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# EFFECT OF DI-TERTIARY-BUTYL PEROXIDE ON IGNITION PERFORMANCE IN A COMPRESSION IGNITION NATURAL GAS ENGINE

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**ABSTRACT**–Experimental study of additives on the ignition performance of a compression ignition natural gas engine is introduced, followed by results of a simulation of its working mechanism. From the experimental results, it is understood that engine ignition performance can be improved when a certain amount of Di-tertiary-butyl peroxide additive is added. If the mass fraction of Di-tertiary-butyl peroxide additive reaches as high as 14.2%, engine ignition can be realized at ambient temperatures with a glow plug temperature of about 750°C. From the simulation results, we verify that the Di-tertiary-butyl peroxide additive, by cracking its radicals at lower temperature, can accelerate reaction rate. Therefore, the additive is able to improve the ignition performance of natural gas significantly.

**KEY WORDS :** Natural gas engine; Di-tertiary-butyl peroxide; Ignition performance; Simulation

## 1. INTRODUCTION

Due to the global environmental pollution and energy crisis, severe emission regulations for internal combustion engines have been established throughout the world. In this situation, many alternative fuels have been studied (Liss, 1991; Heywood, 1981; Aslam *et al.*, 2006). Among alternative gaseous fuels, CNG (compressed natural gas) is now more popular on the market. Comprehensive reviews of the advantages of CNG as an environmentally friendly, clean burning (very low propensity to soot), economical and efficient fuel have been reported in the literature (Fowler *et al.*, 1991; Silviu *et al.*, 2000; Hupperich *et al.*, 1996; Raine *et al.*, 1997).

CNG has been primarily considered to be a spark ignition rather than compression ignition engine fuel, due to its low cetane number. Engineers have continuously desired to adopt CNG as a compression ignition fuel, like diesel, to acquire the high thermal efficiency of CNG engines (Vilmar, 1996; Christensen *et al.*, 1997; XU *et al.*, 2005). However, a compression ignition (CI) natural gas engine is difficult to ignite, due to the low ignitability of methane, which is the primary constituent of natural gas. Several studies reported the use of air pre heating for improving the ignitability of the CI engine (Naber, 1994; Zheng *et al.*, 2005). This method has the advantage of keeping combustion efficiency high, even at low load conditions; meanwhile, it does not require a lot of engine design changes. However, the response from the air pre heating device is not quick enough. Therefore, compression ratio (Hultqvist, 2002) or valve timing (Law *et al.*, 2001) has to be modified to improve ignitability, in some cases. These involve a lot of design changes to get potential performance improvement.

Additives have the capability of improving the ignition performance of natural gas without much modification of core engine design. The effect of additives on improving the ignition performance of compression ignition engines has been broadly studied in recent years. The most common additives are $H_2O_2$, formaldehyde, organic peroxides, nitrates, Di-tertiary--butyl peroxide and butyl oxidized hydrogen, etc. Particularly, organic oxide additives (Naber *et al.*, 1994; Langille *et al.*, 2004; Yap *et al.*, 2006; Peucheret *et al.*, 2005; Goto *et al.*, 1999; Lee *et al.*, 2000; Eng *et al.*, 2003; Ricklin *et al.*, 2002; Yap *et al.*, 2004; Li, 2007) are reportedly being applied in compression ignition LPG engines. In these reports, the works by Daeyup Lee and J.A. Eng are impressive. Daeyup Lee made studies on a compression ignition LPG engine with DTBP (Di-tertiary-butyl peroxide) as an additive to improve ignition performance (Goto *et al.*, 1999; Lee *et al.*, 2000), and the results show that with 5% mass concentration of DTBP, the engine acquires a shorter ignition delay, broader stable running zone and higher thermal efficiency than

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traditional diesel engines, with lower NOx and soot emission. J.A. Eng from GM engine institute made studies on gasoline HCCI (homogeneous charge compression ignition) engines, adopting DTBP as an additive by experiment and simulation (Eng *et al.*, 2003). His research indicates that the lean burn combustion boundary at the light load condition is broadened by a 15% DTBP additive. At a speed of 1000 r/m, the necessary amount of gasoline for stable combustion is reduced from 9 mg to 6.2 mg.

