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POTENTIAL OF OZONE TREATMENT AS A POLLUTION CONTOL METHOD FOR GASEOUS EFFLUENTS FROM INTERNAL COMBUSTION ENGINES

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ABSTRACT

Internal combustion engines are widely used as mobile units in the transport sector and commercially used as stationary units in the power production and agricultural sectors. Emissions from internal combustion engines usually consist of oxides of nitrogen, carbon dioxide, carbon monoxide, sulphur dioxide, and un-combusted hydrocarbons in addition to unconverted oxygen and nitrogen. Generally, the environmental regulations impose limits on these emissions to tolerable values before release to the atmosphere. However, reduction of these emissions is usually carried with difficulty and at high expense. Some of the pollutants so emitted in turn react with the stratospheric ozone in the atmosphere (10-50 km above the surface of the Earth) leading to ozone layer depletion. This paper presents an analysis of a technique which makes use of the ozone reactions in a reaction stage prior to release of gaseous effluents to the atmosphere where NOx and other pollutants such as CO, SO_2 and hydrocarbons are converted into products some of which can be easily cleaned downstream of the process leading to a cleaner exhaust to the atmosphere promoting a cleaner technology and emissions having less impact to environment and the stratospheric ozone layer.

Keywords
Exhaust, pollution, ozone

INTRODUCTION

Internal combustion (IC) engines usually consume liquid or gas petroleum products of varying compositions of carbon, hydrogen, oxygen, nitrogen and sulphur. The combustion reactions within the engine produce carbon dioxide, water vapour, carbon monoxide, traces of hydro carbons, elemental carbon in the form of soot and excess inert nitrogen[1]. In addition, unburnt hydrocarbons are also emitted together with the above exhaust. The proportions in which these gases are produced depend on the amount of air admitted to the internal combustion engine during the induction stroke and the extent of combustion taking place within the engine.

Internal combustion engines are widely employed in the transport, power, processing and agricultural sectors.

It is reported that 236,000 tonnes of nitrous oxides (NOx), 111,000 tonnes of hydrocarbons(HC) and 38,200 tonnes of SO_2 and 17,300 tonnes of particulates(PM_{10}) have been released to the atmosphere by combustion activities of fossil fuels in Malaysia in 1998.[2] It is also reported that 73.8% and 9.3% respectively of the above have been contributed by the motor vehicles and the power stations. The respective contributions in 1999 have been 76.3% and 8.7%. About 50% of the emissions out of the figures presented for motor vehicles seem from the motor cycles.[3].

NOx usually consist of Nitrogen dioxide (NO_2) and nitric oxide (NO). The latter is not considered to be a harmful to health. However, NO reacts with other gases present both in the the atmosphere, to form nitrogen dioxide. Nitrogen dioxide is harmful to health. Sulphur dioxide (SO_2) is produced by combustion of sulphur present in the fuel, particularly diesel. Sulphur dioxide is a hazardous gas which is one of the causes for acid rain. Carbon Monoxide (CO) is produced by incomplete, or inefficient, combustion of fuel. The gas affects the transport of oxygen around the body by the blood. Hydrocarbons which are generally volatile organic compounds (VOCs) consist of 1,3 butadiene, butane and other organic volatiles primarily from vehicle exhausts. These too are regarded as hazardous pollutants. Benzene in the atmosphere either comes from incomplete combustion or evaporation of petrol. Fine particles made up of carbon from combustion and chemical compounds such as sulphates and nitrates generally known as PM_{10}.are also known to be a pollutant from internal combustion engines. Diesel vehicles, typically emit more PM_{10} particles than petrol vehicles.

Several methods used for cleaning the above pollutants from the exhausts of internal combustion engines are presented in the next section.

