

Nonthermal Plasma Approach in Direct Methanol Synthesis from CH₄

Mamoru Okumoto, B. S. Rajanikanth, *Member, IEEE*, Shinji Katsura, *Member, IEEE*,
and Akira Mizuno, *Senior Member, IEEE*

Abstract—Direct methanol synthesis from CH₄ and O₂ has been experimentally studied using pulsed discharge plasma in concentric-cylinder-type reactors. The methanol production becomes efficient with an increase in the average electric field strength of the reactor. A combination of the pulsed discharge and catalysts was tested and was proved to be effective in increasing both the production and selectivity of methanol. In the present stage, about 2% of CH₄ can be converted into other hydrocarbons, and a methanol yield of around 0.5% and selectivity of 38% can be obtained when a catalyst of V₂O₅ + SiO₂ is combined with the pulsed discharge plasma.

Index Terms—Combined effect of plasma and catalyst, direct methanol synthesis, nonthermal plasma, plasma chemical reaction.

I. INTRODUCTION

CONVERSION of hydrocarbon fuels to methanol will promote their efficient utilization, since methanol can easily be converted to hydrogen using low-temperature heat energy, which would otherwise be disposed of [1]. The conventional chemical process for methanol synthesis from CO and H₂ requires high pressure and high temperature [2]. A plasma chemical process is a possible alternative to the conventional methanol synthesis, since chemical reactions can be promoted at lower pressure and temperature conditions. In flue gas cleaning or decomposition of volatile organic compounds, nonthermal plasma process has been widely investigated, and promising results have been obtained [3]–[6]. There are, however, a few reports on direct methanol synthesis using nonthermal discharge plasma. Okazaki *et al.* reported that methanol synthesis can be made from CH₄ and O₂ by pulsed discharge plasma [7]. Eliasson *et al.* reported the possibility of using silent discharge for hydrogenation of CO₂ to produce useful hydrocarbon components [8]. Hijikata *et al.* used glow discharge or spark discharge in reduced pressure condition and produced methanol from CH₄ and H₂O [9]. This experimental

result indicated an important advantage of nonthermal plasma process that can promote endothermic chemical reactions. Energy efficiency of methanol production in these previous works, however, was still insufficient to substitute the conventional method of methanol synthesis. Further studies are necessary to optimize the type of plasma and gas condition and to improve electrical power conversion efficiently and gas conditions. A combination of nonthermal plasma and catalyst might improve methanol production efficiency.

We investigated the methanol synthesis from CH₄ and O₂ using pulsed discharge plasma. In this paper, we present the performance evaluation carried out in regard to the choice of corona electrodes and pulse energizing circuit. In addition, the effect of concentration of reactants (CH₄ + O₂ mixtures) was studied. We also present the results of the combined effect of catalysts and electrical discharges on methanol synthesis.

II. EXPERIMENTAL SETUP

The corona reactor consists of an inner metal electrode and an outer electrode of aluminum foil wrapped around a glass tube. The glass tube eliminates sparking between the electrodes. Fast-rising high-voltage pulses were used in this experiment. Pulsed discharge takes place, which self extinguishes when surface charge builds up on the glass surface. In fast-rising pulsed discharges, high electric field can be established before the formation of space charge and electrons are driven, therefore, the contribution of electrical energy to plasma formation is considered essential [10].

In the present experiment, we tried four types of corona electrodes: straight wire reactor (SWR), barbed plate reactor (BPR), helical wire reactor (HWR), and metal tubular reactor (MTR). The SWR consists of the conventional straight wire as the corona electrode. The BPR assembly consists of a series of rows and columns of steel barbs (pins) fixed on a thin aluminum plate acting as the corona electrode. In the HWR, a helical wire forms the corona electrode. Finally, the MTR consists of a uniform hollow metal tube as the corona electrode.

Table I shows the average electric field strength of these reactors. These values are calculated by dividing the peak voltage by the discharge gap. Methanol production and power transfer efficiency are also tabulated. These values were measured with peak voltage of 25 kV, CH₄:O₂ = 94 : 6, room temperature, and gas residence time of 6.7 s. The power transfer efficiency was calculated as the discharge power (integration of power waveform) divided by the input power.