The motive of our project is to explore whether applying ignition assistant additives is an effective method to improve the ignition performance of CI natural gas engines. In this paper, a series of experimental results are presented on a compression ignition natural gas engine with DTBP applied as a kind of additive. Further work on engine combustion simulations, with and without DTBP additives, is carried out by coupling CFD (computational fluid dynamics) software with a chemical kinetics model. Table 1 illustrates the main physical and chemical characteristics of DTBP.

## 2. ENGINE CONFIGURATION

The engine used for this research is a single cylinder four-stroke engine. Table 2 shows the most important design features of the engine. Besides these features, three measures are tried for improving ignition performance. They are inlet air preheating, glow plug heating in the chamber and additive of DTBP through the air inlet manifold.

Table 1. Main physical and chemical characteristics of ditert-butyl peroxide (DTBP).

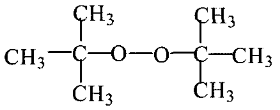
| | |
|---|---|
| Structure of ditert-butyl peroxide (DTBP) |  $CH_3-C(CH_3)_2-O-O-C(CH_3)_2-CH_3$ |
| Boiling point (°C) | 110 |
| Flash point (°C) | 18.3 |
| Ignition temperature (°C) | 165 |
| Half life cycle (at 300°C) | 10 ms |

Table 2. Engine specifications.

| | |
|---|---|
| Bore | 95 mm |
| Stroke | 115 mm |
| Connecting rod length | 210 mm |
| Intake valve opening | 30°C A BTDC |
| Intake valve closing | 25°C A ABDC |
| Exhaust valve opening | 40°C A BBDC |
| Exhaust valve closing | 30°C A ATDC |
| Compression ratio | 19 |
| Fuel | Natural gas |

In the engine fuel system, natural gas is stored in a gas container with a pressure of 20 MPa and delivered through two levels of pressure reduction to reach the final pressure stage of 0.4 MPa. Natural gas is then injected into the inlet manifold through a gas injector. The mixture of natural gas and air inside the inlet manifold flows into a cylinder during the process of the engine air inlet stroke. According to our general understanding, natural gas is considered to be a mixture of lower hydrocarbon gases and consists mainly of methane and small percentages of higher alkanes, such as ethane, propane and butane, and possibly, small fractions of incombustible products like nitrogen and carbon dioxide. The Natural gas used in this study is a blend of five different kinds of gases. They are 92.2% methane, 4.8% ethane, 1.3% propane, 0.7% nitrogen, and 1.0% carbon dioxide.

## 3. EXPERIMENTAL STUDY ON ADDITIVES FOR IMPROVING ENGINE IGNITION PERFORMANCE

The experimental studies on a CI natural gas engine without the additive show that the engine can only be ignited under limited conditions, which means the ignition relies heavily on inlet air temperature and glow plug temperature. Unstable combustion and running speed, even misfiring in many cases, was experienced. It was shown that the engine could not be ignited at inlet air temperatures lower than 225°C, while the glow plug temperature was lower than 1000°C. This was due to the temperature at the end of compression stroke being too low for combustion. Increasing inlet air temperature and glow plug temperature is rather difficult. Therefore, the compression ignition natural gas engine has poor ignition performance if only inlet air preheating and glow plug heating are used.

In order to improve ignition performance of CI natural gas engines, DTBP additives were applied and induced into natural gas fuel and relevant studies were targeted accordingly. A set of facilities were designed to inject additives into the air inlet manifold in the experiment. The facilities consist of a DTBP additive container, additive pump, pressure regulator, pressure gauge, an injector and an ECU. The amount of injected DTBP is controlled by injector opening duration. The process is controlled to let the injected DTBP in the inlet manifold mix in a timely manner with natural gas during the engine air inlet process. The diagram of this system is shown in Figure 1.

