International Journal of Automotive Technology, Vol. 8, No. 1, pp. 1−7 (2007)

1229−9138/2007/032−01

EFFECT OF ADDITIVE ON THE HEAT RELEASE RATE AND EMISSIONS OF HCCI COMBUSTION ENGINES FUELED WITH RON90 FUELS

X.-C. LÜ*, L.-B. JI, W. CHEN and Z. HUANG

Institute of Internal Combustion Engine, Shanghai Jiaotong University, Shanghai 200240, China

(Received 16 September 2005; Resived 23 August 2006)

ABSTRACT−The effect of the di-tertiary butyl peroxide (DTBP) additive on the heat release rate and emissions of a homogeneous charge compression ignition (HCCI) engine fueled with high Research Octane Number (RON) fuels were investigated. The experiments were performed using 0%, 1%, 2%, 3%, and 4% (by volume) DTBP-RON90 blends. The RON90 Fuel was obtained by blending 90% iso-octane with 10% n-heptane. The experimental results show that the operation range was remarkably expanded to lower temperature and lower engine load with the DTBP additive in RON90 fuel. The first ignition phase of HCCI combustion was observed at 850 K and ended at 950 K while the hot ignition occurred at 1125 K for all fuels at different engine working conditions. The chemical reaction scale time decreases with the DTBP addition. As a result, the ignition timing advances, the combustion duration shortens, and heat release rates were increased at overall engine loads. Meanwhile, the unburned hydrocarbon (UHC) and CO emissions decrease sharply with the DTBP addition while the NOx emissions maintain at a lower level.

KEY WORDS : Homogeneous charge compression ignition (HCCI), Additive, Heat release rate, Emission

1. INTRODUCTION

The HCCI combustion is a promising alternative combustion model to conventional spark ignition engines and compression ignition engines, which was identified as a distinct combustion phenomenon about 25 years ago by Onishi *et al.* (1979) and subsequently by Noguchi *et al.* (1989, Najt and Foster, 1983). The HCCI combustion engine combines features from both SI and CI engines, promising the high efficiency of a diesel engine with virtually no NOx and particulate emissions. However, there are several problems are blocking the road to successfully integration of the HCCI concept in automotive applications. The most serious problems are the control of the ignition timing and combustion rate at overall operation ranges (Tanaka *et al.*, 2003a, 2003b). It is widely accepted that HCCI combustion was controlled by chemical kinetics. This means that the ignition timing and combustion rate of HCCI combustion are dominated by fuel properties, air/fuel mixture, temperature and pressure of environmental condition, and operating conditions including engine speed, compression ratio, and coolant temperature, and so on.

Gasoline fuel has RON of approximately 90 to 100. It is difficult to achieve HCCI combustion without accessorial methods. Several potential control methods have been proposed to control the gasoline HCCI combustion (Zhao *et al.*, 2001; Aaron *et al.*, 2001; Yang *et al.*, 2002; Kontarakis *et al.*, 2000): intake charge heating system, exhaust gas recirculation (EGR) (Choi *et al.*, 2004), variable compression ratio (VCR), and variable valve timing (VVT) to change the effective compression ratio and/or the amount of hot exhaust gases retained in the cylinder, *et al.* This paper tries to control the ignition and combustion of gasoline HCCI engine by reformulating the fuel properties.

According to the chemical kinetics (Curran *et al.*, 1998a, 1998b, 2002; Ranzi *et al.*, 1995; Leppard, 1992), low-temperature oxidation plays an important role on hydrocarbons ignition and combustion. At the same time, many researches revealed that some additives such as 2-ethylhexyl nitrate (2-HEN), DTBP, and H_2O_2, *et al.* would produce active radicals and small heat during the low temperature oxidation, and this will accelerate the low temperature oxidations of hydrocarbons. Based on this reason, the authors conducted an experiment to study the effect of additive on combustion and emission of HCCI engines using RON90 fuels. Di-tertiary butyl peroxide, which was widely used as cetane number improver of diesel fuel (Griffiths and Philips, 1990), was

---

**Corresponding author.* e-mail: lyuxc@sjtu.edu.cn

selected as the reformulated additives in this research. In general, the application of additive on low temperature oxidation has a number of effects. Firstly, heat effect - the temperature of the air/fuel mixture will slightly increase with the heat release of the additives decomposition. Secondly, chemical effect - reaction velocities of the air/fuel mixture will be accelerated by the active radicals, which produced during the additives decomposition.

