무성방전 플라즈마 전극구조에 대한 질소산화물 제거효율 연구

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A Study on NOx Removal Efficiency Depending on Electrode Configurations of Silent Discharges

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Abstract : A comparative investigation of an experimental and a simulation of chemical kinetics for NOx removal from silent(dielectric-barrier) discharges is presented. Several types of dielectric-barrier discharges were implemented depending upon the configuration of electrodes. The simulation was based on an approximate mathematical model for plasma cleaning of waste gas. The influence of non-uniform distributions of species due to the production of primary active particles in the streamer channel was taken into account. A comparison of observed experimental to the calculated removal efficiency of NOx showed acceptable agreement.

요 약 : 무성 (유전체 장벽) 방전기구의 질소산화물(NOx) 제거효율에 대한 화학 반응역학의 전산모사 및 실험적 특성이 비교 조사되었다. 방전 전극구조에 따른 여러 종류의 유전체 장벽 방전기구가 구현되었으며 응용 방전환경 별 질소산화물(NOx) 제거특성이 이론적, 실험적으로 고찰되었다. 전산모사 모델링은 유해 배가스에 대한 플라즈마 응용기구의 수학적 근접모델을 기초로 하였고 각 방전광(스트리머) 채널의 주 활성입자 생성에 의한 화학반응 종들의 비균일, 비평형 분포특성을 고려하였다. 모델링 전산모사로 얻어진 질소산화물(NOx) 제거효율은 관찰 실험특성과 오차 허용범위 내의 일치성을 나타내었다.
Key Words : non-thermal plasma, silent(dielectric-barrier) discharge, NOx, chemical kinetics simulation, experimental

1. Introduction

One of the promising technologies for destruction or removal of nitrogen oxides (NO_x) from flue gas streams is the non-thermal plasma discharge. Application of the non-thermal plasma for the pollution control is based on a locally generated high electric field. Due to a high electric field, energetic electrons are generated which produce in turn the active components. These components initiate the sequence of chemical reactions involving molecules of the background gases and toxic impurities. These generated radicals reduce and/or oxidize NO_x molecules. The removal efficiency of NO_x is generally dependent upon the magnitude of applied voltage on electrodes and the intensity of plasma energy. And, electrical discharge techniques can also be implemented in many different ways, depending on the electrode configu- rations and the applied power supplies[1,2]. In this paper, using a

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simulated gas mixture, the performance of a dielectric-barrier discharge reactor with a coaxial cylinder electrode has been investigated in dry conditions. And, a computer simulation results that based on the experimental data are also presented. The employed simulation modelling of chemical kinetics showed generally in a good agreement with the obtained experimental data.

2. Experimental

In this work, two different types of plasma reactors were implemented for the investigation. The fist type reactor(single dielectric barrier discharge reactor) with a 20mm and the second type reactor(dual dielectric barrier discharge reactor) with a 35mm outer diameter had a cylindrical glass chamber as a dielectric barrier between the high voltage and ground electrodes. The glass cylinder provides a dielectric barrier to the development of a discharge, so that high voltage can be applied without breakdown. The external surface of cylindrical reactor glass was covered with an aluminium foil of 1.5mm thickness, which forms the ground electrode. High voltage pulses of positive polarity were applied to the inner electrode. The inner electrode of the first type reactor is consisted of a centrally suspended straight stainless steel wire of 0.8mm in diameter as shown in Fig. 1. The second type reactor is comprised of two cylindrical glass tubes arranged so that the gas flow was directed between two tubes as shown Fig. 2(a). Inside of the inner tube was filled with a titanium dioxide(TiO_2) pellets about 3.5 mm in diameter for the high NO_X reduction rate and the low discharge temperature[6]. The outside of inner tube was wounded with stainless steel wire to form the electrode as shown in Fig. 2(b). Reactor sizes are given in millimeters.

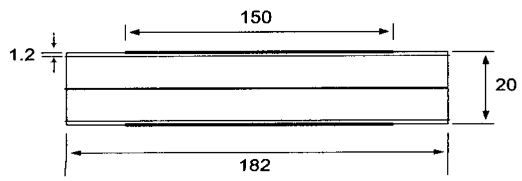

Fig. 1. Schematic diagram of a first type reactor [mm]