CURRENT STATUS OF EXHUST GAS CLEANING

Catalytic converters are usually employed in order to convert the carbon monoxide to carbon dioxide in the exhaust of IC engines. A catalytic converter working under ideal conditions would have an active life of about 100,000 km(4). The ideal working temperature of catalytic converters is within the range of 400°C and 800°C. But due to possible temperature fluctuations below and above the above ideal ranges makes the converters less effective. Further, CO catalytic converters do not convert NOx. The SO_2 can be oxidized to SO3 and subsequently to sulphuric acid by the converter making the catalyst less efficient. Many studies have been carried out in the past to reduce NOx emissions of internal combustion engines. Techniques such as exhaust gas recycling and De-NO_X processes are reported in the literature.(4). The former technique which is recycling part of exhaust gases back to the engine inlet has proved success but with the expense of shaft power and increased levels of carbon monoxide emissions. Use of water emulsified fuel is reported to reduce the NOx emissions by 80-85% and particulate matter by 86-90%.Thermal De-NOx processes where NO is reduced to N_2 by means of catalysts and/or ammonia are also reported(5). Reduction of SO_2 from the emissions has been mainly carried out as a top down control methods of fuel de-sulphurization have been given importance. A two bed catalytic system for NOx/SOx removal has been presented(6) . SO_2 however deactivates the NOx catalysts leading to in efficient De-NOx processes(7,8,9) . The particulates in the exhaust are usually removed by particulate traps as these tend to poison the catalysts downstream.

OZONE AS AN AGENT FOR POLLUTION CONTROL

Ozone has been used in cleaning of water since many years in the past [10].

Several studies are reported on the use of ozone in the oxidation of SO_2 in the flue gases [11,12] Application of ozone in the removal of NOx emissions are also reported in the literature [11].These methods have not been pursued very much apparently because of the slow rate of reactions and the resulting high costs involved [14].

Studies on the removal of hydrocarbons using ozone have been studied by Seo et al.[15] , where methane has been used in his study. The conversions of methane has been reported to be satisfactory.

REACTIONS OF POLLUTANTS WITH ATMOSPHERIC OZONE

Gases such as oxides of nitrogen are well known to their properties of ozone depletion in the stratosphere leading to much concern among the environmentalists. The reactions of atmospheric ozone with NO2 and the subsequent chain reactions can be summarized as follows.[13]

A molecule of NO_2 reacts to form NO and a singlet O atom under the influence of light energy. The extent of the reaction depends on the intensity of the radiation of light.

$$NO_2 + h\nu \rightarrow NO + O \tag{1}$$

Ozone reacts with NO to produce more NO_2 and O_2

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{2}$$

Ozone is degraded by energy from light radiation, producing a charged form of singlet oxygen, [O], and more molecular oxygen. This reaction is reported to proceed at a much slower rate than the first reaction.

$$O3 + h\nu \rightarrow O2 + [O] \tag{3}$$

Some of the charged oxygen atoms react with water molecules to form a hydroxyl radical, [OH] which are fragments of molecules that have at least one unpaired electron, and are highly reactive.

$$[O] + H2O \rightarrow [OH] \tag{4}$$

Carbon monoxide reacts strongly with hydroxyl radicals to form carbon dioxide and $[HO_2]$ radicals.

$$CO + [OH] \rightarrow CO2 + [HO2] \tag{5}$$

The $[HO_2]$ radicals formed above react with the extra NO to form more NO_2 and more [OH] radicals.

$$[HO2] + NO \rightarrow NO2 + [OH] \tag{6}$$

The hydroxyl radicals react with NO_2 to form nitric acid, HNO_3 .

METHOD STUDIED

The method considereded is using dry exhaust gases arresting the reactions (1) and (3) in a reactor by carrying out the ozonization reactions in the absence of any light energy (opaque reactor) thereby assisting the following reactions to be carried forward .

