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Polymer waste recycling over "used" catalysts

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Abstract

Catalytic degradation of high-density polyethylene (HDPE) was carried out under nitrogen using a laboratory fluidised bed reactor operating at 360 °C with catalyst to polymer feed ratio of 2:1 and at 450 °C with catalyst to polymer feed ratio of 6:1 under atmospheric pressure. The catalysts used in this study were ZSM-5, US-Y, ASA, fresh FCC (fluid catalytic cracking) commercial catalyst (Cat-A) and equilibrium FCC catalysts with different levels of metal poisoning were studied. The initial results for polymer degradation at 360 °C (catalyst to polymer ratio of 2:1) in a fluidised bed reactor in terms of the yield of volatile hydrocarbon products were: model catalysts $>$ commercial FCC catalyst $>$ E-Cats. However, when the process conditions more closely resembled to FCC conditions, the fresh commercial FCC catalyst was more favourable in terms of the yield of volatile hydrocarbon products. The degradation of HDPE over E-Cats although reduced was similar to ASA in product selectivity and yield, and the level of metal contamination did not affect the product stream generated. A simple economic evaluation of polymer recycling process is reported showing that a catalytic system based on E-Cats appears comparable in costs to a commercial thermal cracking plant. © 2002 Published by Elsevier Science B.V.

Keywords: High-density polyethylene; Recycling; Catalytic degradation; Fluidised bed; FCC; E-Cats

1. Introduction

Plastics are among the best 'fruits' of the chemical process industry and are used extensively in our lives. Unfortunately, every year, the UK produces 29 million tonnes of municipal waste (equivalent to half a tonne per person [1]) and in 1999, 4 million tonnes of plastic packaging and 2 million tonnes of plastic were landfilled [2]. Municipal and industrial plastic wastes are treated predominantly in three ways, by landfill, incineration and true material recycling. Each of these methods has disadvantages. Landfill treatment and incineration of plastic waste are less desirable due to high cost, poor biodegradability and the possibility of unacceptable emissions [3]. True material recycling (the conversion of scrap polymer into new products) is a popular recovery path but the recycled plastic product often costs more than virgin plastic [4].

An alternative strategy is that of chemical recycling, which has attracted much interest recently [5–8] with the aim of converting waste polymers into basic petrochemicals to be used as feedstock or fuel for a variety of downstream processes. Two main chemical recycling routes are the thermal and catalytic degradation of waste plastics. In thermal degradation, the process produces a broad product range and requires high operating temperatures, typically more than 500 °C and even up to 900 °C [5]. On the other hand, catalytic degradation might provide a solution to these problems by controlling the product distribution and reducing the reaction temperature.

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In this work, we evaluate "used" fluid catalytic cracking (FCC) catalysts [9,10] for the recycling of polymer wastes and compare the economics of the process with current process technology [11].

2. Experimental

2.1. Materials and reaction preparation

Pure high-density polyethylene (HDPE) (ex. BASF) with an average molecular weight of 75,000, as determined by gel permeation chromatography, and a density of 960 kg m^{-3} was used in this study. The catalysts employed in this study are described in Table 1 with relevant characterisation details shown in Table 2. Prior to use, all the catalysts were pelleted using a press (compression pressure = 160 MPa), crushed and sieved to give particle sizes ranging from 125 to 180 μm. The catalysts (0.25–0.30 g) were then activated by heating, in the reactor, in flowing nitrogen (50 ml min^{-1}) to 120 °C at 60 °C h^{-1}. After 2 h, the temperature was increased to 500 °C at a rate of 120 °C h^{-1}. After 5 h at 500 °C, the reactor was cooled to the desired reaction temperature. The particle size of both catalysts (125–180 μm) and polymer (75–250 μm) were chosen as being large enough to avoid entrainment and small enough to be adequately fluidised in a flow of high purity nitrogen at 450–500 ml min^{-1}.