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M. Okumoto, S. Katsura, and A. Mizuno are with the Department of Ecological Engineering, Toyohashi University of Technology, Toyohashi, Aichi, 441-8580 Japan (e-mail: mizuno@eco.tut.ac.jp).

B. S. Rajanikanth is with the Department of High Voltage Engineering, Indian Institute of Science, Bangalore, 560012 India (e-mail: raj@hve.iisc.ernet.in).

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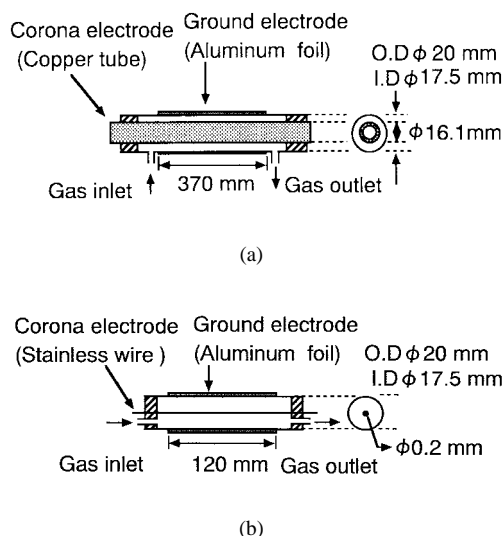


Fig. 1. Reactors used in the experiment. (a) MTR. (b) SWR.

TABLE I
PERFORMANCE EVALUATION OF CORONA REACTORS (APPLIED
VOLTAGE = 25 kV, CH₄:O₂ = 94 : 6, AT ROOM
TEMPERATURE AND ATMOSPHERIC PRESSURE)

Reactor	Average electric field [MV/m]	Methanol concentration [%]	Power transfer efficiency [%]
Straight wire	2.50	0.02	35.5
Barbed plate	2.78	0.08	36.6
Helical wire	4.99	0.12	24.5
Metal tubular	35.7	0.29	48.1

We selected the MTR because of its superior performance in regard to the other electrodes (E : 3.6×10^7 V/m).

Fig. 1(a) shows the schematic of the MTR. The uniform metal tubular reactor consists of a glass tube (OD: 20 mm, ID: 17.5 mm) with a large inner tubular corona electrode (OD: 16.1 mm, ID: 13.7 mm, copper). The discharge gap was 0.7 mm thick. The effective gas volume and length of the reactor were, respectively, 14 ml and 370 mm. The schematic of the SWR is shown in Fig. 1(b). Straight wire (diameter: 0.2 mm, stainless steel) was used for the inner electrode, instead of the tubular electrode of the MTR. The reaction volume and the length of the SWR were 27 ml and 120 mm, respectively.

Different types of electrical circuits were also investigated to achieve higher power transfer efficiency for the selected reactor. Fig. 2(a)–(d) shows the different circuits of the pulse generator using the rotary spark gap switch (RSG) that was used in the present study.

Maintaining a high charging capacitance of the order of 27 nF as shown in circuit 1 [Fig. 2(a)] reduces the ripple in the rectified dc output, but introduces a small dc component in the pulse output. However, the methanol production was high, owing to high power transfer efficiency.

Connecting a high resistance across the reactor as in circuit 2 [Fig. 2(b)] decreases not only the dc component in the pulse, but, also, the power delivered to the reactor.

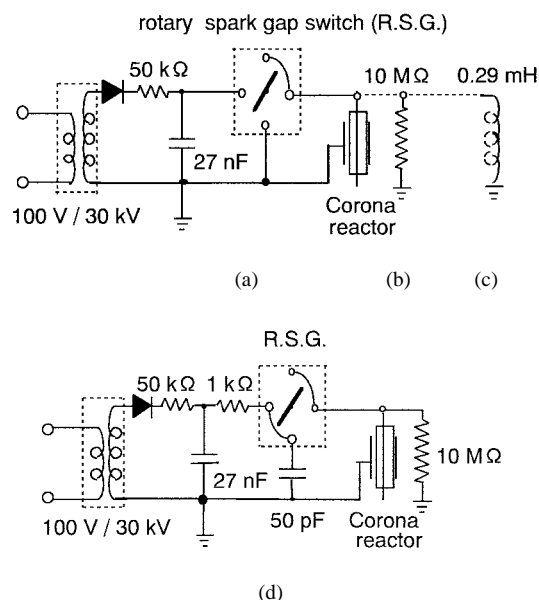


Fig. 2. Evaluation of different circuits.

