

POLYMER WASTE RECYCLING OVER FRESH, STEAM DEACTIVATED AND USED FCC CATALYSTS

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ABSTRACT

Feedstock recycling of high-density polyethylene (HDPE) over fluid catalytic cracking (FCC) catalysts (6:1 ratio) was carried out using a laboratory fluidised bed reactor operating at 450°C, atmospheric pressure and nitrogen environment. Fresh and steam deactivated commercial FCC catalysts with different levels of rare earth oxide (REO) were compared as well as used FCC catalysts (E-Cats) with different levels of metal poisoning. The initial activity of the catalysts was also estimated by hexane cracking in a fixed bed reactor at 450°C. The results of HDPE degradation, in terms of yield of volatile hydrocarbon product, were: Fresh FCC catalysts > steamed FCC catalysts ≈ used FCC catalysts. Overall, the product yields from HDPE cracking showed that the level of metal contamination (nickel and vanadium) did not affect the product stream generated from polymer cracking. The promising results of this study help to establish a more economic catalytic alternative for polymer waste recycling.

Keywords : polymer recycling, feedstock recycling, FCC catalysts, E-Cats

INTRODUCTION

The main challenge with the growing consumption of plastics is to keep pace with waste and waste recovery. The most common method of treating solid wastes is by disposing to landfill. This option is being curtailed under new EU Landfill Directives where 2020 UK levels must be 35% less than in 1995 [1]. In addition, Alam Flora Sdn. Bhd., a single purpose company formed by the HICOM-led Consortium who handles the solid waste management for Central and Eastern Regions of Malaysia, expects that solid waste generated in Malaysia would be doubly-increased in 20 years from 3.2 to 7.7 million tonnes per year, which give a big challenge since most of the 20 landfills have reached to their critical level [2].

APME reports [3] that feedstock recycling has great potential to enhance plastics waste recovery levels. Unfortunately, in 1999, only 364 thousand tonnes of wastes were treated by this method and little change on 1997 figures (Table 1). Also, this process is not quite known in Malaysia. By July 2004, only 77 tonnes of plastics have been recycled from the total recycling percentage by type of material in Malaysia, which mainly by mechanical recycling (Figure 1).

Table 1: Total Plastics Consumption and Waste Recovery, Western Europe (x 1000 tonnes) [1]

	1993	1995	1997	1999
Total Plastics Consumption	24 600	26 100	29 000	33 600
Total Plastics Waste	15 651	17 505	16 975	19 166
Total Plastics Waste Recovered	3 340	4 019	4 364	6 113
Mechanical Recycling	915	1 222	1 455	1 800
Feedstock Recycling	0	99	334	364
Energy Recovery	2 425	2 698	2 575	3 949
% Total Plastics Waste Recovered	21	26	26	32

Recycling Percentage by Material in Malaysia by July 2004

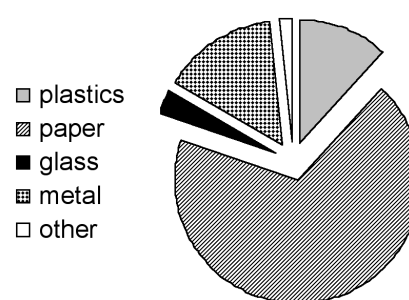


Figure 1: Recycling Percentage by Type of Material in Malaysia by July 2004 [2]

There are two main chemical polymer recycling routes namely thermal degradation, which produces a broad product range and requires high operating temperatures, and catalytic degradation, which may offer an alternative by controlling product distribution and reducing reaction temperatures. The catalytic degradation of polyolefins, which typically 60 – 70 % of polymer waste is in municipal waste streams [3], have been studied using predominantly pure catalysts, namely SiO₂-Al₂O₃ [4], zeolites (ZSM-5, US-Y) and mesoporous materials (such as MCM-41) [5-7]. Strategies adopted predominantly target the formation of a stable hydrocarbon product for downstream processing. Research is scarce on FCC catalysts with only two reports on the use of an equilibrium catalyst (E-Cat). One is to degrade polyethylene and polystyrene at 450°C in a fluidised-bed reactor. A roughly equal mix of gas and oil product was obtained; however, no catalyst detail was mentioned [8]. The other is to degrade polypropylene at 380 °C