The DTBP supply pump is a 12 volt device with a delivery pressure of 0.3MPa. The function of the pump is to deliver additive at a certain pressure into the system. While the pump is working, DTBP inside container is

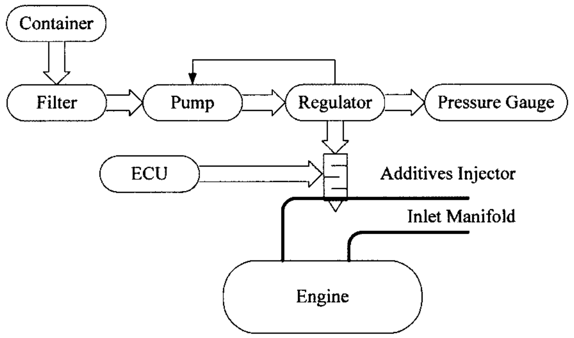


Figure 1. Diagram of DTBP supply system.

delivered to the injector through a filter and pressure regulator which is used to maintain system pressure. The injector is a type of needle lift electromagnetic valve operated at 12 volts. The amount of delivered additive is determined by the electric charging duration of the injector and the pressure difference between the inner system and the outer environment. Since there is no throttle valve in the compression ignition natural gas engine, the pressure difference between the inner system and the outer environment is usually considered constant, so injection quantity is determined by the electric charging duration of the injector. In this case, the ECU controls additive delivery quantity by adjusting the electric charging duration on the injector.

In order to investigate the effect of DTBP quantity on ignition performance in compression ignition natural gas engines, ten different DTBP supply modes at different injection durations and injection intervals are stored in ECU. Table 3 shows the relationship between these DTBP supply modes and corresponding DTBP mass fraction, where supply modes are chosen depending on the status of inlet air temperature and glow plug temperature.

Table 3. The relationship between DTBP supply mode and mass fraction.

| DTBP supply mode | Mass fraction of DTBP(%) |
|---|---|
| A | 4.6 |
| B | 5.3 |
| C | 5.9 |
| D | 6.7 |
| E | 7.8 |
| F | 8.7 |
| G | 9.9 |
| H | 11.3 |
| I | 12.3 |
| J | 14.2 |

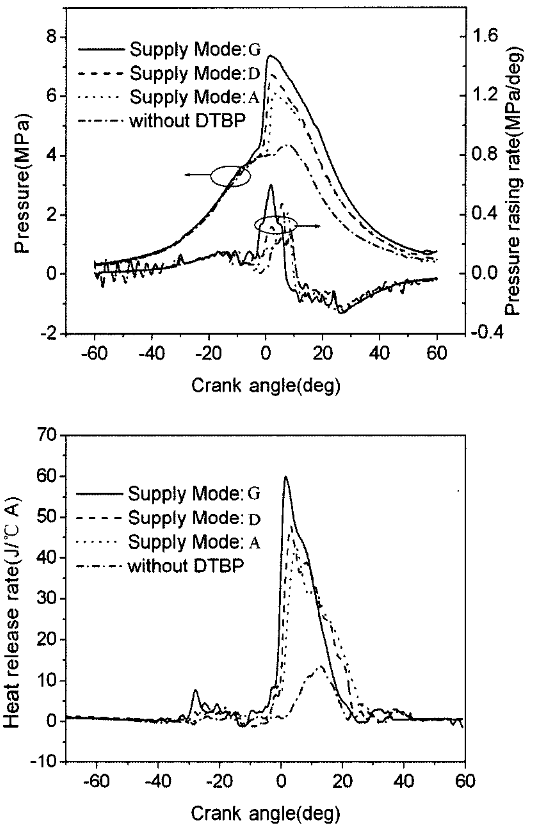


Figure 2. Effect of DTBP supply mode on cylinder pressure and heat release rate. (Excess air ratio: 4.0, Engine speed: 1000 r/min, Inlet air temperature: 150°C, Glow plug temperature: 1120°C).

