

Two-Stage Thermal Gasification of Plastics

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Plastic pellets of polyethylene (PE), polypropylene (PP), and polystyrene (PS) have been gasified by the two-stage thermal degradation process. The first stage is liquefaction of plastics and the second one is gasification of the liquid hydrocarbons produced by the first stage. The total gas yields of PE, PP, and PS were 80, 74, and 6.2 wt% each at 800°C. The main components of the product gas for PE and PP were methane and gaseous olefins such as ethylene and propylene. The formation of carbonaceous residue or coke was very low less than 1wt%. The two-stage pyrolyses of plastics efficiently produce high calorie gas with low coke ratio and produce some aromatic oils including benzene, toluene and xylene as main components.

Introduction

In recent years, recycling of waste plastic is thought to be important and many studies of feed stock recycling have been reported. There have been many studies of liquefaction however few studies have been made for gasification of plastics.

As one of the studies for gasification of plastics, a partial combustion method in a fluidized bed has been developed by Tomita et al. [1]. This method of heating by internal combustion is simple and has high thermal efficiency. However the calorific value of produced gas is relatively low because nitrogen in the combustion air and carbon dioxide mix with product gas. As an example of thermal decomposition by external heating, Sawaguchi et al.[2] studied high temperature thermal gasification of plastics in a fixed bed packed with Raschig rings. They reported that the maximum total gas yields were 75wt% for PE and 65% for PP whereas the carbon deposit increased up to 20-30wt% with increasing temperature.

In the present study, two-stage pyrolytic gasification process by external heating has been developed to improve the quality of gaseous products and the efficiency of gasification. The gasification of waste plastics will expand many other wide possibilities of reuse such as fuels for gas turbines or recycling to monomers as raw material for plastics.

Concept of the two-stage pyrolytic gasification

Fig.1 shows a conceptual diagram of the two-stage pyrolytic gasification of plastics. The first stage is the conversion of plastics to liquid products at relatively low temperature and the second one is the high temperature gasification of the liquid hydrocarbons produced by the first stage. By dividing the process into two stages and by gasifying the distilled oil of the first stage, coking is remarkably reduced compared to single-stage gasification of plastics.

Experimental

Fig.2 shows a schematic diagram of the experimental apparatus for the pyrolytic liquefaction. The principal part was Pyrex glass tube reactor (27mm i.d. and 280mm length)

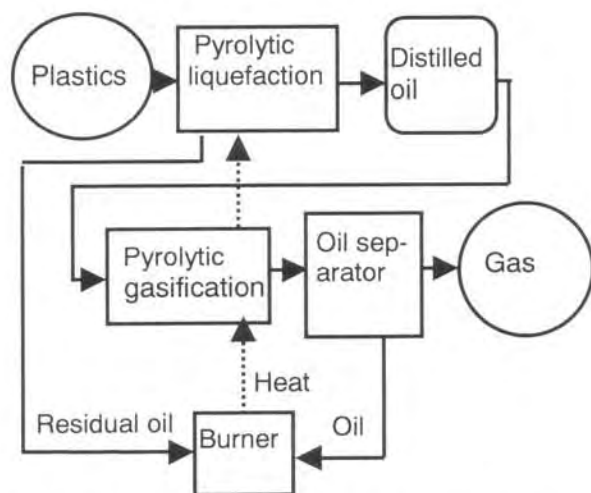


Fig.1 Concept of the two-stage pyrolytic gasification of plastics

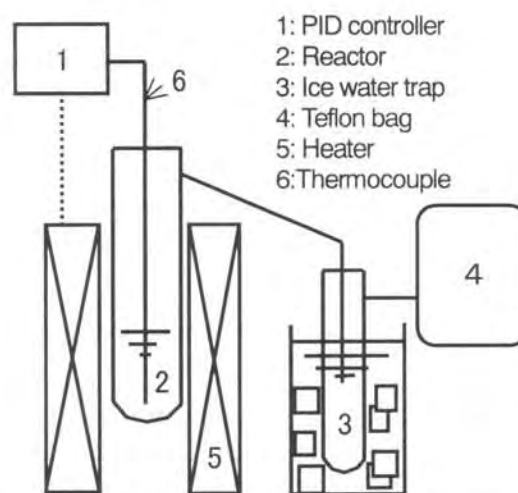


Fig.2 Schematic diagram of the experimental apparatus for the pyrolytic liquefaction