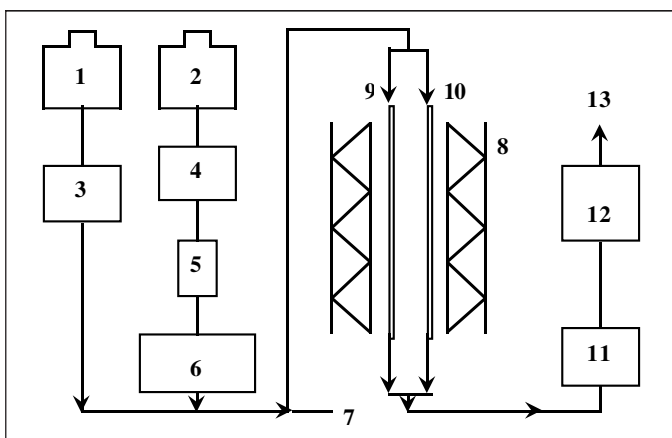
in a semi-batch reactor. However, the product yield was poor compared to pure catalysts such as silica alumina, but the authors commented that increased amounts could be used as the cost was very low [9].

At UMIST, research has focused on commercial catalysts (as well as zeolites) [6, 10-13]. This paper deals with the conversion of polymer using fresh and steam deactivated catalysts as well as E-Cats with differing Ni and V levels, helping to refine costings of catalytic polymer recycling [11] for comparison with current technology [14].

MATERIALS AND METHODS

A. N-HEXANE CRACKING

Catalysts (0.1 g, 125 - 180 μm pellets) were activated at 500°C in a fixed bed quartz glass reactor by heating (1°C/min) in air (50 ml/min). The reactor was then stabilized at 450°C in flowing nitrogen (30 ml/min) and n-hexane (Aldrich, 99.9 %) was passed over the catalyst. The products were analysed by on-line gas chromatography (VARIAN 3400) [10]. A schematic-line diagram of the n-hexane cracking rig is showed in Figure 2.



(1) Dry Air, (2) Dry Nitrogen, (3) Flow Controller, (4) Mass Flow Controller, (5) Flow Meter, (6) 4-tap Bubbler (containing n-hexane at 0°C), (7) Flow Check (8) Furnace, (9) Catalyst Reactor, (10) Blank Reactor, (11) 16-loop Box, (12) GC and (13) To Vent
Figure 2: Schematic Line-Diagram of the n-Hexane Cracking Rig

B. POLYMER CRACKING

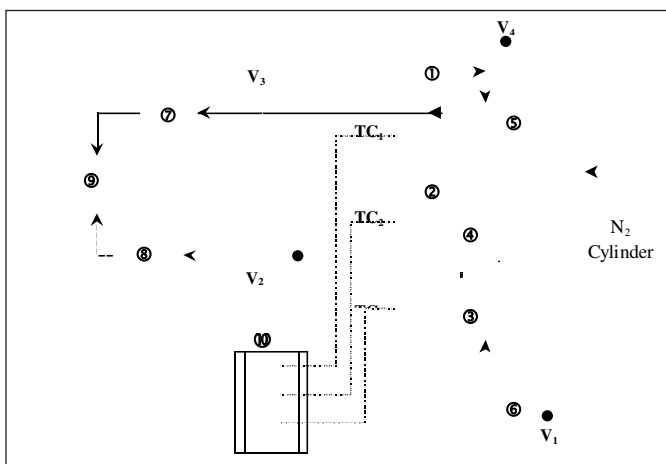
Pure HDPE (ex. BASF) with an average molecular weight of 75 000 (density 960 kg/m³) was used. The catalysts employed in this study are described in Table 2. Polymer-cracking

Table 2 : Catalyst Details (Supplied by Engelhard Corporation, USA)

