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Research Article

Analysis of the Mechanism and the Current Situation of the Plasma Purification Technology for Diesel Exhaust

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Abstract: In this study, the mechanism and the current situation of the plasma purification technology for diesel exhaust is introduced. Research indicates that cleaning the diesel exhaust with the plasma produced by corona discharge or dielectric barrier discharge has too high energy consumption to direct use without catalyst. To solve this problem, the study gives some new ways about cleaning diesel exhaust with arc discharge.

Keywords: Arc discharge, diesel, exhaust, plasma

INTRODUCTION

According to the rules adopted at European conference, the Euro V standard came into effect. This standard is suitable for diesel cars, gasoline cars and light commercial trucks, but the Euro VI is only suitable for diesel cars. The Euro VI and Euro V standards make higher demands on the amount of the PM and NO_x for diesel and gasoline vehicles. According to the standard, the amount of NO_x. emission from diesel car must be less than 180 mg/km, which has been reduced by 27% compared with the amount of Euro IV and the amount of PM has also reduced by 80% compared with Euro IV. So all the diesel vehicles must solve the problem of the emission of PM and NO_x. the vehicle fleet of China is about 225 millions in 2011, which includes 65 million diesel vehicles. Once the new standard put into effect, a large number of diesel vehicles will cannot meet the demands and be not allowed to run. Therefore, the need for a new technology for control the diesel exhaust which accords with the situation of our country is imminent.

The main technological measures on decrease the exhaust of diesel engine often includes inside machine processing and outside machine processing. A large number of structure improvements on diesel engine has been done recently years, but which couldn't meet the more and more strict standards for exhaust emission, so the outside machine processing (post processing technology) attracts more and more attention (Shenhua *et al*., 2001; Yiming *et al*., 2002; Johnson, 2002; Rajanikanth and Ravi, 2002; Rajanikanth *et al*., 2002, 2003; Meixiang and He, 2002).

In the post processing technology, the plasma could not only have a good purifying effect for PM, but also clean NO_x, HC and CO in synchronism (Kai *et al*., 2011; Thomas *et al*., 2000), which overcome the "inborn weakness" of high amounts of PM and NO_x for diesel vehicles. It is a new subject for some experts to study the plasma diesel exhaust purification technology.

THE MECHANISM OF THE PLASMA PURIFICATION TECHNOLOGY

The purification mechanism of the diesel exhaust treated with low temperature plasma as follow: The purpose of cleaning diesel exhaust is achieved by using a series of chemical and physical reactions caused by a large number of high energy electrons, excited particles, atoms and free radicals which be included in the low temperature plasma produced in normal pressure.

In the process of the cleaning exhaust with low temperature plasma, there are kinds of reactions including oxidation reactions and reduction reactions, which depend on the average energy of electrons, the electron density, the gas temperature, the molecular concentration of pollutant gas and the other gas composition (Qingdao and Xueli, 2004).

The exhaust composition of diesel engine is of great difference form that of gasoline. The PM emissions from diesel is generally 30~50 times than gasoline's, or even higher, the NO_x emissions from diesel is as same as gasoline's, but the HC and CO emissions from diesel is less than gasoline's. The low temperature plasma technology is main suitable for PM and NO_x.

The mechanism of low temperature plasma for removing PM: The mechanism of the low temperature plasma could remove PM as follow Guibing (2004): with the action of OH and O, the soot oxidation degradation into CO and H_2; with the adsorption and reduction of the NO_x, the soot also could oxidate degradate into NO and N_2. To form a hypothesis, PM consists of C and H, could be expressed as CxHy

