

# A PRELIMINARY INVESTIGATION OF SYNGAS AND TAR PRODUCTION BY OXIDATIVE PYROLYSIS OF POLYPROPYLENE WITH ELECTRON INJECTION

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## ABSTRACT

This study reports the component of syngas and tar produced from oxidative pyrolysis of polypropylene with electron-injected air using a laboratory-scale reactor. This experiment was conducted using a cylindrical fixed bed reactor. The feedstock tested in this study was polypropylene. During experiments, the feedstock was heated by an electric heater to 500, 600, and 700°C with or without electron injection into the air. Under all experimental conditions, oxidative pyrolysis occurred immediately after the start of the test. The analysis results of syngas and tar samples show no significant effects of electron injection at 500°C while significant effects were observed at 600°C and 700°C. Electron injection gave a clear impact on syngas and tar production during the oxidative pyrolysis of polypropylene.

**Keywords:** pyrolysis, oxidative pyrolysis, incomplete combustion, polypropylene

## 1. INTRODUCTION

The production of polypropylene (hereinafter called "PP") reached over 100,000,000t in 2016 in the world and PP applications have been expanded more and more [1]. On the other hand, the growing generation of waste PP in proportion to PP production has attracted great concerns in terms of waste management and environmental pollution. In this context, the conversion of waste PP into the gaseous, liquid, and/or solid fuels by some thermal techniques like pyrolysis, gasification, and hydrothermal carbonization is promising not only to reduce waste PP disposal but also to save fossil fuel consumption<sup>[2-5]</sup>. Tar produced from the thermal decomposition of PP is a problem for clean syngas production. So, removal, decomposition, and/or cracking of tar are usually necessary. Recently, effective

reforming of tar-containing artificial syngas using plasma-assisted oxidative steam<sup>[6]</sup> and enhancement of syngas production using electron injection<sup>[7]</sup> were reported. In this study, the authors investigated the effects of electron injection into the air on the oxidative pyrolysis of PP in regards to the syngas production and tar generation.

## 2. MATERIAL AND METHODS

### 2.1 Material

In this study, river sand was used as a supporting material of the fixed bed reactor and the feedstock was PP manufactured by Japan Polypropylene Corporation (NOVATEC-PP, BC03C).

### 2.2 Experimental methods and conditions

The schematic diagram of the experimental equipment is shown in Fig.1. An electron generator that was used in this experiment was ITM-F201 device, produced by Andes Electric Company Japan.

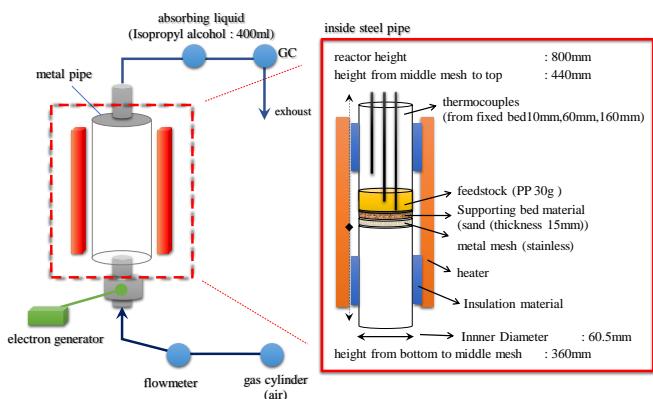


Fig.1 Schematic diagram of the experimental equipment

Electron was injected into the air using one or ten electron generators before the air was supplied into the reactor. When an electron was not injected, only air was supplied. Experimental conditions are summarized in Table 1.

Table 1 Experimental conditions

| Case                         | 1       | 2      | 3        | 4       | 5      | 6        | 7       | 8      | 9        |
|------------------------------|---------|--------|----------|---------|--------|----------|---------|--------|----------|
| experiment ID                | 500 OFF | 500 ON | 500 ON10 | 600 OFF | 600 ON | 600 ON10 | 700 OFF | 700 ON | 700 ON10 |
| number of electron generator | 0       | 1      | 10       | 0       | 1      | 10       | 0       | 1      | 10       |
| temperature °C               | 500     |        |          | 600     |        |          | 700     |        |          |
| feed stock                   |         |        |          | PP      |        |          |         |        |          |
| feed stock weight g          |         |        |          | 30      |        |          |         |        |          |
| air flow rate L/min          |         |        |          | 0.100   |        |          |         |        |          |

The reactor was heated to the target temperature (500, 600, or 700 °C) and then the feedstock was thrown into the reactor. The experiment ID was defined by “temperature + number of electron generators.” For example, 500OFF, 500ON, and 500ON10 indicate that the temperature was 500°C without electron injection, the temperature was 500 °C with the usage of 1 electron generator, and the temperature was 500 °C with the usage of 10 electron generators, respectively.

