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

Minoru Genta
Fumitoshi Yano
Yuichi Kondo
Wataru Matsubara
Setsuo Oomoto

Post-consumer PET (polyethylene terephthalate) bottles have been recycled into fiber and sheet products ever since the Containers and Packing Recycling Law came into effect in 1997. There has been a growing need, however, for a chemical recycling process. In this process, post-consumer PET bottles are recycled into monomers that can be used as feed stocks for the recycled production of PET bottles for beverages. It is believed that such a process would be much more suitable for a recycling-oriented society. Mitsubishi Heavy Industries, Ltd. (MHI) has been developing a chemical recycling process that uses supercritical methanol in order to depolymerize PET material into its constituent monomers within a short time. During the development stage, it was found that the chemical recycling process developed by MHI (Mitsubishi Process) can recover monomers with qualities that are equivalent to those of the original monomers produced from petroleum. The results of feasibility studies have also shown that the Mitsubishi process can be economically feasible.

1. Introduction

The production of PET bottles has been on the rise mainly for beverage bottle use these past several years (330 000 tons in 1999, 360 000 tons in 2000) and is expected to increase further because of their convenience.

On the other hand, 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 (22.8% in 1999, 34.5% in 2000) 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 (40 000 ton in 1999, 69 000 ton in 2000).

However, the sales volume of recycled fiber and sheet products is coming to be saturated, so that there is concern that these products will be unable to cope effectively with the increase in the collection of post-consumer PET bottles in near future.

Taking into consideration the above tendency, MHI began development of a chemical recycling process for depolymerizing post-consumer PET bottles into monomers for use as feed stocks for manufacturing PET resin[2], utilizing supercritical methanol (methanolysis)[1].

MHI 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. MHI is currently undergoing the development and verification test of Mitsubishi process at a MHI pilot plant.

This report presents an introductory overview of the Mitsubishi process from the viewpoint of the feasibility of the "B to B" recycling of PET bottles.

2. Conditions for establishing a B to B recycling business

In order to commercialize the B to B recycling business, the following three challenges need to be addressed.

(1) Technical aspect: The quality of the recycled monomers must be equivalent to the virgin monomers produced from petroleum.

(2) Economic aspect: Economical feasibility of the business must be established to ensure profitability.

(3) Aspects unique to recycling business: Post-consumer PET bottles must be available in an amount necessary to productively operate a recycling plant.

3. PET-recycling system by Mitsubishi process

3.1 Recycling flow sheet

Fig. 1 shows the flow sheet of a PET recycling system, with a comparison of the Mitsubishi process using supercritical methanol and a conventional process. **Fig. 2** shows an outline flow sheet of the Mitsubishi process. It can be seen that post-consumer PET bottles are flaked by a PET bottle shredding section, after which the flakes of the PET bottles are sent on to the depolymerization (with supercritical methanol) section.