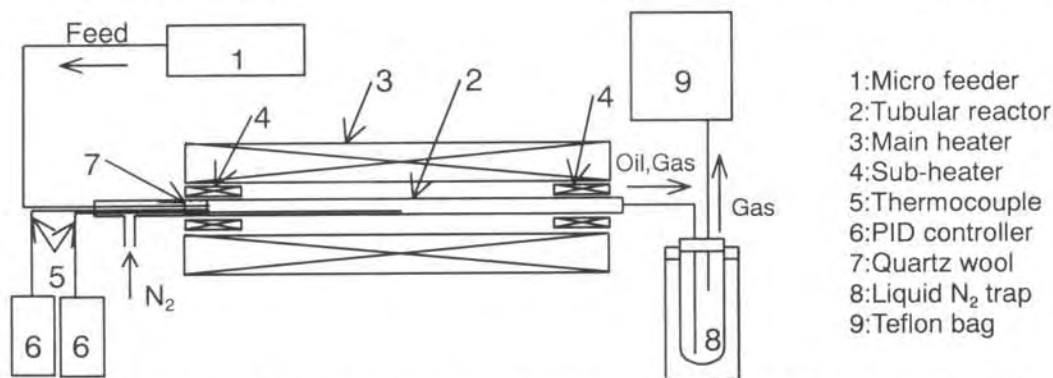


Fig.3 Schematic diagram of the experimental apparatus for the pyrolytic gasification

heated in an infrared furnace under atmospheric pressure by batch operation. Low-density PE pellets (Mitsubishi Chemical, M430), PP pellets (Japan Polyolefins, PM900A), or PS fragments (crushed plastic box) of 10 grams were loaded in the reactor. After purging with N_2 stream, the reactor was heated at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ up to 470°C (for PE) or 450°C (for PP and PS) and was held for 10 min. The outlet of the reactor was connected to an ice water cooled trap in order to condense the liquid products, which was referred to a distillate and was gasified in the second stage. Gaseous products through the ice water trap were collected in a Teflon bag. The material remained in the reactor was referred to residue.

Fig.3 shows a schematic diagram of the experimental apparatus for the pyrolytic gasification. A syringe type micro feeder was used to feed the oil made in the first stage of liquefaction. Nitrogen gas was also fed with the oil to adjust residence time. The reactor was a quartz tube (10 mm i.d. and 600 mm length) heated by electric heater at a constant temperature between 700 and $850\text{ }^\circ\text{C}$. Sub-heaters were equipped in both inlet and outlet of the reactor to reduce the temperature drop around there and to keep the temperature uniform through the reactor. Thus, the effective length of the reactor was 350 mm in which the temperature difference was less than $30\text{ }^\circ\text{C}$ and effective volume (V) was 27.5 cm^3 . The space-time was defined as V/F , where the flow rate (F) is a sum of the flow rate of nitrogen carrier gas and the product gas. The outlet of the reactor was connected to a liquid nitrogen trap. A Teflon bag was connected to the outlet of the trap. After degradation run, the trap was soaked into a water bath at a room temperature so that condensed gases evaporated into the Teflon bag.

Table 1 Product yields for liquefaction (wt%)

	Temp.	Distillate	Residue	Gas
PE	470°C	87.3	9.7	3
PP	450°C	85.0	14.0	1.0
PS	450°C	92.1	7.9	0