In this paper, 90% iso-octane-10% n-heptane blends (by volume for all), named as RON90 was used as the test fuel. The different reformulated fuels were obtained by adding 1%~4% DTBP to RON90. The experimental studies were carried out for one cylinder in 4-cylinder DI diesel engine. The effects of DTBP additive on gasoline HCCI combustion were evaluated. Furthermore, the cooled EGR on HCCI combustion using RON90 with DTBP additive were also investigated.

2. EXPERIMENTAL APPARATUS

A four-cylinder, four-stroke high-speed direct injection (DI) diesel engine was employed as an experimental engine. One cylinder of the prototype engine was reformed for operating with HCCI combustion, the other cylinders running with original DI diesel engine. The intake pipe and exhaust system of the test cylinder were separated with the other cylinders, and an individual injection pump was used to supply the test fuel through port injection. Furthermore, a controllable EGR system was used to investigate the effect of cooled EGR on HCCI combustion. The specifications of the test cylinder are shown in Table 1, and the photo graph of experimental system is shown in Figure 1.

To insure the repeatability and comparability of the measurements for different fuels and operating conditions, the intake charge temperature was fixed at 20°C (without EGR), held accurately to within ± 2°C; while in the cooled EGR tests, fixed inlet temperature of 30 °C, held accurately to within ± 2°C. The coolant-out temperature remains at 85°C, held accurately to within ± 2°C. The engine speed was kept at 1,800 r/min.

The cylinder pressure was measured using a Kistler model 6125A pressure transducer. The charge output from this transducer was converted to an amplified voltage using a Kistler model 5015 amplifier. The 1,440 pulses per rotation (4 pulses per crank angle) from a shaft encoder on the engine crankshaft were used as the data acquisition clocking pluses to acquire the cylinder pressure data. Pressure data was recorded using a high-speed memory. For each measuring point, the pressure data of 50 consecutive cycles were sampled and recorded. The pressure trace for a specific condition was obtained by averaging the sampled pressure data of 50 cycles.

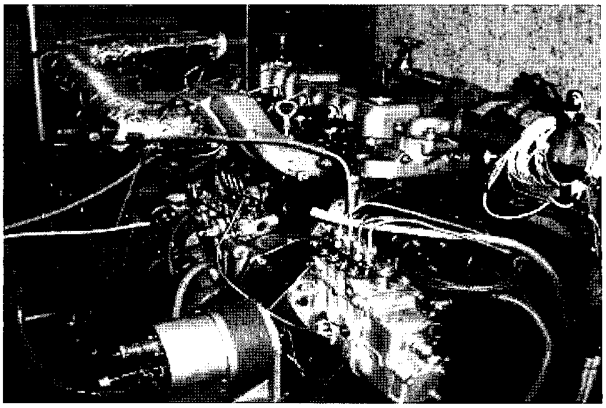


Figure 1. Experimental systems.

Emission of UHC, CO_2, CO, and NOx were measured with an emission analyzer (AVL Di Gas 4000). The percentage of EGR rate is determined by comparing the CO_2 concentration in the intake ($CO_{2\ \mathrm{Intake}}$) pipe and exhaust system ($CO_{2\ \mathrm{Exhaust}}$) using the following equation:

$$EGR(\%)=\frac{CO_{2\ Intake}}{CO_{2\ Exhauste}}\times 100$$

3. DEFINITION OF COMBUSTION PARAMETERS

Some basic combustion parameters of HCCI engine are shown in Figure 2. $HRR_{max,1st}$ and $HRR_{max,2nd}$ are defined as the maximum value of heat release in the first-stage and second-stage combustion. SOI_{1st} is defined as the start of ignition of the first-stage combustion. The SOI_{2nd} is the start of ignition of the second-stage combustion, which is specified crank angle corresponding to 10% of the magnitude of the peak of heat release on the rising

Table 1. Specifications of the single-cylinder HCCI engine.

