

## Dechlorination Characteristics of Vinyl Chloride under Decomposition and Reuse of Household Waste Plastics as Solid Fuel

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The decomposition characteristics of vinyl chloride are studied as a function of pressure. Vinyl chloride samples are decomposed in the pressure range from 0.01 to 1000 kPa and the residual chlorine contents of the decomposed samples are measured. The residual chlorine contents are decreased by the decompression. Based on these experimental results, a dechlorination apparatus is developed and applied to actual household waste plastics.

### Introduction

Polyvinyl chloride (PVC) is one of the major polymers consumed in Japan [1]. Vinyl chloride (PVC and additives) accounts for about 10% of household waste plastics gathered by municipalities [2]. The chlorine content of these waste plastics derived from PVC is about 3%. Pretreatment to decrease the chlorine content is needed in order to reuse the household waste plastics as fuels. The conversion from waste plastics into fuels is very attractive because the waste plastics have the same calorific values as petroleum. The household waste plastics are mainly composed of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), vinyl chloride (PVC and additives) and alien substances such as paper, aluminum foil, and foods. Also, these waste plastics include additives (mainly calcium carbonate), plasticizers (typically DOP), and various kinds of the other plastics [2-3].

In Japan, hydrochloride separation from household waste plastics by PVC decomposition has been applied using extruders in several oil reclamation plants [2-6]. The waste plastics are heated to about 300 °C to 350 °C in the extruders. At that temperature range, PVC is decomposed (PE, PP, PS are not decomposed) and chlorine is separated from the waste plastics as hydrochloride gas. The waste plastics in the extruders are pressurized by kneading and generation of hydrochloride gas. In the high pressure, hydrochloride gas can easily react with calcium carbonate, metals and organic matters which are included with the waste plastics.

Pure PVC without stabilization additives cannot be used because of its low thermal, thermo-oxidative, and light stability. Thermal stability, degradation, and stabilization mechanisms of vinyl chloride have been studied minutely in order to stabilize PVC properties [7]. There are a few studies about chloride removal by vinyl chloride decomposition [8-9]. In this paper, the decomposition characteristics of vinyl chloride are studied as a function of pressure. Vinyl chloride samples, which contain calcium carbonate, are decomposed in the pressure range from 0.01 to 1000 kPa and the residual chlorine contents are measured.

### Experimental apparatus

Figure 1 shows an experimental apparatus. The experimental apparatus consists of a decomposition tube, electric heater, pressure gauge, buffer tank, and vacuum pump. The inner diameter of the decomposition tube is 10 mm and the outer diameter is 20 mm. Vinyl chloride samples are set in the tube as shown in fig.1. A thermocouple to measure the temperature of the decomposition tube is installed in the hole at the tube bottom. The decomposition tube is made from nickel, which has good heat conductivity to provide a uniform temperature distribution, and high corrosion-proof characteristics to the hydrochloride. The inner volume of the decomposition tube is 7.2 cc, and the buffer tank 602.8 cc. The inner volume of the apparatus is changed by the buffer tank valve.

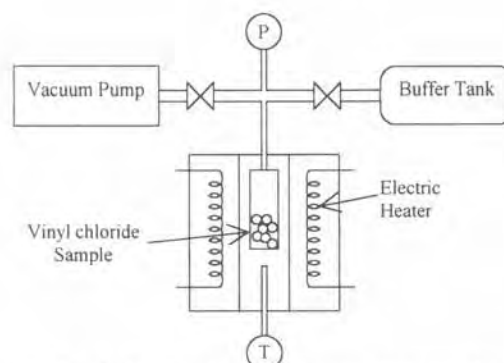


Figure 1: Schematic diagram of experimental apparatus

Prior to the decomposition process, the decomposition tube and the buffer tank are reduced to a pressure of 0.01 kPa and the vacuum pump valve is closed. Then, the sample is heated gradually to the prescribed temperature of 350°C. PVC samples in the tube are decomposed. In the series of the experiments, PVC samples containing 30% calcium carbonate are used.