The air was fed from the bottom of the reactor at the flow rate of 0.100 L/min, which was insufficient for complete combustion within 400 minutes. Therefore, PP was thermally decomposed by oxidative pyrolysis in this study. During the experiments, tar in the syngas was collected by impinger bottles filled with 400 ml isopropyl alcohol (IPA) and cooled in an ice bath. The syngas composition was measured by GC (490 Micro GC System, United State) after tar collection. The weight of tar in the syngas was calculated by measuring the weight of IPA before and after the experiments. The repetition number of experiments was the same at the reaction temperatures of 500°C and 600°C; 3 times for OFF, one time for ON, and 3 times for ON10. While at the reaction temperature of 700°C; 5 times for OFF, one time for ON, and 5 times for ON10.

### 2.3 Characterization of products

In this study, syngas composition ( $H_2$ ,  $O_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ , and  $C_3H_8$ ) was measured continuously. The tar collected from the syngas was analyzed by the gas chromatography-mass spectroscopy (GCMS-QP2020 NX, Japan) equipped with a capillary column (SH-Rxi-5 Sil MS, length: 30 m, internal diameter: 250  $\mu m$ , film-thickness: 0.25  $\mu m$ ).

## 3. RESULTS AND DISCUSSIONS

### 3.1 Results

#### 3.1.1. Syngas composition

The time change of the concentration of oxygen in the syngas is shown in Fig. 2. The oxygen concentration decreased to less than 1% within at least 10 minutes from the start of the experiment.