Table 1
Summary of catalysts used

Catalysts	Commercial name	Suppliers
ZSM-5	ZSM-5 zeolite	BP Chemicals, Sunbury-on-Thames, UK
US-Y	Ultrastabilised Y zeolite	Crosfield Chemicals, Warrington, UK
ASA	Amorphous silica alumina	Crosfield Chemicals, Warrington, UK
Cat-A	Fresh commercial FCC catalyst	Engelhard, NJ, USA
E-Cat 1	Equilibrium catalysts	Engelhard, NJ, USA
E-Cat 2	Equilibrium catalysts	Engelhard, NJ, USA
E-Cat 3	Equilibrium catalysts	Engelhard, NJ, USA

Two types of polymer cracking experiments were carried out:

(a) 360 °C with a catalyst/polymer (C/P) ratio of 2:1;
(b) 450 °C with a catalyst/polymer (C/P) ratio of 6:1 (more closer resembling FCC conditions).

2.2. Analysis

A schematic diagram of the fluidised bed reactor is shown in Fig. 1 and a detailed operation procedure has been reported previously [5,12]. Volatile products leaving the reactor were passed through a glass-fibre filter to capture catalyst fines. A three-way valve was used to route product either into a sample gas bag or to an automated sample valve system with 16 loops. Tedlar bags, 15 l in capacity, were used to collect time-averaged gaseous samples. The bags were replaced at intervals of 5 and 10 min throughout the course of the reaction. The multiport sampling valve allowed frequent, rapid sampling of the product stream at 0.5 and 1 min intervals. Gaseous products were analysed using a gas

Table 2
Summary of catalyst details

Catalysts	Si/Al	Al_2O_3 (wt.%)	REO[a] (wt.%)	TSA[b] (m^2/g)	Ni (ppm)	V (ppm)
ZSM-5	17.5	–	–	391	–	–
US-Y	6.2	–	–	603	–	–
ASA	2.6	25.0	–	274	–	–
Cat-A	2.0	32.5	1.2	384	–	–
E-Cat1	ND[c]	42.5	1.3	175	171	217
E-Cat2	ND	29.4	1.6	127	5400	6580
E-Cat3	ND	37.4	2.8	155	1520	3920

[a] Rare earth oxide.
[b] Total surface area (BET).
[c] Not determined.

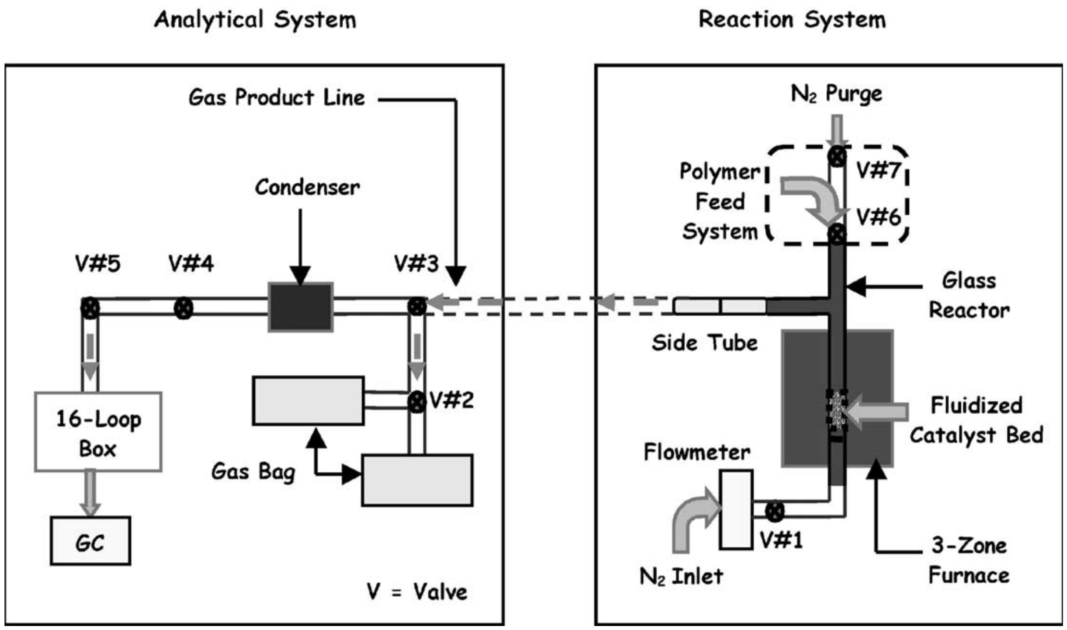

Fig. 1. Schematic diagram of fluidised bed reactor rig.

chromatograph (VARIAN 3400) equipped with: (i) a thermal conductivity detector (TCD) fitted with a Molecular Sieve 13X packed column (1.5 m × 0.2 mm i.d.) and (ii) a flame ionisation detector (FID) fitted with a PLOT Al_2O_3/KCl capillary column (50 m × 0.32 mm i.d.). A calibration cylinder containing 1% C_1–C_5 hydrocarbons (Linde Gas, UK) was employed to help identify and quantify the gaseous products.