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad 1.08\exp(12-2.720/RT) \tag{7}$$

$$O_3 + NO_2 \rightarrow)2NO_3 \qquad 7.22\exp(10-4.865/RT) \tag{8}$$

$$O_3 + CO \rightarrow CO_2 + O_2 \qquad 5.02\exp(2-23.15/RT) \tag{9}$$

$$O_3 \rightarrow O_2 + O \qquad 5.8\exp(14-23.15/RT) \tag{10}$$

$O_2+O \rightarrow O_3$ 2.4exp(13-5.6/RT) (11)

Where the rate constants are cm mol kcal units[13]

$SO_2+O \rightarrow SO_3$ 3.6×10^{14}.exp(1000/RT) (12)

$O_3+O \rightarrow 2O_2$ 3×10^{13}.exp(-6000/RT) (13)

$SO_2+O_2 \rightarrow SO_3+O$ 6.5×10^{14} .exp(-10,800/RT) (14)

Where rate constants are in cm mol s units.[11]

Once the above reactions occur in the reactor the stream is processed downstream by means of scrubber or porous absorber removing the acidic SO3 and NO3.

The layout scheme of the proposed process is given in Figure 1.

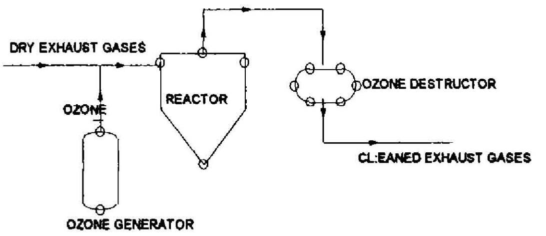


FIGURE 1 . LAY-OUT OF THE PROCESS CONSIDERED

ANALYSIS

The above reactions have been modeled in the process shown in Figure 1 where the reactor is assumed to be of CSTR(opaque)type. Simulations were carried out for a typical worst case of an exhaust composition of a diesel engine having the following exhaust gas compositions[1];

CO = 1000ppm NOx= 1000ppm
SO2= 300 ppm NO = 200ppm
HC =600 ppm

Ozone injections to constitute ozone concentrations of 5000 ppm, 10000 ppm and 50,000 ppm in the exhaust gas ere used in the simulations. Reactor temperatures of 300°C, 500°C and 800°C were studied.

Possible free radical formation reactions are not taken into account in the simulations.

RESULTS AND DISCUSSION

Figures 2A to 2B present the variation of residence time with the conversion of NO present in the exhaust to NO2. As expected, the conversions are seen to be faster with increased ozone concentrations and with increased temperature. At 500°C the conversions of 50% could be achieved during reactor residence times of about 100 s. An increased temperature to 800 °C is seen to give conversions of NO to NO2 to around 70%.

FIGURE 2A .PLOTS OF RESIDENCE TIME VS CONVERSION OF NO FOR T=300 C

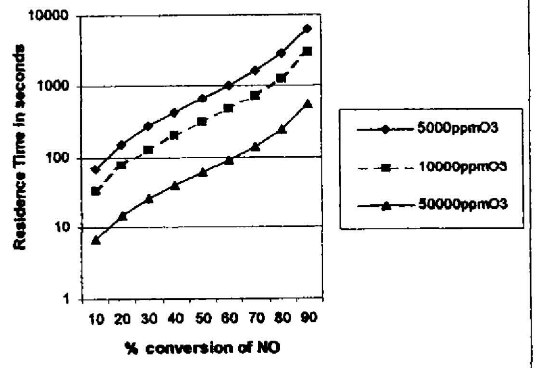
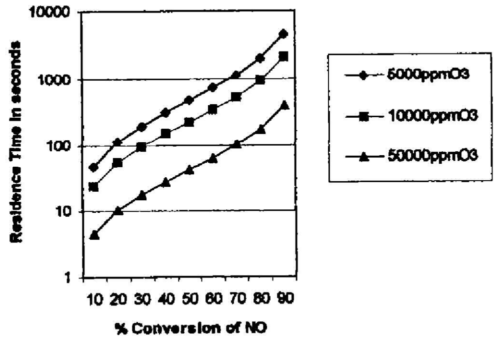