Fig.4 Gas chromatogram of the liquefaction products of polyethylene

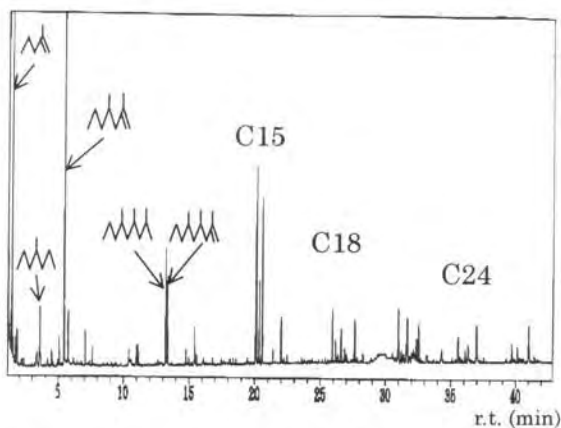
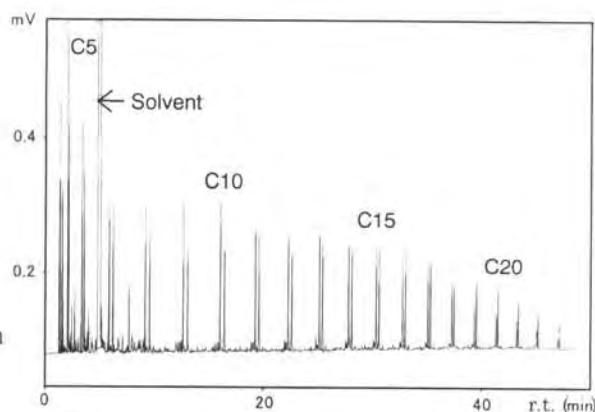


Fig.5 Gas chromatogram of the liquefaction products of polypropylene

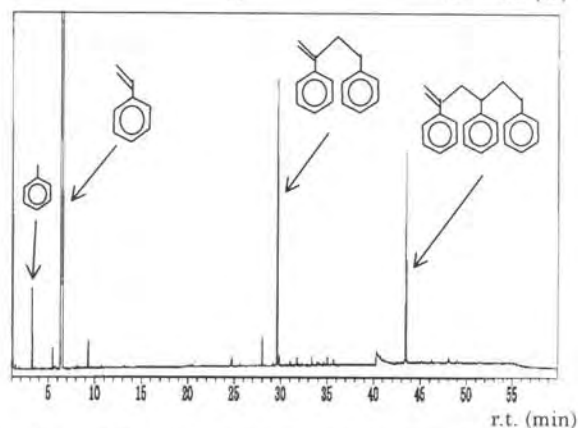


Fig.6 Gas chromatogram of the liquefaction products of polystyrene

The remained product in the trap was referred to the product oil. The coke and the carbonaceous compounds stuck to the wall of the reactor were referred to residue. Oil and gas products were analyzed by GC and GC-MS (Shimadzu, GC17A and GC-MS QP5000).

Results and Discussions

Table 1 shows the product yields for the pyrolytic liquefaction. In the liquefaction stage the yields of the gaseous products are very low because the reaction temperature is relatively low. Figs. 4-6 show the gas chromatograms of distillates in this liquefaction stage. The main products from PE degradation are n-paraffins and 1-olefins. As can be seen from Fig.4 the liquid hydrocarbon products from PE were distributed in a wide range of carbon number. Fig.5 shows that the products from PP were mostly iso-paraffins and iso-olefins. As in the case of polyethylene, the peaks in the chromatogram correspond approximately to those of dimers, trimers, and oligomers. Larger peaks can be seen in every three carbon numbers for PP. The products from PS were mostly monomer, dimer and trimer as seen in Fig.6.

Figs.7-9 are the experimental results of gasification using the apparatus shown in Fig.3. Fig.7 shows the dependence of the gas yields on the gasification temperature for PE. From Fig.7 the yields of methane and ethylene increase with the temperature, whereas gaseous products heavier than C3 components decrease with the temperature. The total gas yield shows the maximum at 750°C. Fig.8 shows the dependence of the oil yields on the gasification temperature for PE. In Fig.8, the yield of BTX(Benzene, Toluene, Xylene) increases with the temperature. This means the gas components having carbon numbers larger than 3 turn to BTX by intermolecular condensation at the high temperature.

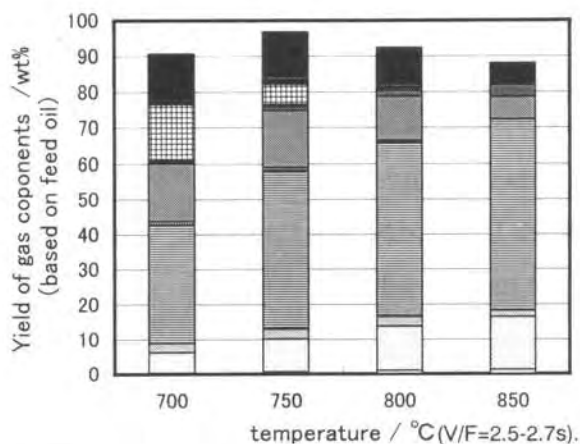


Fig.7 Dependence of the gas yields on the gasification temperature for polyethylene

