Pulse corona induced plasma chemical process: a horizon of new plasma chemical technologies

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Abstract - A very intense corona discharge can be produced by applying a sharp rising, narrow pulse high voltage between corona and counter electrodes of a corona system. Because of an extremely increased spark voltage electrons are highly accelerated even under ordinary gas pressure, while ions with much larger mass are not effectively accelerated as a result of too short pulse duration time. Hence, a strongly non-equilibrium plasma with a high electron temperature and low ion and molecular temperatures is produced. A number of gas phase reactions, such as DeNOx, DeSOx and control of hazardous and toxic gaseous pollutants like mercury vapour from incineration plants, can be effectively realized, where the pollutants are converted into solid aerosol particles, with or without additive agents like ammonia, to be easily removed in downstream precipitators. This also opens a new way of producing ultra-fine particles of various exotic materials. Treatment and dry processing of various surfaces under ordinary pressure (and also reduced or increased pressures) are also possible.

1. INTRODUCTION

The author investigated with his co-worker a possibility of enhancing DeSOx and DeNOx in E-beam method from a thought that copious electrons, produced by ionizing collision of primary high energy electrons and remaining with low energy after performing useful chemical reactions, could be regenerated in energy by applying an electric field. The results of experiments were very positive (1), but only under the condition that corona discharge took place. Furthermore, the use of DC voltage produced a comparatively large ionic current to cause quite a high electric loss. This suggested that a very narrow pulse high voltage or microwave high voltage must be used for exploitation of such effect in order to avoid energy loss due to acceleration of ions. A great technical difficulty to proceed with this idea was the lack of power supplies which must be high in efficiency, low in cost, and durable enough to allow a long term continuous operation. The microwave was discarded because of its too high cost and too low efficiency in power supply. A sharp rising, very narrow pulse voltage was only one possibility in view of its cost. The author and his co-workers succeeded to develop a very efficient, low cost, and reliable nanosecond or submicrosecond pulse power supply using a rotary spark gap for fast switching of a condenser in combination with its phase-selective AC charging (2). Fig. 1 indicates its circuit diagram, and Fig. 2 a photograph of one of the pulse power supply which can energize 2,000 m² in terms of total counter electrode area. This pulser can be directly connected to the load when it is small, but in the case when load capacity is large, the use of the corona transmission line (3) should be most effective in both plasma chemical performance and energy efficiency. This uses a long corona wire, zig-zag formed, on which such a narrow pulse voltage proceeds in a form of a travelling wave without losing its original rise and duration times, thus producing its essential activity and uniformity along the entire length of the wire.

After completing the nanosecond pulse power supply and the circuit technologies for an effective use of the pulse, the author and co-workers started (1) DeNOx and DeSOx tests in laboratory and an incineration plant, (2) tests of mercury vapour control at the incineration plant, and (3) ozone production test in laboratory. Based on these test results theoretical considerations were also made on the mechanism of the pulse corona induced plasma chemical process (PPCP).

The author is convinced at this stage that PPCP could provide a number of cost-effective means for oxidizing and other applications. In the following our test results are presented together with the discussion on the results.
2. TEST RESULTS

2.1 Correlation between E-beam and PPCP (pulse corona induced plasma chemical process)

At first tests were made to clarify if a cross-correlation exists, as expected before, in the overall effect of reactions between E-Beam and PPCP, or if they are independent in their effects. Fig. 3 indicates a typical result which were obtained for NO gas in dry air with negative pulse corona, where ammonia was added. The curves with E-Beam only do not indicate any change up to 11 kV/cm, where sharp changes occur in both NO and NO₂ concentrations. However, these changes are exactly those which happen with PPCP without the aid of E-Beam. Hence, it can be concluded that no cross-correlation exists between E-Beam and PPCP. Hence E-Beam process and PPCP must be considered separately.
2.2 Effect of pulse peak field intensity

The effect of PPCP begins to appear only after corona onset as shown in Fig. 4 in which the corona starts at $E_p=5$ kV/cm ($E_p$: peak voltage $V_p/(\text{gap})$). This figure also includes the effect of E-Beam which produced initial drops of NO and NOx. With increasing field NO indicates a gradual drop to become zero at $E_p=12$ kV/cm, while NOx rises concurrently, as a result of NO oxidation, up to 11.5 kV/cm, beyond which it suddenly drops. In other words, the dominant active species producing NO removal is different from those for NO oxidation, and the formers are produced beyond a much higher threshold value of $E_p$. It is anticipated from Fig. 5 indicating the effect of humidity (4), and Fig. 6 indicating the effect of oxygen (5), that O and O$_3$ are likely to be dominant for NO oxidation while OH radical is likely to be essential for NOx removal.