Figure 2 shows the effect of the mass fraction of DTBP on cylinder pressure, pressure rising rate and heat release rate. The DTBP supply modes are A, D and G, respectively, and the corresponding mass fractions are 4.6%, 6.7% and 9.9%. It was found that the engine could not be ignited without the DTBP additive at this condition. When the DTBP additive is added, the engine is then ignited, as other conditions remain unchanged. Furthermore, with increasing DTBP quantity, the ignition advances, and peak pressure and the pressure rising rate increases. The phasing of peak pressure moves forward as well. The mass fraction of DTBP is above 6.7%, the ignition occurs before TDC. If the mass fraction of DTBP is further increased to 9.9%, the heat release rate and cylinder pressure rising rate are relatively high. Therefore, the amount of DTBP additive should be controlled. Otherwise, the excessive pressure rising rate will lead to engine knocking.

Figure 3 shows the required glow plug temperatures for engine ignition at different modes of DTBP additive supply. As seen from the figure, the engine can realize compression ignition when DTBP is added at ambient air

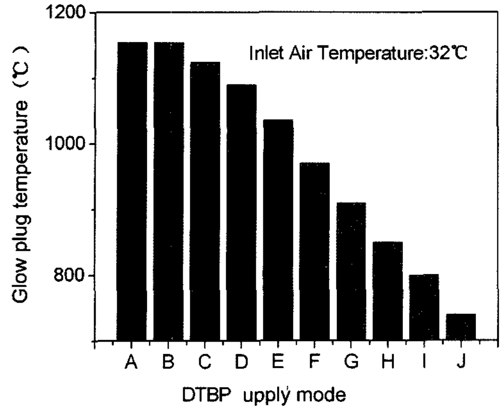


Figure 3. Effect of DTBP supply mode on necessary glow plug temperature.

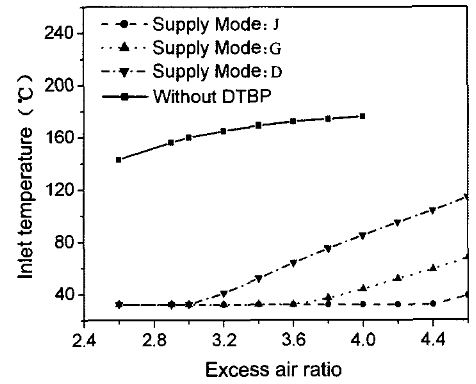


Figure 4. Effect of DTBP supply mode on ignition limit.

temperatures (without air preheating). If the mass fraction of DTBP reaches as high as 14.2% (mode J), engine ignition can be realized at ambient temperatures with glow plug temperatures about 750°C. Moreover, the required glow plug temperature varies with DTBP supply modes. For example, at mode G, the required glow plug temperature is 910°C, but at mode D, it is 1090°C. Therefore, it is obvious that DTBP additives can improve the ignition performance of compression ignition natural gas engines.

Figure 4 illustrates the effect of DTBP on the ignition limit. The four lines in the figure represent misfiring boundaries with or without DTBP at different supply modes. The three DTBP supply modes are mode D, G and J, which correspond with mass fractions of DTBP of 6.7%, 9.9%and 14.2% respectively. The areas under each line indicate different misfiring zones. It can be found from the figure that the misfiring zone gets smaller and smaller with increasing DTBP quantity and the misfiring boundaries move towards high excess air ratio area and low inlet air temperature area. For example, the engine can work stably at an excess air ratio of 3.6 at ambient temperatures when adopting mode J of the DTBP supply, whereas, the engine requires the inlet air temperature to be as high as 170°C to get stable ignition, even at the same excess air ratio as in the cases where no DTBP is added. Consequently, DTBP involvement can lead to engine stable combustion at leaner gas mixture conditions, which is very important for improvement of engine running stability at low load conditions.