Figure 2 shows typical temperature and pressure changes in the decomposition tube. The final temperature is settled at 350 °C (623.15K) and the sample mass is 0.5234g. When the temperature exceeds about 250°C, the pressure begins to increase. This pressure increase corresponds to the gas production by the PVC decomposition. When the decomposition of the PVC sample has been completed, the pressure increase is stopped. The decomposed gas is mainly composed of hydrochloride. The final hydrochloride pressure is determined by the PVC sample mass and the inner volume of the apparatus. The experiments are conducted by changing the PVC sample masses and the inner volume. The final pressures are varied from 0.1 kPa to 1000 kPa. In the case of pressure above 100 kPa, the buffer tank valve is closed. After the decomposition, the decomposition tube is cooled to room temperature, and the solid residue is obtained. The residual chlorine content of the residue is measured by the chlorine analyzer ML-3000 of Mitsubishi-bunseki Corp. In the analyzer, the residue is decomposed at 1100°C in a mixed gas flow of 60% oxygen, 40% argon and a small amount of water vapor. The residue is decomposed under the hydrogen supplied from the water vapor. The chlorine in the residue is entirely removed as hydrochloride gas by the excess hydrogen supply. The total amount of chlorine in the residue is determined by coulometric titration.

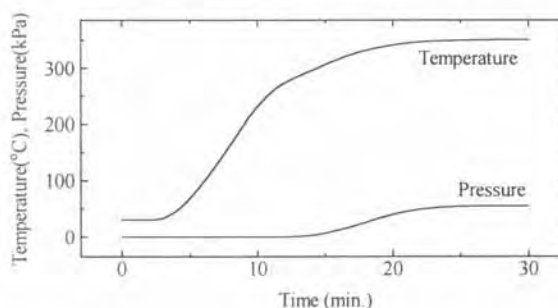


Figure 2: Measured pressure and temperature change in degradation of PVC

## Results and Discussions

Figure 3 indicates the residual chlorine concentration as a function of the end pressure of the vessel. Obviously, the residual chlorine is increased by the increased pressure. Especially, the residual chlorine is multiplied in the higher pressure than the atmospheric pressure. The decomposition tube temperature is kept at 350°C for 10 minutes after the completion of gas generation. The steady states are established in all the experiments. It is considered that some chemical equilibrium state exists in the dehydrochlorination process of PVC with calcium carbonate inclusion.

These results indicate that the decomposition of vinyl chloride should be conducted under low pressure in order to decrease the chlorine concentration from waste plastics. Japanese household waste plastics include calcium of a few percent by weight. Calcium carbonate is one of the major additives to the vinyl chloride. We have developed a dechlorination apparatus for the household waste plastics based on the experimental results.

Figure 4 shows a schematic diagram of the developed dechlorination apparatus. The apparatus is composed of a hopper, a dechlorination furnace, a discharger of dehydrochlorinated plastic fuel, a condenser, a vacuum pump, and a gas treatment system. The waste plastics are moved into the hopper, and the hopper is evacuated to remove oxygen. Then, the waste plastics are fed into the dechlorination furnace. The furnace is depressurized and heated to about 330-350°C (At this temperature range, vinyl chloride is decomposed and the other kinds of plastic are mostly not decomposed [10]). Cutters set around the shaft are rotating in the furnace. The waste plastics are stirred by the rotating cutters and heated gradually by heat transfer from the furnace wall. Also, new surfaces, where the hydrochloride emission occurs, are created in the plastic by the cutter. The generated hydrochloride is emitted only from the surface of the melted plastic. If there is no creation of new surfaces, the generated hydrochloride by PVC decomposition is contained in the melted plastics as bubbles. The creation of new surfaces accelerates the hydrochloride emission. Also, the hydrochloride pressure around the PVC in the waste plastics is kept at a low level by the decompression in order to accelerate hydrochloride emission and evacuation. Effective dechlorination can be achieved by the creation of new surfaces and decompression.

The actual household waste plastics and the test sample are dehydrochlorinated and the residual chlorine concentrations are measured. Table 1 shows the chlorine concentration changes by treatment in the developed dechlorination furnace. The tested household waste plastics, gathered by municipalities, contains about 10% vinyl chloride, 5% metallic elements and salt of about 0.3%.

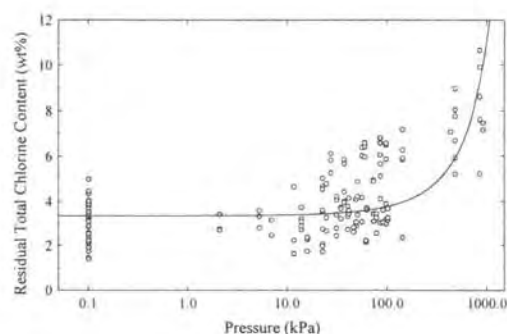


Figure 3: Residual chlorine concentration change in the residues obtained by the decomposition of vinyl chloride samples.

