PYROLYSIS OF MIXED PLASTICS IN THE FLUIDIZED BED USING HARD BURNT LIME AS BED MATERIAL

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Abstract: A mixture consisting of 40 wt% PS, 20 wt% PE, 20 wt% PP and 15 wt% PET were pyrolyzed in the presence of both steam and nitrogen, using a fluidized bed reactor with hard burnt lime (HBL) as bed material. The experiments were carried out at 600 °C and 700 °C. In opposite to soft burnt lime, HBL showed good fluidizing properties and little erosion. Since both CaO and $Ca(OH)_2$ are widely used as aggregates in order to fix HCl and catalyze the degradation of organic acids, the purpose of this research was the investigation of the impact on the product distribution and the ability of HBL to support the degradation of PET. Compared with experiments applied in the presence of quartz sand, the gas yield increased, while the wax fraction was strongly reduced. In the presence of HBL, the benzene yield rose strongly due to the decarboxylation of PET.

1. Introduction

The pyrolysis of mixed plastics is one of the useful feedstock recycling techniques. Waste plastics consist mainly of poly(ethylene) (PE), poly(propylene) (PP), poly(styrene) (PS), and poly(ethylene terephthalate) (PET). Polyolefines, such as PE, and PP, and PS, can be converted into oil via thermal decomposition. However, the thermal decomposition of PET causes not only corrosion and blocked pipes, but also the reduction of the oil yield by the generation of sublimating substances, such as terephthalic acid (TPA) and benzoic acid. As a countermeasure against these difficulties, hydrated lime ($Ca(OH)_2$)was introduced into the process in order to avoid the problems mentioned above [1]. On the other hand, the pyrolysis of PET in a steam atmosphere in contact with $Ca(OH)_2$ or CaO at above 520°C led to a high yield of benzene without the production of sublimating substances[2,3]. We suggest that the application of this reaction to the pyrolysis of mixed plastics, using a fluidized bed reactor with hard burnt lime (HBL) as bed material, might also be able to eliminate the problems, caused by sublimating materials.

2. Experimental

2.1 Material

The material used in these experiments was mixed virgin plastics, consisting of 40 wt% PS, 20 wt% PE, 20 wt% PP, and 15 wt% PET (Aldrich) with the particle sizes of less than 500 μm. HBL was received from Okutama Kougyou.

2.2 Pyrolysis experiment

The experiments were carried out in a fluidized bed reactor (Fig.1) at 600 °C and 700 °C in nitrogen and steam atmosphere (0, 70 vol%, 7.5 l min^{-1} at room temperature). The steam was generated at 250 °C and piped through an isolated tube into the reactor. The sample (200 g) was fed into the hot reactor at 70-123 g h^{-1}. HBL (500 g) with a particle size of 300-500 μm was used as bed material. The product oil and wax were gathered in cooling units, cooled with water and ethanol, and an electrostatic precipitator. The collected oil and wax ware distilled, using the fluorine cut at 295 °C. Gas samples were collected in a gas bags. The gas composition was analyzed by GC-TCD, using a packed column. The distilled oil was analyzed qualitatively by GC-MS with a HP-5MS capillary column. The quantitative analysis was carried out by GC-FID with capillary column of the same type. The wax was fractions were analyzed by FT-IR. The bed material was analyzed by XRD.

