



Hydrocracking of mixed polymer waste, NovaCrack

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Enhanced Feedstock Recycling – NovaCrack™

Aaron Akah¹, Jesus Hernandez-Martinez² and Arthur Garforth²

¹Chemicals Division, Research and Development Centre, Saudi Aramco, Dhahran, Saudi Arabia;
²School of Chemical Engineering, Centre for Nanoporous Materials, University of Manchester, UK

Since plastics are extremely stable, decomposition in a landfill occurs over extended periods, and with the introduction of more stringent environmental regulation and rising landfill costs there is an increasing need to redirect plastic waste from landfill towards recycling options, enhancing recovery of raw materials.

There are two major routes for the recycling of plastic waste; mechanical and feedstock. The most widespread approach to *feedstock recycling* is the *pyrolysis (or cracking)* of the plastic waste. However, this process requires high operating temperatures (typically 500°C – 900°C) with a subsequent large adiabatic temperature drop across the reactor (fixed bed or fluidised) which combined with catalyst deactivation results in significant processing issues^{1,2}. Work at Manchester³ from 1994 focussed on a fluidised bed reactor where there are advantages in terms of heat and mass transfer. HDPE cracking was carried out using pure zeolites and fresh, steam deactivated and “equilibrium” catalysts (E-Cats) with different rare earth oxides and Ni and V loadings (Table 1).

Table 1: Catalyst details (supplied by Engelhard Corporation now BASF, Iselin, USA)

Catalyst	Commercial name	REO (wt%)	UCS (Å)	MSA (m ² /g)	ZSA (m ² /g)	Ni (ppm)	V (ppm)
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	^a Steam deactivated FCC catalyst	0.8	24.3	90	198	-	-
Cat-7S	^a 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

^a Steaming conditions: 4h/1061 K/100% steam

The effect on product distribution of zeolite type and the influence in the formulated FCC catalyst can be seen in the changing yields of paraffins and olefins (Fig. 2 and Table 2).

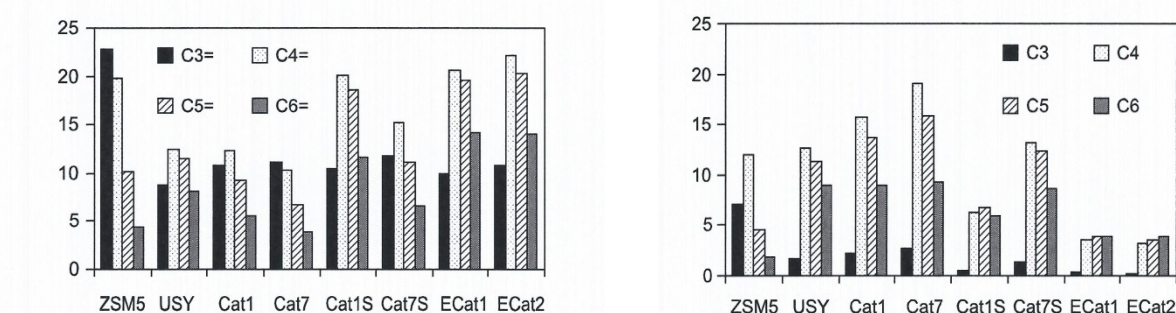


Fig. 2: Selected olefin and paraffin products (wt%) for fluidised catalytic cracking at $T = 723$ K; $C/P = 6:1$

The anticipated loss in reactivity is also seen from fresh to steam deactivated FCC catalysts and rare earth stabilisation in Cat 7/7S activities compared to Cat 1/1S. There appeared little effect in the significant increase in Ni and V loading in the ECats tested suggesting a “waste catalyst for waste recycling” strategy might be appropriate as the cost of disposal increases significantly.

