

Studies on The Dechlorination and Oil-Production Technology of Waste Plastics with High Efficiency

Kiyoshi Saito* and Hideo Narita

Resources and Energy Division

Hokkaido National Industrial Research Institute

Tsukisamuhigashi 2-17-2-1, Toyohiraku, Sapporo, 062-8517 Japan

E-mail: narita@hniri.go.jp Fax: +81-11-857-8944

The recycle technology of waste plastics has been developed. This system is constituted by a dechlorination process and a two-stage pyrolysis process. And, this system can produce both of solid fuel and liquid fuel from PVC containing waste plastics. Natural zeolite and synthetic zeolite were used as catalysts for two-stage pyrolysis process. These technologies make it possible to produce nonpolluting, high-calorie solid fuel and a mixture of gasoline and kerosene.

Introduction

The total output of plastic production of 1998 amounted to 15.2million tons[1] in Japan. The principal products are polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP) and polystyrene (PS), which account for 70% of the total amount. Sixty percent of the production output is scrapped as used plastics every year. In urban waste plastics, PVC is inevitably mixed with waste plastics, creating many management problems since PVC produces hydrogen chloride during combustion or thermal decomposition, which may corrode combustors and cause air pollution. For this reason, most municipal bodies reclaim these waste plastics, although some of them incinerate waste plastics after removing PVC.

In response to the need to recycle plastics, the Hokkaido National Industrial Research Institute (HNIRI) has developed the dechlorination and oil production technology from waste plastics.

Experiment

Sample

Soft PVC and PE (LDPE) were used as feed samples, and the properties are shown in Table 1. Natural zeolite, which is produced in Oshamanbe, was used as a catalyst for first pyrolysis stage. Natural zeolite was activated by being calcined for three hours at 550°C. Synthetic zeolite (ZMS-5) was used for secondary pyrolysis stage.

Apparatus

A diagram of a twin-screw extruder[2] is shown in Fig. 1. The thermal decomposition part was 300mm long with an inner diameter of 26mm. Two rods, 285mm long and 14mm in diameter, were

Table 1 Properties of feed sample

		PE	PVC
Size	(mm)	4.0φ×2.0	4.0φ×2.5
H	(%)	12.20	6.67
C	(%)	85.50	49.80
N	(%)	0.00	0.00
O	(%)	0.70	5.80
Cl	(%)	0.00	38.75
Ash	(%)	0.10	1.32
Calorific value	(cal/g)	11,130	6,210
Specific gravity	(g/cm ³)	0.588	0.710

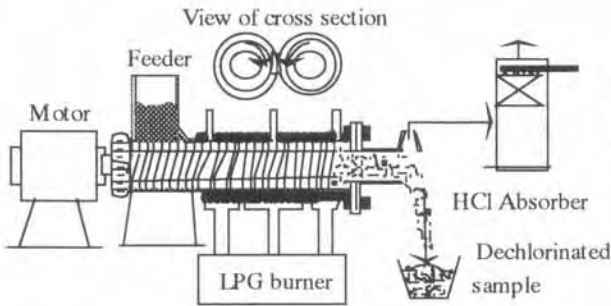


Fig.1 Diagram of twin-screw extruder

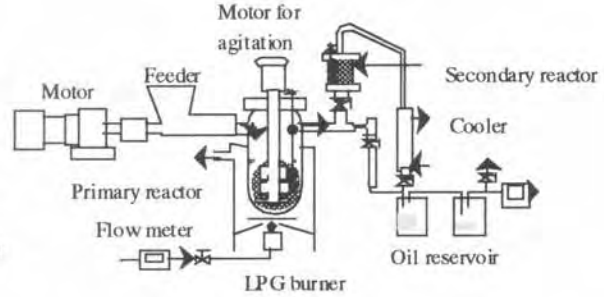


Fig.2 Two-stage catalytic pyrolysis process

fitted in parallel. The dead volume was about 0.2 litre. A schematic diagram of the two-stage catalytic pyrolysis process[3] is shown in Fig. 2. The system consists of a screw feeder, a first-stage catalytic bed (inner diameter, 105mm; height, 550mm), a second-stage catalytic bed (inner diameter, 65mm; height, 300mm), a condenser, a vessel, and a gas meter. The first stage bed was filled up to 200mm with natural zeolite, and the reaction time was calculated using that height. The second bed was filled with ZMS-5 zeolite. The dechlorinated sample was heated at 260°C and continuously supplied to the first bed. The decomposed product in the first stage flowed into the second bed and was decomposed further. The final product was condensed at 10°C and separated into gas and oil.

Results and Discussion

Dechlorination Reactions

The effects of the PVC mixing ratio on the dechlorination reaction are shown in Figs. 3 and 4. The PVC mixing ratios were 10 and 40wt%, and the reaction temperatures were 340°C to 380°C. The sample feed rate in the dechlorination process varied from 1.10kg/h to 3.36 kg/h.