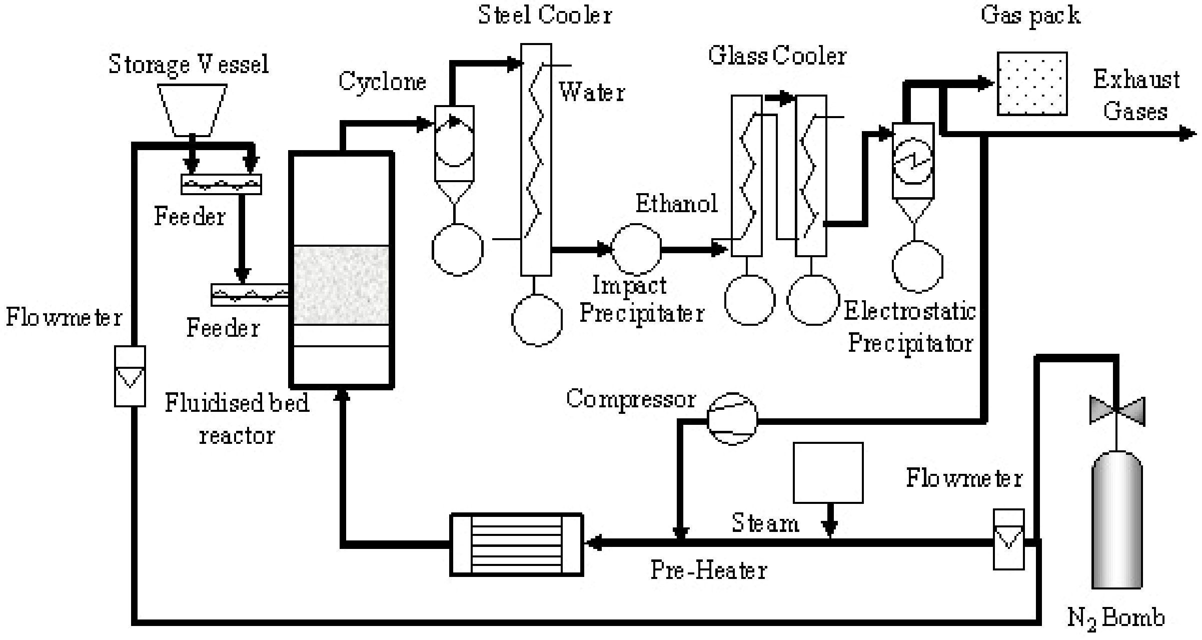

Fig.1 Experimental setup

3. Result and Discussion

Fig. 2 shows the yields of the pyrolysis of mixed plastics at 600 °C and 700 °C. In the case of HBL was used in place of sand as bed material in N_2 atmosphere at 600 °C, the yield of wax was decreased from 35.8 wt% to 10.0 wt%. On the other hand, the yields of the gases rose from 17.4 wt% to 40.9 wt%. The addition of HBL caused also the degradation of PET, increasing the benzene yield from 0.01 wt% to 3.6 wt%. Fig.3 shows the FT-IR spectra of wax (a) using HBL as bed material, in N_2 atmosphere, (b) HBL, in steam (c) sand, in N_2 (d) Sand, in steam, and (e) TPA, each obtained at 600 °C. The FT-IR spectra of (c), (d) and (e) display the absorption bands of the C=O stretching vibrations (around 1150 cm^{-1}) and the C-O stretching vibrations (around 1700cm^{-1}) derived from TPA. These were not visible it the FT-IR spectra of (a) and (b), indicating the degradation of TPA derived from PET in the presence of HBL. In the presence of HBL, the amount of waxes decreased by 25.8 wt%. Since the degradation of the TPA, derived from PET, can be accounted for a maximum of 12.8 wt% in the absence of HBL, another 13.0 wt% of waxes, derived from other plastics, were converted into lighter compounds.

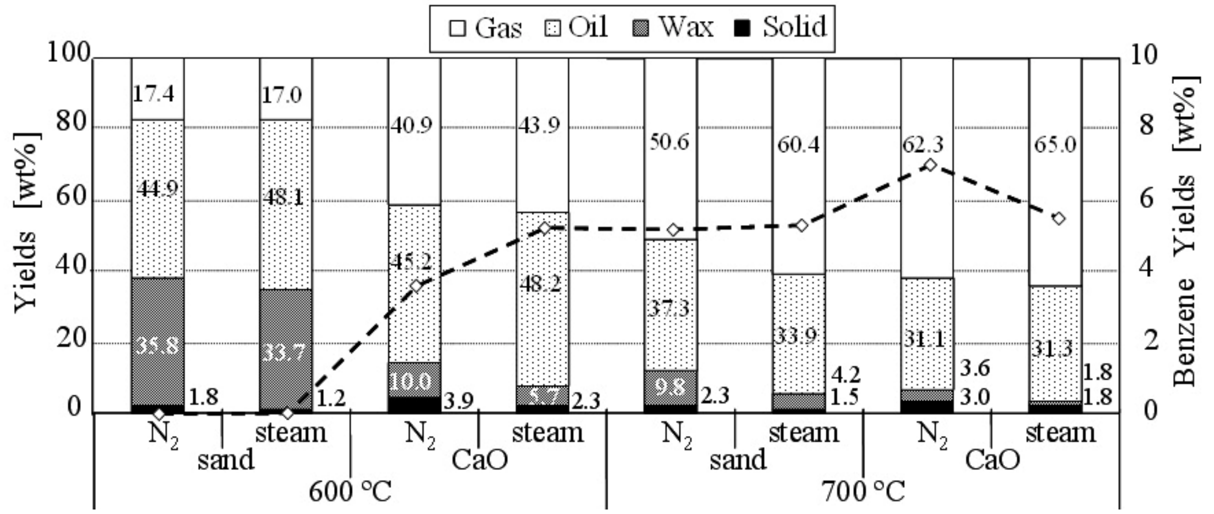

Fig.2 Yields of the pyrolysis of mixed plastics with different bed materials and fludizing gases at 600℃ and 700℃

There is a possibility that PET inhibits the decomposition of other plastics. Under this consideration, HBL prevents the inhibition of the degradation of plastics by PET. Assuming that benzene was derived solely from PET, the change of the benzene amount from 0.01 wt% to 3.6 wt% means that the benzene yield increased from 0.06 % to 24 %. When steam was used as fluidizing gas, the yields of waxes and solids decreased due to steam cracking. Moreover in the case of using HBL as bed material, steam addition increased the benzene yield from 24% to 35 %, caused by the hydrolysis of PET promoting the production of terephthalic acid which was decomposed to benzene and CO_2.