Bore × stroke	98 (mm) × 105 (mm)	Advanced angle of injector open	285 BTDC
Displacement (l)	0.782	Inlet valve open	16 BTDC
Compression ratio	18.5: 1	Inlet valve close	52 ABDC
Nozzle type	pintle	Exhaust vale open	66 BBDC
Injector open pressure	5.5MPa	Exhaust vale close	12 ATDC

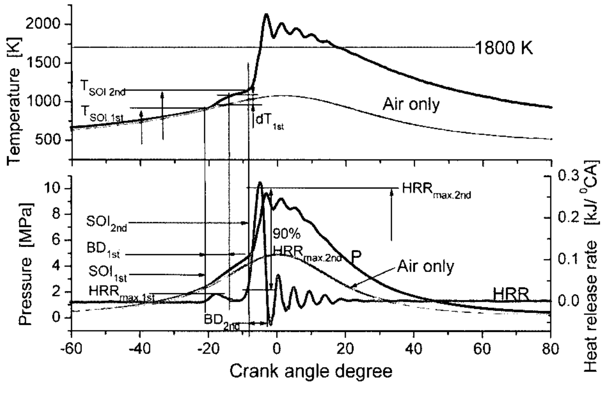


Figure 2. Definition of symbols and combustion parameters.

side of the curve. BD_{1st} is defined as the combustion duration of the first-stage reaction. BD_{2nd} is the burn duration of the second-stage combustion, which is the distance between the SOI_{2nd} crank angle and the crank angle corresponding to 10% of the magnitude of peak of heat release on the falling side of the curve. $T_{SOI,1st}$ is the in-cylinder gas temperature corresponding to the SOI_{1st}. $T_{SOI,2nd}$ is the in-cylinder gas temperature corresponding to the SOI_{2nd}. dT_{1st} and dP_{1st} are the temperature rising and pressure rising during the first-stage combustion compared to the pressure and temperature with air only at the crank angle corresponding to the end of the first-stage combustion.

4. RESULTS AND DISCUSSION

4.1. In-cylinder Pressure and Heat Release Rate

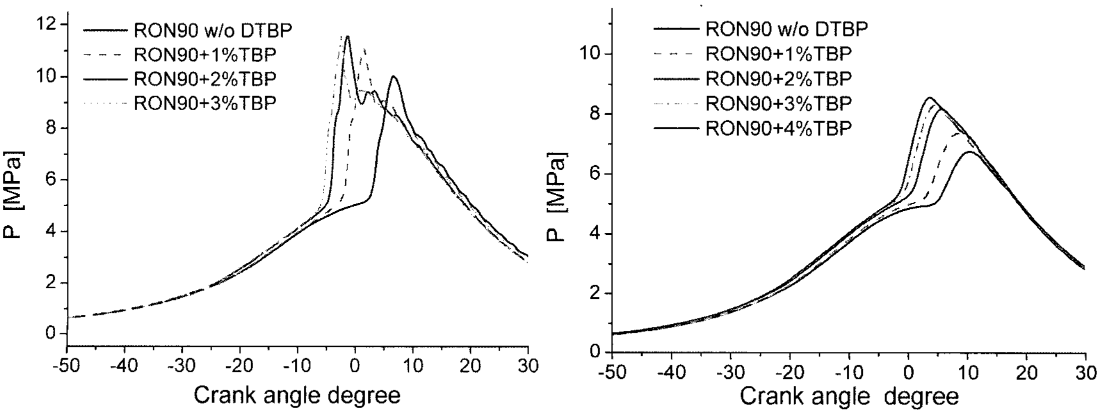
Figure 3 shows the comparison on in-cylinder pressure of HCCI combustion using RON90 with and without DTBP additive. Figure 4 show the heat release rate of RON90 HCCI combustion with different percentage of DTBP additive. The falling edge of the heat release curves can be very noisy due to the acoustic phenomena in the cylinder (knocking-like pressure oscillation). This phenomenon can also be found from other researches report (Flowers *et al.*, 2001). It is found that the ignition timing advances, the maximum gas pressure increase, and the peak value of the heat release also increase with the DTBP addition for different operating conditions. Then, the detail combustion characteristics and emissions of HCCI combustion are investigated for the RON90 with DTBP additions.