TABLE II
POWER TRANSFER EFFICIENCY AND THE METHANOL PRODUCTION
(MTR, INPUT POWER = 7 W, CH₄:O₂ = 94 : 6, AT
ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE)

Circuit No.	Power transfer efficiency [%]	Methanol concentration [%]
Circuit 1	52.2	0.31
Circuit 2	42.7	0.19
Circuit 3	10.6	0.11
Circuit 4	10.7	0.01

Connecting a high inductance across the reactor as in circuit 3 [Fig. 2(c)] produces a slightly faster wave front compared to circuit 2. The total power consumption increases, but the power consumed in the reactor decreased, and the methanol production decreased.

Circuit 4 shows a combination of resistance and a capacitance as in Fig. 2(d). This circuit stabilizes the repetition rate of the pulses better than the previous circuits, but the pulse crest voltage decreases, thereby affecting the power transfer efficiency and decreasing the methanol production.

Table II shows the power transfer efficiency and the methanol production of the four circuits studied. The analysis was carried out using the MTR at a constant input power of 7 W. The pulse repetition rate was 250 Hz. The gas mixture was CH₄ + O₂ (94:6) at room temperature, with gas residence time of 6.7 s. As seen from the table, circuit 1 [Fig. 2(a)], without any additional R , L , or C , produces high methanol output (about 0.3%) with a maximum power transfer efficiency of 52.2%. It should be noted that a considerable amount of methanol can also be generated using circuit 2, which has the advantage of maintaining low dc component in the output voltage. Circuits 3 and 4 recorded low power transfer efficiency and, hence, can be discarded.

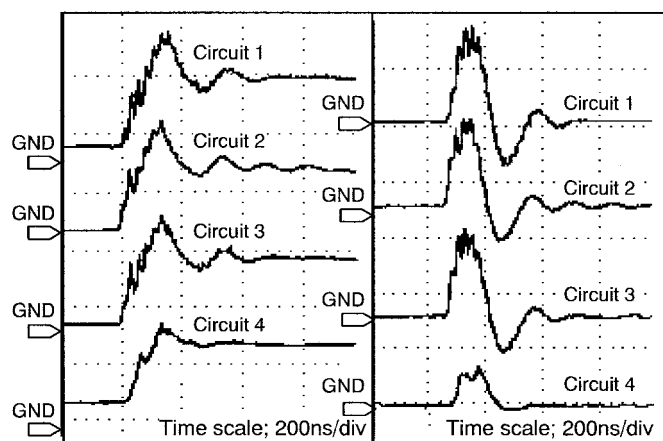


Fig. 3. Waveform of voltage and current for the four circuits studied (MTR, input power; 7 W, at room temperature and atmospheric pressure). (a) Voltage [10 kV/div]. (b) Current [50 A/div].

Fig. 3 shows the voltage and current waveforms of the four circuits.

Further studies on methanol synthesis were carried out using circuit 1. The pulse rise time was about 40 ns.

For measurement of voltage and current waveforms, a digital oscilloscope (Tektronix TDS644A), a voltage divider (Tektronix P6015A), and a current probe (Tektronix P6021) were used. The input power was measured by a digital power meter (YOKOGAWA 2534) inserted at the ac power input line. Analysis of the gas sample was carried out using gas chromatography (GC17A, Shimadzu, Column: G-Columun 950).

III. RESULTS AND DISCUSSION

Methanol synthesis was carried out under dynamic gas flow condition with $\text{CH}_4 + \text{O}_2$ gas mixture. CH_4 concentration was changed in a limited range from 94% to 98% to avoid explosion. The experiments were conducted at room temperature.

Fig. 4 shows the effect of residence time on methanol levels for the gas mixture studied. An overall high methanol production was observed at all gas residence times for a gas mixture ratio of 94:6. The maximum methanol concentration reached 0.5%.