Catalyst	Commercial Name	wt% REO	Å UCS	m ² /g MSA	ppm ZSA	Ni	V
Cat-1	Fresh Commercial FCC Catalyst	0.8	24.4	112	264	-	-
Cat-7	Fresh Commercial FCC Catalyst	9.6	24.7	90	331	-	-
Cat-1S	*Steam Deactivated FCC Catalyst	0.8	24.3	90	198	-	-
Cat-7S	*Steam Deactivated FCC Catalyst	9.6	24.5	72	241	-	-
E-Cat 1	Equilibrium FCC Catalysts	1.3	24.3	76	99	171	217
E-Cat 2	Equilibrium FCC Catalysts	1.6	24.3	32	95	5400	6580

*Steaming Conditions: 4 h/ 788°C/ 100% Steam

experiments were carried out in a fluidised bed reactor under nitrogen at 450°C/min with a catalyst to polymer (C/P) ratio of 6:1. A schematic-line diagram of the polymer cracking rig is showed in Figure 3, whereas a detailed operation procedure and product analysis has been reported previously [10, 12].



① Polymer Feeder, ② 3-Zone Furnace, ③ Sintered Distributor, ④ Fluidising Catalyst, ⑤ Fluidised Bed Reactor, ⑥ Flow meter, ⑦ 16-loop Automated Sample Valve in Heated Box, ⑧ Gas Bag, ⑨ Gas Chromatograph, ⑩ 3-Zone Digital Controller
Figure 3: Schematic Diagram of Polymer Cracking Rig

RESULTS AND DISCUSSION

Hexane cracking and polymer degradation proceed by a carbocation mechanism, where the initially formed ions experience chain reactions via isomerisation and β -scission (monomolecular processes) and hydrogen transfer and oligomerisation (bimolecular processes) [15].

A. N-HEXANE CRACKING

Reactions of paraffins on zeolites are generally treated using simple first-order kinetic expressions [16]. However, cracking catalyst deactivation occurs at such a rapid rate that, in quantifying the rates of cracking, the kinetics of conversion must be treated simultaneously with deactivation kinetics. By following the conversion (χ) of n-hexane over the catalyst as a function of time using a time-on-stream theory of decay from a general rate of reaction term [17], an estimate of initial catalyst activity ($\ln t = 0$) can be made (a plot of $\ln(-\ln(1-\chi))$ vs. $\ln t$ is a straight line).

The deactivation of a constant weight of catalyst was studied for a fixed flow of n-hexane in nitrogen (W/F = 27 g.h/mol, at 450°C) for up to 120 minutes. The total number of acid sites (Bronsted and Lewis), initial activities and product distributions are detailed in Table 3.

As expected, fresh FCC catalysts (Cat-1 and Cat-7) were the most active, cracking between 3 - 5% of the n-hexane feed. FCC catalysts are regenerated with steam in the FCC process and consequently lose some framework aluminium, creating defects and resulting in a lowering of acidity [18]. The presence of rare earth oxide (REO) hinders this dealumination and hence, the catalyst activity is better maintained. Indication of this stabilisation was shown in the results of hexane and polymer cracking over Cat-7S compared to Cat-1S. Cat-1S, E-

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Table 3: Initial Conversion and Product Distribution for n-Hexane Cracking at Time-on-Stream (TOS) of 1 min

	Cat-1	Cat-7	Cat-1S	Cat-7S	E-Cat1	E-Cat2
Bronsted + Lewis, $\mu\text{mol/g}$	606	637	116	254	28	18
Conversion, wt%	5.04	3.07	0.13	0.88	0.15	0.22
Product Distributions (moles per 100 moles converted)						
C ₁ -C ₄	182	189	148	159	172	146
C ₅ -C ₉	12	9	30	24	19	31
BTX	0	0	0	0	0	0
Paraffins	88	84	53	64	53	36
Olefins	101	108	124	114	139	141

Cat1 and E-Cat2 showed similar low activities with increased olefin yield (primary cracking products) as catalytic activity reduced.

B. POLYMER CRACKING

At 450°C, the products from polymer cracking were mostly gases in the range C₁ - C₉, coke and unreacted polymer. As expected, trends in polymer cracking (Table 4) were comparable with those of n-hexane cracking and reflected the different nature of catalysts under study.

