Feedstock Recycling by Pyrolysis of Plastics in a Fluidized Bed

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Pyrolysis of mixed plastic wastes and elastomers is a variable and cost-effective process to recover feedstocks for the petrochemical industry. The Hamburg process, using an indrectly heated fluidized bed, can be varied to produce mainly monomers, aliphatic hydrocarbons, or aromatics. At temperatures of 500 °C, polymethylmethacrylate (PMMA) is depolymerized to more than 98 % of the monomer. Similar results are obtained with polytetrafluorethylene. Polystyrene as feed gives up to 75 % of styrene and 10 % of oligomers. First demonstration plants are running for feedstock recycling of PMMA in a fluidized bed. For mixed plastic fractions from household waste separation with a low PVC content, the pyrolysis oil contains less than 10 ppm of chloroorganic compounds. In a collaborative effort with BP Chemicals and other linked European companies, the fluidized bed process is used to recycle mixed plastic wastes as refinery and petrochemical feedstocks.

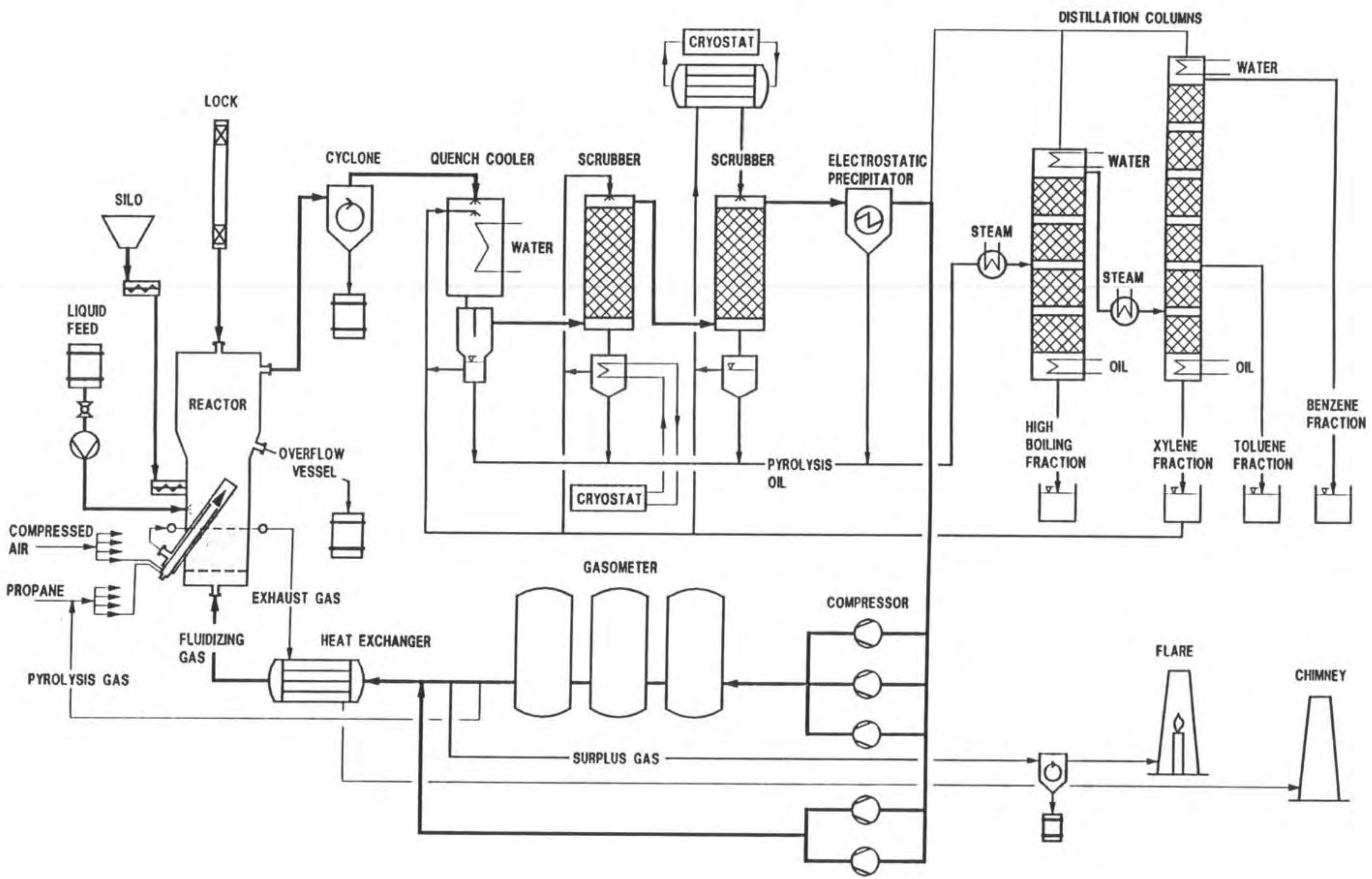
Introduction

Pyrolysis is the thermal degradation of macromolecules in the absence of air. Pyrolysis simultaneously generates oils and gases which are suited for chemical utilization or generation of energy. The advantage of pyrolysis over combustion is a reduction in the volume of product gases by a factor of 5 to 20 which leads to considerable savings in the gas conditioning equipment. Furthermore, the pollutants are concentrated in a coke-like residue matrix. It is possible to obtain hydro-carbon compounds as gas or oil.