The remaining solids deposited on the catalyst after the catalytic degradation of the polymer were considered as ‘residues’ and contained involatile products and coke. The amount and nature of the residues were determined by thermogravimetric analysis (TA Instruments, SDT 2960 Simultaneous DTA–TGA) as described elsewhere [13].

3. Results and discussions

3.1. Overall

Catalytic pyrolysis products (P) are grouped together as hydrocarbon gases ($<C_5$), gasoline (C_5–C_9) and residues to enable the overall pyrolysis processes to described more easily. The term ‘yield’ as used in this paper is defined by the relation:

$$\text{Yield (wt.\%)} = \left(\frac{\text{P(g)}}{\text{Polymer fed(g)}}\right) \times 100 \qquad (1)$$

At the reaction temperatures used in this study, the products from polymer cracking were mostly gas phase (in the range C_1–C_9). The products from polymer degradation (Table 3a and b) have been characterised as gas, liquid, coke and involatile residues. The gaseous product stream was characterised by GC and carbon chain length and degree of unsaturation determined. Mass balances of 90 ± 5% were obtained for all experiments.

3.2. Model catalysts

The products from polymer cracking shown in Fig. 2a and b reflect the different nature of both the zeolitic pore structure and the predominant type of acidity found in the catalysts. At the lower temperature of 360 °C, ZSM-5 yielded predominantly olefinic

Table 3
Summary of product distributions

Products	ZSM-5	US-Y	ASA	Cat-A	E-Cat1	E-Cat2	E-Cat3
(a) $T = 360\,^{\circ}\mathrm{C}$ (C/P =2:1)							
Gaseous	87.1	70.4	86.9	79.8	69.2	60.1	67.9
Liquid	0.0	0.0	0.0	0.0	0.9	3.3	4.8
Coke	1.5	7.3	2.2	9.1	0.8	1.0	1.6
Involatile	11.4	22.2	10.8	11.1	29.1	35.6	25.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gaseous product distribution							
C_1–C_4	72.6	38.1	45.7	42.6	25.2	26.7	25.0
C_5–C_8	24.6	59.4	54.3	54.6	74.7	73.3	74.7
BTX	2.7	2.5	0.0	2.8	0.2	0.0	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total paraffins	16.1	48.7	6.8	48.7	18.4	17.8	20.2
Total olefins	81.2	48.8	93.2	48.4	81.5	82.2	79.5
(b) $T = 450\,^{\circ}\mathrm{C}$ (C/P =6:1)							
Gaseous	83.7	69.6	79.2	75.8	83.3	83.8	82.5
Liquid	2.0	0.6	0.0	0.7	1.8	1.7	1.8
Coke	2.4	9.7	5.0	13.3	1.9	1.3	1.5
Involatile	11.9	20.2	15.8	10.3	13.0	13.2	14.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gaseous product distribution							
H_2	0.007	0.000	0.001	0.002	0.001	0.001	0.002
C_1–C_4	68.6	36.6	41.5	55.5	35.2	34.4	32.7
C_5–C_9	23.1	60.2	58.0	40.4	63.4	64.3	66.4
BTX	8.3	3.2	0.5	4.1	1.4	1.3	0.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total paraffins	27.0	49.0	15.8	64.4	23.7	23.7	25.8
Total olefins	64.7	47.8	83.6	31.5	74.9	75.0	73.3

materials (~83 wt.%) in the very narrow range of C_3–C_5 as well as being resistant to coke formation, and was as might be expected with its restricted channels and smaller pore-openings.

The amorphous silica alumina (ASA, largely weaker Lewis acid sites) yielded almost 95 wt.% unsaturated olefin products over C_3–C_7 carbon range and as a consequence of its lower acidity, had low levels of coke. The larger pore-openings and internal supercages of US-Y allowed bulky bimolecular reactions to occur. Consequently, a wide carbon number distribution (C_3–C_8) with a 50:50 balance of paraffins and olefins was produced as well as much higher observed levels of coke compared with ZSM-5. At the higher temperature of 450 °C and higher catalyst to polymer ratio, the results were similar but with increased paraffin yields and coke levels.

