Development of PVC Dechlorination Process

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To utilize effectively all waste plastics containing polyvinyl chloride(PVC), the removal of chlorine in PVC has been studied. A newly designed rotary kiln characterized by indirect heating and coke addition was adopted to PVC dechlorination process. Coarse coke was supplied to prevent an agglomeration of PVC particle and its sticking to an inner wall of kiln during PVC dechlorination. The heat for dechlorination was supplied from the outer tube of kiln so as to minimize the amount of processed gas containing HCl. Basically, it was verified that the rotary kiln could be smoothly operated due to the presence of coke particle. Dechlorination efficiency of PVC increased with increases in the processing temperature and retention time in kiln. From these results, it was concluded that an optimum reaction conditions to give 95 % of dechlorination efficiency were the processing temperature of 350 °C, the retention time of over 15 min and the PVC/Coke weight ratio of 1.0. It was estimated that the application of this process enable to utilize effectively industrial and municipal waste plastics containing PVC in the blast furnace.

1. Introduction

Waste plastics has shown rapid increase due to changes of life style and its amounts reached around 9 million tons at 1996[1]. We have already presented a method for utilizing the waste plastics by injecting it into a blast furnace as a raw material to further develop environmental conservation and resource recycling[2]. In this process, waste plastics excluding polyvinyl chloride (PVC) can be used as a reducing agent for coke and pulverized coal. The recycling of PVC has been hampered due to the corrosion of blast furnace facilities by hydrogen chloride. To promote waste plastics recycling, PVC dechlorination process is desired. This report describes the development of PVC dechlorination process.

2. Concept of PVC dechlorination process

From the view points of physical and chemical properties of PVC, the following points were taken into consideration for development of PVC dechlorination process. Coarse coke is supplied to prevent an agglomeration of PVC particle and its sticking to an inner wall of kiln during PVC dechlorination. PVC is dechlorinated by indirect heating to reduce

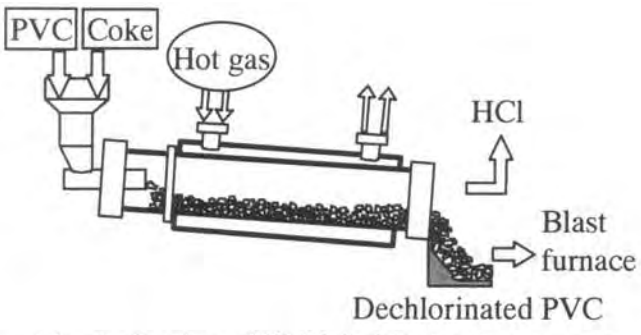
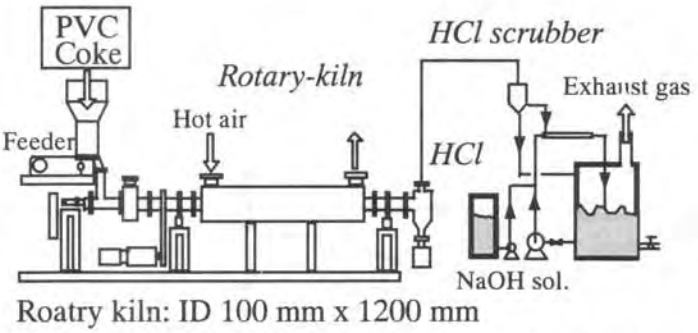


Fig. 1. Outline of PVC dechlorination process.

a generated gas processing apparatus from PVC dechlorination. Co-current gas flow is applied to prevent over-heating of PVC. Figure 1 shows the outline of PVC dechlorination process developed by NKK. The dechlorinated plastics can be used as blast furnace materials. Chlorine is recovered as hydrochloric acid .

3. Experiment

PVC dechlorination experiments were carried out by the apparatus as shown in Fig. 2. This apparatus consists of a rotary kiln furnace with an indirect heating and a processing apparatus of the generating gas. The newly-designed rotary kiln furnace with the size of 0.1 m ID and 1.2 m length can be processed 5 kg/h of a rigid PVC. Nitrogen was supplied into the rotary kiln in order to prevent PVC oxidation. The influence of reaction conditions on dechlorination were examined by the change of heating gas temperature and rotation of kiln. Processing temperature of PVC was represented as a temperature of gas generated at the end of kiln. PVC tested are various products that contain different chlorine content, 3 kinds of rigid PVC (PVC-1(Cl: 51.4 wt%): using for a board, PVC-3(55.2 wt%): using for a pipe, PVC-4(50.3 wt%): pellet for industrial material) and 3 kinds of soft PVC (PVC-2(41.0 wt%): PVC sheet, PVC-5(40.0 wt%): laminated with PE sheet, PVC-6(19.0 wt%): laminated with paper), respectively.



Roatry kiln: ID 100 mm x 1200 mm

Fig. 2. Experimental apparatus of PVC dechlorination.