2.3 Effect of polarity of pulse voltage

This is very complicated, as shown in Figs. 7 and 8. At room temperature positive pulse always produces much better performance than negative one, although energy based efficiencies are the same (5). However, with the

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Fig.6 Effect of Oxygen (Negative; Dry)

Fig.7 Effect of Polarity on NO Removal

Fig.8 Effect of Polarity on NO$_2$ Removal
increase in temperature the tendency reverses, as shown in the above figures (4), at least in clean gas (room air + NO) conditions. However, in a combustion gas from an incinerator boiler plant these differences between positive and negative polarities in the performance disappears, while energy efficiency is always better in positive pulsing PPCP (6). The difference in gas lies in much higher concentrations of water (17%), CO (10%), CO (300 ppm), and HCl (350 ppm) and existence of fine particulate in combustion gas. The superiority of using negative pulsing for PPCP may open a way to applying PPCP inside an electrostatic precipitator, where both particulates and gaseous pollutants (NOx, SOx, mercury vapour, etc.) could be simultaneously removed. All these results tell that a careful preliminary test must be made on a case by case basis to avoid a risk due to a drastic change of PPCP characteristics caused by a small change in gas composition.

2.4 SOx removal

The laboratory tests indicate that SO2 can only removed after NO and NO2 have been removed by PPCP. In the practical combustion gases, however, SO2 is the first to be removed, followed by NO and NO2 removal. It is anticipated that, in combustion gas which includes particulate, SO2 converted from SO2 will be rapidly absorbed on the particulate surface to avoid its reverse decomposition into SO2. This scavenging effect of SO2 is likely to be an essential factor which enhances SOx removal by PPCP in combustion gases. The active species dominant for DeSOx by PPCP is likely to be OH radical.

2.5 Effect of corona power, pulse frequency and gas residence time

The PPCP effect is determined by a parameter \((P/Q)/T_g^{1/2}\) where \(P = \) corona power, \(Q = \) gas flow rate, and \(T_g = \) gas residence time (Fig. 9) (5). At room temperature the PPCP effect is a linear function of pulse frequency, as shown in Fig. 10, while at an elevated temperature a deviation occurs from the straight line. A number of test data indicate that the pollutant concentration shows an exponential decay with the gas residence time and pulse frequency (Fig. 11) (4).

2.6 Effect of ammonia

Addition of ammonia produces a substantial improvement in the removal of NOx, while it has a much less effect on NO removal. NOx fast indicates a rise owing to NO oxidation, arriving at peak, and drops. This peak value is reduced to the half of that without ammonia addition at room temperature (5). However, at an elevated temperature this advantage of ammonia is lost, and the performance becomes deteriorated by ammonia addition in DeNOx. Its effect on DeSOx at an elevated temperature is not yet clear.

2.7 Effect of pulse rise time

The pulse rise time has a substantial effect on the performance of PPCP. Shorter the rise time the more the intensive and elongated are the pulsed streamers, and better is the PPCP performance. In the application of PPCP in a very large plant having a very large inter-electrode capacity, it is difficult to reduce the rise time below 500 - 1000 ns, even if the high frequency oscillation part of the pulse leading edge be used. The only way of overcoming this difficulty is to use the travelling wave mode, as described above.
2.8 Control of mercury vapour in combustion gas

The test made at an incineration plant for PPCP removal of Hg vapour from combustion gas indicated a drastic result (6). Within 2 seconds gas residence time mercury vapour with 0.5 mg/Nm³ (0.06 ppm) could be 100% converted into solid particulates (oxides and chlorides) in a wide range of gas temperature (30 - 300 deg.C) with a pulse frequency of 50 Hz. The mercury removal was enhanced by the addition of HCl or Cl₂. The larger residence time did not produce a substantial improve (at a reduced voltage), while lowering of residence time caused a substantial drop in performance. This tells that a certain quantity of radicals must be produced to fully oxidize Hg vapour, while beyond this quantity no improvement occurs. In other words, the reaction speed is likely to be very high.

3. FUNDAMENTAL MECHANISM OF PPCP

The mechanism is divided into electrical one and chemical one. The electrical one is that PPCP enables a highly non-equilibrium plasma with a high electron temperature and low ionic and molecular temperatures to occur under normal pressure, as described previously. This is a unique feature resulted by a sharp rising, narrow pulse high voltage applied to a corona system which has a strong electron source (corona electrode). The chemical mechanism is not yet fully understood, although a number of analysis have been presented (7, 8). It is certain that electrons having an adequately high energy (upper tail of Dryvestin distribution) would produce copious active species: O, O₂⁺, N, O₂⁻, OH⁻ radical, etc. Some of the theoretical calculations indicate reasonably good approximations of the test results, while others very different results.

4. CONCLUSION

The unique feature of PPCP for various applications under ordinary gas pressure is indicated with many examples. It is expected that PPCP would provide a new area of plasma chemical process in many applications.

REFERENCES