Liquid phase fuel reforming at room temperature using non-thermal plasma

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Introduction

Hydrocarbon fuel reforming is a very important technology for a variety of applications. For example in cracking process, it is necessary to get various useful hydrocarbon gases and oils. Hydrogen manufacturing from hydrocarbon fuels is also important and could be used for many applications. These applications introduced the fuel cells used in stationary electric power production and in vehicular propulsion, such as refueling stations for hydrogen-powered vehicles. Hydrogen manufacturing is also needed for many industrial applications. Many catalytic methods were investigated for fuel reforming to get the gas phase hydrocarbons and H_2. However, almost catalysts are composed by valuable metals and materials. Then, catalytic methods require high temperature, around 300°C to 800°C to get the activation for reforming.

Recently, a novel technology of plasma and catalytic processes were studied by many researchers for hydrocarbon reforming[1-3]. In this study, a new type of plasma reactor was investigated for fuel reforming at room temperature. Positive square pulsed high voltage generates strong plasma in the oils. We expected that liquid oil change to gas and solid.

Experimental setup and procedure

Plasma reactor and a power source. Liquid phase plasma reactor consists of a plastic column vessel, metal plate as both, high voltage and ground electrodes and metal chips. Aluminum or copper plates and chips were investigated as the electrodes. Reactor was filled with 100ml of iso-octane or diesel oil. A magnetic stirrer and a stirring bar to stirr the oil and metal chips were placed into the reactor. Spark plasma, including light and heat, was generated by the high voltage in many points of contact between the metal electrodes and chips. It was a spark discharge including light and shock wave.

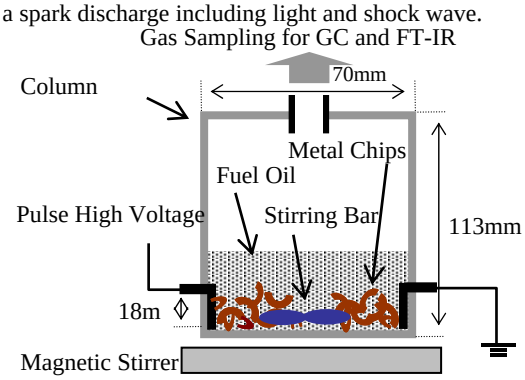


Figure1 Liquid phase plasma reaction

The plasma reactor was driven by positive pulsed square high voltage generated by a rotary spark gap (RSG) switch. The rise time of the pulsed voltage was about 40nsec, and the repetition frequency of the pulse was set at 240Hz. The high voltage applied was about 10kV peak to peak. During the rising time, spark discharges are produced and few amperes of current are flow to reform the hydrocarbon fuels.

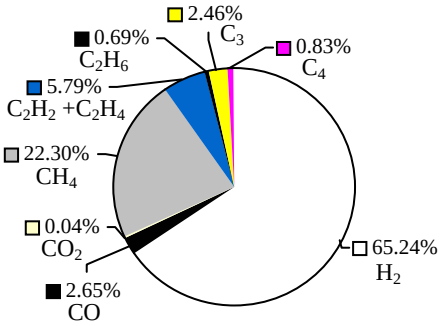
Characterization Methods. Much gas and black powder were generated from the oil during plasma operation. H_2, N_2, O_2, CO, CO_2 and many low molecular hydrocarbons were detected and analyzed by GC-FID(Shimazu 14B) equipped with a metanizer(GL Science MT-21), GC-TCD(Shimazu 8A) and FT-IR(Bio-rad FTS3000). The black power was inspected using E-SEM and analyzed by XRD after evaporation of liquid oils.

For the E-SEM and XRD analysis, samples were prepared as follows: carbon powder deposited on the bottom of the reactor was taken, with a pipette, filtered with a quartz fiber filter (Whatman QM-A) and dried during 6h in an oven at 200°C.