It should be noticed that the HCCI combustion operated stably with RON90 only at the condition of the coolant temperature higher than 92°C when the inlet temperature remains at 20°C, and the combustion quality and emissions deteriorate with the decrease of the equivalence ratio, inlet charge temperature, and coolant temperature. Based on this reason, the combustion parameters of RON90 showed in the following figures were obtained on the condition of the coolant temperature at 92°C~95°C, while the inlet charge temperature remains at 20°C.

4.2. Effect of DTBP on the First-stage Combustion

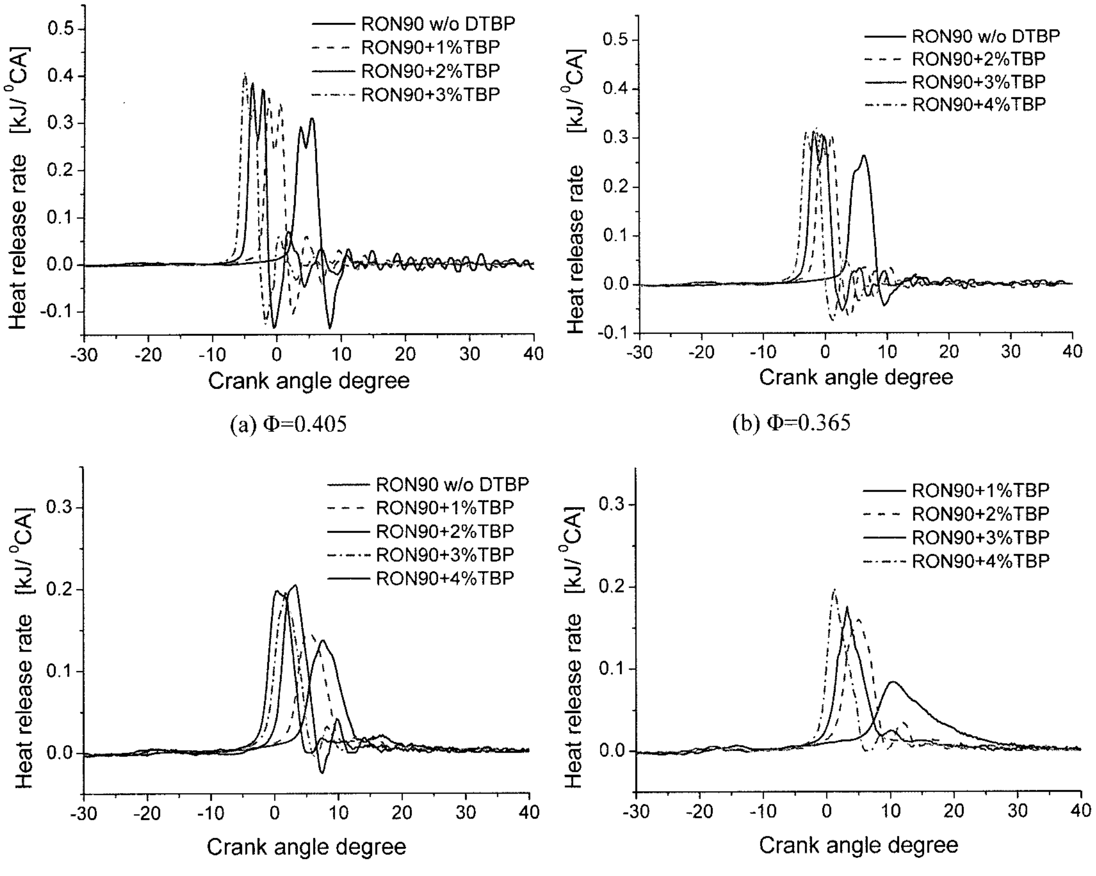
According to the low-temperature reaction mechanism, the first-stage ignition of hydrocarbon fuels is largely associated with ketohydroperoxide species decomposition at a temperature between 800 K and 850 K, and the end of the first-stage occurs when the temperature reaches the NTC zones. That means, the onset of the first-stage combustion is decided by the time that the air/fuel mixtures reaches the decomposition temperature. Any methods that shorten the time to achieves the "threshold temperature" of ketohydroperoxide species decomposition will accelerate the low temperature reaction, and result an early cool flame reaction.

Figure 5(a) shows the comparison of additive volume



(a) Φ=0.405 (b) Φ=0.318

Figure 3. Effect of DTBP additions on in-cylinder pressure of HCCI combustion (n=1800 r/min).