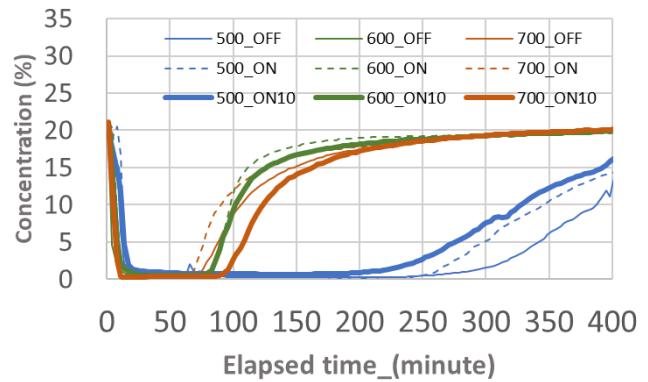


Fig. 2 Concentration of oxygen in the syngas

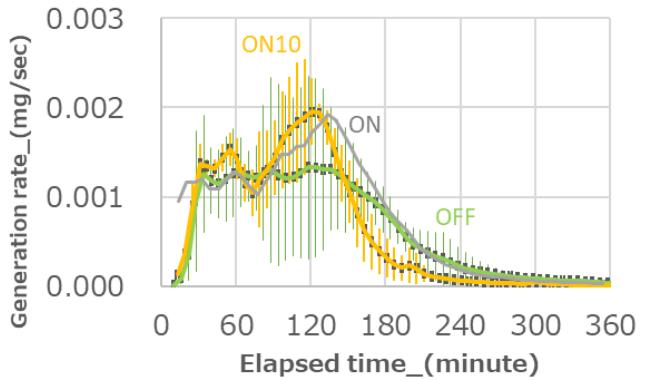


Fig. 3 Generation rate of  $H_2$  at 500°C

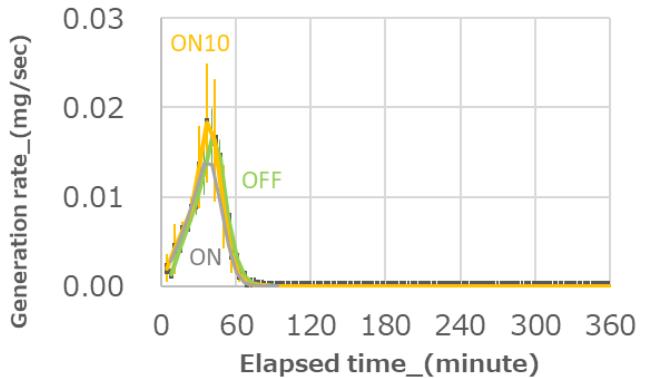


Fig. 4 Generation rate of  $H_2$  at 600°C

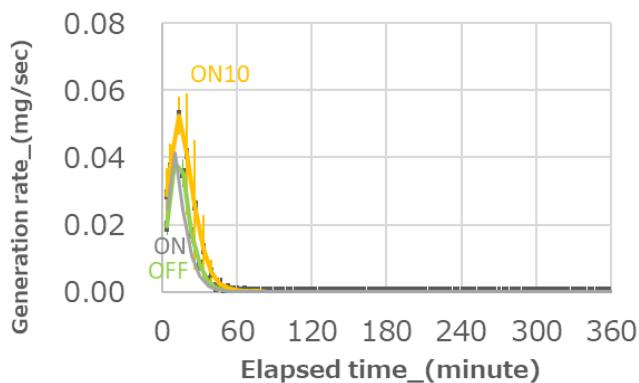


Fig.5 Generation rate of  $\text{H}_2$  at 700°C

Thereafter, the reaction proceeded under the oxygen-depleted condition for at least 80 minutes at all temperature conditions. The time changes of the production rate of  $\text{H}_2$  calculated from its concentration and the  $\text{N}_2$  concentration as well as the  $\text{N}_2$  flow rate at 500°C, 600°C, and 700°C are shown in Figs.3-5, respectively. No significant difference was observed among the cases of OFF, ON and ON10 at 500°C and 600°C. On the other hand, at 700°C, the reaction was enhanced in the case of ON10.

### 3.1.2. Tar

Table 2 shows the collected tar weights in the cases of OFF and ON10. The experiments were repeated three-times, three-times, and five-times at 500°C, 600°C, and 700°C, respectively. At each temperature, the average tar weights in the case of OFF were larger than in the case of ON10. However, as shown in this table, there were no statistically significant differences between the two cases, so additional experiments are needed.

Table 2 Tar concentration in the exhaust gas

|                            | 500<br>OFF   | 500<br>ON10                                   | 600<br>OFF                                     | 600<br>ON10                                   | 700<br>OFF                                     | 700<br>ON10                                    |
|----------------------------|--|---|--|---|--|--|
| 1                          | 85 g/Nm <sup>3</sup>                                   | 134 g/Nm <sup>3</sup>                         | 413 g/Nm <sup>3</sup>                          | 174 g/Nm <sup>3</sup>                         | 472 g/Nm <sup>3</sup>                          | 308 g/Nm <sup>3</sup>                          |
| 2                          | 215 g/Nm <sup>3</sup>                                  | 76 g/Nm <sup>3</sup>                          | 222 g/Nm <sup>3</sup>                          | 176 g/Nm <sup>3</sup>                         | 340 g/Nm <sup>3</sup>                          | 243 g/Nm <sup>3</sup>                          |
| 3                          | 64 g/Nm <sup>3</sup>                                   | 114 g/Nm <sup>3</sup>                         | 192 g/Nm <sup>3</sup>                          | 100 g/Nm <sup>3</sup>                         | 325 g/Nm <sup>3</sup>                          | 197 g/Nm <sup>3</sup>                          |
| 4                          | -  | -   | -  | -   | 209 g/Nm <sup>3</sup>                          | 224 g/Nm <sup>3</sup>                          |
| 5                          | -  | -   | -  | -   | 198 g/Nm <sup>3</sup>                          | 135 g/Nm <sup>3</sup>                          |
| Average                    | 121 g/Nm <sup>3</sup>                                  | 108 g/Nm <sup>3</sup>                         | 276 g/Nm <sup>3</sup>                          | 150 g/Nm <sup>3</sup>                         | 309 g/Nm <sup>3</sup>                          | 221 g/Nm <sup>3</sup>                          |
| Unbiased dispersion        | 6,719  | 854   | 14,360   | 1,897   | 12,569   | 3,973  |
| Standard error             | 25.9   | 9.2   | 37.9   | 13.8  | 35.5   | 19.9   |
| t                          | 4.30   | 4.30  | 4.30   | 4.30  | 2.78   | 2.78   |
| Error of the mean          | 111.5  | 39.8  | 163.0  | 59.3  | 98.4   | 55.3   |
| Confidence interval (95% ) | max 233 g/Nm <sup>3</sup><br>mini 10 g/Nm <sup>3</sup> | 148 g/Nm <sup>3</sup><br>68 g/Nm <sup>3</sup> | 439 g/Nm <sup>3</sup><br>113 g/Nm <sup>3</sup> | 209 g/Nm <sup>3</sup><br>91 g/Nm <sup>3</sup> | 407 g/Nm <sup>3</sup><br>211 g/Nm <sup>3</sup> | 277 g/Nm <sup>3</sup><br>166 g/Nm <sup>3</sup> |

Figs.6 and 7 show the GC-MS chromatograms of tar collected in the cases of 500OFF and 500ON10, respectively.