3.3. US-Y and FCC catalyst (Cat-A)

As expected, the FCC commercial catalyst (Cat-A, Fig. 3a) produced a balanced paraffinic and olefinic product stream (mainly C_3–C_8) similar to that of US-Y. Both catalysts had high levels of coke. However, when the laboratory conditions more closely resembled FCC process conditions, Cat-A produced significantly larger amounts of paraffins (>60 wt.%, Fig. 3 b). This increased activity in the FCC catalyst compared to US-Y may be explained by the presence of rare earth oxide on the FCC catalyst and also indicate extra activity due to the FCC matrix [9,10].

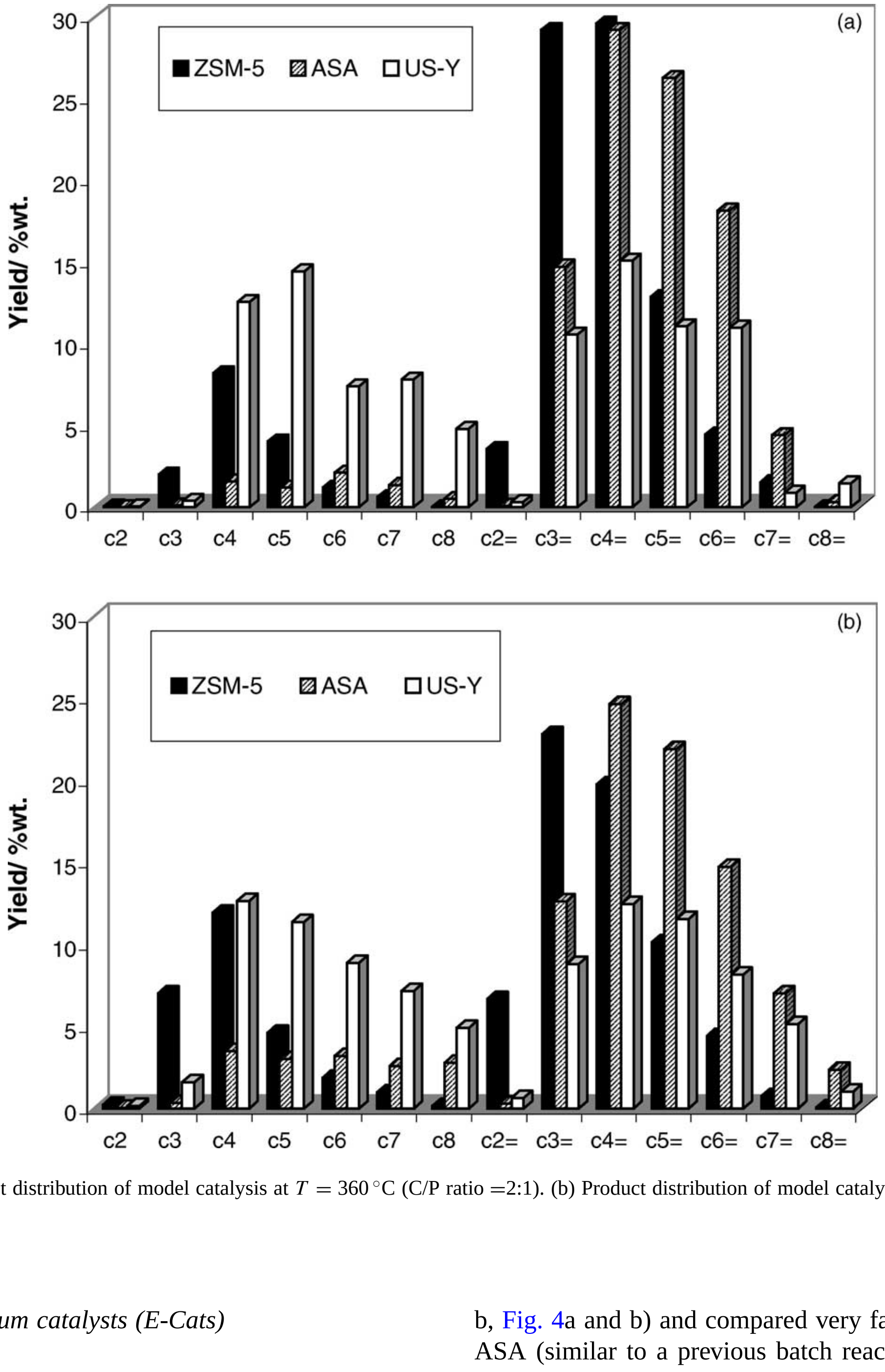

Fig. 2. (a) Product distribution of model catalysis at $T = 360\,^{\circ}$C (C/P ratio =2:1). (b) Product distribution of model catalysts at $T = 450\,^{\circ}$C (C/P ratio =6:1).