## 4. RESEARCH ON THE MECHANISM OF THE EFFECT OF ADDITIVES ON IGNITION PERFORMANCE

In this paper, CFD simulation is applied to study the combustion mechanisms of CI natural gas engines by coupling them with a chemical kinetics model when a DTBP additive is used.

CFD simulation has been effectively used as an important tool in modern engine design and development (Zhang *et al.*, 1998; Soylu *et al.*, 2003). The CFD software used in this research is AVL's FIRE. This software builds its flow kinetics model on the basis of the mass conservation law, the momentum conservation law and the energy conservation law, and then classifies its calculations to several controlled zones with the help of a finite element (FE), then solves multi-dimension N-S equations and transportation equations in every controlled zone. The finite volume method is used to discretize the partial differential equations governing the mean fluid motion. The Eular implicit scheme is used for temporal integration to ensure unconditional numerical stability, while a hybrid central/upwind differencing scheme is utilized for spatial derivatives. The popular PISO algorithm is then used to solve the resulting algebraic equations

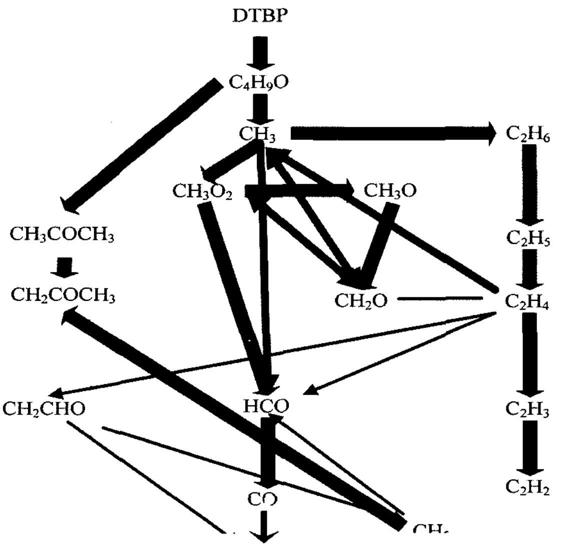


Figure 5. DTBP chemical reaction map.

(AVL CFD Solver).

According to features of the compression ignition of homogeneous combustion gas, it can be regarded that ignition and combustion are controlled by chemical kinetics. The chemical kinetic mechanism used in this study is built by combining two mechanisms from natural gas (53 species and 325 chemical equations) (http://www.me.berkeley) and DTBP (39 species and 126 chemical equations) (Griffiths *et al.*, 1990; Hidaka *et al.*, 1994). The reaction route of the DTBP mechanism is shown in Figure 5, where the applied temperature is from 1102 K to 1921 K and the pressure is between 1.2 atm and 2.7 atm.

The DTBP reaction route indicates that there is a weak -O-O- radical in the DTBP, causing a very short half life cycle. At low temperatures, from 600 K to 700 K, the radical is very easy to dissolve and forms tertiary-butyl peroxide radicals ($(CH_3)$ 3CO·). The tertiary-butyl peroxide radicals will break up into active methyl radicals. The methyl radicals will react with oxygen to form hydroxide radicals (OH·). The main reaction equations are as follows:

$(CH_3)_3COOC(CH_3)_3 <=> 2(CH_3)_3CO$
$(CH_3)_3CO <=> CH_3+(CH_3)_2CO$
$CH_3+O_2+M <=> CH_3O_2+M$
$CH_3O_2+CH_3O_2 <=> O_2+CH_3O+CH_3O$
$CH_3O+O_2 <=> CH_2O+HO_2$
$CH_3O_2+HO_2 <=> CH_3O+OH+O_2$

The calculated and experimental data are compared at the two operating cases indicated in Table 4. The boundary conditions used in the calculations are summarized in Table 5.

