

DECHLORINATION OF PVC IN CATALYTIC PYROLYSIS OF PACKAGING PLASTIC WASTES

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Abstract

PVC is frequently present in plastic wastes giving rise to the presence of chlorine in pyrolysis products, which is rather detrimental for their potential applications mainly due to chlorine environmental hazards. The use of zeolites has been proved to be beneficial for the pyrolysis process and it has been demonstrated that a low temperature dechlorination step prior to the pyrolysis process significantly reduces the chlorine content in the liquid products. In this paper the combination of both, catalyst and dechlorination step, is explored. A mixture of PE, PP, PS, PET and PVC has been pyrolysed in a 3.5 dm³ semi-batch reactor at 440 °C for 30 min using a ZSM-5 zeolite as catalyst. A previous low temperature (300 °C) dechlorination step has been carried out both with and without catalyst. It has been proved that the application of such dechlorination gives rise to a 75 wt% reduction of chlorine in the liquid fraction. However, such step has a negative influence on the catalyst, which loses some catalytic activity. The optimum procedure in terms of quality and chlorine content of the products is first a low temperature step and then the catalytic pyrolysis step.

Keywords: stepwise pyrolysis, feedstock recycling, catalytic decomposition, plastic wastes, dechlorination.

1. Introduction

PVC is one of the most widely used polymers. However, the presence of chlorine in the PVC backbone is the key concern when it comes to waste PVC management, due to the chlorinated compounds which can arise during waste treatment operations as a consequence of the molecular instability of PVC towards heat and light [1]. Pyrolysis is a process which has received renewed attention in the last years for recycling plastic wastes, converting them in potentially useful liquids and gases. In the pyrolysis process (heating in an oxygen free atmosphere), the organic components of the material are decomposed generating liquid and gaseous products while the inorganic ingredients (fillers, metals, etc.) remain practically unaltered in the reactor. When PVC containing samples are pyrolysed, the pyrolysis process can be improved by means of a previous low temperature step in order to remove chlorine from the original sample as HCl, which evolves as a gas at temperatures around 300 °C, preventing the generation of chlorinated compounds in the liquid fraction [2]. On the other hand, it is well known that the use of catalysts enhances the quality of pyrolysis products. Therefore, the objective of this paper is to study the effectiveness of the previous dechlorination step when catalyst is used in the pyrolysis process, in order to obtain high quality pyrolysis liquids with low contents of chlorine.

2. Materials and Methods

A mixture of 40 wt% PE, 35 wt% PP, 18 wt% PS, 4 wt% PET and 3 wt% PVC in pellet size (≈3 mm) was used for the pyrolysis experiments. The catalyst used was a

commercial ZSM-5 zeolite; in all the experiments it was used as received and in a plastic/catalyst ratio of 10/1.

The pyrolysis experiments were carried out using an unstirred stainless steel 3.5 dm³ reactor in semi-batch operation. In all the experiments, 100 g of plastic sample were placed into the reactor; nitrogen was passed through at a rate of 1 dm³ min⁻¹ through all the run, and the vapours leaving the reactor flowed to a series of running water cooled gas-liquid separators where the condensed liquids were collected. The uncondensed products were passed through an activated carbon column and collected as a whole in Tedlar plastic bags.

Three different pyrolysis methods were explored. 1) "Conventional catalytic pyrolysis", in which the plastic sample was mixed with the catalyst and the system was heated at a rate of 20 °C min⁻¹ to 440 °C, and maintained there for 30 min. 2) "Catalytic stepwise pyrolysis", in which the plastic sample was mixed with the catalyst, a previous dechlorination step was carried out at 300 °C during 60 min and then the temperature was raised at 20 °C min⁻¹ to 440 °C to complete the pyrolysis process. 3) "Non catalytic dechlorination step + catalytic pyrolysis", in which the dechlorination step was applied to the plastic sample alone (without catalyst) and then the catalyst was added, carrying out the final pyrolysis as in the other methods. The amount of solids remaining in the reactor and the liquids condensed in the gas-liquid separators were weighed after pyrolysis and the pyrolysis yields were calculated as weight percentage with respect to the raw material pyrolysed. Gas yields were normally determined by difference. Method 5050 of the Environmental Protection Agency (EPA) of the United States was used for chlorine determination. Additionally, pyrolysis liquids were also analysed by GC-MS.