3.4. *Equilibrium catalysts (E-Cats)*

Equilibrium catalysts are ‘used’ FCC catalysts with different levels of metal contamination (Table 2). Typically, all E-Cats yielded a predominantly olefin product (≥80%) in the range of C_3–C_8 (Table 3 a and b, Fig. 4a and b) and compared very favourably with ASA (similar to a previous batch reactor study [7]). More hydrogen transfer was observed when E-Cats were used with approximately double the amount of paraffins generated at 360 °C than with ASA. Increased temperature generated more paraffins with

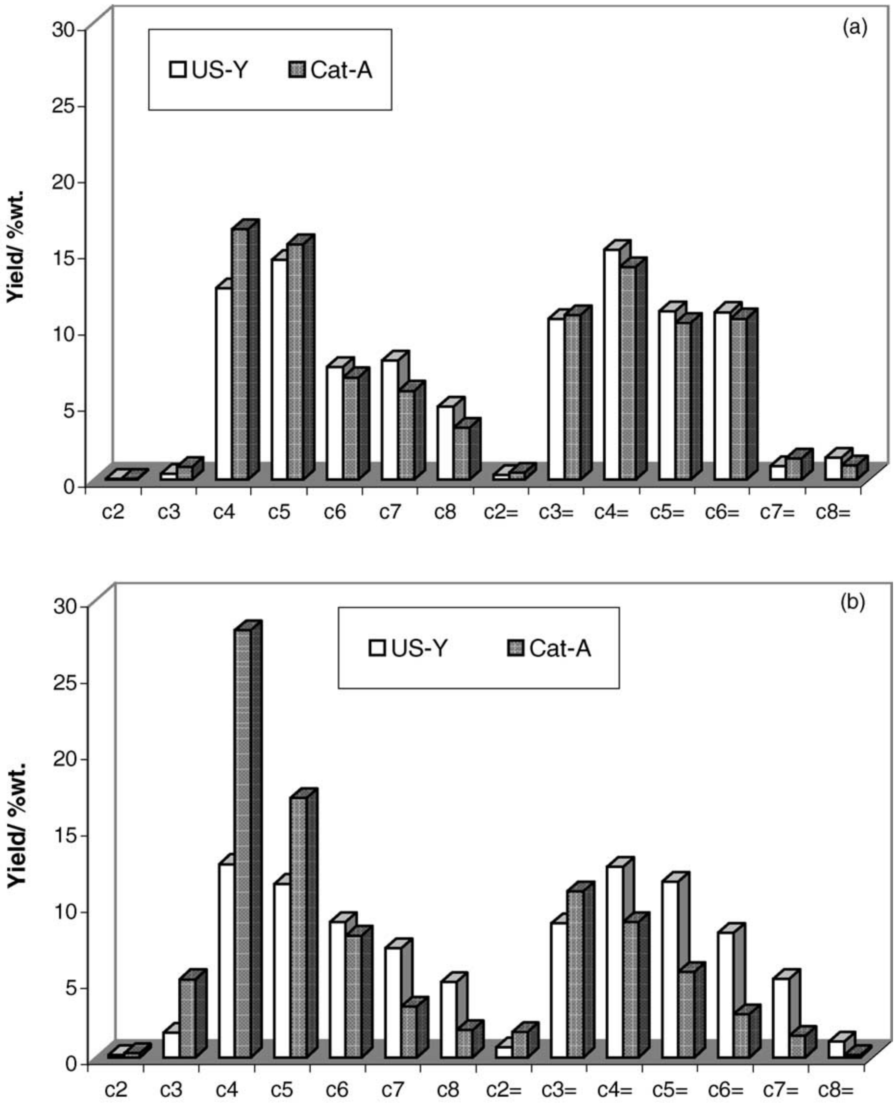

Fig. 3. (a) Product distribution of US-Y and Cat-A at $T = 360\,^{\circ}\mathrm{C}$ (C/P ratio =2:1). (b) Product distribution of US-Y and Cat-A at $T = 450\,^{\circ}\mathrm{C}$ (C/P ratio =6:1).