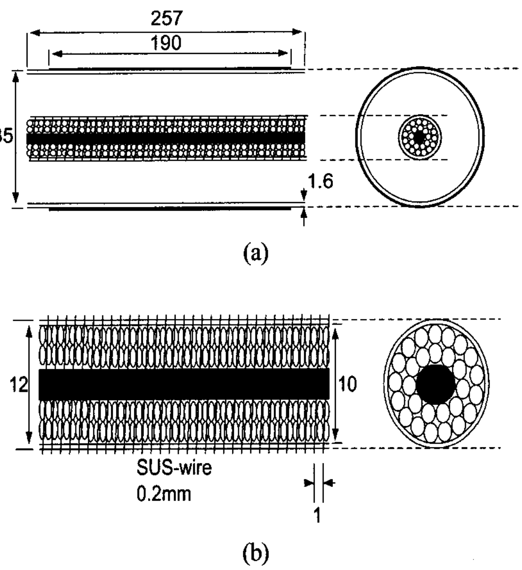

Fig. 2. Schematic diagram of a second type reactor [mm] (a) geometrical dimension of a reactor (b) inside geometry of inner tube of (a)

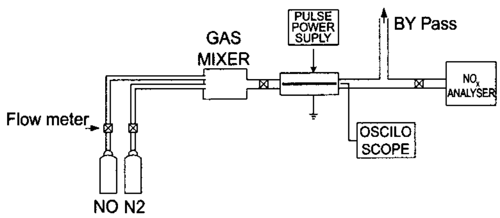

Fig. 3. Schematic diagram of the experimental set-up

A rotating spark gap switch was used to generate the square wave pulses by chopping the DC voltage supplied from DC high voltage generator(Pulse Electronic Engineering, 50kV). The repetition frequency of pulses was 240Hz. The output voltage, current and the discharge power were measured using a digital oscilloscope(Tektronix TDS 702A), along with a 1000:1 high voltage divider(Tektronix P6015A) and a current transformer(Tektronix AM503B) with a current probe(Tektronix A6303). A schematic diagram of the experimental apparatus is shown in Fig. 3.

The deposited energy into the gas changed due to applied voltage with an amplitude from 15 to 20kV at the fixed frequency. The initial NO gas of 1400ppm with a N_2 balance gas was used and mixed with a dry air to control the variable NO concentration of 300-800ppm. The flow rate was varied from 2 to 4 l/min. NO and NO_x concentration at the input and the output of reactor were measured with a chemiluminescence $NO/NO_2/NO_x$ analyzer(Advanced Pollution Instrumentation, model 200AU). It is important to point out that in the experiments the gas flowing into the discharge reactor consists of dilute amounts of NO in only N_2. NO and NO_x concentration were measured in dependence on the deposited energy into the gas.

3. Chemical Kinetics Modelling

For description of experimental results, the approximate mat1hematical model for plasma cleaning of pollutant gas and the simulation tools of radical had been used[3,4]. The spatial non-uniformity of gas parameters associated with the existence of many microdischarge channels in a discharge chamber and sequence of discharge pulses were taken into account. The discharge characteristics in experiment such as a specific energy input into a gas per pulse(W_{dc}), a total deposited energy, a number of pulses in the experiment were included in the simulation. Parameters of microdischarge in modelling: a specific energy input into microdischarge channels(W_{st}) and a part of this energy(q) which is spent on the active species production, a fraction of the reactor volume filled by microdischarges ($F_0 = W_{dc}/W_{st}$) have been chosen according to the model[3,4]. The parameter q depends on the set-up design and includes some deviations from the theoretical assumptions. It must be adjusted in order to reach agreement with experimental and calculated results for all flow rates for the same experimental set-up and matrix gas composition.

In given work the calculations were made for the average electric field of microdischarge E=100kV/cm. This value was chosen because a high voltage was used in these experiments, and, on the other hand, to satisfy a characteristic value of electron density ($\sim 10^{14}cm^{-3}$) and density of filling($F_0 \sim 10^{-2}$) in a barrier discharge. The concentrations of active species were defined using G-factors corresponding to E=100kV/cm, and the specific energy for active species production of qW_{st}. G-factor is the number of particles of each sort in dissociative process per 100 eV of absorbed energy. G-factors from literature were properly refined to obtain the G-factors for the considered gas composition[7-10].

4. Results and Discussion

4.1. First type reactor

It was assumed that only part(q=0.75) of specific energy W_{st}=0.0075J/cm^3 is spent to produce the active species in this barrier discharge. Under these conditions the concentration of nitrogen atoms and electrons were $3\times10^{14}cm^{-3}$ and $3.6\times10^{14}cm^{-3}$ correspondingly. The value of F_0 is changed from 10^{-2} up to 10^{-1} in dependence on the value of W_{dc} for the first and second types of reactors. The value of W_{dc} was changed from 1.7×10^{-4}J/cm^3 up to 8×10^{-4}J/cm^3. Since the electric field is not known exactly, the sensitivity of its value had been examined. The calculations showed that in general only concentration of nitrogen atoms(N) is the value, which determines the agreement between calculations and experimental data.