(a) Φ=0.405

(b) Φ=0.365

(c) Φ=0.318

(d) Φ=0.295

Figure 4. Effect of additive on the heat release rate at the same conditions (RON90).

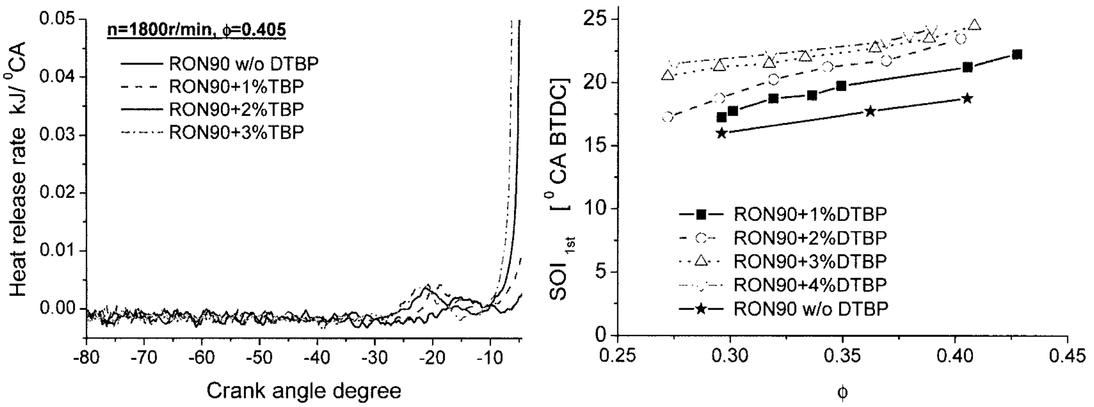
on low-temperature heat release for a specific fuel/air equivalence ratio (Φ). It can be found from this figure that two-stage combustion and NTC phenomena were observed for all fuels, and the DTBP plays an important role on low temperature heat release and hot ignition timing. Figure 5(b) illustrates that, for a specific equivalence ratio, the ignition timing of the first-stage combustion advances remarkably with the increase of the DTBP volume. Furthermore, the ignition timing slightly advances with the increase of equivalence ratio for all fuels. While, DTBP addition plays little effect on the initial temperature and the end temperature of the first stage reactions, this can be seen from Figure 5(c) and Figure 5(d). The cool flame occurred at 820 K, and ended about 950 K for all fuels.

4.3. Effect of DTBP on the Second-stage Combustion

Figure 6 gives the comparison of the second-stage combustion characteristics. The ignition timing of the second-stage combustion occurred after the top dead center for RON90 without DTBP addition. While, when the 2%~3% DTBP additive were added to the RON90 fuel, the ignition timing was advanced to near the TDC. This is very important to improve the combustion quality, thermal efficiency, and emissions for lower engine loads conditions. Figure 6(b) shows that DTBP addition plays a moderated effect on the initial temperature of the second-stage combustion, and the hot combustion occurred at 1125 K.

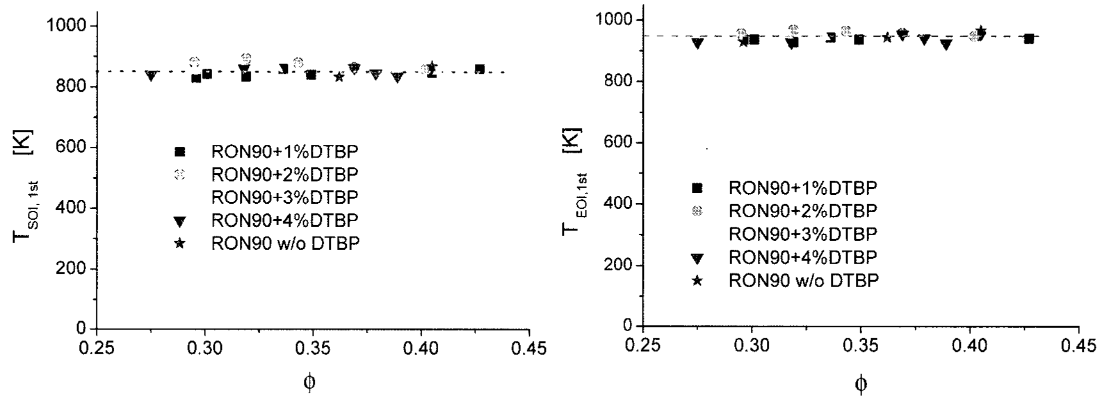
Figure 6(c) shows the burn duration of the second-stage combustion vary with the DTBP volume in RON90 fuels. The figure revealed that the burn duration substantially decreases with the DTBP addition at lower engine loads. For a specific fuel, the burn duration shortens with the increase of the equivalence ratio. But, there has little difference of burn duration for all fuels when the equivalence ration larger than 0.35.

