Development of Chemical Recycling Process for Post-Consumer PET Bottles by Methanolysis in Supercritical Methanol

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In recent years, Chemical Recycling from PET Bottle to PET Bottle (B to B) by depolymerizing polyethylene terephthalate (PET) to yield monomers as its raw materials, has been gaining greater interest as ideal means of recycling. Mitsubishi heavy industries LTD (MHI) has been developing "Chemical Recycling Process for Post-Consumer PET Bottles by Methanolysis in Supercritical Methanol".
Based on results of the fundamental study and laboratory test, we have constructed the Bench Test Plant. This plant consists of Depolymerization in Supercritical Methanol section with a continuous reactor and Monomer purification section. We have operated this plant stably for roughly total 400 hours. We recovered diethyl terephthalate (DMT) and ethylene glycol (EG) as monomer from Post-Consumer PET Bottles in this Plant. The qualities of those recycled monomers that were produced in the laboratory test were equivalent to those of virgin monomers that are produced from petroleum. The recycled DMT produced on laboratory test was converted into pure terephthalic acid (PTA) by Hydrolysis with batch type reactor. The purity of this recycled PTA was equivalent to that of virgin PTA. The results suggested that our process would make The Bottle-to-Bottle Chemical Recycling Process to come in practical. Further, the results of our feasibility studies have also shown that our PET recycling process could be economically feasible.

1. Introduction

The production of PET bottles has been on the rise mainly for beverage bottle use these past several years and is expected to increase further because of their convenience. Recycling of post-consumer PET bottles has been gaining a great interests and several recycling methods have been proposed. Especially, in Japan since the Containers and Packing Recycling Law came into effect in 1997, the collection rate of post-consumer PET bottles by local municipalities has increased dramatically (34.5% in 2000, 40.1% in 2001) with the possibility of exceeding 50% in 2005. Sales volume of products recycled from post-consumer PET bottles is also expanding to a large extent for fiber and sheet products (69,000 ton in 2000, 95,000 ton in 2001). However, the sales volume of recycled fiber and sheet products is coming

to be saturated. Therefore these recycled products would be effectively unable to cope with increasing collection volume of post-consumer PET bottles in near future.

Taking into consideration the above tendency, MHI has began development of a chemical recycling process for depolymerizing post-consumer PET bottles into monomers for use as feed stocks for manufacturing PET resin [1, 2], utilizing supercritical methanol [3]. We intends to establish an ideal recycling system consisting of a recycle flow from PET bottles to PET bottles (so called B to B (Bottle to Bottle) recycling) while minimizing the consumption of natural resources and the generation of wastes by making this process practicable.

This report presents an overview of the Mitsubishi process and the trace of our development.

2. PET-recycling system by Mitsubishi process.

2.1 Recycling process flow

Fig. 1 shows the flow sheet of a PET recycling system, with a comparison between the Mitsubishi process using supercritical methanol and a existing recycling process.

