In Situ Removal of HCl in Copyrolysis Process of Fertilizer / Cattle Manure and Polyvinyl Chloride

Chanatip Samart and Apinya Duangchan
Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand

Abstract: An alternative method of hydrogen chloride removal in PVC pyrolysis used cattle manure and fertilizer. Preliminary study of thermal decomposition of PVC, cattle manure and fertilizer showed decomposition at the range 230-320°C. Releasing of HCl from PVC degradation and of ammonia from cattle manure and fertilizer degradation happened in this temperature. The ammonia reacts with HCl and becomes ammonium chloride. Copyrolysis of PVC and cattle manure or fertilizer was studied in a semi-batch reactor under nitrogen atmosphere. HCl was absorbed in sodium hydroxide and the removal efficiency was determined by back titration of the remaining sodium hydroxide. The HCl removal efficiencies increased from 40% to 80-85% when the amounts of cattle manure and fertilizer was increased from 1 to 6 times of PVC at 450°C and the removal was nearly complete at 600°C. Solid and liquid yield increased when the amount of manure fertilizer was increased. The main gas products were propane and carbon monoxide. The pH of the solid carbon was 5-6 for copyrolysis of PVC with fertilizer and 7 with cattle manure. Fixed carbon of the solid product was less than 20%.

Keywords: HCl Removal, PVC, Copyrolysis, Cattle Manure, Manure Fertilizer.

1. INTRODUCTION

In recent year, a lot of plastic wastes are accumulated because most plastics are not degraded. A common method to reduce plastic wastes is recycling. There are four types of recycling. Primary recycling is the reprocessing of scrap plastic. Secondary recycling is the remolding of plastic waste. Tertiary recycling is the conversion of plastic waste to petrochemical feedstock or fuel oil. The last one is quaternary recycling which produces energy from plastic wastes. The primary and the secondary recycling have limits in use because products from these recycling have low mechanical properties. The quaternary recycling produces air pollution from combustion reaction. Therefore, tertiary recycling is an appropriate method to reduce plastic waste.

Pyrolysis reaction is a type of tertiary recycling. It is a thermal decomposition of organic materials in the absence of air. Plastic waste is converted to fuel oil or feedstock. There are many researchers who study pyrolysis of plastic waste in different ways. Kaminsky and Kim [2] studied pyrolysis of mixed plastic in a lab scale fluidized bed reactor. They determined the composition of products and compared with technical process. The concentration of chloro-organic was lower in technical process due to long residence time. Wong and Broadbelt [3] studied pyrolysis of polypolypropylene and polystyrene binary mixture. The overall conversion of binary mixture was higher than the average conversion of pure case. Cilez et.al. [4] pyrolyzed virgin and waste of polypolypropylene and polyethylene and polystyrene mixtures by thermal gravimetric technique for kinetic study. The results showed impurities in waste plastic affected liquid product. Pyrolysis of plastics has been developed to commercial scale. However, pyrolysis process has a problem if polyvinyl chloride (PVC) exists in plastic waste. Pyrolysis of PVC causes corrosion problem from the hydrogen chloride produced. Many researchers have studied different methods of hydrogen chloride removal in pyrolysis of plastic waste. Yoshioka et.al. [5] decomposed PVC by oxidative degradation NaOH solution. The PVC was converted to carboxylic acid. Some metal oxide can be used in hydrogen chloride removal. It was changed to metal chloride form. Bhaskar et.al. [6] used calcium carbonate carbon composite in hydrogen chloride adsorbent. This adsorbent showed high efficiency, it gave chlorine free liquid product for consecutive six batch processes. Zhou et.al. [7,8] studied catalytic dechlorination using Al-Mg and Al-Zn composite oxide catalyst. However, these metal oxides have some cost when it is scaled up to a commercial plant.

An alternative method of hydrogen chloride removal in low operating cost is investigated in this study. The non-value substance such as cattle manure can be used in hydrogen chloride removal. While the manure is heating, ammonia gas is produced and reacted with hydrogen chloride. Ammonium chloride is formed. This research is aimed to study copyrolysis of PVC with cattle manure to remove hydrogen chloride.

2. EXPERIMENT

2.1 Pyrolysis reaction

Pyrolysis reaction was carried out in a semi-batch reactor. The 700 ml cylindrical stainless steel reactor was placed in an electrical furnace. The process diagram is shown in Fig 1. Polyvinyl chloride (PVC) was obtained from VinyThai Public Company, Thailand. It was mixed with cattle manure at various ratios and loaded in the reactor. The reaction was run in two steps. First step, the reactor was heated to 250°C for dechlorination reaction and remained at this temperature for 30 min. After that the reactor was heated to pyrolysis temperature. Liquid was condensed by a condenser and collected in a flask. The gas product passed through sodium hydroxide solution. The remaining hydrogen chloride was absorbed and the gas products were collected in a gas sampling bag.

2.2 Analysis of product

In pyrolysis reaction, there are three types of products; solid, liquid and gas. The proximate analysis of solid product was followed ASTM D3172-89. The heating value of liquid product was determined by bomb calorimeter (model PAR 1261) and gas product was analyzed by gas chromatograph (model varian CP3800). The amount of sodium hydroxide remained in the solution after the reaction was analyzed to determine hydrogen chloride removal efficiency.
3. RESULT AND DISCUSSION

3.1 Study of thermal decomposition of PVC, cattle manure and manure fertilizer

Thermal decomposition was studied by thermal gravimetric analysis (TGA). The degradation profile of PVC had two steps as shown in Fig 2. The first step is dechlorination in the temperature range 230-320°C. The last step is the breaking of carbon-carbon backbone at temperature higher than 400°C.