Figure 6(d) is the comparison between maximum rate of heat release (HRR_{max}) and the crank angle corresponding to the HRR_{max} and equivalence ratio. The peak values of the heat release rate reflect the combustion velocity of HCCI combustion during the high temperature stage, which is always dominated by the equivalence ratio. The experimental results also verified that the peak values



(a) Cool flame

(b) Ignition timing of the first-stage combustion



(c) Onset temperature of the first-stage combustion

(d) Final temperature of the first-stage combustion

Figure 5 Effect of additive on the first-stage combustion parameters of RON90 HCCI combustion.

increases with the equivalence ratio, while DTBP addition shows a little effect on the peak values. But, the figure also shows that the DTBP addition plays an important effect on the crank angle corresponding to the HRR_{max}.

4.4. Effect of DTBP on Emissions

CO and UHC emissions of HCCI combustion are key problems which should be overcome. Figure 7 gives the CO and UHC emissions for different engine loads. CO emissions from internal combustion engines are controlled primary by the fuel/air equivalence ratio. For fuel-rich mixtures, CO concentrations decrease steadily with the increase of equivalence ratio. For lean fuel mixtures, equivalence ratio has a slightly effect on CO emissions. CO emissions from HCCI engines are controlled by the chemical kinetics. CO formation is one of the basic reaction steps in the hydrocarbon oxidation mechanism, which may be summarized as follows (Heywood, 1988):

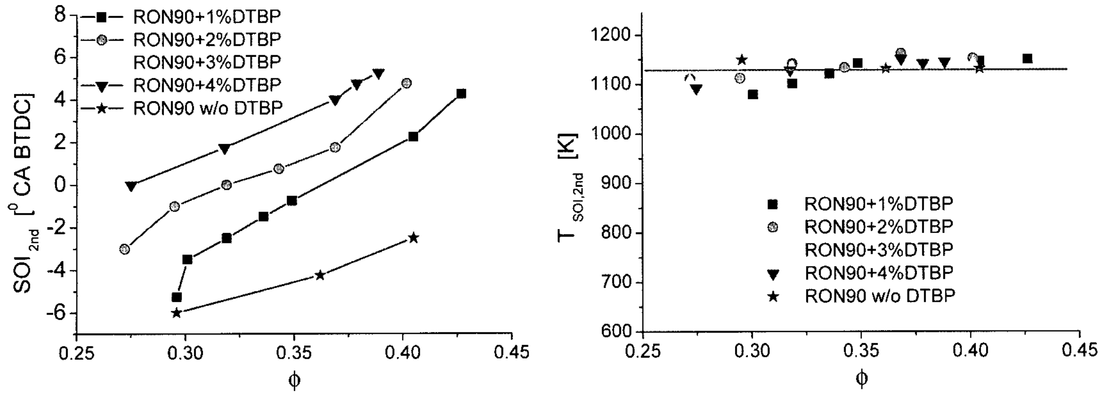
$$RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO$$

Where R stands for the hydrocarbon radical. CO is a result of incomplete combustion in intermediate temperature regions where the OH radical concentration becomes significantly diminished, resulting in less conversion of CO to CO_2. Figure 7 shows that the CO and UHC emissions gradually decrease with the increasing of the equivalence ratio and DTBP addition. In particular, at low equivalence ratio, CO emission of RON90 with additive is much lower than that of RON90 without DTBP addition. In fact, UHC emissions essentially increase linearly with later ignition timing. The combustion advances with the increase of DTBP volume in RON90 fuel, this leads to a lower UHC levels.