Fig. 5 shows the variation of the power transfer efficiency as a function of the reactor input power. This result indicated that the efficiency was almost constant at all input powers for the $\text{CH}_4 + \text{O}_2$ mixture. Fig. 6 shows the voltage, current and power waveforms. In this case, the output voltage was maintained constant at 24 kV. The discharge power was calculated by integration of the power waveform and multiplied by the pulse frequency.

Fig. 7 shows the variation of the spark gap loss and the discharge power as a function of the input power. The spark gap loss was less than 1.5 W at any input power. The discharge power can be further improved by reducing the loss in the dc charging circuit.

An attempt was made to study the combined effect of catalysts and electrical discharges on methanol synthesis. An SWR was used. Four types of catalysts, $\text{WO}_3 + \text{SiO}_2$,

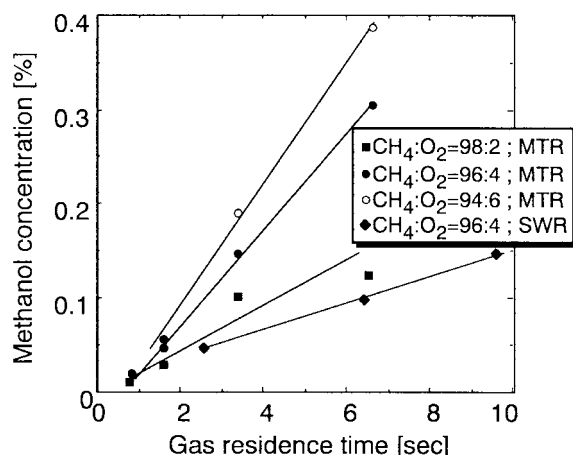


Fig. 4. Methanol synthesis with $\text{CH}_4 + \text{O}_2$ (input power = 7 W, at room temperature and atmospheric pressure).

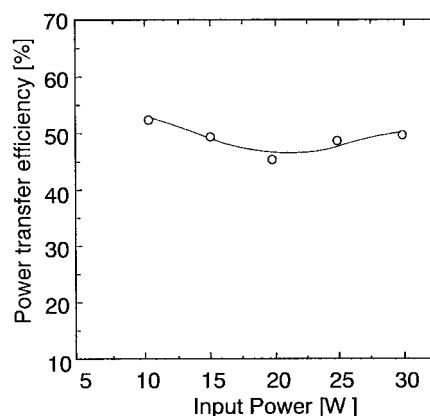


Fig. 5. Effect of input power on power transfer efficiency in circuit 1 (MTR, $\text{CH}_4:\text{O}_2 = 94 : 6$, at room temperature and atmospheric pressure).

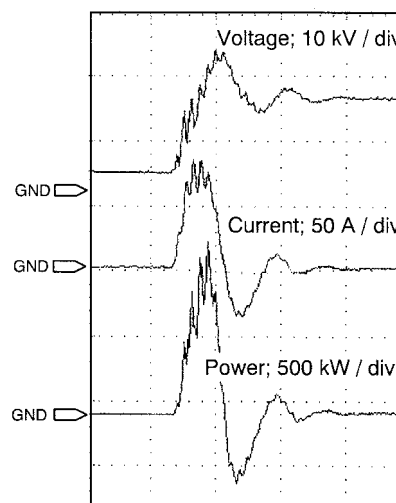


Fig. 6. Typical oscillograms of voltage, current, and power (MTR, applied voltage = 24 kV, $\text{CH}_4:\text{O}_2 = 96 : 4$, at room temperature and atmospheric pressure). Time scale: 200 ns/div.

$\text{MoO}_3 + \text{SiO}_2$, $\text{NiO} + \text{ZnO} + \text{CdO}$, and $\text{V}_2\text{O}_5 + \text{SiO}_2$, were subjected to the combined reaction. These catalysts were prepared by mixing with equal proportions of catalysts

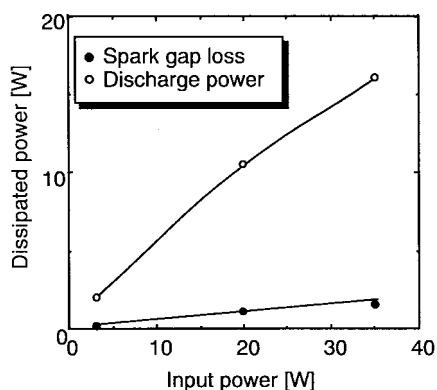


Fig. 7. Variation of dissipated power measured at different nodes in circuit 1 (MTR, CH₄:O₂ = 94 : 6, at room temperature and atmospheric pressure).