4. Results and Discussion

4.1. Effect of coke addition on PVC dechlorination

To clarify the appropriate dechlorination conditions, various reaction conditions using PVC-1 were tested. Figure 1 shows the effect of PVC/Coke weight ratio on dechlorination efficiency. Dechlorination efficiency was not changed over the range of 0.5 to 2.0 of PVC/coke weight ratio. For the conditions with high ratio of PVC/coke, an agglomeration phenomenon due to the softened PVC was observed. On the other hand, the hydrocarbons yield by PVC pyrolysis was not changed over the range of 0.5 to 2.0 of PVC/coke weight ratio. Its yield gave 10 to 15 %. From the results, supply of coarse coke with PVC was effective to prevent an agglomeration of softened PVC particle and to promote heat transfer to PVC layer in a kiln. Therefore, 1 to 2 of PVC/Coke weight ratio was more suitable to this process.

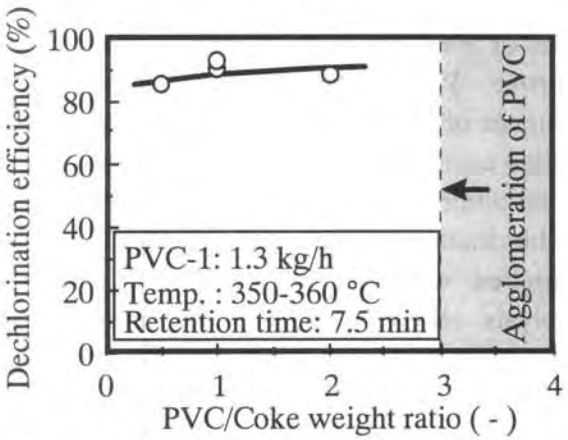


Fig. 3. Effect of PVC/Coke weight ratio on dechlorination efficiency.

4.2. Effect of reaction conditions on PVC dechlorination

Figure 4 shows the effect of processing temperature and retention time on dechrolination

efficiency and pyrolysis efficiency under conditions with 1 of PVC/Coke weight ratio using rigid PVC. Pyrolysis efficiency which indicates PVC decomposition to hydrocarbons was calculated by mass balance. The dechlorination efficiency increased as the processing temperature and retention time of PVC in a kiln increased. Gaseous hydrocarbons, benzene, toluene and tar were generated by PVC pyrolysis simultaneously with HCl generation. However, pyrolysis efficiency based on PVC feeding rate were not dependent on these reaction conditions and it had about 10%.

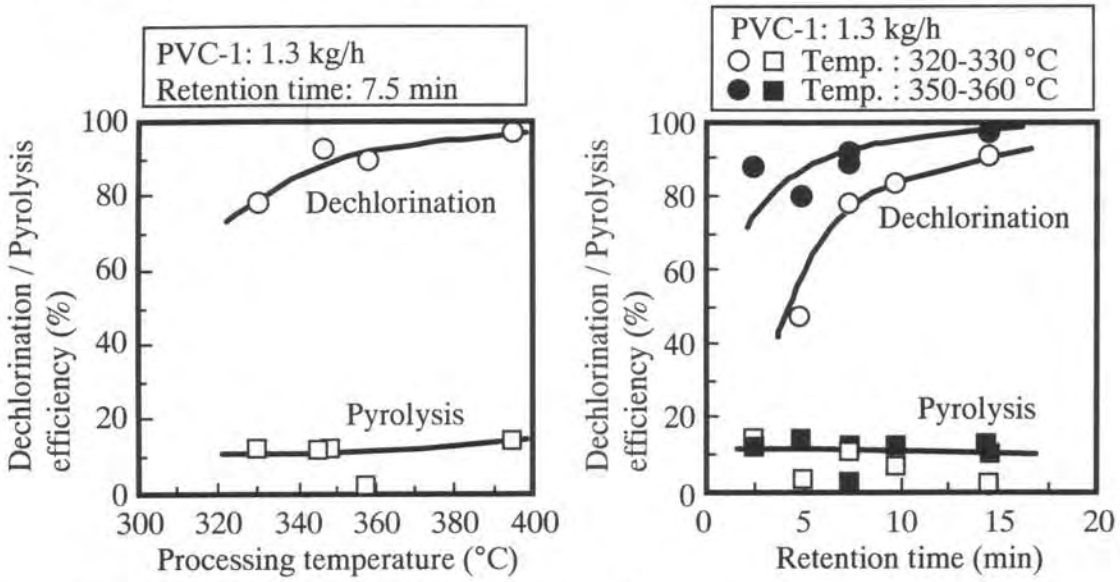


Fig. 4. Effect of reaction conditions on dechlorination / pyrolysis efficiency.