The pyrolysis is complicated by the fact that plastics show poor thermal conductivity while the degradation of macromolecules requires considerable amounts of energy. Pyrolysis of plastics has been studied in different research groups in melting vessels, blast furnaces, autoclaves, tube reactors, rotary kilns, and fluidized bed reactors [1,2]. Rotary kiln processes are particularly numerous. They are marked by a wide spectrum of feeds and products and by relatively long residence times of the waste in the reactor whereas fluidized bed reactors show short residence times and higher quality of products.

The fluidized bed has a number of special advantages for pyrolysis because of its good heat and mass transfer and because the reactor can easily be sealed. On the other hand, the fluidized bed is sensitive to fibers and high amounts of metals and fillers.

Fig. 1 Scheme of the Fluidized Bed Process used for the Pyrolysis of Plastics



Materials and Methods

The collected mixed plastics from household separation by the DSD Germany contains in average

Polyolefins	65 wt%	Polystyrene	14 wt%
PVC	4 wt%	Other plastics and paper	9 wt%
Inorganic materials	4 wt%	Moisture	4 wt%

Figure 1 shows the scheme of the pilot plant for the pyrolysis of plastics. The core of the plant is a fluidized bed reactor with inner diameter of 450 mm. A fluidized bed of quartz sand with a temperature of 400 to 800 °C is used for the feedstock recycling of plastics that are fed into the reactor through a double flap gate or a screw. Pyrolysis gas preheated to 300 °C is used to create the swirl in the fluidized bed. The heat input takes place indirectly through heat radiation fire pipes which are heated by pyrolysis gas [3].

The exhaust gases are then directed through a heat exchanger. The product gases emerging from the fluidized bed are separated from residual carbon und fine dust in a cyclone and are then cooled by quench coolers. The condensed oil fractions are distilled in two distillation columns. The gas, largely stripped of liquid products, passes to an electrostatic precipitator and is compressed in five diaphragm compressors, connected in parallel, and stored in three gas tanks, each 0,5 m^3 in volume. Part of the gas serves as fuel for the radiation heating tubes, while the remainder, preheated by hot fuel gases in the heat exchanger, is used for fluidizing the sand bed. The excess gas is burnt in a flare.

Results and Discussions

For some polymers such as poly(methylmethacrylate) (PMMA), poly(tetra-fluoroethylene) (PTFE), polystyrene (PS) it is possible to win back the monomers [4,5]. The pyrolysis of PMMA by 450 °C produces up to 97 wt% of methylmethacrylate; other components are carbondioxide, methylacrylate, methylisobutyrate - each of same less than 1 wt%. About 76 % of the monomeric styrene could be recovered by pyrolysis of PS. Other products are oligomers, α-methylstyrene and toluene. The liquid has to be purified to give polymerization grade styrene. Table 1 shows the products from the pyrolysis of PTFE by different temperatures.

Table 1 Pyrolysis of PTFE, products in wt%

Temperature (°C)	605	650	700
tetrafluoroethylene	78,5	75,9	60,2
hexafluoropropene	4,6	5,2	6,0
cyclo-octafluoropropene	3,7	5,9	16,1
deca-fluorobutane	4,1	+	+
octa-fluorobutene	0,04	+	+
carbon dioxide	5,4	8,3	5,8
carbon black	0,6	0,5	0,4

Depending on the process parameters between 40 to 90 % of polyolefins were recovered as oil. The other fractions are gas and a residue containing fillers and impurities (heavy metals). Ethylene, propene, butene, and butadiene are the most valuable feedstocks in the gas fraction.

In a collaborative effort with BP Chemicals and other linked European companies, the fluidized bed process is used to recycle mixed plastic wastes as refinery and petrochemical feedstocks [6]. At 510 to 530 °C high yields of up to 85 % of a purified, waxy distillate hydrocarbon are obtained (Table 2).

Table 2 Products from the Pyrolysis of Polyolefins (PE, PP) and mixed plastics (Mix) in wt%

Temperature Feed	530 PE	510 PP	510 Mix
Ethylene/Ethane	2,8	1,5	1,1
Propylene	1,8	3,0	1,5
Other gases	3,0	1,8	2,1
C_5-C_{10}	6,9	15	14
C_{11}-C_{20}	9,9	13	5,7
Aromatics	0,3	0,1	0,1
Waxes	75,3	65,6	75,5

The gas with a heat of combustion of some 47 MJ/kg can be used for the indirect heating of the fluidized bed. The hydro carbons C_5-C_{20} and the waxes can be used as feedstock for crackers.

Conclusions

Some pilot plants are built up for the pyrolysis of PMMA into valuable feedstocks. But today no process has reached a stage of industrial size for the feedstock recycling of mixed plastics in a fluidized bed.

References

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