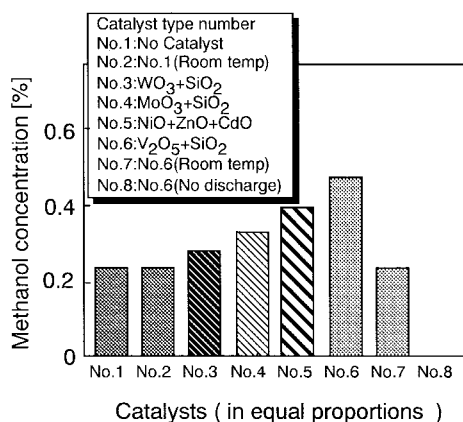


Fig. 8. Combined effect of catalysts and pulse discharge on methanol synthesis (SWR, CH₄:O₂ = 96 : 4, input power = 7 W, gas residence time = 11.2 s, 120 °C, atmospheric pressure).

component in powder form. Catalysts mixture ratio (wt. %) was 50:50 for WO₃ + SiO₂, MoO₃ + SiO₂, V₂O₅ + SiO₂, and 30:30:40 for NiO + ZnO + CdO. Total weight of catalysts was 1.5 g for all types of catalysts. The mixture was then applied uniformly over a thin glass-fiber tube in the form of slurry (mixed with water) and then dried at 120 °C overnight. The glass-fiber tube was inserted inside the reactor concentrically. The gas line (length: 1 m) and the reactor were placed inside a convection oven (TABAI LC222). The system was heated to 120 °C, and 30 min later, HV pulses were applied. We measured the gas temperature at the exit of the reactor.

Fig. 8 shows the comparison of methanol concentration with different catalysts. Experimental conditions were as follows: CH₄:O₂ = 94:6; gas residence time = 6.7 s; and the input power = 7 W. Fig. 9 corresponds to a typical GC output without catalyst. The chart indicated the presence of CH₃OH, C₂H₄, CH₃CHO, and C₂H₅OH. Table III shows the CH₄ conversion and the product selectivity for various catalyst combinations on methanol production. The selectivity was calculated using the area of gas chromatography and was the ratio of the area of a product and the total area of all products. A combination of these catalysts demonstrated both higher methanol production (Fig. 8) and higher selectivity

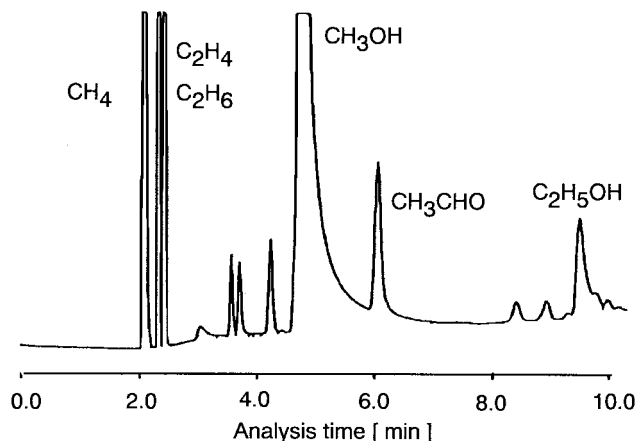


Fig. 9. Gas chromatography analysis of the products on methanol synthesis (MTR, CH₄:O₂ = 94 : 6, input power = 7 W, at room temperature and atmospheric pressure, GC-FID & G-column 950, Col. temp. = 70 °C).