For simplicity, catalytic polymer degradation products (P) were grouped together as hydrocarbon gases (< C₅), gasoline (C₅ ~ C₉), aromatic hydrocarbon (BTX), liquids (trapped inside the side tube and the reactor) and carbonaceous deposits (trapped on the catalyst - TGA). Polymer Reacted (PR) was the weight difference between polymer feed and unreacted polymer (on the wall of the reactor and on the catalyst (TGA)). The term "yield" was used to examine the mass balance of the overall pyrolysis, and was defined by the relationship as follows:

$$\text{Yield (wt \%)} = \left(\frac{P(g)}{PR(g)} \right) \leftrightarrow 100 \quad (1)$$

Based on 0.1 g of polymer feed, fresh commercial FCC catalysts converted about 85 - 90 % of their feeds to gaseous, liquid and carbonaceous products. On the other hand, the less active steamed and equilibrium catalysts showed only 60 - 70 % conversion to the volatile products (Figure 4).

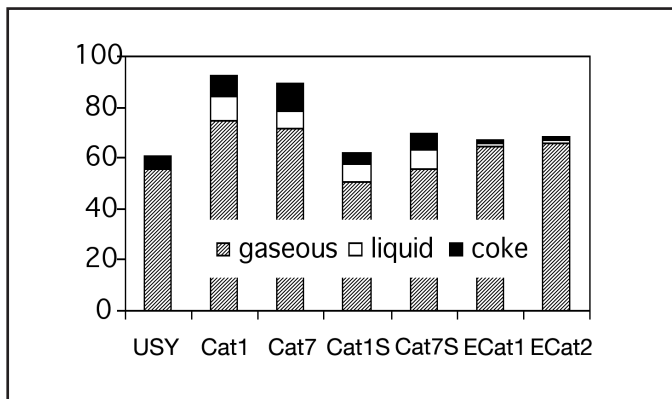


Figure 4: Total Product Yield (wt%) at T = 450 °C; C/P = 6:1

Table 4: Weight % of Product Distributions at T = 450 oC; C/P = 6:1

	US-Y*	Cat-1	Cat-7	Cat-1S	Cat-7S	E-Cat1	E-Cat2
Gaseous	55.9	75.0	71.8	50.4	55.8	64.5	65.8
Liquid	0.5	9.0	6.8	7.2	7.8	1.4	1.4
Coke	4.5	6.5	7.2	3.0	4.9	1.5	1.2
Involatile	39.1	9.5	14.2	39.4	31.5	32.6	31.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Gaseous Product Distribution							
C1-C4	36.6	44.4	47.4	38.4	44.4	35.2	37.1
C5-C9	60.2	52.2	48.8	60.2	52.8	63.4	62.6
BTX	3.2	3.4	3.8	1.4	2.8	1.4	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total Gaseous Product							
Paraffins	48.8	53.7	60.0	31.4	48.7	23.6	23.0
Olefins	47.8	42.5	35.7	67.1	48.6	74.9	76.6

*Results for US-Y reported earlier [11]

