FEEDSTOCK RECYCLING OF NITROGEN CONTAINING POLYMERS BY FLUIDIZED BED PYROLYSIS

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Abstract

The increasing use of plastics and the high crude oil price prefer the research to pyrolyze mixed plastics into gas and oil. Well established are the use of polyolefins, PMMA, PET, and polystyrene as feedstocks for recycling by pyrolysis. One problem for cracking mixed plastics into suitable products is the contamination of nitrogen containing polymers. These materials produce by higher pyrolysis temperatures high amounts of toxic components, such as HCN and nitriles. Pure polyamides (Pa 6 and Pa 6.6) and polyuretanes (PUR) were used as feedstock in a fluidized bed pyrolysis process by temperatures of 810°C. Acryl nitrile butadiene styrene copolymers (ABS) were pyrolyzed by 800°C in a plant with a throughput of 3 kg/h. It was one goal of the study to investigate the concentration of HCN and nitiles in the pyrolysis products. In mixed plastics pyrolysis the concentration of HCN and nitiles decrease lineary with the amount ot nitrogen containing polymers. That makes it possible to calculate the amount of hazard compounds.

Keywords: *Fluidized bed pyrolysis, polyamide, nitrogen containing polymers, gas and oil*

1. Introduction

The pyrolysis of mixed plastics is receiving attention since the crude oil price is increasing rapidly and as a route for the disposal of the large quantities of plastic wastes collected by different systems. Mechanical recycling can be preformed solely on single polymer plastic waste since a market can be found only if the recycled products show a high quality. The more complex and contaminated the waste, the more difficult it is to recycle it mechanically. The pyrolytic route is favored because of the high rates of conversion into oil and gas which can be obtained. The gas with a high caloric value may be used as fuel for heating in the process. Some processes to recycle plastics by pyrolysis are near to be commercialized such as pyrolysis in vessels, autoclaves, rotary kilns and fluidized bed reactors (1,2).

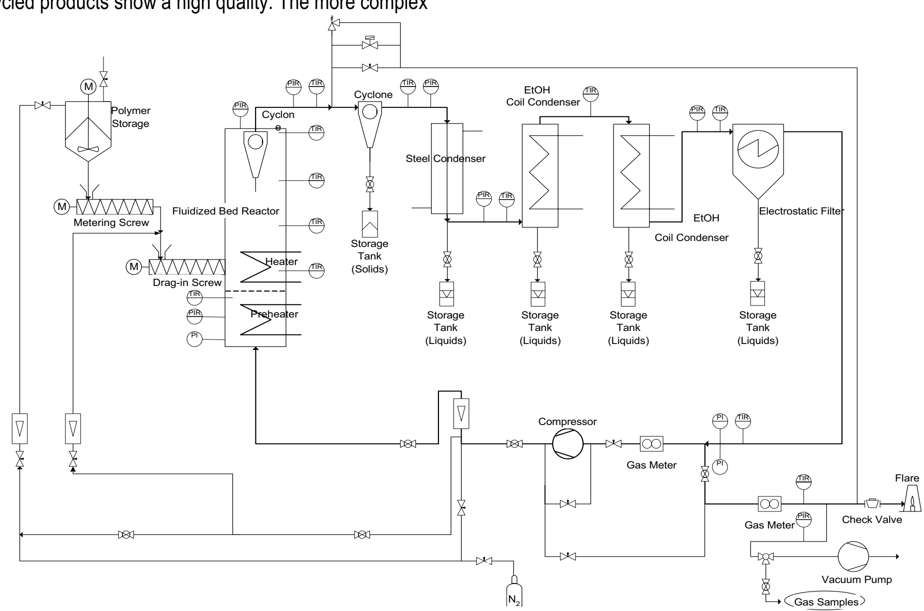

Fig. 1. Flow scheme of the used fluidized bed process.

For the commercial use it is necessary to know the content of toxic compounds in the gas and oil products which are produced by pyrolysis of mixed plastics. Beside PVC as feedstock which produces high amounts of HCl, the content of nitrogen containing products are of interest, such as brussic acid (HCN), nitriles, and isocyanates. These compounds are produced from nitrogen containing polymers.