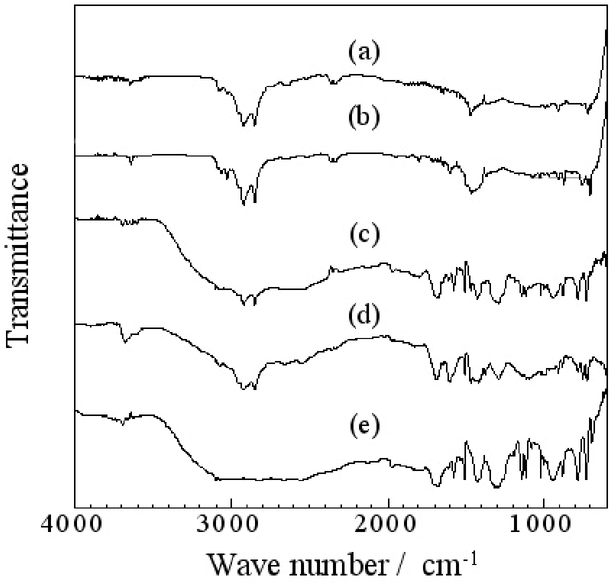

Fig.3 FT-IR spectra of wax(a) HBL N_2(b) HBL Steam(c) Sand N_2 (d)Sand Steam(e)TPA

At 700 °C, the yields of the pyrolysis of mixed plastics with different bed materials and fluidizing gases (Fig.2), did not indicate significant changes in the presence of HBL, assuming that the degradation of TPA to benzene and other component at 700 °C was little affected by HBL. When steam was added, decreasing yields of waxes and solids were observed, comparable to the reaction at 600 °C. However, another rise of the benzene yield was not observed indicating that at this temperature the pyrolysis rate is faster than hydrolysis rate.

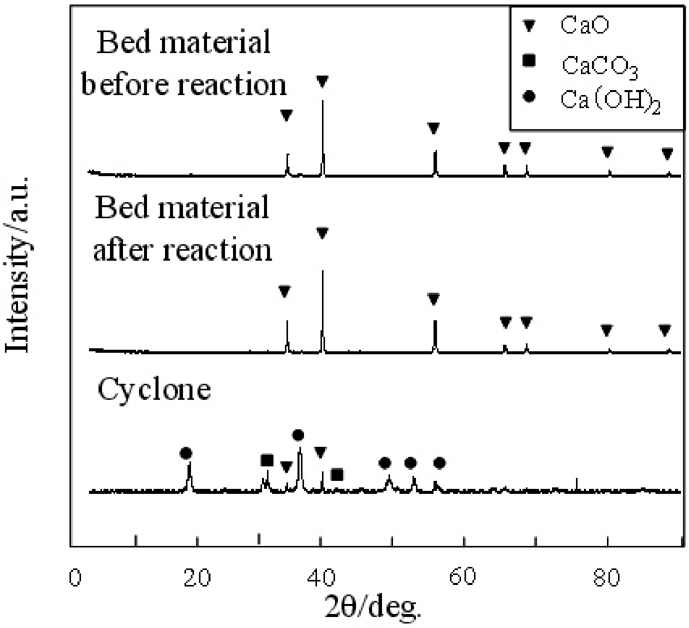

Fig.4 XRD of the HBL before and after the reaction and the cyclone fraction

Fig.4 shows the XRD of the HBL before and after the reaction and the cyclone fraction, obtained after the experiment at 600 °C in steam atmosphere. The HBL, obtained from the cyclone, consisted of CaO, $Ca(OH)_2$, and $CaCO_3$. CaO formed $Ca(OH)_2$ in the presence of steam. $CaCO_3$ was produced by the absorption of CO_2 after the degradation of TPA. However, the HBL that remained in the bed did not show any changes due to the regeneration of $CaCO_3$ after the end of the experiment during the cooling down procedure. The high dynamic of this process, shows that HBL can be used for long reaction cycles, without being replaced or regenerate.

4. Conclusion

Using HBL as bed material and steam as fluidizing gas can reduce the yields of waxes and increase the yields of gases. When HBL is used as bed material at 600 °C, the yields of useful products, such as oils and gases, becomes comparable to those at 700 °C. This indicates that HBL is an efficient catalyst for the feedstock recycling of mixed plastics by pyrolysis.

Possibility of reuse of HBL was confirmed.

References

[1] M. Shioya, K. Wakai, M. Fukushima, and H. Ibe, *Towards maximizing recycling rate in Sapporo plastics liquefaction plant, the 4th ISFR* ***2007***.

[2] T. Yoshioka, E. Kitagawa, T. Mizoguti and A. Okuwaki, Chemistry Letters, 2004, 33,282-283.

[3] T. Yoshioka,T. Handa , G. Grause,Z. Lei, H. Inomata, T. Mizoguchi *,J. Anal. Appl. Pyrolysis,* **2005**,*73*,139–144.