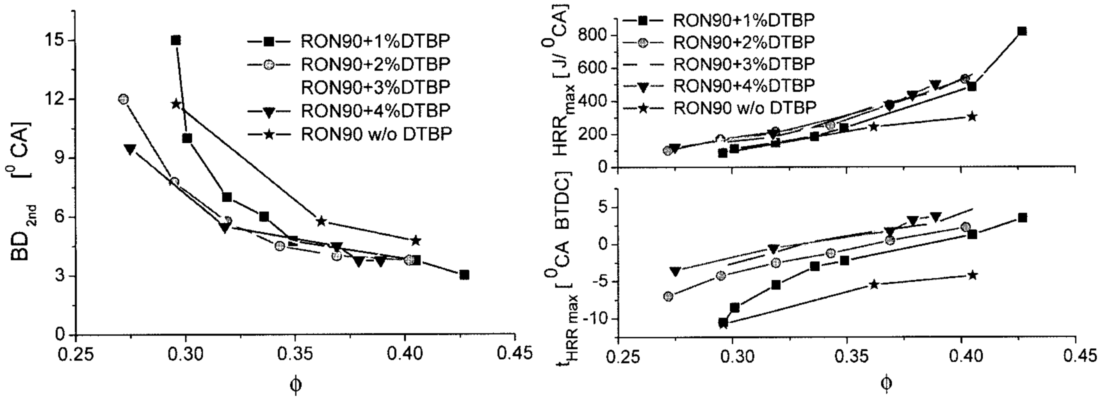
NOx emissions of HCCI engines are very low because the super dilution fuel/air mixtures are used. This can be verified from Figure 7b. At a wide operating range, NOx levels are less than 20 ppm. While, as the equivalence ratio exceeds to a certain value (for instance, 0.40), NOx emissions increase remarkably. The maximum NOx emission was recorded at 100 ppm for RON90 with 1% DTBP addition. At this point, the IMEP achieves to 6.5 bar.

5. CONCLUSIONS

In this study, the effect of the DTBP additive on the heat

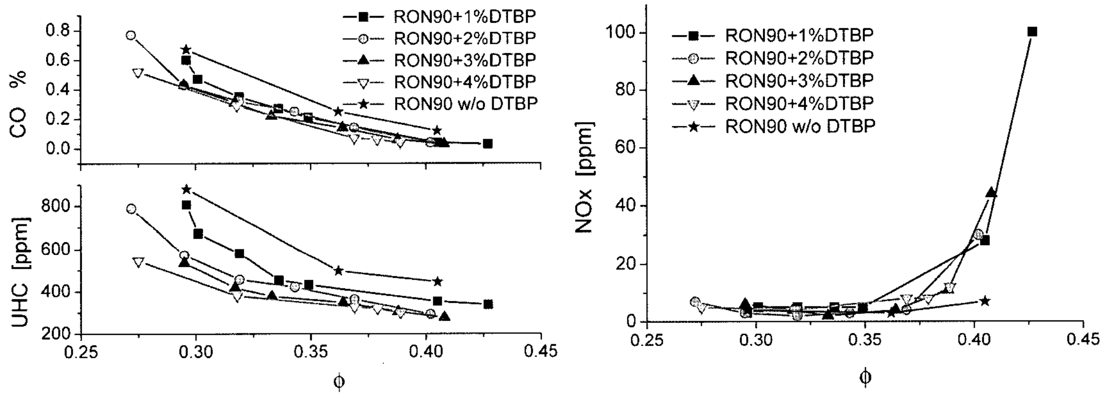


(a) Ignition timing (b) Initial temperature of the combustion



(c) Burn duration (d) Peaks of heat release rate and its crank angle

Figure 6. Effect of additive on the second-stage combustion parameters of RON90 HCCI combustion.



(a) (b)

Figure 7. Effect of DTBP additions on HCCI emissions.

release rate and emissions of HCCI engine fueled with RON90 fuel was investigated. Some conclusions can be obtained as follows:

(1) The HCCI combustion operated stably with RON90 only at the condition of the higher coolant temperature and/or higher inlet charge temperature. While, the operating range of HCCI combustion using high RON fuel can be expanded to low temperature and low loads with DTBP addition.

(2) The first ignition phase of HCCI combustion was observed at 850 K, and ended at 950 K, and the hot ignition occurred at 1125 K for all RON90 with and without DTBP addition at different engine working conditions.