Fig.6 GC-MS chromatogram of collected tar (500OFF)



Fig.7 GC-MS chromatogram of collected tar (500ON10)

From Figs.6 and 7, we can see that the peak of propane,1,1'-[ethylidenebis(oxy)]bis- is higher in the case of ON10 than in the case of OFF but there are no significant differences in other peaks at 500°C. On the other hand, as shown in Figs.8-11, significant differences can be observed between OFF and 10ON cases at 600°C and 700°C. At these reaction temperatures, when electrons were injected, the number and the height of peaks in the chromatogram are smaller than those without electron injection. For example, clear peaks of 3-Hexadecene ( $\text{C}_{16}\text{H}_{32}$ ), 3,7,11-Trimethyl-1-dodecanol ( $\text{C}_{15}\text{H}_{32}\text{O}$ ), Oxalic acid, cyclohexyl tetradecyl ester ( $\text{C}_{22}\text{H}_{40}\text{O}_4$ ), 2-Isopropyl-5-methyl-1-heptanol ( $\text{C}_{11}\text{H}_{24}\text{O}$ ), 1,22-Docosanediol ( $\text{C}_{22}\text{H}_{46}\text{O}_2$ ), 2-Hexyl-1-decanol ( $\text{C}_{16}\text{H}_{34}\text{O}$ ) can be found without electron injection. These peaks are much higher than in the case of ON10.

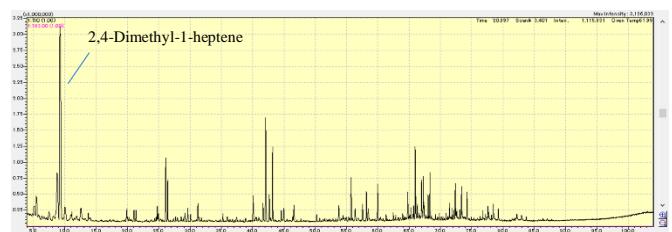


Fig.8 GC-MS chromatogram of collected tar (600OFF)

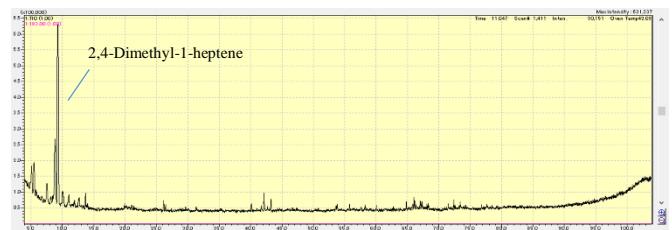


Fig.9 GC-MS chromatogram of collected tar (600ON10)

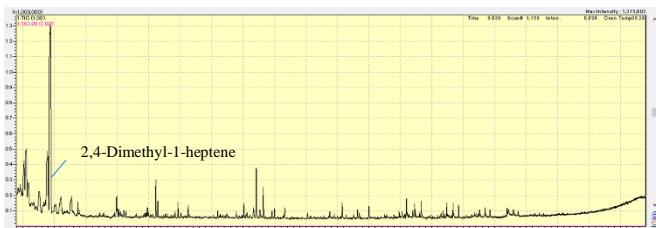


Fig.10 GC-MS chromatogram of collected tar (700OFF)

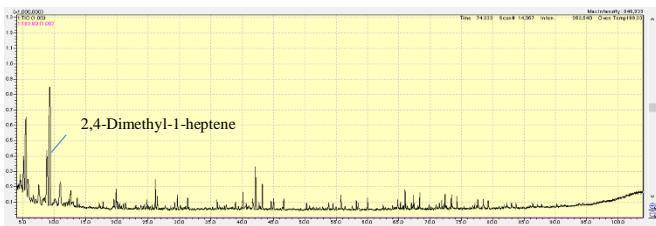


Fig.11 GC-MS chromatogram of collected tar (700ON10)

### 3.2 Discussions

In this study, no significant effects of electron injection were observed at the reaction temperature of 500°C. Tamer et al. reported that there was no significant effect of electron injection on the composition of the syngas when polyethylene was pyrolyzed alone at 500°C<sup>[7]</sup>, which is consistent with the present results. On the other hand, the gas production rate was enhanced and tar production was suppressed by increasing the amount of electron injected at 600°C and 700°C. At these reaction temperatures, it is considered that electron injection promoted the decomposition of tar into gas components. According to Ref.7, the injected electrons collide with the pyrolysis gas in the pyrolysis zone generating secondary electrons. These secondary electrons produce ions and radicals which accelerate the decomposition of tar.

### 4. CONCLUSIONS

Polypropylene was thermally decomposed at 500°C, 600°C, and 700°C under the oxidative pyrolysis condition with/without electron injection. At 500°C, no significant effects of electron injection were observed. On the other hand, at 600°C and 700°C, the gas production rate was enhanced and tar production was suppressed by increasing the amount of electron injected. It was suggested that electron injection promotes the oxidative pyrolysis reaction.

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