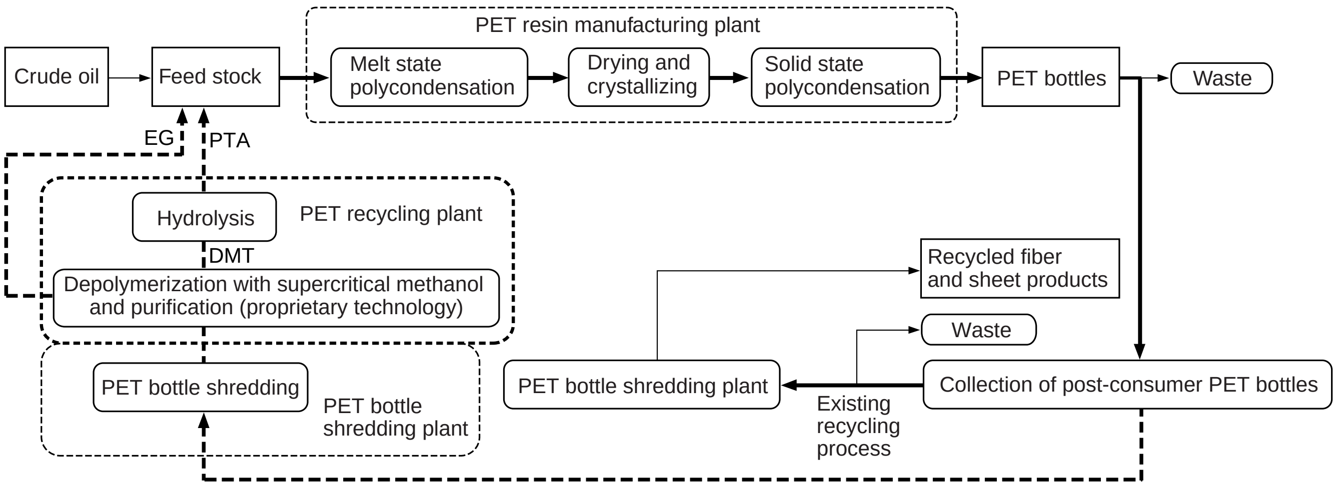

Fig. 1 Flow sheet of Mitsubishi chemical recycling process of post-consumer PET bottles using supercritical methanol, including a comparison with the conventional process

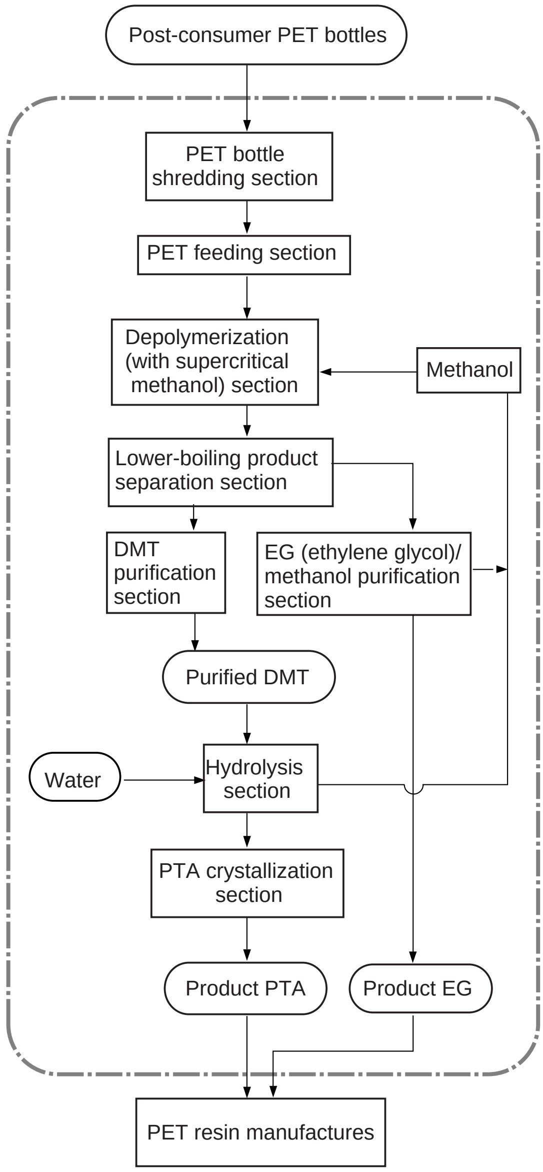

Fig. 2 Outline flow sheet of PET chemical recycling process using supercritical methanol (Mitsubishi process)

In this section, the flakes are depolymerized into DMT (dimethyl terephthalate) and EG (ethylene glycol) through a methanolysis reaction by supercritical methanol[3]. The model formula of the reaction is shown in **Fig. 3.** The mixture of depolymerized DMT, EG, and excess methanol is then sent on to a lower-boiling product separation section to be separated into DMT and EG/ excess methanol, which in turn are sent to the respective purification section to be purified by distillation. The purified DMT monomer is further converted into PTA (highly purified terephthalic acid) in the hydrolysis section[4]. EG is purified from the mixture of EG and excess methanol in the EG/methanol purification section. Finally, the converted PTA and purified EG are then delivered to existing PET resin production plants, thereby forming an ideal cyclical type recycling system.

3.2 Features of the Mitsubishi process

The Mitsubishi process is characterized by a combination of a newly developed high-reaction-velocity PET-depolymerizing process by supercritical methanol and an existing DMT hydrolysis process for converting PET into PTA, which is a feed stock monomer for producing PET. Another feature of this process is that it is provided with a process where impurities such as foreign plastics that might contaminate the collected post-consumer PET bottles are eliminated in accordance with the properties of the impurities. The advantages of using supercritical methanol are as follows.

(1) Utilization of the high reactivity of supercritical fluid makes it possible to complete the reaction quickly, so that the both the depolymerization section and the reactor can be made compact. **Table 1** shows a comparison of both processes of methanolysis with supercritical methanol and the conventional depolymerization. As can be seen in Table 1, the Mitsubishi process with supercritical methanol can complete the depolymerizing reaction in the shortest period of time.