ASA but a greater a yield was still observed when HDPE was degraded over E-Cats. Most importantly, the level of nickel (Ni) and vanadium (V) contamination did not greatly affect the product stream generated. The results are very encouraging and have significant impact on the economics of a catalytic polymer degradation process employing catalysts of zero market value.

3.5. Simple economic evaluation

An economic evaluation of the BP process for the thermal recycling of polymer waste [11] and several alternative catalytic recycling routes has been attempted. In brief, the technologies are:

- *BP process*. Using a thermal-cracking process over fluidised sand with a reaction temperature of 500 °C

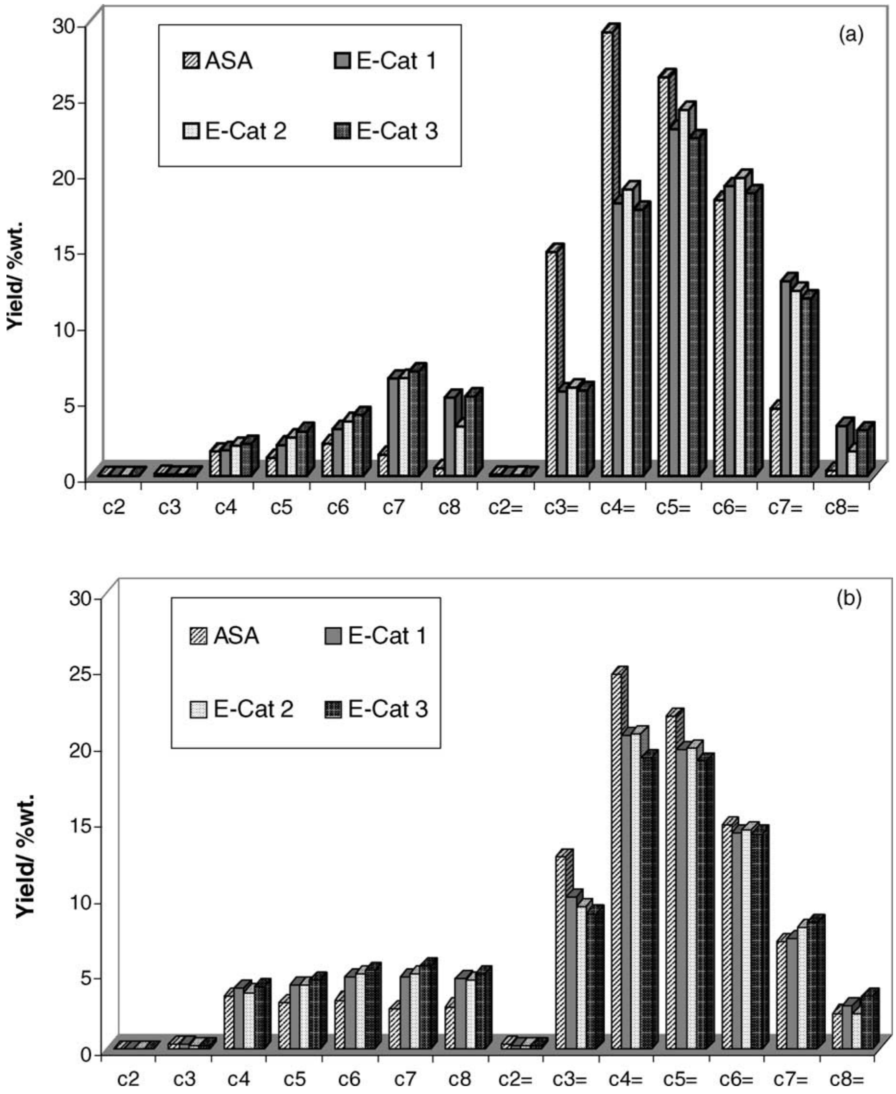

Fig. 4. (a) Product distribution of ASA and three "used" E-Cats at $T = 360\,^{\circ}\mathrm{C}$ (C/P ratio =2:1). (b) Product distribution of ASA and three "used" E-Cats at $T = 450\,^{\circ}\mathrm{C}$ (C/P ratio =6:1).

yielding a product range up to C_{50}. Typical process and feed preparation costs are estimated at £250/te and BP predicts that a government subsidy of £120/te is required to break even [4].

