exhaust emissions in Mexico. *Fuel*, 83(14-15): 2065–2074.

Thummadetsak T, Wuttimongkolchai A, Tunyapisetsak S, Kimura T, 1999. Effect of gasoline compositions and properties on tailpipe emissions of currently existing vehicles in Thailand. SAE paper, No. 1999-01-3570.

Uehara T, Takei Y, Hoshi H, Shiratani K, Okada M, Esaki Y, 1997. Study on combustion chamber deposit formation mechanism-influence of fuel components and gasoline detergents. SAE paper, No. 971722.

Van den Brink P J, McDonald C R, 1995. The influence of the fuel hydrocarbon composition on NO conversion in 3-way catalysts: the NO*x*/aromatics effect. SAE paper, No. 952399.