FIGURE 2B. PLOTS OF RESIDENCE TIME VS CONVERSION OF NO FOR T=500C



The conversion of NO2 to NO3 for three inlet ozone concentrations of 5000-50000 ppm and for reactor temperatures of 300°C, 500°C and 800°C are shown in Figures 3A to 3C. Conversions of NO2 to NO3 seems to be slower than conversions of NO under similar conditions. However conversion up to about 70% at

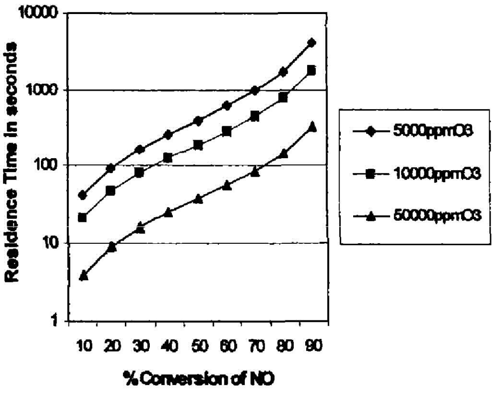


FIGURE 2C.PLOTS OF RESIDENCE TIMES VS CONVERSION OF NO FOR T=800C

reactor residence times of about 100s is seen to be possible under 800oC and with ozone concentrations of 50000ppm.

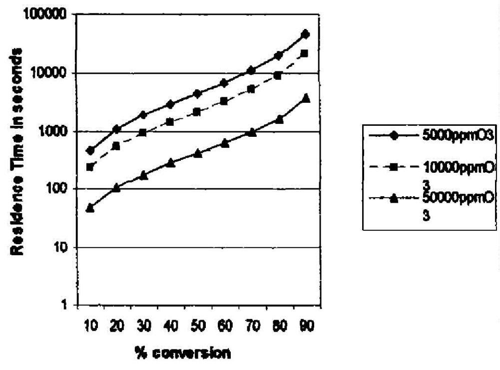


FIGURE 3A. PLOTS OF RESIDENCE TIME VS CONVERSION OF NO2 FOR T=300 C

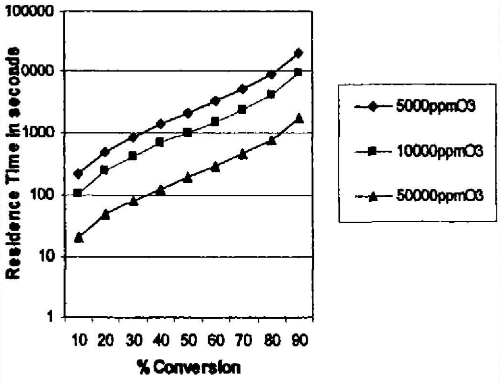


FIGURE 3B.PLOTS OF RESIDENCE TIME VS CONVERSION FOR OF NO2 FOR T=500C

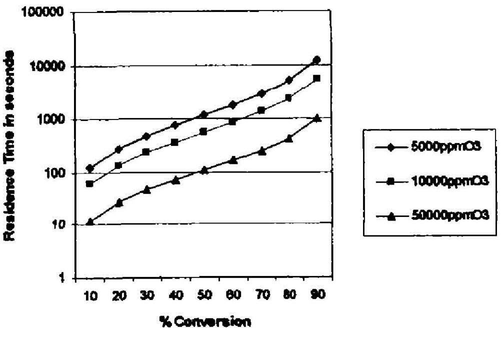


FIGURE 3C.PLOTS OF RESIDENCE TIMES VS CONVERSION OF NO2 FOR T=800C

The respective variation of residence times with the conversion of CO are shown in Figures 4A to 4C below. A study of residence time requirements for satisfactory conversion of CO to CO2 is observed to be too high, usually above 1000 s , which make the conversion impractical commercially, specially in the case of a gas flow CSTR reactor.