(3) The chemical reaction scale time decreases with the DTBP addition, as a result, the ignition timing advances, the combustion duration shortens, and the combustion efficiency improves for lower engine load

(4) The UHC and CO emissions decreased sharply with the DTBP addition, while the NOx emissions maintain at a lower level.

ACKNOWLEDGEMENTS–This work was supported by the Nature Science Foundation of Shanghai (Grant No. 06ZR14045), and the Basic Research Program of Shanghai (Grant No. 05DJ14002).

REFERENCES

Aaron, O., Hua, Z. and Nicos, L. (2001). Experimental studies on controlled auto-ignition (CAI) combustion of gasoline in a 4-stroke engine. *SAE Paper No.* 2001-01-1030.

Choi, G. H., Han, S. B. and Dibble, R. W. (2004). Experimental study on homogeneous charge compression ignition engine operation with exhaust gas recirculation. *Int. J. Automotive Technology* **5, 3,** 195–200.

Curran, H. J., Gaffuri, P., Pitz, W. J. and Westbroo, C. K. (2002). A comprehensive modeling study of iso-octane oxidation. *Combustion and Flame,* **129**, 253–280.

Curran, H. J., Gaffuri, P., Pitz, W. J. and Westbrook, C. K. (1998a). A comprehensive modeling study of n-heptane oxidation. *Combustion and Flame*, **114**, 147–179.

Curran, H. J., Pitz, W. J. and Westbrook, C. K. (1998b). Oxidation of automotive primary reference fuels at elevated pressures. *Proc. Combustion Institute*, **27**, 379–387.

Flowers, D., Aceves, S. M. and Martinez-Frias, J. R., Smith, Au, M., Girard, J. and Dibble, R. (2001). Operation of a four-cylinder 1.9L propane fueled homogenous charge compression ignition engine: Basic operating characteristics and cylinder-to-cylinder effects. *SAE Paper No.* 2001-01-1859.

Griffiths, J. F. and Philips, C. H. (1990). Experimental and numerical studies of the combustion of di-tertiary butyl peroxide in the presence of oxygen at low pressure in a mechanically stirred closed vessel. *Combustion and Flame*, **81**, 304–416.

Heywood, J. B. (1988). *Internal Combustion Engine Fundamentals*. McGraw-Hill. New York.

Kontarakis, G., Collings, N. and Ma, T. (2000). Demonstration of HCCI using a single cylinder four-stroke SI engine with modified valve timing. *SAE Paper No.* 2000-01-2870.

Leppard, W. R. (1992). The autoigition chemistries of primary reference fuels, olefin/paraffin binary mixtures, and non-line octane blending. *SAE Paper No.* 922325.

Najt, P. M. and Foster, D. E. (1983). Compression-ignited homogeneous charge combustion. *SAE Paper No.* 830264.

Noguchi, M., Tanaka, T. and Takeuchi, Y. (1979). A study on gasoline engine combustion by observation of intermediate reactive products during combustion. *SAE Paper No.* 790840.

Onishi, S., Jo, S. H., Shoda, K., Jo, P. D. and Kato, S. (1979). Actived thermo-atmosphere combustion (ATAC)-a new combustion process for internal combustion engines. *SAE Paper No.* 790501.

Ranzi, E., Faffuri, P. and Faravelli, T. (1995). A wide range modeling study of n-heptane oxidation. *Combustion and Flame*, **103**, 91–106.

Tanaka, Shigeyukii, Ayala, Ferrann, K. and James, C. (2003a). A reduced chemical kinetic model for HCCI combustion of primary reference fuels in a rapid compression machine. *Combustion and Flame* **133, 4,** 467–481.

Tanaka, Shigeyukii, Ayala, Ferrann, K., James, C. and Heywood, J. B. (2003b). Two-stage ignition in HCCI combustion and HCCI control by fuels and additives. *Combustion and Flame* **132, 1-2**, 219–239.

Yang, J., Culp, T. and Kenney, T. (2002). Development of a gasoline engine system using HCCI technology-The concept and the test results. *SAE Paper No.* 2002-01-2832.

Zhao, H., Peng, Z. and Ladommatos, N. (2001). Understanding of controlled autoignition combustion in a four-stroke gasoline engine. *Proc. Instn. Mech. Engre.*, **215**, Part D, 1297–1310.