The comparative results of experimental data and calculations in Fig. 4 show NO conversion for a flow

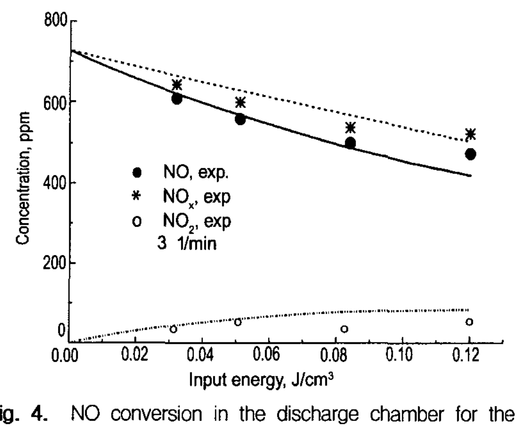

Fig. 4. NO conversion in the discharge chamber for the first type reactor; curves: result of the modelling [3l/min, 730ppm]

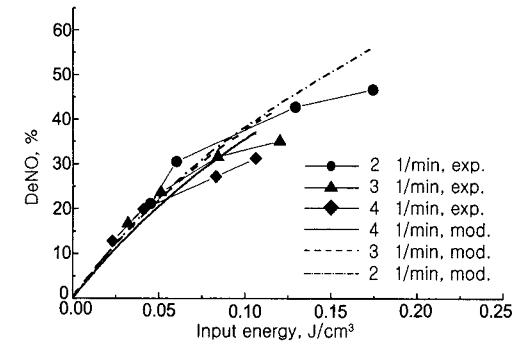

Fig. 5. Conversion of NO for several flow rates and different initial NO concentrations for the fist type reactor: 2 l/min, 699ppm; 3 l/min, 730ppm; 4 l/min, 771ppm.

rate of 3 l/min and initial NO concentration of 730ppm. Fig. 5 illustrates NO conversion ratio for the different initial NO concentrations and flow rates. In general the results of modelling have revealed satisfactory agreement with experiments. Some discrepancy observed at high deposited energy is connected to the heating of gas at 80-100C (experimental value).

4.2. Second type reactor

Four different types of discharge depending on method of voltage applying were considered for this reactor. Three different discharges were implemented for electrode configurations: a-apply, b-earth; a-earth, b-apply; a-earth, b-apply, c-earth have been described with identical parametes of microdischarge, where "a" is a metallic rod of 2.3mm in diameter inside of small tube, "b" is SUS-wire, "c" is a foil. It was assumed that W_{st}=0.0075J/cm^3 and q=0.25. In this case, the concentration of nitrogen(N) atoms and electrons were equal to 10^{14}cm^{-3} and 1.2×10^{14}cm^{-3} correspondingly. The fourth discharge was generated as an electrode configuration of b-apply, c-earth , and the value of q was accepted 0.4 for the same value of W_{st}. The concentration of nitrogen(N) atoms and electrons were 1.6×10^{14}cm^3 and 1.9×10^{14}cm^{-3}.

Decomposition efficiency of NO and NO_x are presented for a discharge with electrode configuration of a-earth, b-apply, c-earth in Fig. 6 for several flow rates and different initial NO concentrations. In general, taking into account of some possible experimental discrepancies, the modelling is in a good agreement with experiments, especially for NO removal efficiency.

Some difference at the large amount of deposited energy apparently is connected with a local heating of the gas in a microdischarge channel, which is more than the typical average temperature in a gas(final temperature measured in experiments was approximately 380K). The difference between experimental and calculated results for NO2 concentration is more appreciable for the discharge configuration of a-earth, b-apply, c-earth than for the configuration of b-apply, c-earth. This may be connected with a non-uniform filling by microdischarge channels of a reactor volume.