(2) The Mitsubishi process does not require any catalyst

Table 1 Comparison with conventional technology * Conversion: 80%

Solvent for depolymerization	Reaction temperature (°C)	Reaction pressure (MPa)	Reaction time	Catalyst	Recycled monomers	References
Supercritical methanol (MHI)	300	15	10 minutes	Not used	DMT/EG	MHI proprietary technology
Supercritical methanol (Others)	300	6	30 minutes	Not used	DMT/EG	Reference (5)
Subcritical methanol (MHI)	230	6.5	5 hours*	Not used	DMT/EG	MHI proprietary technology
Liquid methanol	180	2.5	5 or more hours	Used	DMT/EG	Reference (5)
Ethylene glycol	190 to 200	3 to 4	5 or more hours	Used	BHET	Reference (5)

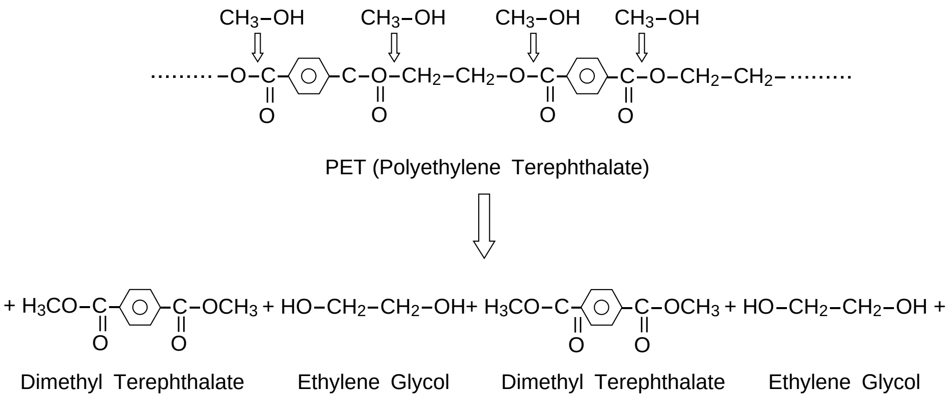

Fig. 3 Reaction model formula of methanolysis process of PET
Supercritical methanol acts on the ester bonds of PET, so that methanolysis occurs.

Fig. 4 Test apparatus of continuous PET depolymerization process
The figure shows an external view of the laboratory apparatus for methanolysis with supercritical methanol process.

for the depolymerization, so that the operation of the reaction is simplified and the separation of catalyst is not necessary.

(3) In conventional depolymerization with EG (Glycolysis process), special purification operation must be taken because the depolymerization product contains components with high boiling points exceeding 400°C, such as BHET (bis-hydroxyethyl terephthalate). In the Mitsubishi process, however, normal distillation can be applied because the depolymerize products consist of DMT (boiling point: 288°C) and EG (boiling point: 198°C). The lower boiling points and absence of any need for any special steps means that both purification sections can be simplified.

Table 2 Quality of recycled monomers

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

The advantages of conversion to PTA can be summarized as follows.

(1) Converted PTA is usable as a feed stock for producing PET resin, so that it can be sold to existing PET resin manufacturers.

(2) Since only the PET resin manufactured from PTA is used as the raw material of PET bottles in Japan at present, the bottle to bottle recycling system can be readily operated using existing domestic manufacturing and distributing systems.

3.3 Qualities of recovered monomers

Trial production of DMT and EG was performed using the continuous depolymerization apparatus and continuous distillation apparatus shown in **Figs. 4** and **5**. In those trial tests, PET flakes produced from post-consumer PET bottles are taken as the feedstock. Trial production of PTA from obtained DMT was performed. **Table 2** shows a comparison of the purities of recycled