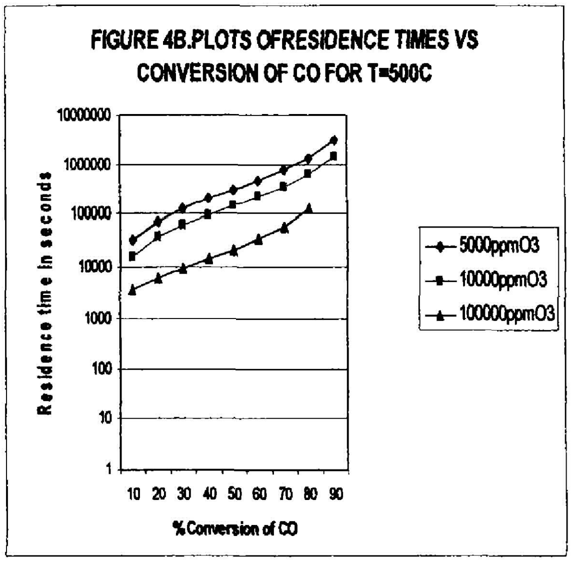


FIGURE 4B.PLOTS OFRESIDENCE TIMES VS CONVERSION OF CO FOR T=500C

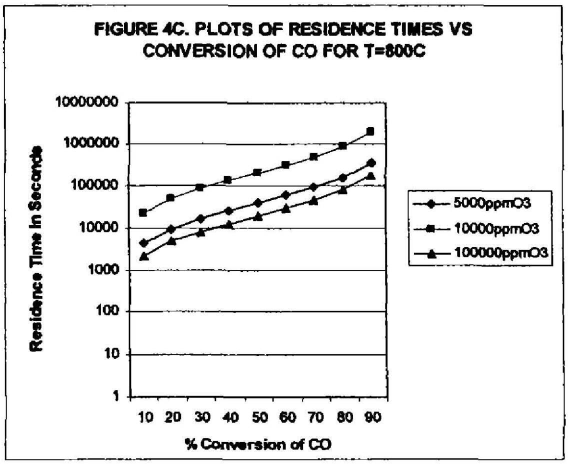


FIGURE 4C. PLOTS OF RESIDENCE TIMES VS CONVERSION OF CO FOR T=800C

Simulation results for residence times for different conversions of SO2 are presented in Figures 5A to 5C. The results demonstrate a fast conversion compared with the other reactions so far considered. Conversions up to 70 to 80% seem to be possible at low residence times around 1s or below and at temperature of around 800°C .