Fig. 2 Thermal decomposition of PVC.

The decomposition profile of cattle manure and manure fertilizer is shown in Fig 3. At temperature range of 100-120°C, evaporation of moisture occurs and at temperature greater than 250°C nitrogen compound decomposes to ammonia gas and hydrocarbon compound. Cattle manure decomposed easier than manure fertilizer about 8%.

Fig. 3 Thermal decomposition of manure fertilizer and cattle manure.

As shown in Fig 2 and 3, temperature range of dehydrochlorination of PVC and decomposition of nitrogen compound from manure was in similar temperature range. Therefore, manure can be used for hydrogenchloride removal.

3.2 Study of hydrogen chloride removal

The HCl removal efficiencies of manure fertilizer: PVC and cattle manure: PVC at different ratios are shown in Fig 4. The removal efficiencies at reaction temperature of 450°C increased from 40 % to 80-85% by mol when the amount of nitrogen compound was increased to six times of PVC. At low amount of nitrogen compound, the removal efficiencies of different nitrogen compound were not different at all temperatures. At reaction temperature of 450°C, the efficiencies of cattle manure were more than manure fertilizer when nitrogen compound had more than three times of PVC amount. Since cattle manure provided ammonia more than manure fertilizer that showed in TGA results.

Fig. 4 HCl removal efficiencies of manure fertilizer and cattle manure at different ratios.

The removal efficiencies of both nitrogen compounds at 600°C were higher than at 450°C. At 600°C, manure fertilizer can removed HCl higher than cattle manure and the removal was nearly completed at the PVC: manure fertilizer ratio of 1:6.

3.3 Study of product yields

Product yields of copyrolysis PVC and manure fertilizer at different ratios and at reaction temperature of 450°C are shown in Fig 5. Solid and liquid yield increased from 30%wt and 10%wt to 65%wt and 19%wt respectively and gas yield decreased from 51 to 16%wt when the ratio of PVC: manure fertilizer was increased from 1:1 to 1:6. Yields of liquid and solid product increased and gas products decreased due to the removal of chlorine from gas phase to liquid and solid phase.

Solid and liquid products yields increased from 35%wt to 48%wt and 20%wt to 31%wt respectively and gas product decreased from 45%wt to 20%wt when the amount of cattle manure was triple. When the amount of cattle manure increased more than three times of PVC, all product yields were constant.
3.4 Analysis of gas products

The compositions of gas product from copyrolysis of PVC and manure fertilizer at different ratios are shown in Fig. 9. Most gas products consisted of propane and carbon monoxide. Carbon monoxide gas came from manure fertilizer which has oxygen atom in structure.

3.5 Analysis of liquid products

The heating value of liquid products was analyzed by bomb calorimeter. Heating value of the liquid product was in the range of 2.31–7.7 KJ/g. The heating value of product from copyrolysis PVC with manure fertilizer at reaction temperature 450°C increased from 2.31 to 6.03 KJ/g when the amount of manure fertilizer was increased to six times and heating value of product from PVC and cattle manure mixture increased from 3.63 to 7.68 KJ/g when the ratio of PVC: cattle manure was from 0.33 to 0.20. The amount of nitrogen compound affected the heating value of liquid product.

3.6 Analysis of solid product

The solid products were analyzed for proximate analysis followed ASTM D3172-89. The fixed carbon in solid product from copyrolysis PVC and manure fertilizer at different ratios at 450°C is shown in Fig. 11. The weight percent of fixed carbon decreased from 5.0 to 1.4 but ash increased from 55.5%wt to 65.0%wt when the amount of manure fertilizer was increased to six times of PVC. Many ashes came from soil in fertilizer.
Fig. 11 Proximate analysis of solid product from co-pyrolysis of PVC with manure fertilizer at different ratios at 450°C.

The proximate analysis of solid product from co-pyrolysis PVC and cattle manure in Fig 12 showed increasing of ash and fixed carbon, however, volatile matter decreased when the amount of cattle manure was increased. Cattle manure had higher fixed carbon than manure fertilizer.

Fig. 12 Proximate analysis of solid product from co-pyrolysis of PVC with cattle manure at different ratios at 450°C

The pH of solid products was studied. Solid product from pure cattle manure provided pH = 8 and pH decreased to pH=7 when it was mixed with PVC and cattle manure due to acidity from PVC. The pH of solid product from PVC and manure fertilizer was below 7.

Fig. 13 pH of solid product from co-pyrolysis of PVC with manure fertilizer and PVC with cattle manure at 450°C

4. CONCLUSION

Cattle manure and manure fertilizer can remove hydrogen chloride from PVC pyrolysis. The efficiency of removal is nearly 100%. The product yields are affected by amount of nitrogen compound. Manure fertilizer provide high amount of solid product. Mainly gas product is propane. It can be used as fuel. The heating value of liquid product is in the range of 2.31- 7.7 KJ/g. Water must be separated before use as fuel oil. The amount of fixed carbon in co-pyrolysis of PVC with cattle manure is higher than manure fertilizer and pH of the solid is in neutral range. Solid product can used as a new material for activated carbon.

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REFERENCES