For the sample containing 10wt% PVC, the following reaction times and temperatures were required to attain a 99.9wt% dechlorination rate as shown in Fig. 3: 5.6 min (1.80 kg/h) for 340°C, 4.4 min (2.30 kg/h) for 360°C and 3.4 min (2.93 kg/h) for 380°C. For the sample containing

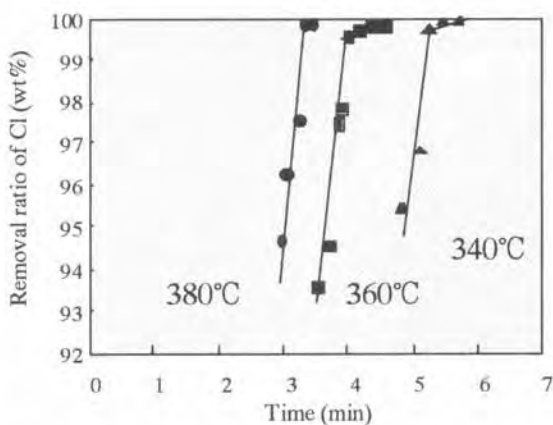


Fig.3 Relationship between residence time and Cl removal rate (PVC:10wt%)

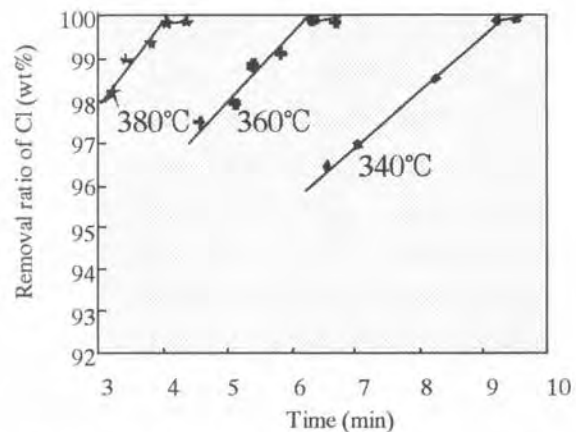


Fig.4 Relationship between residence time and Cl removal rate (PVC:40wt%)

40wt% PVC, longer reaction times were required as shown in Fig.4: 9.2 min (1.10 kg/h) for 340°C, 6.3 min (1.60 kg/h) for 360°C, and 4.0 min (2.30 kg/h) for 380°C. This suggests that elevating the reaction temperature can reduce the reaction time for high PVC containing samples. Table 2 shows the results of elemental analysis, density, ash contents and calorific value of processed sample containing 10wt% PVC. After processing, the 10wt% PVC sample had C and H contents similar to those of PE, and the density was increased from 0.605g/cm³ to 0.830g/cm³.

Table 2 Properties of dechlorinated sample

Temperature (°C)	340	360	380
PVC Contents (wt%)	10	10	10
Removal ratio of Cl (wt%)	99.93	99.91	99.90
Residence time (min.)	5.6	4.4	3.4
Feed rate of sample (kg/h)	1.79	2.29	2.93
H (%)	11.0	10.4	9.2
C (%)	86.2	7.9	87.5
N (%)	0.0	0.0	0.0
O (%)	0.0	0.0	0.0
Specific gravity (g/cm ³)	0.830	0.838	0.832
Ash Content (wt%)	0.08	0.09	0.09
Calorific Value (cal/g)	10,510	10,730	10,530

Furthermore, the calorific value was about 10,000cal/g, which is also similar to that of PE.

Product yields in catalytic pyrolysis process

The yields of oil, gas and residue at first stage, are shown in the right part of Fig. 5. The reaction temperatures was varied from 430°C to 460°C and feed rates were 0.76kg/h. As shown in this figure, the gas yield in the first stage increased from 5.1wt% to 10.1wt% and the oil yield decreased from 86.7wt% to 82.1wt% as increase in temperature.

The yield of residue in the first stage was 5.9wt% for each temperature. The integrated operation was done connecting with first stage and second stage. The first stage temperature was 440 °C, and the second-stage temperature was varied from 280°C to 360°C by 20 °C, and the feed rate was varied from 0.60 kg/h to 0.95kg/h. As shown in the left part of Fig.5, gas yields increased as increasing in temperature, on contract,