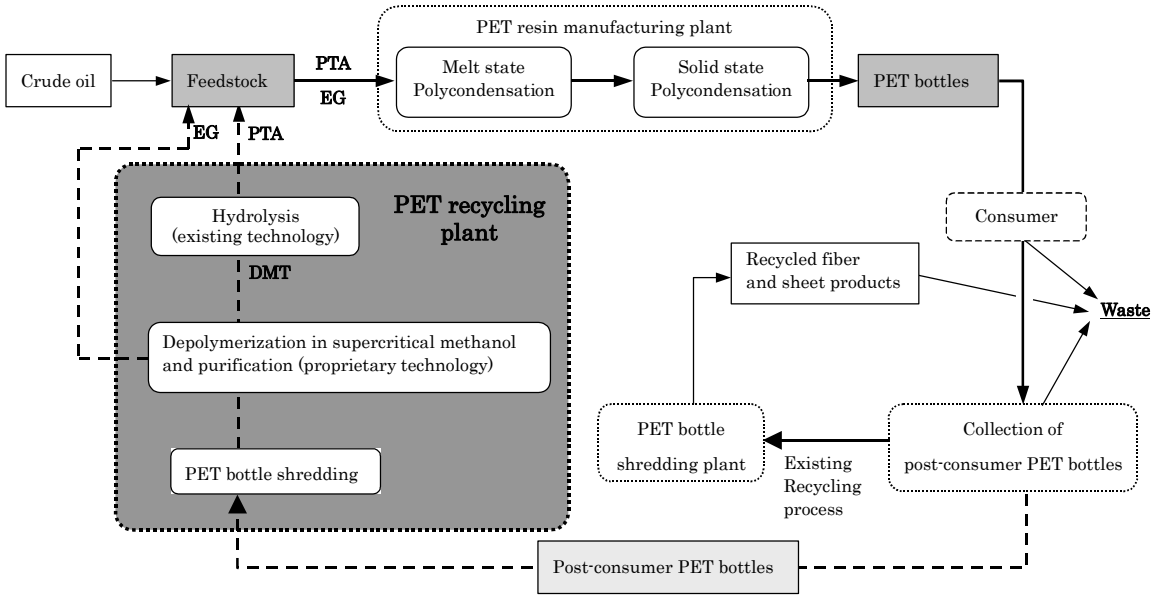

Fig. 1 Flow sheet of a PET recycling system

Fig. 2 shows an outline flow sheet of the Mitsubishi process. The Mitsubishi process consists mainly 4 sections, (the PET bottle shredding section, the depolymerization with supercritical methanol section, the separation and purification section and hydrolysis section). Post-consumer PET bottles are flaked by the PET bottle shredding section. PET flakes are sent to the depolymerization with supercritical methanol section. In this section, the PET flakes are depolymerized into DMT and EG by methanolysis in supercritical methanol. The model

formula of this reaction is shown in Fig. 3. The mixture of depolymerization products (DMT, EG), and excess methanol are then sent on to the separation and purification section. In this section, DMT, EG and methanol are purified by distillation and other methods. The purified DMT monomer is further converted into PTA in the hydrolysis section [4]. The model formula of this reaction is shown in Fig. 4. Finally, PTA and EG are then sent to existing PET resin production plants, thereby an ideal recycling system can be completed.

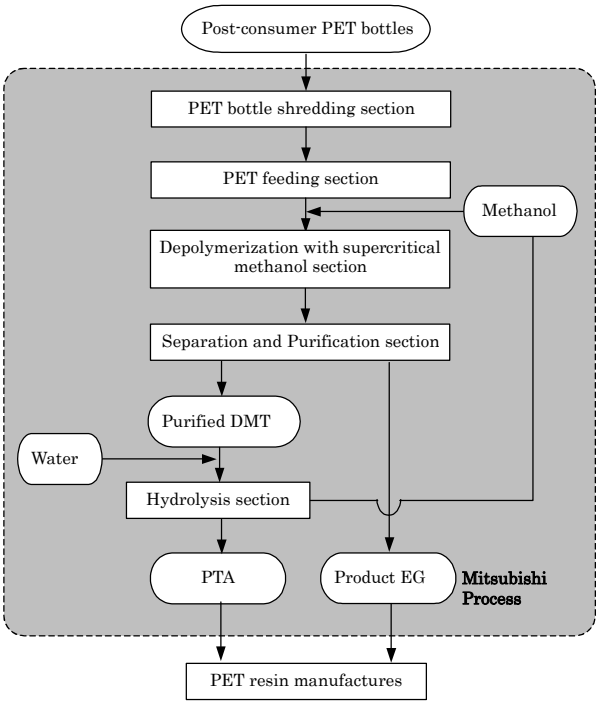

Fig. 2 Outline flow sheet of the Mitsubishi process

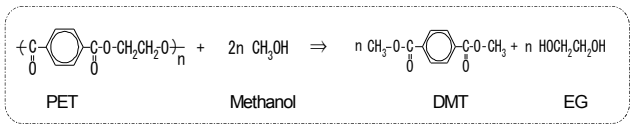

Fig.3 The model formula of methanolysis reaction in supercritical methanol

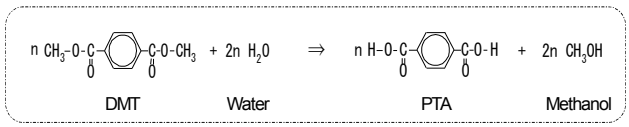

Fig.4 The model formula of DMT hydrolysis reaction

2.2 Features of the Mitsubishi process

The Mitsubishi process is characterized by a combination of a newly developed PET-depolymerizing process with supercritical methanol and an existing DMT hydrolysis process for converting PET into PTA, which is a feed stock monomer for producing PET.

Another features of this process are as follows.