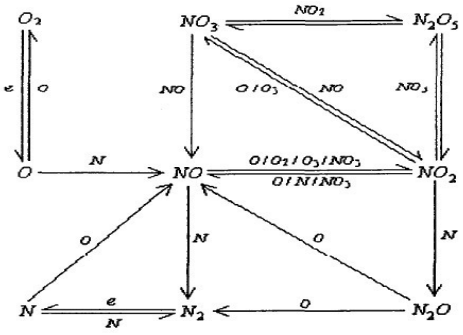

Fig. 1: The transformation of NO_x of diesel exhaust

(Dorai *et al*., 2000), so the degradation ways of the soot as following formate:

$$(CXHY) + OH \rightarrow (CX\text{-}1HY)\text{-}C\text{-}OH \quad (1)$$

$$(CXHY) + O \rightarrow (CX\text{-}1HY)\text{-}C\text{-}O \quad (2)$$

$$(CXHY) + NO_2 \rightarrow (CX\text{-}1HY)\text{-}C\text{-}NO_2 \quad (3)$$

$$(CXHY) + NO_2 \rightarrow (CX\text{-}1HY)\text{-}C\text{-}ONO \quad (4)$$

$$(CX\text{-}1HY)\text{-}C\text{-}OH \rightarrow (CX\text{-}1HY) + CO + 1/2H_2 \quad (5)$$

$$(CX\text{-}1HY)\text{-}C\text{-}O \rightarrow (CX\text{-}1HY) + CO \quad (6)$$

$$(CX\text{-}1HY)\text{-}C\text{-}NO_2 \rightarrow (CX\text{-}1HY) + NO + CO \quad (7)$$

$$(CX\text{-}1HY)\text{-}C\text{-}ONO \rightarrow (CX\text{-}1HY) + NO + CO \quad (8)$$

The above reactions begin with soot absorbed OH and O to generate association of C-OH and C-O and absorbed NO_2 to generate association of C-NO_2 and C-ONO. As the associations degradation into N_2, NO and CO, the mass of soot reduced promoting the soot degradation by using NO_x is one of the effective ways to improve the purification efficiency for diesel exhaust.

The mechanism of low temperature plasma for removing NO_x: The results of current research show that the low temperature plasma could not only remove PM in the diesel exhaust, but also remove NO_x. The transformation of NO_x of the diesel exhaust in the reaction system of the low temperature is shown in Fig. 1 (Xudong *et al*., 2003). In addition to electron-molecular collusion reaction, there isn't reaction of any other charged particles in Fig. 1. This is because that in the process of removing NO_x, the reactions between neutral object and neutral object take the lead and the reactions between charged particles could be ignored (Penetrante *et al*., 1996).

In the plasma chemical reaction shown in Fig. 1, the electron just played an excitation role in the beginning. The active substance play an important role in the discharge chemical reaction. The process of discharge enhanced the activity of substance and caused reactions, some of which are difficult or cannot occur in the normal temperature and pressure. So the amount of active material is very important for the whole reaction system. Enhancing the excitation ability of the high energy electrons to obtain more active materials is very useful to remove the NO_x in the diesel exhaust.

THE CURRENT SITUATION OF THE STUDY ON THE CONTROL OF DIESEL EXHAUST WITH LOW TEMPERATURE PLASMA TECHNOLOGY

Control the diesel exhaust with low temperature plasma technology: American Northwest Research Institute made a real vehicle study on packed bed discharge reactor in DISI and non DISI light diesel engine respectively. The study shows that the efficiency of removing PM could reach 60%, that of NO_x could be more than 40%, some CO would be generated and the reactor also run in the transient operating conditions (Fanick and Bykowski, 1994).

Fujjj and Rea designed a needle-plate wet reactor, which could remove 95% NO_x and 100% PM whose sizes are more than 0.3 μm in the diesel exhaust test (Fujii *et al*., 2001).

Masuda Senichi used plasma produced by high voltage pulse power supply discharge to decompose NO_x in the diesel exhaust and the test shows that the low temperature plasma technology is useful for removing NO_x of the diesel exhaust (Masuda, 1993).

In China, the study on the application of low temperature plasma in the diesel exhaust purification begins in the early 1990s, but has developed rapidly. Shanghai Jiaotong University put forward a new method about using low temperature plasma to assist catalytic oxidation reduction reaction and remove PM and NO_x and conduct an exploratory research (Lin *et al*., 2004).