Most of PVC products contain a plasticizer to improve PVC properties. Therefore, the influence of PVC property on dechlorination was studied using PVC-2. Figure 5 shows the effect of retention time on PVC-2 dechlorination. Dechlorination efficiency of soft PVC was lower compared with that of rigid PVC, while its pyrolysis efficiency became higher than rigid PVC, in spite of the same reaction conditions. Dechlorination of soft PVC was a little different from that of rigid PVC because of its property. In the case of the rigid PVC, its dechlorinated plastics particle was porous materials foamed along with the removal of HCl. On the other hand, for the soft PVC of thin material, an agglomerated particle shrunk by heating was obtained. It was considered that the defference of pyrolysis efficiency depended on plasticizer in PVC, and also dechlorination efficiency was influenced by its shape. It was reported that the chlorine in PVC was eliminated as a hydrogen chloride by free radical mechanism[3]. Furthermore, in the presence of other polymer such as polystyrene, the radical generated from

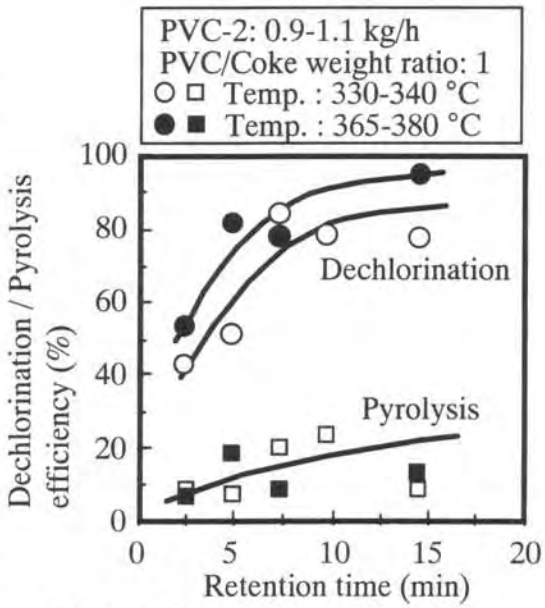
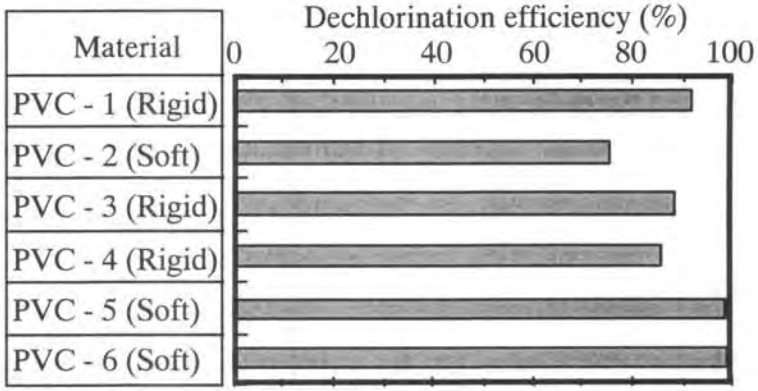


Fig. 5. Effect of retention time on dechlorination / pyrolysis efficiency.

polystyrene pyrolysis affects the dechlorination of PVC[4]. Therefore, it is considered that the radical generated from pyrolysis of plasticizer in soft PVC affected the dechlorination. From the above results, it was concluded that an optimum reaction conditions to give 95 % of dechlorination efficiency were the processing temperature of 350 °C, the retention time of over 15 min and the PVC/Coke weight ratio of 1.0.

4.3. Application to various PVC products

To apply all of PVC products to this process, various PVCs with different Cl content were tested. Figure 6 shows the dechlorination efficiency of various PVC. The efficiency of all PVC had about 90 % except PVC-2. PVC-5 and PVC-6 gave high dechlorination efficiency in spite of soft PVC and laminated with PE and paper. From this results, it can be suggested that the laminated PE and paper do not affect the PVC dechlorination. In either case, these dechlorinated plastics obtained by this process is suitable to the injection into the blast furnace.



PVC feed rate: 0.8-1.35 kg/h, PVC/Coke weight ratio: 1
Retention time: 7.5 min, Processimg temp.: 345-360 °C

Fig. 6. Dechlorination efficiency of various PVC products.

5. Conclusions

Through the basic research of PVC dechlorination using the rotary kiln furnace characterized by indirect heating, the following results were obtained.

(1) Coarse coke was effective to prevent an agglomeration of softened PVC particle and to promote heat transfer to PVC layer in a kiln.

(2) An optimum reaction conditions to give 95 % of dechlorination efficiency were the processing temperature of 350 °C, the retention time of over 15 min and the PVC/Coke weight ratio of 1.0.

On the basis of fundamental researches, the 1000t/y pilot plant installed in Keihin works which was supported in part by a grant from the Japan PVC Environmental affairs Council and the Plastic Waste Management Institute has been successfully operated. It can be concluded that this process contributes to the favorable recycling of waste plastics.

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