TABLE III
EFFECT OF CATALYST ON THE METHANOL PRODUCTION AND THE SELECTIVITY (SWR, CH₄:O₂ = 94 : 6, INPUT POWER = 7 W, GAS RESIDENCE TIME = 11.2 S, ATMOSPHERIC PRESSURE)

Catalyst Type	Temp (°C)	CH ₄ Conv. [%]	Product selectivity [%]			
			CH ₃ OH	C ₂ H ₆	C ₂ H ₄	CH ₃ CHO
No Catalyst	25	1.24	30.0	31.5	31.0	2.50
	120	1.18	30.5	29.7	28.5	3.70
WO ₃ +SiO ₂	120	1.39	35.1	28.8	27.3	4.18
MoO ₃ +SiO ₂	120	1.65	29.3	24.9	23.9	3.60
NiO+ZnO+CdO	120	1.77	34.1	27.1	26.8	2.70
V ₂ O ₅ +SiO ₂	25	1.25	29.3	31.1	30.5	2.10
	120	1.99	37.9	26.5	24.2	3.37
(No Discharge)	120	-	-	-	-	-

(Table III). Conversion of CH₄ to other hydrocarbons was also enhanced with the use of catalysts. The catalyst of V₂O₅ + SiO₂ produced the highest methanol output of about 0.5%, selectivity of about 38%, and CH₄ conversion of 1.99%.

We also checked the effect of reaction temperature on the combined reaction of catalyst and plasma discharge using V₂O₅ + SiO₂. As shown in Fig. 8 (Type Nos. 7 and 8), no effect of catalyst was observed when the reaction temperature was shifted to room temperature. The behavior was different from those without catalysts, which demonstrated no temperature effect on methanol production (Type Nos. 1 and 2 in Fig. 8). Because ordinary catalytic reaction proceeds above 300 °C, this result suggests that the production of methanol attributed to surface reaction of the catalysts is promoted by discharge plasma. Even though the promotion effects of catalysts were observed, the fundamental mechanism and characterization of function of catalysts are still unknown and, therefore, further investigations are necessary.

IV. CONCLUSION

Relative performance analysis of the reactors using pulsed discharge plasma strongly indicates the dependence of methanol production on the average electric field. The power

transfer efficiency can also be improved at higher electric field. A higher charging capacitance increases both the power transfer efficiency and methanol production.

The combination of catalysts and pulsed discharge plasma is effective in increasing the methanol yield and selectivity for CH_4 and O_2 . The catalyst combination of $\text{V}_2\text{O}_5 + \text{SiO}_2$ yielded the highest methanol output (ca. 0.5%), selectivity (ca. 38%), and CH_4 conversion (ca. 2%) from $\text{CH}_4 + \text{O}_2$, for the range of catalysts studied.

The present value of methanol yield of the plasma process seems very low compared to that of the commercial synthetic process. However, this yield value was obtained in the one-pass process. Considering that a methanol yield of a few percent is required in one-pass in commercial plants, the present yield by the plasma process is not too low. The nonthermal plasma process can possibly be comparable when the process is further improved to give a two to three times higher yield value.