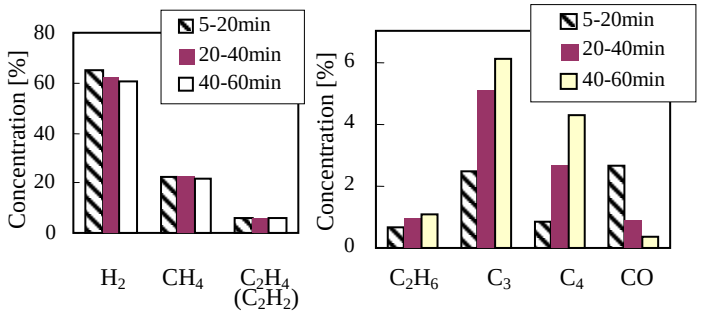
Results and Discussion

The reforming process of iso-octane and diesel oil was investigated using plasma reactor at room temperature, in this study.

The generated gas compounds from iso-octane from 5 to 20 minutes are shown in Fig1 (A). Generation of gases was in the following order to H_2> CH_4 >> C_2H_4 >> CO, C_2H_6, C_3, C_4. More than 60% of H_2 gas was generated during high voltage application. Focusing the H_2 and CH_4, 86% of selectivity (H_2+CH_4) was obtained from the gas generate in this case. Fig.1 (B) shows the time elapse change of the gas compounds. The H_2 and CH_4 concentrations gradually decreased with the increment of CO_2 and CO concentrations in this case. Proportionally, the C_2H_6, C_3, and C_4 hydrocarbons gradually increased with time. On the other hand, black powder was rapidly obtained in the liquid phase when starting at high voltages, and this powder also increased with the time. After the plasma application, the temperature of the liquid iso-octane was increased at around 55°C to 65°C



(A) Generation of gas compounds from iso-Octane (5-20min)



(B) Time elapse change of gas compounds from iso-octane

Figure2 Gas compounds generation and time elapse change from liquid phase iso-octane using liquid phase plasma reactor

After the experiments, the surface of both electrodes and the aluminum chips had many black points. These aluminum chips did not have such points before the experiment. Moreover almost all chips decreased their size losing their edges. E-SEM (E-SEM-2700) photograph show aluminum particles around sub-micro meter to several ten micro-meter in diameter. Aluminum and carbon were detected by X-ray micro analyzer (HORIBA EDX). On the other hand, a large aluminum peak was obtained from XRD (RINT 2500) measurements. These results indicated that iso-octane was reformed to gas and solid by high voltage application through electrodes and contact points of aluminum chips. At the same time, aluminum electrodes and chips were melted by the heat generated by the shock wave with spark discharge.

Gas generation rate using plasma reactor with aluminum chips is shown in Fig.3. The total gas flow rate included H_2, CH_4 and other hydrocarbons obtained were 17ml/min and 80ml/min for an applied power of 10W and 32W respectively. In this case, H_2 gas was flowed at 11ml/min and 52ml/min with an energy efficiency of 8.6g/kWh. Gas generated rates were proportional to the input energy in this case.

On the other hand, electrolysis has about 20g/kWh of energy efficiency to get H_2 from water[1][4]. Almost catalytic methods could get very large amount of H_2 compared with the electrolytic method and this method. However, catalysts need a very high temperature of more than 400°C to get high concentration of H_2 gas. Liquid plasma method and electrolysis also could be driven at room temperature. Moreover, plasma method has the possibility of fuel cracking control, producing the various carbon compounds and other many reactions. Focusing only in H_2 generation for industrial application, it requires large amount of H_2 generation efficiency. We must explore the catalytic reactions by combination of plasma and catalysts.