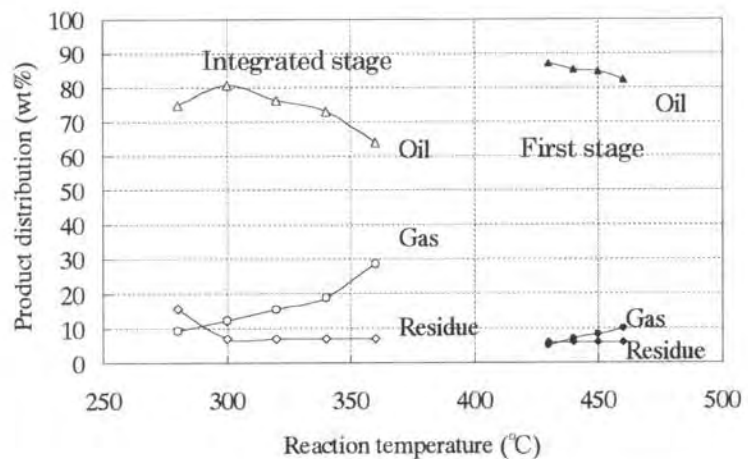


Fig.5 Product yield at first and integrated stage

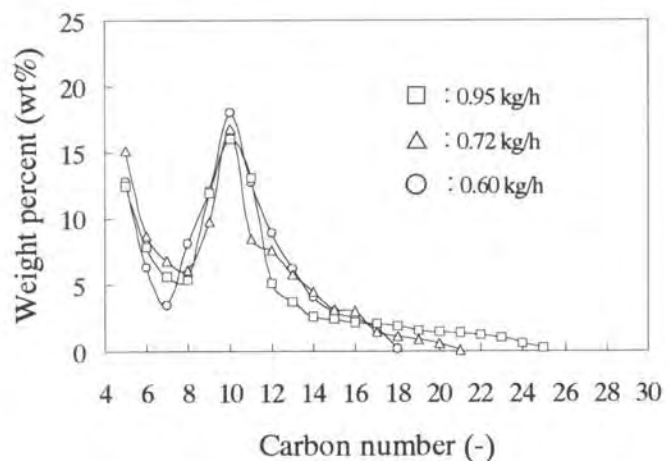


Fig.6 Carbon number distribution of produced oil

oil yields were decreased. And it was found that 300°C was the optimum temperature to produce maximum oil yields. The produced oil was clearly transparent and had low viscosity. This suggests that catalytic reactions proceeded further in the second stage. The yield of residue in the integrated stage was 7.1wt% except 280°C, and it can be said that the residue yields was almost 1.2wt% in second stage.

Quality of produced oil

The molecular distributions of produced oil in the integrated stage were shown in Fig. 6. The molecular weight distributions of produced oil were varied as the reaction time. When the reaction time was shorter, that was rather widely distributed between C_5 to C_{25} , and it was getting narrower as increase in the reaction time, and distributed between C_5 to C_{18} . In accordance with molecular weight distribution,

the distillate of oil were varied, and these were distributed from gasoline fraction to kerosene fraction. The type analyses of products were carried out to investigate the chemical properties of produced oil. The contents of n-paraffin and olefin were decreased as increase in reaction time, and these were mainly converted to aromatics as shown in Fig. 7

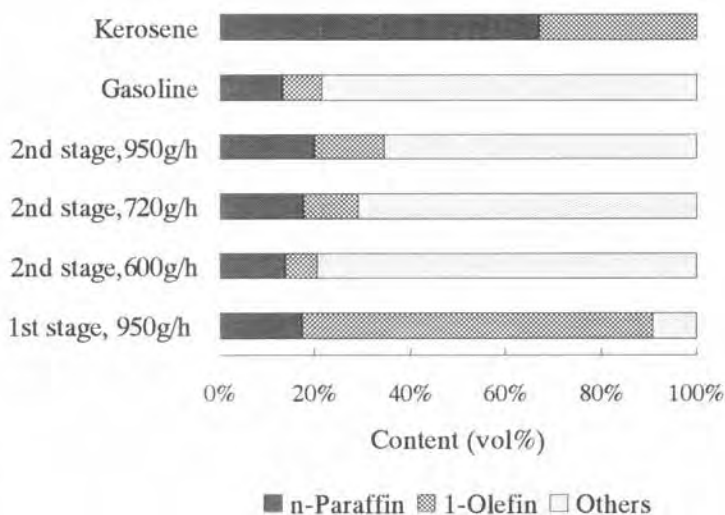


Fig. 7 Type analyses of produced oil etc.

Conclusion

- 1) A dechlorination and oil producing process was developed by using bench scale equipment to realize effective reuse of waste plastics.
- 2) Samples containing 10wt% and 40wt% PVC were provided for the dechlorination process which demonstrated a removal rate of 99.9wt% and a short reaction time.
- 3) Dechlorinated samples were provided for the two-stage catalytic decomposition system and lighter oil was produced at high conversion efficiency using synthetic zeolite as the catalyst in second stage.

References

- [1] K. Saito, History of oil production from waste plastics, PLASPIA, No.104, Plastic Sokushin Kyogikai (1998)
- [2] K. Saito, Development of dechlorination and oil production process of waste plastics, Chemical Engineering, 39, 1(1994)
- [3] K. Saito, Oil production Technology of Waste Plastics by using Catalytic Cracking, Kagaku-kougyo-nippousha, No.9, 35(1996)