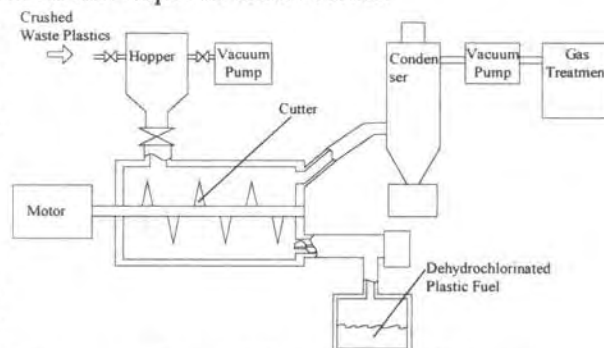


Figure 4: Schematic diagram of dehydrochlorination apparatus.

The test sample is a vinyl chloride mixture 10% (PVC 44%, DOP 30% and calcium carbonate 26%) and polypropylene (PP) 90%. The chlorine concentrations of those two at source are nearly the same. In the case of the test sample, the residual chlorine concentration is on the order of 0.1%. The good dehydrochlorination performance of the dechlorination furnace is confirmed from this low residual chlorine content. Whereas, the residual chlorine content increased to about 0.5% for the case of the household waste plastics. It is considered that the 5% metallic elements and the 0.3% salt contained in the mixed plastics caused this relatively high residual chlorine content compared to the test sample result.

Table 1: Dechlorination characteristics

Sample	Total Chlorine(wt%)		Calorific Value
	Source	Residual	
Vinyl chloride 10% Polypropylene 90%	2.46	0.06 ∧ 0.16	10940
Household Waste Plastics	2~4	0.4 ∧ 0.6	10000

### Conclusion

Vinyl chloride samples are decomposed, and the changing pressure and residual chlorine concentrations are measured. The residual chlorine concentration is decreased by the decompression. The decomposition of vinyl chloride from waste plastics should be conducted under low pressure in order to decrease the chlorine concentration.

### References

1. "Plastic Products, Plastic Waste and Resource Recovery" (Japanese), Japan PVC Environmental Affairs Council, 1997.
2. "Haipurasuchikkuno Samarurisakuru Kisogijyutu Data Shuu," (Data Book on Thermal Recycle of Waste Plastic) (Japanese), Plastic Waste Management Institute, 1994.
3. "Production and Shipping Results of Plasticizer" (Japanese), Vinyl and Polymers, Vol.39, No.6, 24, 1998.
4. Yoshioka, T.; Okuwaki A. "Chemical Recycling of Poly (Vinyl Chloride) to Raw Materials" (Japanese), Chemical Industry (Kagakukogyou), 563-570, 1994.
5. Yoshioka, T.; Okuwaki A. "Recycle Technology of Waste Plastics to Raw Materials and Fuel Oil" (Japanese), Chemical Industry (Kagakukogyou), 313-324, 1997.
6. Mikata N. "Special Issue / The Recent Condition and Task of Resource and Task of Converting Technique (2). Technique for Intermediate Processing and Recycling. The Recent Condition and Task of Converting Technique for Plastic Wastes into Oil" (Japanese), Urban Cleaning (Toshiseiso), 569-580, 1993.
7. Ivan, B. "Thermal Stability, Degradation, and Stabilization Mechanisms of Poly(vinyl chloride)," Adv. Chem. Ser., 1996, 249, 19-32.
8. Takahasi, H.; Isido, S.; Abe, Y.; Sato, T.; Saito, H. "Studies on Dehydrochlorination Equipment for Waste PVC" (Japanese), Technical report of Mitsubishi Heavy Industries, 10, 781-786, 1973.
9. Saito, K. "Pollution Free Conversion Technology of Waste Plastics for Recycle Use" (Japanese), Science and Industry (Kagakuto Kougyou), 66, 438-445, 1992.
10. Mikata, N.; Hasimoto, S.; Takeuchi, T.; Nishiyama, H. "Research in Thermal Decomposition Characteristics of Plastic Waste" (Japanese), Technical report of Nippon Steel, 360, 38-45, 1996.