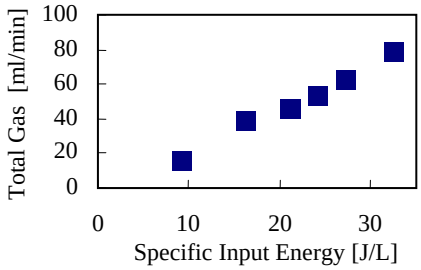


Figure3 Gas generation rate using plasma reactor with aluminum chips

Reforming of diesel oil was also investigated in this study. Fig.4 shows the gas compounds generation and the time-elapse change using the liquid phase plasma reactor. Comparing Fig.4 with Fig.2, it is clearly different the amount of N_2 and O_2 formed during the first 20 minutes as it is shown in Fig.4 (a). On the other hand, N_2 and O_2 disappeared during the next 20min as it is shown in Fig.4 (b). It can be suggested that N_2 and O_2 gas were already present into the diesel oil, and they were rapidly derived to the gas phase when plasma was applied. The amount of gases generated were in the following order: H_2> C_2H_4 >> CH_4 >> CO, C_2H_6, C_3, C_4 in the case of (b). Ethylene selectivity is very high compared with the iso-octane case.

Fig.5 shows the XRD pattern of black powder from diesel oil using three types of metal chips and electrodes. Type I using aluminum electrodes and chips, type II using copper, and type III using a mixture of aluminum (2g) and copper (9g) chips.

When using aluminum chips, aluminum peaks and Al_4C_3 peaks were obtained. Only when using copper chips, its corresponding peaks appeared. When using aluminum and copper chips mixed type their corresponding peaks appeared. However, many small peaks also appeared for the copper-aluminum mixed type, which seems to be sulfur and copper compounds (CuS_2 or Cu_8S_5). These results suggested that plasma might transform some compounds into solid crystals in the diesel oil, indicating this, a way for the removal of compounds by plasma treatment at low temperature.

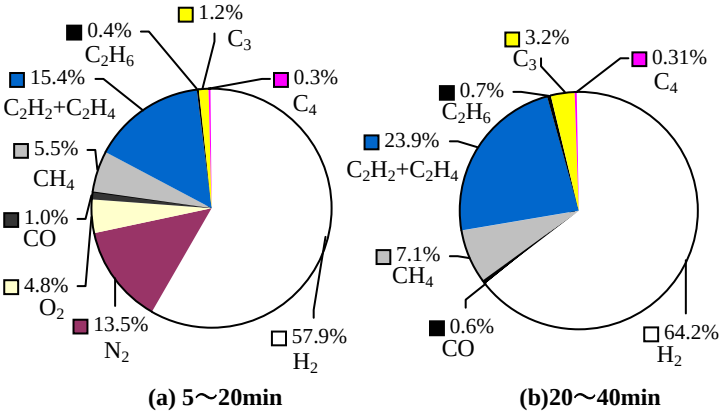


Figure4 Gas compounds generation and time elapse change from diesel oil using liquid phase plasma reactor

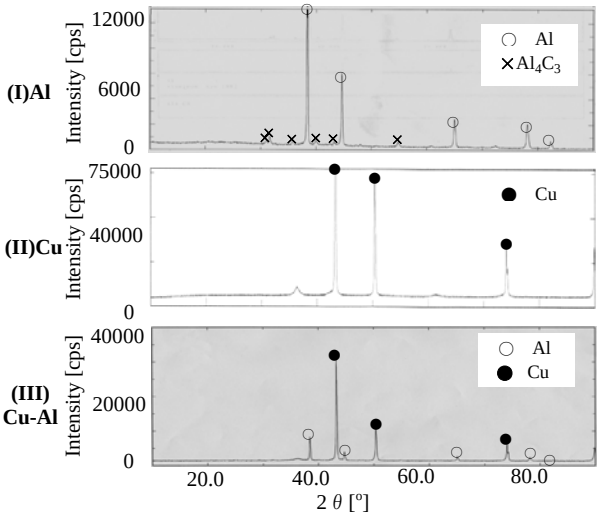


Figure5 XRD patterns of black carbon powder using aluminum, copper and aluminum-capper mixed metallic fragments

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