2. Materials and Methods

For the experiments were used polyamide 6 (PA 6), polyamide 6.6 (PA 6.6), polyurethane (PUR), and acrylonitrile-butadiene-styrene copolymers (ABS).The nitrogen content in PA 6 and PA 6.6 was 12 wt% in ABS 3 wt%.

The pyrolysis experiments were carried out in a laboratory scale fluidized bed reactor with a throughput of 1-3 kg/h of polymers (Figure 1). The reactor consist of a steel tube (length 770 mm, 154 mm inside diameter). The gas distributor is a steel plate with 108 tubes. The fluidized bed of fine sand (0.3-0.5 mm) is heated indirectly by electricity. Nitrogen or steam are used as fluidizing gas, but during the experiments it is displaced by gaseous pyrolysis products. The feed material is inserted into the reactor, using two screw conveyers. The product gases are cooled in different separation units. Carbon black and fine sand are precipitated in a cyclone.

The product fractions obtained were analyzed by different capillary GC-columns and registered with TCD_ and FID-detectors. The reactor sand used and the precipitates in the cyclone were combusted in a furnace to constant weight. The loss in weight was balanced as carbon black and inorganic fillers. All results of the analysis of the organic product fractions were combined together to form a total mass balance.

3. Results and Discussion

Table 1 gives an overview on the product composition of the different polymers pyrolyzed.

Table 1. Pyrolysis of PA, PUR, ABS.

Feed:	PA 6	PA 6.6	PUR	ABS
Pyrolysis T	810 °C	810 °C	750 °C	800 °C
Fluidizing gas	pyro-gas	steam	steam	pyro-gas
Products:				
Gas (wt%)	52	52	53	32
HCN	8.5	8.7	0.5	5.9
Nitriles	9.2	9.0	8.0	4.1
Oil	25.4	26.2	19.8	44
Tar/C	22.6	21.8	27.2	24

Gas with over 50 wt% is the main fraction for polyamides and polyurethane as feedstock by a pyrolysis temperature of 810°C. Using ABS the main product fraction with 44 wt% is oil. HCN formed reaches 8.5 or 8.7 wt% for PA 6 or PA 6.6 while this is only o.5 wt% for PUR and 5.9 wt% for ABS.

The gas fraction (Table 2) contains mainly CO, methane, ethane and HCN. The HCN concentration reaches values of over 18 wt% for PA and ABS as feedstock.

Table 2. Pyrolysis gas of PA, PUR, ABS

Feed:	PA 6	PA 6.6	PUR	ABS
Pyrolysis T	810 °C	810 °C	750 °C	800 °C
Products:wt%				
Hydrogen	0.6	1.2	1.3	3.2
CO	26	31	46.7	5.7
CO_2	2.1	3.4	3.7	3.0
Methane	12.4	16.1	24.7	45.9
Ethene	22.6	21.3	10.3	10.0
Ethane	2.8	3.1	0.8	1.0
Propene	1.9	2.4	0.4	0.9
HCN	18.4	18.9	2.0	18.3
Others	13.2	2.6	10.1	12.0

Main components in the oil are by a pyrolysis temperatures of 750 -810°C benzene, toluene, naphthalene and nitriles. Table 3 shows the concentrations of some nitriles in the product oil.

Table 3Nitriles concentration in the oil fraction

Feed:	PA 6	PA 6.6	PUR	ABS
Pyrolysis T	810 °C	810 °C	750 °C	800 °C
Products:wt%				
Acetonitrile	1.4	1.2	0.9	1.3
Acrylonit.	2.4	3.4	0.3	0.4
Benzonit.	0.4	1.0	5.9	2.8
Propionit.	0.3	0.8	0.1	0.1

All nitriles together give a concentration of 5-8 wt% in the products. Mixed plastics collected by household waste separation contain about 2 wt% of PA, PUR; and ABS. The concentration of toxic HCN and nitriles can be calculated to be less than 0.2 wt% in pyrolysis products.

References

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