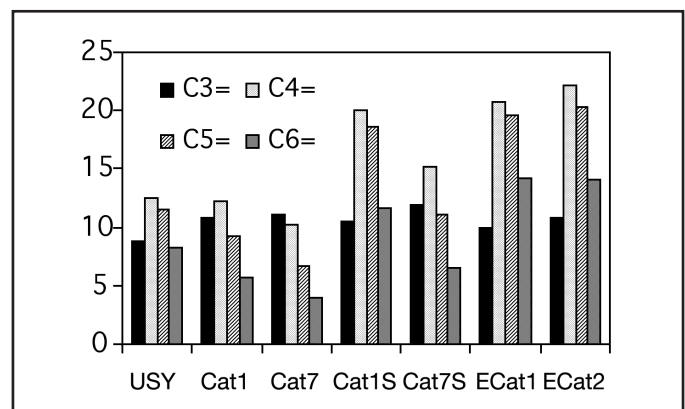


Figure 5: Selected Olefin Products (wt%) at T = 450 °C; C/P = 6:1

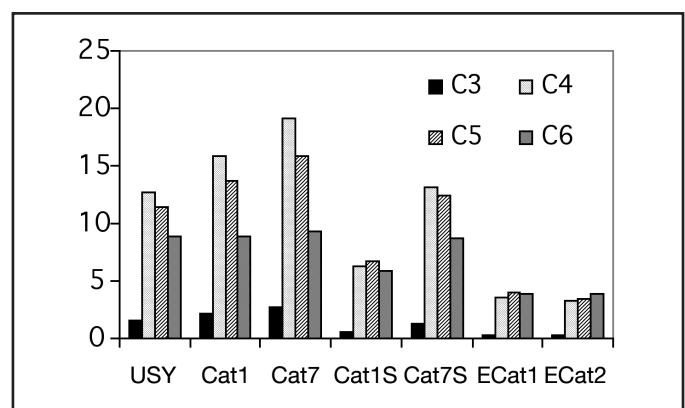


Figure 6: Selected Paraffin Products (wt%) at T = 450 °C; C/P = 6:1

Figures 5 and 6 show selected olefin and paraffin products, respectively, for the catalysts. A major active component in FCC catalysts is the zeolite US-Y and hence, product yields of pure zeolite and FCC catalysts were compared.

Again, the level of activity of the various catalysts was reflected in the amount of primary (olefin) versus secondary

(paraffin) products observed with the high acidities of both fresh catalysts (Cat-1 and Cat-7, Table 2) producing a high yield of secondary products. The E-Cats showed negligible loss in overall conversion of HDPE due to metal contamination and produced an olefin-rich degradation products compared with steam deactivated Cat-1S and Cat-7S. Evidence of high REO stabilization of steam deactivated catalyst, Cat-7S, was noted with a yield of balanced primary and secondary products (Figures 5 and 6).

The ratio of iso-butane to iso-butene (Figure 7) indicated the amount of hydrogen transfer that had occurred during the cracking process. The result illustrated that more bimolecular hydrogen transfer occurred in US-Y, fresh FCC catalysts and Cat-7S. Reduced acidity and deactivation of the Cat-1S and E-Cat1 and E-Cat2 showing much reduced hydrogen transfer.

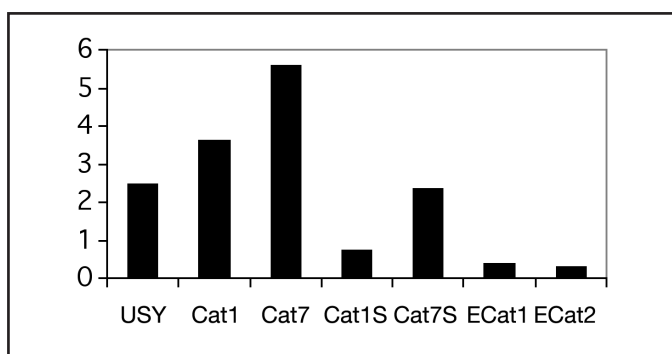


Figure 7: Hydrogen Transfer Indication: $iC_4/iC_4=$

CONCLUSION

Results reported here demonstrate that waste FCC catalysts, namely E-Cats [18], can catalyse the degradation of polyolefins and suggest improvements to current technology, such as the BP process in Grangemouth [14] using fluidised sand to thermally crack polymer waste at 500 °C.

Although E-Cats contaminated with heavy metals, such as nickel and vanadium, cause unwanted by-products in dehydrogenation reactions and destroy the catalyst components in FCC [18], and very less active as reported from n-hexane cracking, their use in catalytic recycling of waste polymers has been demonstrated. E-Cats would lower the operating temperature, improve the yield and selectivity of volatile products, produce potentially more valuable olefinic feedstocks than a thermal process alone and would lead to a more economic polymer waste recycling process.

Consequently, catalytic recycling of plastic wastes has the potential of contributing valuable chemical feedstock to petrochemical industries and refineries. Collection, sorting and transportation costs are the major barriers to the economic large scale processing of municipal polymer waste.

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