Chongqing University made a study on the plasma produced by high pulse corona discharge. The study shows that the efficiency of the purification for NO could be above 50% and the produce is main NO_2 without too strong wind (Yang *et al*., 2002).

Related research made great achievement but it is still need to study on the theory.

The current situation of the study on the generation mode of plasma under normal pressure:

The generation mode of plasma: The generation mode of low temperature plasma includes three kinds as gas discharge, thermal ionization and radiation based on the theory. The latter two need high temperature combustion, explosions, shock waves or X ray, UV. So it is difficult to apply in the purification technology for diesel exhaust.

According to generation mechanism, the gas pressure range, the nature of power and the geometry of electrodes, the gas discharge plasma includes following modes:

- Glow discharge
- Arc discharge
- Corona discharge
- Dielectric barrier discharge
- RF discharge
- Microwave discharge

Glow discharge could generate under low pressure, but it is very low pressure. Corona discharge could generate under atmospheric pressure by using asymmetric electrodes (needle-plate electrodes and needle-needle electrodes), but it is difficult to obtain large volume plasma. Dielectric barrier discharge is a combination of the advantages of the two previous ones, it could generate large volume plasma under atmospheric pressure. RF discharge and microwave discharge are belongs to non-electrode discharge, could avoid electrode contamination and obtain pure plasma, but it needs low pressure. One of the demands of purification for diesel exhaust is atmospheric pressure and there are only three modes which include arc discharge, corona discharge and dielectric barrier discharge could generate plasma under normal pressure. Most of the related studies focus on corona discharge and dielectric barrier discharge, but little on arc discharge in the current situation.

The study on corona discharge and dielectric barrier discharge: Tsinghua University designed a lightweight corona discharge device and made a experiment of removing NO by using cold plasma (Wenhua and Xudong, 2004). Meixiang *et al*. (2005) and Okada (1983) made a basic research on removing NO_x by using dielectric barrier reactor under imitative condition of diesel exhaust. The result indicates that the low temperature plasma could be used to remove NO_x, but the efficiency of that NO could be converted into N_2 become lower and the energy consumption increases when the feed gas contains O_2. Many domestic and foreign experts (Miyamoto and Ogawa, 1988; Salvat, 2000; Coroller, 2002; Shangxiu, 1989) studied the influence of various components as O_2, H_2O, HC and NO_x on the purification of NO_x and the results show that the exist of O_2, H_2O, HC could be useful for the oxidation of NO into NO_2, but not for degeneration of NO into N_2.

Now the research institute home and abroad usually use many different methods (for example, DPF and SCR (Qingyun, 2001; Cooper and Thoss, 1992; Hammerle *et al*., 1995; Page *et al*., 1999; Chandler *et al*., 2000; Meixiang *et al*., 2005)) to reduce PM and NO_x simultaneously to meet more and more strict standard. Besides PM, NO_x and CO, there is a lot of O_2. That using the oxidation-reduction reaction between NO_x and PM from diesel engine itself to generate CO_2 and N_2 is a post-processing technology with good application future. Yashida (Yamazoe and Teraoka, 1990) made a study on the possibility of the oxidation and reduction reaction between soot-O_2-N_2 for the first time and the result indicates that the oxidation reaction between NO and C could occur under low temperature (300°C). The findings of the studies of Johnson Matthey company (Neeft *et al*., 1996) and Su Qingyun are shown in Fig. 2.