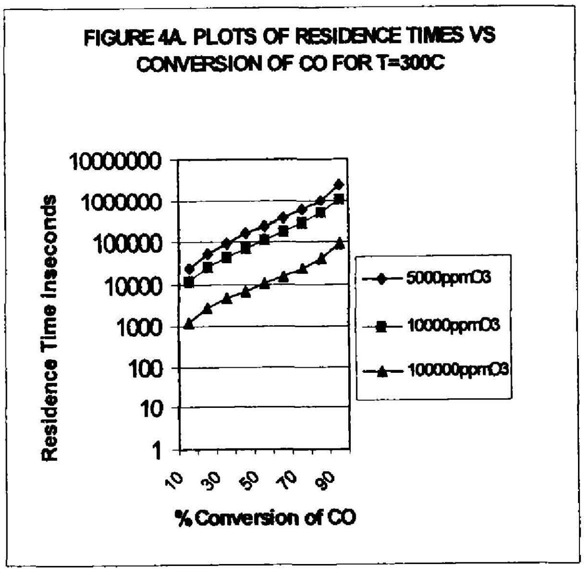


FIGURE 4A. PLOTS OF RESIDENCE TIMES VS CONVERSION OF CO FOR T=300C

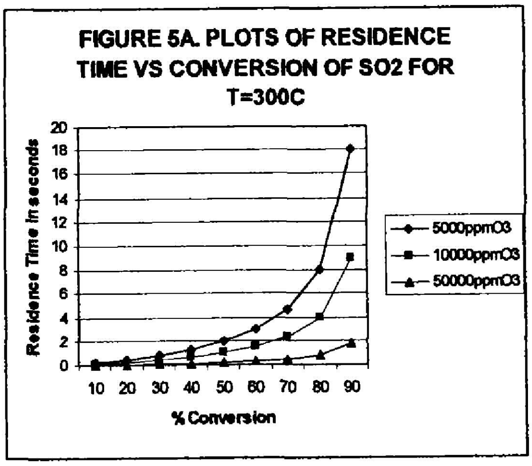


FIGURE 5A. PLOTS OF RESIDENCE TIME VS CONVERSION OF SO2 FOR T=300C

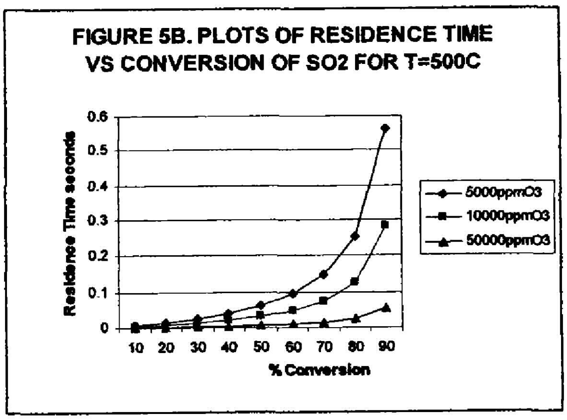
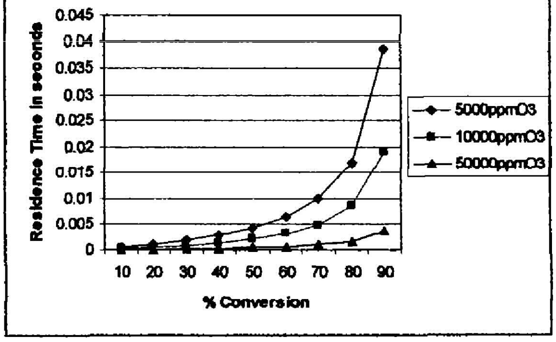


FIGURE 5B. PLOTS OF RESIDENCE TIME VS CONVERSION OF SO2 FOR T=500C

FIGURE 5C.PLOTS OF RESIDENCE TIME VS CONVERSION OF SO2 AT T=800C



CONCLUSION

From the above study, it can be concluded that a potential exists for cleaning of pollutants other than carbon monoxide from the exhaust of a typical internal combustion engine using ozone as a treatment agent at temperatures around 800°C. Conversions of carbon monoxide is seen to be very low even at temperature around 800°C indicating the impracticality of using ozone as a treatment agent for conversion of carbon monoxide. Studies may be required to investigate the conversion of carbon dioxide to carbon monoxide through ozone under catalyzed reactions.

The products leaving the reactions are generally acidic having SO3 and NO3 which are fast reactive in absorbents making easier for their removal downstream and thereafter discharge of cleaner gases to the atmosphere.

The study did not consider the reactions of ozone with hydrocarbons, moisture and carbon particulates. Removal of PM10 particulate carbons through reactions with ozone is promising even though its study has not been included in the current paper. Studies of removal of hydrocarbon and PM10 carbons using ozone will be required to be carried out in the future.

The results of the theoretical simulations carried out need to be verified experimentally in order to ascertain the accuracy of the model and also for further improvements of the model.

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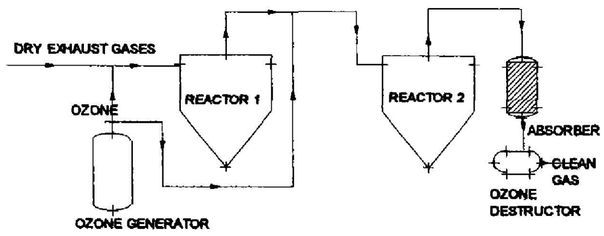

FIGURE.6 . LAY-OUT OF THE PROCESS PROPOSED