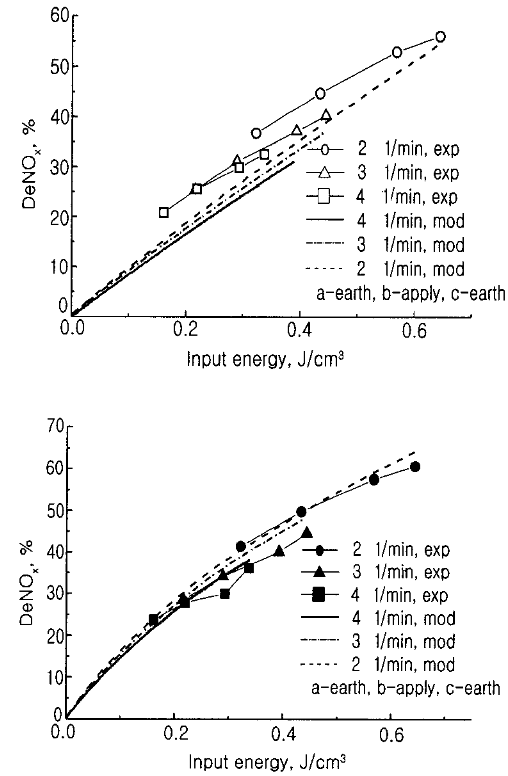

Fig. 6. Decomposition of NO_x and NO for a discharge configuration of a-earth, b-apply, c-earth for several flow rates and different initial NO concentrations for the second type of reactor: 2 l/min, 701ppm; 3 l/min, 738ppm; 4 l/min, 781ppm.

The value F_0 is larger by a factor of 2-4 for a configuration of a-earth, b-apply, c-earth. In this case the discharge is very strongly located near to the central electrode and more intensive than in a configuration of b-apply, c-earth (observed fact in experimental). In the region of central electrode the temperature is high and the rate constant in reaction

$$NO + O + M \Rightarrow NO_2 + M,$$
$$k = 9.1 \times 10^{-28}\ T^{-1.6}\ cm^6/(molecule^2\text{-}s),$$

will be smaller, as a consequence of NO_2 concentration will also be rise slower. Whereas the rate constant of conversion NO into N_2 will be same for several types of discharges :

$$N + NO \Rightarrow N_2 + O,\ k = 3.1 \times 10^{-11} cm^3/(molecule\text{-}s)$$

The integral input of the reaction

$$NO_2 + O \Rightarrow NO + O_2,\ k = 6.5 \times 10^{-12} \exp(120/T) cm^3 / (molecule\text{-}s)$$

will be smaller by a factor of 2-4. The rate constants of reactions were utilized from many sources and are quoted in the reference of [3,4]. One can see that the concentrations of NO and NO_2 depend on temperature. Under the large amount deposited energy, the temperature increases, the conversion of NO to NO_2 decreases, and the concentration NO_2 almost does not change. The main conversion of NO in a mixture N_2-NO is conversion to N_2 and O_2.

Fig. 7 presents the comparison of NO and NO_x decomposition efficiency for several types of discharge in the first and second types of reactors for the flow rate of 4 l/min and similar initial NO concentration. The similar results were obtained for other flow rates. One can see that a configuration of b-apply, c-earth is more effective than other discharge configurations for a second reactor. Their efficiency is approximately similar and equal to 230eV for removal of one NO molecule. For configuration of b-apply, c-earth the average energy cost is near to 170eV. This value for the fist type reactor was equal to near 100eV in N_2-NO mixture and appreciable smaller than that for reaction in[5].

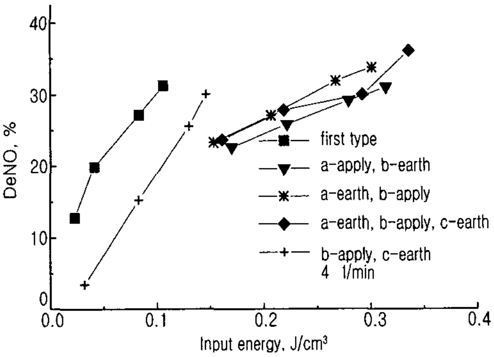

Fig. 7. NO decomposition efficiency for discharge configurations. [NO]0=780 ppm smaller than that for reactors in [5].

5. Conclusions

Removal efficiency of NO_x in N_2 was investigated for the plasma reactor when a high pulse voltage could be applied without breakdown. The results of modelling are close to experimental results. The NO removal depended on initial NO concentration, flow rate, deposited energy, electrode configurations of discharge and temperature. The better reduction NO and NO_x performance were obtained in lower initial NO concentrations and decreasing gas flow rate. The discharge with straight wire configuration of inner electrode was more effective than other types of discharges. For real mixtures(air, flue gas and others) this reactor may be very effective because the energy cost for N_2 dissociation is much lower than that in air or flue gas for O_2 or H_2O for the same electron mean energy. In correspondence with experiment, such type of rector could be more suited at the lower input energy when an increasing temperature is small. A good agreement between experimental data and calculations gives opportunity to simulate the removal process in these types of reactors and predict of its efficiency for other gases.

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