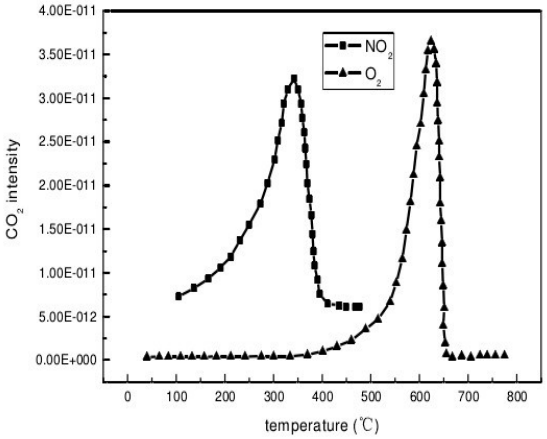

Fig. 2: The performance comparison curve of NO_2 and O_2 oxidated PM respectively

Figure 2 shows that the oxidation of NO_2 for soot is stronger than that of O_2 (Neeft *et al*., 1997). The findings of Cooper's experiments show that NO could be oxidated into NO_2 with the catalytic Pt and the NO_2 could further oxidate soot (Nejar *et al*., 2007). Penetrante coming from Lawrence Livermore National Laboratory of America devoted himself to research on post-processing technology with plasma (Penetrante *et al*., 1999). The team lead by him made theoretical and experimental analysis on the feasibility of this method and pointed out that the energy consumption is too high when plasma is used to clean HC and PM directly and plasma reactor should be used with catalytic device. So, no matter corona discharge or dielectric barrier discharge, it is difficult to put into real use that only using plasma remove PM and NO_x simultaneously and the catalytic materials must be assisted to reduce the energy consumption.

CONCLUSION

Facing with more and more strict standard, the plasma PM/NO_x post-processing integrated control technology would be the development trend of diesel exhaust post-processing strategies. Recent years, the studies mainly on corona discharge and dielectric barrier discharge are more and more widely and the application is also progressing rapidly. Because of the disadvantage of high energy consumption it must be used with catalytic, which increase the cost and secondary pollution in the process. To solve this problem, this study put forward the new idea about the application of arc discharge in the purification of the diesel exhaust.

RECOMMENDATIONS

The disadvantage of corona discharge is that the electron has enough energy only in a small range near electrode and the electron far away from electrode can obtain little energy so the free radicals and some active materials only produced near the electrode. A lot of energy could be wasted on inefficient ionic mobility and molecular vibration easily so that the energy efficiency per unit volume reduced. Compared with corona discharge, despite dielectric barrier discharge could produced large space uniform discharge, but a considerable part of electrical energy converted into heat energy, so the energy is still not high.

There are two ideas to solve the problem of high consumption in the process of the purification of the diesel exhaust. The first one is using catalytic to increase the purification efficiency. The second one is enhancing the electron excitation ability to increase the active materials at the beginning of the generation of plasma, which could promote the interaction between components in the diesel exhaust to increase the efficiency.

I think that the second ideas could be achieved with arc discharge. Since it was invented by Patel, the carbon dioxide laser has been consider as gas laser with high energy conversion efficiency and strongest output. The working substance of gas laser mainly consists of two gas of CO_2 and NO_x. CO_2 is the main gas which generates plasma radiation and NO_x is the auxiliary gas. Document (Wenzheng *et al*., 2009) introduced the effect of temperature and pressure for the laser running and pointed out when the temperature goes up and NO_x exists, in the discharge space, the glow discharge would be unstable contraction and transition to arc discharge gradually. According to the principle of gas laser, we could use CO_2 and NO_x in the diesel exhaust. Through discharge excitation, the transition of CO_2 molecular from low energy level to high energy level forms population inversion. In this process, because of negative nature of the oxides of nitrogen, they trapped a large number of electrons to form negative ionics, so the discharge is unstable and forms arc discharge. Because arc discharge use the components of itself to form plasma environment, so form the arc discharge (Weihong, 2007), not only its efficiency would be increase, but also its energy consumption would be lower than other discharge mode.

In the early 1990s, Czenichovski (1994) put forward gliding arc discharge non-equilibrium plasma technology. Some people besides Du Changming studied on the methods of removing PAH and carbon black particles (Changming *et al*., 2006) in the soot simultaneously using gilding arc discharge. These studies show that the method of removing PM and NO_x simultaneously using arc discharge plasma is feasible in theory. Now our team is actively working on related theoretical and experimental research.

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