- : H₂
- ▨: C₂H₄
- ▩: iso-C₄H₁₀
- ▧: 1-C₄H₈
- : 1,3-C₄H₆
- : CH₄
- ▨: C₃H₈
- ▩: n-C₄H₁₀
- ▧: iso-C₄H₈
- : CH₂
- ▨: C₂H₆
- ▩: C₃H₆
- ▧: t-2-C₄H₈
- : cis-2-C₄H₈

Fig.9 shows the comparison of the gas yields among PE, PP and PS. The gas yields for PS is very low compared to PE and PP. This is because styrene monomer, dimer, and trimer hardly decompose at this temperature. The total gas yields of PE and PP were 92wt% and 87wt% each based on the feed oil i.e. 80wt% and 74% respectively based on the weight of each polymers. The total gas yields obtained in this study are higher than the yields of single stage gasification by Sawaguchi et al.[2] and the formation of coke is very low in this two-stage gasification. Sub products such as the oil in the gasification stage and the residue in the liquefaction stage can be used as heat sources in the pyrolysis.

Conclusions

Two-stage pyrolytic gasification produces high calorie gas with high efficiency of gasification and with low coke formation. The total gas yields for PE was 80wt% and for PP was 74wt% based on the weight of each polymers at 800°C. The main components of the product gas for PE and PP were methane and gaseous olefins such as ethylene and propylene. Aromatic oils including benzene, toluene and xylene were produced as Sub-products.

References

1. Tomita, O.; Bae, S.K.; Kajiuchi, T.; Akehata, T. *Kagaku Kougaku Ronbunshu* 1993, 19, 736-744
2. Sawaguchi, T.; Kuroki, O.; Ikemura, T. *Bull. Japan Petrol. Inst.* 1977, 19, 124-130

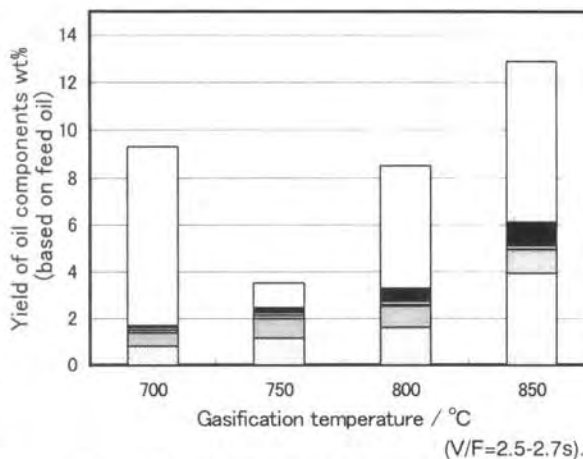


Fig.8 Dependence of the oil yields on the gasification temperature for polyethylene.

- : Benzene
- ▨: Ethylbenzene
- ▩: o-Xylene
- : Toluene
- ▨: m-Xylene, p-Xylene
- : Naphthalene
- : Others

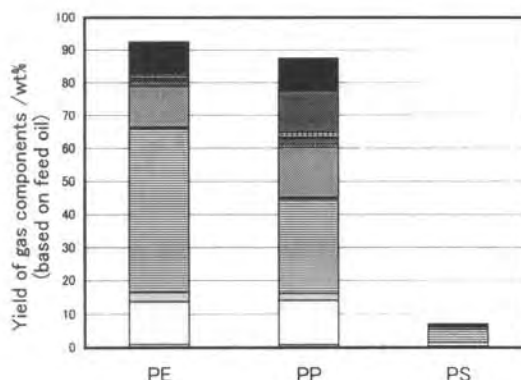


Fig.9 Comparison of the gas yields
PE: Polyethylene PP: Polypropylene
PS: Polystyrene (800°C V/F=2.6 s)

- : H₂
- ▨: C₂H₄
- ▩: C₂H₂
- ▧: t-2-C₄H₈
- ▦: cis-2-C₄H₈
- : CH₄
- ▨: C₃H₈
- ▩: iso-C₄H₁₀
- ▧: 1-C₄H₈
- : 1,3-C₄H₆
- ▨: C₂H₆
- ▩: C₃H₆
- ▧: n-C₄H₁₀
- ▦: iso-C₄H₈