

Feedstock recycling of heterogeneous chlorine rich polymer waste

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This study describes the investigations of a back-to-feedstock method for heterogeneous chlorine rich containing plastic waste streams, which has been developed at the Eindhoven University of Technology (TUE).

In a lab-scale reactor PVC has been gasified with the aid of steam at 850°C into a gas consisting of H₂, CO, CO₂, CH₄ and HCl. The process is carried out in a fluidised bed reactor with the use of alumina as a catalytic bed material.

The experiments have shown that the HCl-recovery strongly depends on the presence of calcium in the feed. For virgin PVC the HCl-recovery was complete without detectable amounts of chlorinated hydrocarbons. The organic part of the waste could be completely converted to syngas, without the formation of tars. It appeared that the formation of tars strongly depended on the quality of the bed material and the process conditions.

This study has shown that the investigated back-to-feedstock method is a promising and energetic interesting route for solving the chlorine rich polymer waste problem. The HCl can be recovered as a 30wt% solution (muriatic acid) and used as feedstock for the vinyl chloride (VC) production. The remaining gases can function either as a syngas or as a fuel gas for energy recovery with high efficiency e.g. via a combined cycle system.

Introduction

With a total consumption of 5.4 Mton in Western Europe in 1994, PVC is one of the major bulk polymers [1]. Although most PVC products show a long service life, they will become waste at a certain point in time. In the Netherlands the bulk of the PVC-waste is incinerated with the municipal waste, since law prohibits dumping by landfill. The processing of PVC in municipal waste incinerators is however much disputed because of the corrosion of HCl and dioxin formation. Only a very small part of the PVC-waste is recycled at this moment by mechanical recycling (28 kton/y in Western Europe, 1994, [1]). Mechanical recycling of PVC is restricted to the homogeneous and easy obtainable part of the PVC waste e.g. production waste, pipes and window frames. Moreover, it has become apparent that mechanical recycling is limited because of down-cycling effects and difficulties in getting a clean enough raw material.

Back-to-feedstock recycling can cope with the heterogeneous and contaminated part of PVC waste but is still in its infancy. The presence of PVC in back-to-feedstock processes for Mixed Plastic Waste (MPW) often leads to technical complications (corrosion of HCl, HCl-removal and gas cleaning) and to high costs. Pyrolysis experiments of MPW at the University of Hamburg by Kaminsky [2] have shown that the PVC content of the input material cannot exceed 2-3%, making preliminary dehydrochlorination or separation of PVC necessary. Sole pyrolysis of PVC has been investigated extensively on different scales by Balcerek [3], Scott [4] and Wu [5]. Also the sole incineration of PVC waste with HCl recovery has been studied by Schaub [6], but this research has not yet resulted in a feasible process. Pyrolysis of PVC results in the production of large quantities of char and tar and the formation of chlorinated

hydrocarbons [2,3] mainly chlorobenzene. Research by Oudhuis [7] shows that incineration of PVC leads to a substantial increase in the formation of chlorinated dibenzodioxines and dibenzofuranes in the flue gas. By using steam as gasification agent these problems can be overcome.

Figure 1 shows a general overview of the hydrothermal recycling process for PVC waste as studied. PVC is converted into HCl and a gas mainly consisting of CO, H₂, CO₂ and CH₄ with the aid of steam. HCl can be recovered for utilisation in for instance Vinyl Chloride Monomer (VCM) production and the caloric gas can be used for energy recovery. The inorganic solids present in the waste, will be separated from the product gas by conventional separation technology.

A bubbling fluidised bed has been selected as a reactor for hydrothermal treatment [8]. This type of reactor is characterised by excellent heat and mass transfer and a constant temperature throughout the reactor. Some other advantages of the use of a fluidised bed reactor are the easy sealing of the system, the absence of moving parts in the hot zone and the easy withdrawal of bed material for regeneration. The bed is fluidised by steam, partly derived from recirculated effluent of the HCl recovery. The energy for direct or indirect heating of the fluidised bed reactor originates from partial incineration of the high caloric hydrocarbon fraction by introduction of air.

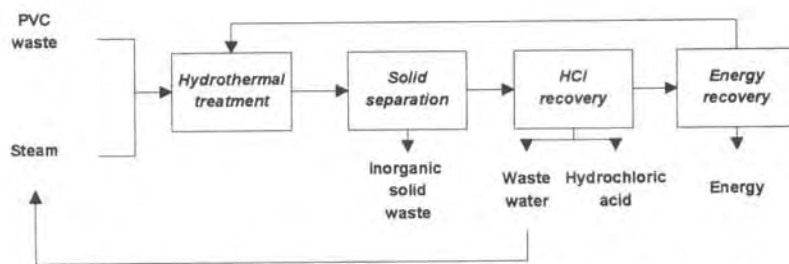


Figure 1 Schematic flow diagram of hydrothermal recycling of PVC waste.

Experimental parameters

A lab scale gasification unit was used to study hydrothermal treatment of PVC-waste [9,10]. The centre of this unit is a bubbling fluidised bed reactor with an inner diameter of 65 mm and a length of 500mm. The construction material of the reactor is quartz glass. The reactor is embedded in an oven, to keep the bed at the desired temperature (typically 1000 to 1300 K).