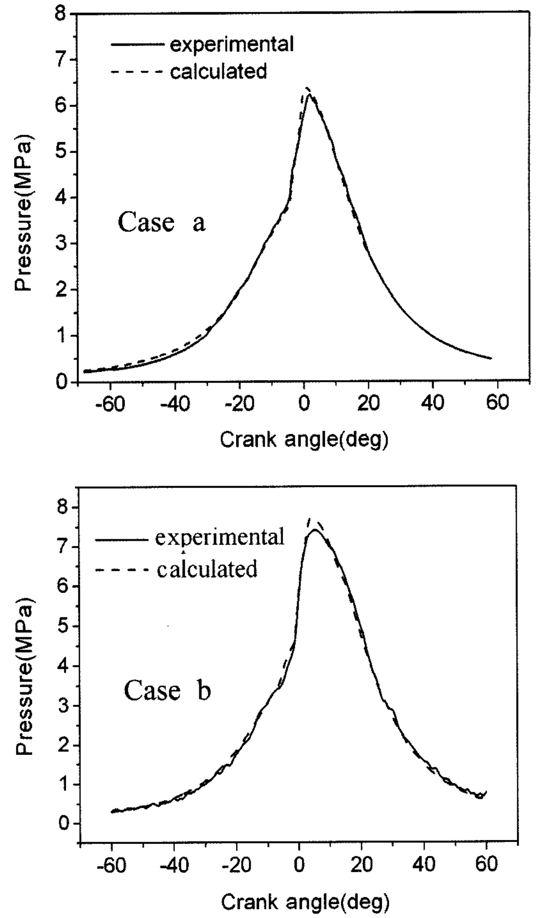


Figure 6. Comparison between calculated and experimental pressure curves.

Figure 6 illustrates a comparison between calculated and experimental pressure curves for case a and case b, respectively. It is indicated that the calculated maximum pressure, ignition timing and combustion duration are in good agreement with the measured results in both cases. Therefore, the combustion simulation model used in this

Table 4. Conditions in experiments.

| | Case a | Case b |
|---|---|---|
| Glow plug temperature | 1000°C | 1000°C |
| Inlet air temperature | 130°C | 150°C |
| Engine speed | 1200 r/min | 1200 r/min |
| Excess air ratio | 3.0 | 2.5 |
| Mass fraction of DTBP | 5.9% | 5.9% |

Table 5. Boundary conditions in calculation.

| | |
|---|---|
| Liner temperature | 440 K |
| Piston head temperature | 500 K |
| Cylinder head temperature | 480 K |

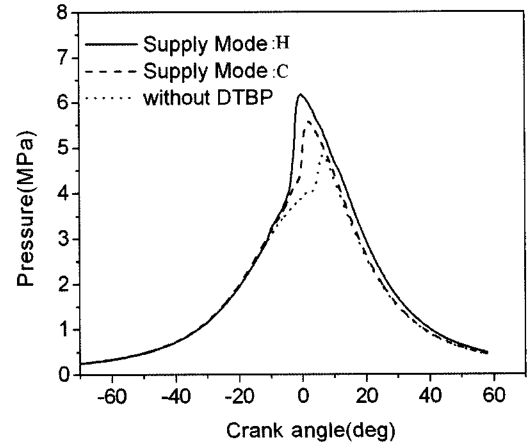


Figure 7. Effect of DTBP on combustion (Excess air ratio: 3.8, Speed: 1200 r/min, Inlet air temperature: 140°C, Fuel supply rate: 1.23 kg/h).