1) Utilization of the high reactivity of supercritical fluid makes it possible to complete the reaction quickly so that the depolymerization with supercritical methanol section and the reactor can be constructed compact.
2) The Mitsubishi process does not require any catalyst for the depolymerization, and so the operation of the reaction is simplified and the separation unit of catalyst is not necessary.
3) In conventional depolymerization with EG, special purification operation must be taken because the depolymerization product contains components with high boiling points

exceeding 673 K, such as bis-hydroxyethyl terephthalate (BHET). In the Mitsubishi process, however, normal distillation can be applied because the depolymerization products consisting of components with low boiling points (DMT (boiling point: 561 K) and EG (boiling point: 471 K)). The separation of components with low boiling points and an absence of any need for any special steps make the purification and purification sections to be simplified.

4) Since PET bottles are made from only the PET resin that is manufactured from PTA in Japan, the Mitsubishi process can utilize existing domestic PET manufacturing and distributing systems without special appreciations.
5) The Mitsubishi process can eliminate impurities such as foreign plastics that might contaminate the collected post-consumer PET bottles.

3.Experiment and Results

3.1 Fundamental study

Fig. 5 shows the photo of test apparatus which consists of the batch type reactor (about 91 cm^3) for Fundamental study. Table 1 shows a comparison between our depolymerization methods and the conventional depolymerization methods. As Table 1, our depolymerization method with supercritical methanol can complete the depolymerizing reaction in the shortest period of time.

Fig.5 Test apparatus of Fundamental study

Table 1 Comparison with conventional technology

Solvent for Depolymerization	Reaction Temp. (K)	Reaction Press. (MPa)	Reaction time	Catalyst	Recycled monomers	References
Supercritical methanol (MHI)	573	15	10 min	Not used	DMT/EG	MHI proprietary technology
Supercritical methanol	573	8	30 min	Not used	DMT/EG	Reference [5]
Subcritical methanol (MHI)	503	6.5	5 hours	Not used	DMT/EG	MHI proprietary technology
Liquid methanol	453	2.5	5 or more hours	Used	DMT/EG	Reference [5]
Ethylene glycol	463-473	3 to 4	5 or more hours	Used	BHET	Reference [5]

3.2 Laboratory scale test

Laboratory scale test was performed using the continuous depolymerization apparatus and continuous distillation apparatus shown in Fig. 6 and Fig. 7. In the course of Laboratory scale test, PET flakes produced from post-consumer PET bottles are taken as the feed stock. DMT produced on this test was converted into PTA by Hydrolysis with batch type reactor. Table 2 shows a comparison of the purities of recycled DMT, EG, and PTA monomers with those of virgin monomers. The purities of recycled monomers were equivalent to those of their comparable virgin monomers. Further, results of the impurities analysis showed that the recycled monomers have the same level of qualities as those of the virgin monomers. These results showed that the Mitsubishi process could be successfully applied to B to B recycling.

Fig.6 The continuous depolymerization apparatus

Fig.7 The continuous distillation apparatus

Table.2 Quality of Recycled monomer

Recycled monomers	Purity of recycled monomers (%)	Purity of virgin monomers (%)
PTA	99.9	≧ 99.9
DMT	99.9	≧ 99.9
EG	99.0	≧ 99.0

3.3 Bench scale test

Based on results of the fundamental study and laboratory test, we constructed the Bench Test Plant shown in Fig.8 to optimise the operation condition and to confirm the ability of stable operations. This plant consists of Depolymerization in Supercritical Methanol section with a continuous reactor and Monomer purification section. We operated this plant stably for a total of roughly 400 hours and with 80 – 90 % monomer yield.

Fig.8 The Bench Test Plant

4. Economics

The Containers and Packing Recycling Law implemented in 1997 states that commercializing enterprise, which sell recycled products, can gain a disposal commission from The Japan Container and Packaging Recycling Association in accordance with the amount of recycled products in the bidding. The results of our feasibility studies have also shown that a B to B recycling using the Mitsubishi process would be feasible in a plant that has a capacity of 20,000 to 40,000 tons/year of post-consumer PET bottles treatment within the scope of the application of this law

5. Conclusion

Research and development work undertaken by us showed that high purity monomers equivalent to the virgin monomers would be recovered. And it was shown that the Mitsubishi process would be economically feasible. We are planning to collect the plant operation data for designing a commercial plant at the pilot test, and to establish the commercialisation scheme for PET recycling.

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