- *UMIST technology*. Using a fluidised bed catalytic cracking process over waste catalysts (E-Cats). Two conditions have been studied to date, yielding a narrow product range up to C_{10} and at lower temperatures (i.e. 360 and 450 °C) compared to the BP process.

A simple estimate of the costs of catalytic recycling of polymer waste has been attempted based on process and feed preparation expenditure similar to those quoted for the BP thermal pilot plant (25–50 kte per year) [11]. Table 4 details the process expenditure, income and gate fee required for economic viability. Expenditure has been calculated based on process, feed preparation and catalyst costs and ignoring transportation, sorting and cleaning costs. Catalyst prices are based on average market prices [14,15] and the

Table 4
A simple economic comparison of thermal and catalytic cracking of polymer waste

	Catalytic fluidised bed[a]				Thermal, sand[b]
	US-Y	FCC	ASA	E-Cats	
Process expenditure					
Catalyst (\$/lb)[c]	2–5	1	1.5–3.5	0	–
Catalyst (£ M/p.a.)[d]	693	198	446	0	–
Catalyst and process (£ M/p.a.)[e]	702	207	455	9	9
Process income					
Gas product (£ M/p.a.)[f]	3.5	4.7	3.8	4.0[g]	Refinery
Gate fee (£/te)[h]	18,600	5400	12,000	135	66–133

[a] All calculations based on 25–50 kte p.a. processing of polymer waste at 450 °C and catalyst: polymerratio =6:1.

[b] All information quoted for BP thermal cracking pilot plant.

[c] Average catalyst price.

[d] Total catalyst usage with regeneration and losses (60%) typical of FCC operations.

[e] Process cost assumed to be similar to BP estimate.

[f] Average price for hydrocarbons product streams.

[g] No financial estimate available for down-stream benefit of hydrocarbon product stream in BP thermal process although £4.0–6.5 M/p.a. could be projected based on gate fee.

[h] Gate fee = (process expenditure − process income)/annual average tonnage.

income for the recycling process estimated on the average market prices of the product stream obtained [16,17]. The gate fees quoted in Table 4 are an estimate of the level of government subsidy required for the polymer recycling process to break even. The gate fee projected by BP for its thermal process suggests that £65–133/te of plastic waste is required from the UK government. From our estimates, the costs of a polymer recycling process based on fresh catalysts (such as US-Y, ASA or FCC) would be prohibitive with subsidies ranging from £6000 to 19,000/te of plastic waste (Table 4).

On the other hand, E-Cats with high levels of metal contamination (such as E-Cat 2) have zero value and hence costs are dramatically reduced. We estimate that the UMIST technology using 450 °C and a 6:1 catalyst to polymer feed ratio would require an approximate subsidy of £135/te of waste comparing favourably with that of the BP process. In addition, the lower operating temperatures and selective product streams generated for downstream processing may be more economically favourable.

More stringent EU legislation on the designation of materials disposed of by landfill and the rising cost of landfill may further benefit the catalytic process. If refiners are charged for the disposal of E-Cat, then this further reduces the level of government subsidy required and the gate fee will be reduced further (approx. £11/te based on current UK landfill charges for chemical waste disposal [1,2]).

4. Conclusion

The use of catalysts in the pyrolysis of polymer waste significantly reduces the required reaction temperature and improves the yield of volatile products as well as provides better selectivity in the product distribution.

The initial results obtained using E-Cats are promising and suggest improvements to current technology (such as the possible replacement of fluidised sand to thermally crack polymer waste). The use of a catalytic recycling process based on E-Cat’s would lower the operating temperature and produce potentially more valuable feedstocks. The degradation of HDPE over E-Cats yields a predominantly olefinic stream in the range of C_3–C_8 similar to that of ASA. A simple economic study suggests that a gate fee (£135–170/te) dependent on the process temperature and catalyst to feed ratio used compares competitively with current thermal cracking technology.

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