3. Results and Discussion

The liquid, gas and solid yields (weight %), obtained with the three mentioned pyrolysis methods are presented in Table 1.

Table 1. Pyrolysis yields (wt%)

	Liquids	Gases	Solids
Method 1	56.9	40.4	3.2
Method 2	69.0	29.0	2.0
Method 3	56.8	41.2	2.0

If the pyrolysis yields of methods 1 and 2 are compared, when the previous dechlorination step is carried out in presence of the catalyst an increase in liquid yield and a decrease in gas yield compared with the conventional catalytic experiment is produced. This fact suggests that the zeolite losses some activity during the dechlorination step. In addition, Table 4 shows that when the catalyst is added to the sample after the dechlorination step, almost the same yields as in the conventional catalytic experiment are obtained, which confirms that the dechlorination step caused the loss of activity of the zeolite.

Figure 2 shows all the compounds identified in the pyrolysis liquids by GC-MS grouped in three categories according to their carbon number: C5–C9, C10–C13 and >C13.

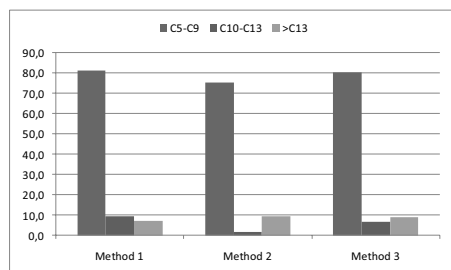


Fig. 1. C5-C9, C10-C13 and >C13 fractions of the pyrolysis liquids (% area).

As it can be seen, C5-C9 is the main fraction of the pyrolysis liquids in a conventional catalytic experiment, ranging more than 80% area. The formation of light hydrocarbons in the pyrolysis of polyolefinic plastic wastes in presence of ZSM-5 zeolite has been reported before [3], and it is very interesting since C5-C9 is the gasoline carbon number range. When the dechlorination step is carried out in presence of the zeolite, the percentage of light (C5-C9) and medium (C10-C13) hydrocarbons significantly decrease (75.5 and 1.5% area respectively), and the yield of heavy hydrocarbons increases up to 9.5% area. This fact is in agreement with the previously mentioned loss of activity of the catalyst that is produced during the previous step. In fact, when the catalyst is added after the dechlorination step, the C5-C9 yield is quite similar to that of the conventional catalytic run.

Table 8 shows the percentage of chlorine in the products obtained after each experiment.

Table 2. Chlorine in the pyrolysis fractions (wt%)

	Liquids	Gases	Solids
Method 1	1.2	1.0	0.4
Method 2	0.3	3.0	0.4
Method 3	0.3	2.2	0.4

It can be seen that the chlorine content of the liquids after a conventional catalytic pyrolysis run is 1.2 wt%, which is quite high and may condition the potential application of such liquids. When the dechlorination step is applied, the chlorine content of the liquids decreases in both cases (from 1.2 to 0.3 wt%), which is equivalent to a 75% reduction of chlorine in the liquids with respect to the conventional catalytic pyrolysis liquids. Since chlorine evolves as HCl (mainly generated in the first step), Table 8 shows higher contents of chlorine in the gases when the previous dechlorination step is used (2.2 - 3.0 wt%) than that obtained in conventional catalytic pyrolysis (1.0 wt%). As it has been mentioned before, the objective of this previous step is precisely to separate the chlorine as HCl, since in an industrial process HCl could be absorbed in alkaline solutions by means of wet scrubbers and the gases generated in the subsequent pyrolysis step would be free of chlorine.

4. Conclusions

Catalytic pyrolysis is an attractive alternative for recycling mixed plastic wastes. However, the presence of PVC in the original sample leads to the generation of chlorinated chemicals which are part of the pyrolysis liquids, and this is very detrimental for their potential applications. The liquids chlorine content can be reduced up to more than 75 wt% compared to conventional catalytic pyrolysis by means of a previous dechlorination step at 300° C during 60 min. However, the authors have proved that when the catalyst is mixed with the sample from the beginning of the process, the previous dechlorination step significantly decreases the catalyst activity, giving rise to liquids with a higher content of heavier hydrocarbons. On the other hand, the addition of the catalyst after the thermal dechlorination step has been found to be an efficient method to obtain almost the same results as in the conventional catalytic process, in terms of products yield and quality, and at the same time the high reduction in the chlorine content of the liquids.

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