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REFERENCES

- [1] K. Hijikata, "Total energy system in the future," in *Proc. IEA Int. Conf. Technology Responses to Global Environmental Challenges*, 1991, pp. 359–370.
- [2] T. Inui and T. Takeguchi, "Effective conversion of carbon dioxide and hydrogen to hydrocarbons," *Catalysis Today*, vol. 10, no. 1, pp. 95–106, 1991.
- [3] A. Mizuno, A. Chakrabarti, and K. Okazaki, "Application of corona technology in the reduction of greenhouse gases and other gaseous pollutants," in *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Series, vol. 34, pt. B. Berlin, Germany: Springer-Verlag, 1992, pp. 167–185.
- [4] K. Fujii, M. Sugaya, R. Tsuji, Y. Yokosawa, and M. Higashi, "Plasma creation for efficient NOx reductions in exhaust gas from a diesel engine," in *Proc. 8th Int. Symp. Plasma Chemistry*, 1987, pp. 840–844.
- [5] T. Yamamoto, K. Ramanathan, P. A. Lawless, D. S. Ensor, and J. R. Newsome, "Control of volatile organic compounds by an AC energized ferroelectric pellet reactor and a pulsed corona reactor," in *Conf. Rec. IEEE-IAS Annu. Meeting*, 1989, pp. 2175–2179.
- [6] T. Oda, R. Yamashita, T. Takahashi, and S. Masuda, "Products analysis of low temperature surface discharge plasma processing of gaseous organic compounds by using GC-MS," in *Conf. Rec. IEEE-IAS Annu. Meeting*, 1994, pp. 1563–1569.
- [7] K. Okazaki, S. Nishimura, A. Mizuno, and K. Hijikata, "Direct conversion of methane to methanol by a pulsed silent discharge," presented at the 29th Symp. Heat Transfer, Osaka, Japan, 1992.
- [8] B. Eliasson, F. G. Simon, and W. Egli, "Hydrogenation of CO_2 in a silent discharge," in *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Series, vol. 34, pt. B. Berlin, Germany: Springer-Verlag, 1992, pp. 321–337.
- [9] K. Hijikata, "Reforming of CH_4 to CH_3OH by corona-discharge, principle of exergy reproduction," Ministry of Education, Japan, Abstracts of Research Project 256, 1995, p. 4.
- [10] S. Masuda and H. Nakao, "Control of NOx by positive and negative pulsed corona discharges," *IEEE Trans. Ind. Applicat.*, vol. 26, pp. 374–383, Mar./Apr. 1990.



Mamoru Okumoto was born in Tokushima, Japan, in 1972. He received the B.S. and M.S. degrees in electrical engineering in 1995 and 1998, respectively, from Toyohashi University of Technology, Toyohashi, Aichi, Japan, where he is currently working towards the Ph.D. degree in environmental engineering.

He is involved in research on nonthermal pulsed plasma chemical reaction for reforming hydrocarbon fuels and the combined effect of plasma discharge and catalysts.



B. S. Rajanikanth (S'89–M'89) was born in Bangalore, India, in 1965. He received the B.E. degree in electrical engineering from Bangalore University, Bangalore, India, in 1987 and the M.S. and Ph.D. degrees in high voltage engineering from the Indian Institute of Science, Bangalore, India, in 1990 and 1993, respectively.

He was a Post-Doctoral Research Fellow at Toyohashi University of Technology, Toyohashi, Aichi, Japan, from October 1994 to March 1996. He then joined Kirloskar Systems Limited, Bangalore, India, where he was the Head of the Research and Development Department. He was a Visiting Researcher at Tokyo Metropolitan University from October 1996 to December 1996. He is currently an Associate Professor in the Department of High Voltage Engineering, Indian Institute of Science, Bangalore, India. His research interests include electrostatics applications and corona physics.



Shinji Katsura (M'97) was born in Shizuoka, Japan, in 1962. He received the B.S. degree from the Department of Electronic Engineering, Mie University, Tsu, Japan, in 1984 and the M.S. and Ph.D. degrees from the University of Tokyo, Tokyo, Japan, in 1986 and 1993, respectively, both in chemical engineering.

He worked under a Post-Doctoral Fellowship at the Institute of Physical and Chemical Research (RIKEN), Japan, where he was engaged in a human genome research project. Since October 1993, he has been with Toyohashi University of Technology, Toyohashi, Aichi, Japan, where he is currently an Associate Professor in the Department of Ecological Engineering. He is currently involved in research on the application of micromanipulations of single DNA molecules in human genome analysis and the combination of discharge plasma with catalysis.



Akira Mizuno (M'84–SM'97) was born in Aichi, Japan, in 1951. He received the B.S. degree from Nagoya University, Nagoya, Japan, in 1973 and the M.S. and Ph.D. degrees from the University of Tokyo, Tokyo, Japan, in 1975 and 1978, respectively, all in electrical engineering.

He was with Ishikawajima-Harima Heavy Industries Company, Ltd. during 1978–1981. Since April 1981, he has been with Toyohashi University of Technology, Toyohashi, Aichi, Japan, where he is currently a Professor of Ecological Engineering. He is involved in research on applied electrostatics and high-voltage engineering. From December 1982 to April 1984, he was a Visiting Research Fellow in the Department of Physics, Florida State University, Tallahassee, where he was engaged in a project involving electron beam charging and precipitation of aerosols and industrial dusts.