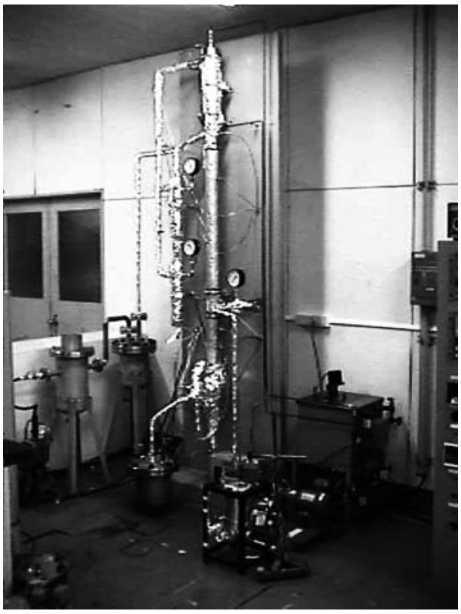

Fig. 5 Test apparatus of continuous purification process

EG, DMT, and PTA monomers with those of their virgin monomer counterparts[5]. The purities of recycled monomer were equivalent to those of their comparable virgin monomers. Further, results of the analysis of the impurities contained in the recycled monomers showed that monomers having the same level of quality as those of the virgin monomers could be recovered. Evaluations by chemical manufacturers of the recycled PTA also showed the material to have the same level of quality as that of the virgin PTA. The trial production runs showed that the Mitsubishi process could be successfully used to recycle into monomers that have the same qualities as those of their virgin monomer counterparts.

4. Economic feasibility of PET recovery process

The Containers and Packing Recycling Law implemented in 1997 states that a recovered product commercializing enterprise can gain a disposal commission corresponding to the amount of recycled products in the bidding from The Japan Container and Packaging Recycling Association (**Fig. 6**). Since the results of the feasibility study came within the scope of the application of this law, it has been shown that a "B to B" recycler using the Mitsubishi process would become feasible in a plant that has a capacity of 20 000 to 40 000 tons/year of post-consumer PET bottles.

5. Availability of post-consumer PET bottles

In order to make post-consumer PET bottle-recycling economically feasible, it is necessary to collect 20 000 to 40 000 tons of post-consumer PET bottles per year. Accordingly, recycling plants should be installed in areas that are able to collect the required amount. In addition, the recycling system should be closely connected to the area where the plant is installed and its vicinity. This

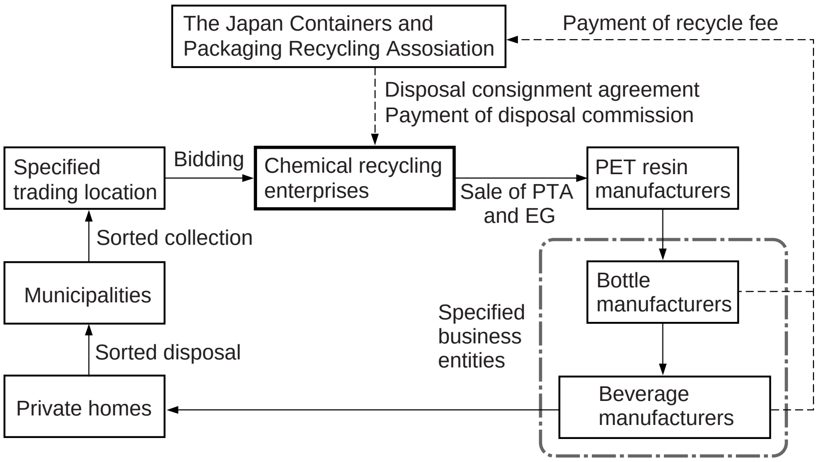

Fig. 6 Commercialization scheme for PET recycling

is a key to making the recycler successful. MHI thus intends to develop such systems together with the recycling technology, taking the concept outlined above into consideration.

6. Conclusion

Research and development work undertaken by MHI into PET bottle-recycling technology showed that high purity monomers equivalent to the virgin monomers would be recovered. And it was shown that our process would be feasible. MHI is planning to acquire the plant operation data for designing a commercial plant at the pilot plant, and to build the commercialization scheme for PET recycling.

References

(1) Sueoka, Y. et al., Chemical Recycling Techniques for Plastics, Mitsubishi Juko Giho Vol.36 No.3 (1999) pp.146-149

(2) Kondo, Y., Genta, M., Development of PET depolymerization into monomer process by Supercritical Methanol, the 9th Symposium on Material Recycling Technology (2001) pp.27-30

(3) Goto, M. et al., Plant & Process 41-2 (1999) pp.47-51

(4) Anton Schoengen, JP Patent S57-53332

(5) Sako, T., Chemical Process Technology using Supercritical fluid, The Seminar on Most-Advanced Technology by NEDO (1998-11)

Kobe Shipyard & Machinery Works


Minoru Genta


Fumitoshi Yano


Yuichi Kondo

Hiroshima Research & Development Center,
Technical Headquarters


Wataru Matsubara


Setsuo Oomoto