PVC-waste was fed in the form of 20-mm PVC-bars from the top, directly into the bed. The product gases are quenched (20 °C) and scrubbed to separate hydrochloric acid. The amount of HCl in the product gases is continuously determined by automatic titration. The composition of the product gas is continuously analysed on-line, by two parallel-connected Chrompack Micro gas chromatographs. The standard deviation in the GC-measurements of all gaseous products was below 1%. The excess gas is burned in a flare. Tar and condensables, present at the surface of the reactor outlet and in the gas cleaning and separation section, are washed off and extracted from the water phase with hexane after the experimental run is finished. Subsequently this solution is analysed with GC-MS. Gasification experiments were performed using virgin PVC and cable waste as feedstock. The two different types of bed

materials, applied in these experiments, were quartz sand and porous alumina powder (AKZO NOBEL, porous alumina catalyst carrier A survey of the experimental parameters can be found in [9,10].

Results and discussion

Table 1 shows the experimental results of the steam gasification of virgin PVC over quartz and alumina as bed material and cable waste (38% PVC, 24% CaCO₃ and 38% plasticizer and other plastics). Changing the bed material from quartz to alumina increases the carbon to gas conversion from 25% to 69% at the temperature of 1150K. Also the HCl recovery is complete and the char, tar and condensable production is greatly reduced. These experiments show that alumina is a much better material for the gasification of PVC. For actual waste the same results are feasible except for the HCl recovery, which is much lower due to the presence of calcium in the cable waste. (Part of the HCl reacts with Ca to CaCl₂).

Table 1: Quantities and composition of the gasification products. T=1150K, PVC-feed= 0.3 g/min, $\tau_{\text{steam}}=4\text{s}$.

Output quantities	Virgin PVC Quartz-sand	Virgin PVC Alumina	Cable waste Alumina
Carbon to gas conversion [wt%]	25	69	55
HCl-recovery [%]	92	98	51
Composition product gas [vol% of product gas]			
Hydrogen	64	62	56
Carbon monoxide	25	14	18
Carbon dioxide	5	19	18
Methane	9	6	6
C2-C5	<<1	<<1	<< 1
Totals	103	101	99

Table 2. Quantities and composition of the steam gasification of virgin PVC with alumina. PVC-feed= 0.24 g/min., $\tau_{\text{steam}}=11-12\text{s}$.

Product quantities [wt% of total PVC input]	1150 K	1200K	1250 K
Gas	85	101	120
HCl	54	54	54
Char, tar & condensables	16	9	5
Composition product gas [vol% of product gas]			
Hydrogen	60	58	60
Carbon monoxide	14	16	21
Carbon dioxide	20	18	17
Methane	5	4	3
C2-C5	<<1%	<<1%	<<1%
Totals	99	96	101
Carbon to gas conversion [wt%]	69	87	99

Table 2 shows that the conversion to gas can be complete when increasing the reaction temperature to 1250 K. The CO₂/CO ratio shifts to slightly lower values with increasing temperature, as can be expected from thermodynamic equilibrium calculations. The hydrogen and methane concentrations remain virtually unaffected by the rise in temperature. The strong effect of temperature on the amount of tar and condensables indicates that the high activation energy for cracking of tar determines the product outcome. Considering this and the effect of residence time, described in the former chapter, it can be concluded that the amount of tar and condensables in the product is determined by kinetics and can be controlled by residence time and temperature. This implicates that PVC can be converted to hydrochloric acid and almost 100% fuel gas, without extensive fouling by tar and char, using alumina as bed material and a temperature of 1250 K.

Conclusions

Quartz sand proved to be an unsuitable bed material for gasification of PVC at 1150 K, because the conversion to gas was limited to 25% and large amounts of tar and char were released. A substantial improvement of conversion to 69% was achieved by utilisation of porous γ -alumina powder instead of quartz sand. This improvement can mainly be attributed to the catalytic activity and large specific surface of the alumina powder. The gaseous fraction consisted of hydrogen chloride, hydrogen, carbon monoxide, carbon dioxide and methane. The rest of the carbonaceous fraction was recovered as tar, char and condensables. No chlorine containing organic compounds like chlorobenzene could be detected in these products. The carbon to gas conversion could be raised to approximately 100% by increasing the reactor temperature to 1250 K. The presence of calcium lowers the HCl-recovery.

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References

1. Association of Plastic Manufacturers Europe (APME), Information system on plastic waste management in Western Europe, p. 19 and 57, 1996.
2. W.Kaminsky, *Die Angewandte Makromolekulare Chemie*, 1995, **232**, 151-165.
3. W.Balcerek, Ph.D. Thesis, University of Hamburg (1979).
4. D.S.Scott, S.R.Cernik, J.Piskorz, D.St.A.G.Radhein, *Energy & Fuels*, 1990, **4**, 407-411.
5. C.Wu, C.Chang, J.Hor, S.Shih, L.Chen, *The Chemical Engineering Journal*, 1994, **55**, 87.
6. M.Schaub, *Polymer Recycling*, 1995, **3**, 191-196.
7. A.Oudhuis, P.de Wit, P.Tromp, J.Moulijn, *J.Anal.Appl.Pyr.*, 1991, **29**, 321.
8. M.J.P. Slapak, J.M.N. van Kasteren, A.A.H. Drinkenburg, *Proceedings of the 1st International working seminar on Reuse, Eindhoven University of Technology, Eindhoven, The Netherlands, 1996*, p.267-276.
9. M.J.P. Slapak, J.M.N. van Kasteren, A.A.H. Drinkenburg, *Polymers for Advanced Technologies*, 1999, **10**, 1-7.
10. M.J.P. Slapak, Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1999.