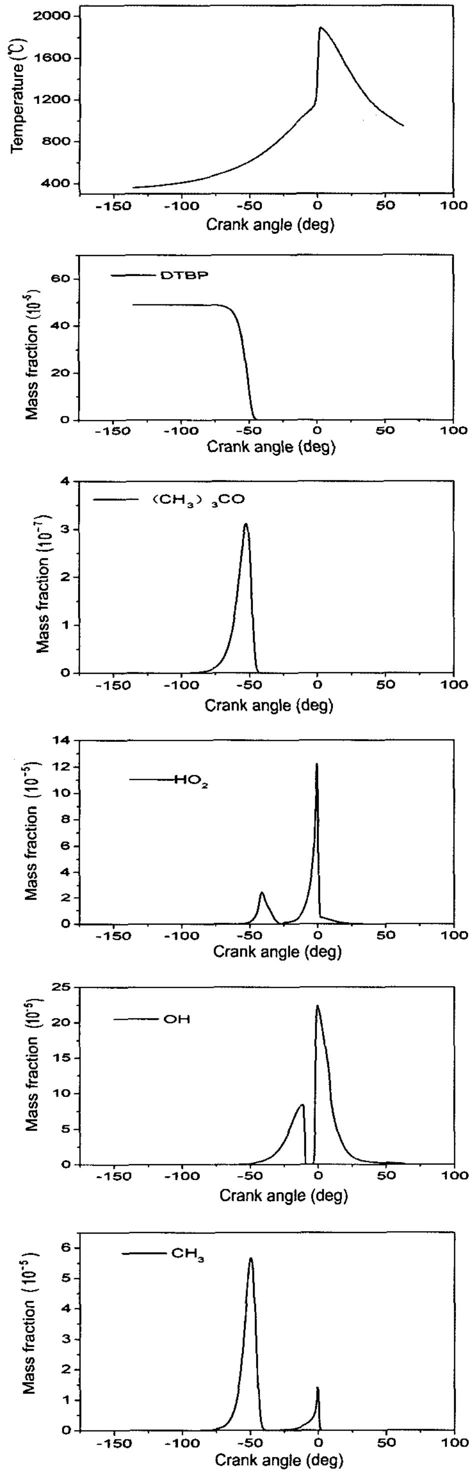


Figure 8. Effect of DTBP on the Mass Fraction of Combustion Production and Temperature (DTBP supply mode H, Supply rate of fuel: 1.23 kg/h).

study represents the practical combustion process well and can be adopted for further intensive simulation.

One of the simulated results is given in Figure 7. As it can be seen, the retarded ignition timing of compression ignition natural gas engine is at 5°CA ATDC without DTBP, and advances to 0°CA BTDC and 3°CA BTDC at DTBP supply modes C and H, respectively. The simulation work by the author also verifies that DTBP additive can improve the ignition performance of natural gas engines.

Figure 8 shows a simulated transition trace of gas temperature and a formation trace of main reaction species in the combustion process of CI natural gas engines with DTBP additives. It can be seen that at the middle stage of the compression stroke, while the in-cylinder temperature reaches 600 K, DTBP begins dissolving and forming a large amount of active species such as $(CH_3)_3CO$, $CH_3$, $CH_3O$, $HO_2$, OH, etc. These active species enhance the concentration of the total active species, which, in turn, accelerate chain reaction speeds and promote natural gas ignition advancement.

## 5. CONCLUSIONS

(1) In order to improve thermal efficiency of natural gas engines and reduce exhaust emissions, a new compression ignition combustion system is established. In this system, a DTBP additive is adopted to improve the ignition performance of this combustion system.

(2) CFD simulation on the new compression ignition combustion system is established successfully by adopting a DTBP mechanism. The CFD model is verified by experimentation, where there is good agreement between the simulation and experimental results.

(3) The simulation results indicate that the involvement of the DTBP additive can cause a large amount of active free radicals ($(CH_3)_3CO$, $CH_3$, $CH_3O$, $HO_2$, OH, etc.) at low temperature, so as to accelerate the chain reaction rate and improve the compression ignition performance of natural gas.

(4) DTBP can greatly improve ignition performance of compression ignition natural gas engines. With DTBP at a mass fraction of 14.2%, the engine can be ignited smoothly at ambient temperature when the glow plug temperature is at about 750°C.

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