Table 2: Product distributions and Catalyst details (supplied by Engelhard Corporation now BASF, Iselin, USA)

Products	ZSM-5	US-Y	Cat-1	Cat-7	Cat-1S	Cat-7S	E-Cat1	E-Cat2
Gaseous	83.7	55.9	75	71.8	50.4	55.8	64.5	65.8
Liquid	2.0	0.5	9.0	6.8	7.2	7.8	1.4	1.4
Coke	2.4	4.5	6.5	7.2	3.0	4.9	1.5	1.2
Involatile	11.9	39.1	9.5	14.2	39.4	31.5	32.6	31.6
Total	100	100	100	100	100	100	100	100
Gaseous product distribution								
C1 - C4	68.6	36.6	44.4	47.4	38.4	44.4	35.2	37.1
C5 - C9	23.1	60.2	52.2	48.8	60.2	52.8	63.4	62.6
BTX	8.3	3.2	3.4	3.8	1.4	2.8	1.4	0.3
Total	100	100	100	100	100	100	100	100
Total gaseous product								
Paraffins	27	49	54	60	31	49	24	23
Olefins	65	48	43	36	67	49	75	77

Before design predictions could be made, an understanding of the interface between the polymer and the catalyst must be developed. The mechanism of interaction is highly complex, with three phases (liquid polymer, solid catalyst and gaseous products), mass transfer by diffusion, convection and bulk flow as well as cracking-type reactions with a large number of products. Fig. 3 shows a scanning electron micrograph (SEM) of a finely blended mixture of high density polyethylene (HDPE) and ZSM-5 after heating from ambient to 573 K and the melted polymer can be seen to have completely “wetted” the zeolite particles (Fig. 3).

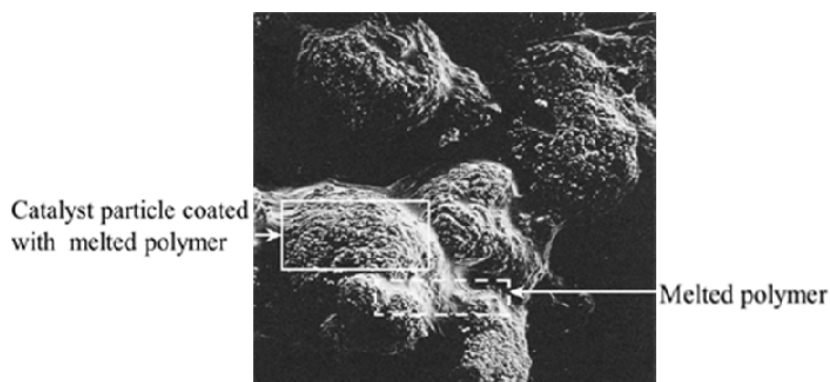


Fig. 3: Mixture of HDPE/Catalyst, 200 times magnification³

A more energy neutral option to catalytic cracking of plastics is that of **hydrocracking**, which in the presence of a suitable catalyst not only offers the potential for the selective recovery of useful chemical fractions, but is also tolerant of the presence of heteroatoms such as chlorine or fluorine in the plastic. The hydrocracking process offers the opportunity to produce medium chain hydrocarbons such as naphtha and diesel fuel.

The focus of work on hydrocracking has been batch reactor studies on polymers or blends of polymers with coal or vacuum gas oil (Table 3). Since 2005, work at Manchester has demonstrated that the mildly exothermic process can be carried out at much reduced temperatures (200°C–350°C) whilst maintaining production/conversion yields comparable to the cited literature values. Most importantly, significantly shorter reaction times (typically 5 mins) now make continuous processing of polymer waste a possibility (Table 3).

Table 3: Comparison of Batch reactor studies on pure polymer and blend mixtures

Reference	T(°C)	H ₂ P(psig)	t (min)	F/C	Gas(%)	Liq(%)
Ding,Anderson 1995 ⁴	375	1000	60	3/2	50	50
Walendziewski 2002 ⁵	380	450	120	10/1	17	75
Karagoz Yanik 2002 ⁶	435	650	60	20/1	60	31
Garforth <i>et al</i> , Pure Polymers ⁷	225-310	500-800	5	10/1-20/1	10-30	70-90
Garforth <i>et al</i> , Polymer Blends ⁸	310-400	800	5	10/1	20	80

Key parameters of mixing, temperature of reaction, pure and mixed polymer feeds were investigated. As expected increasing T increased lighter product yield (Fig. 5). Reducing H₂ pressure increased coke yield and decreased catalytic activity (Table 4).

Table 4: Product distribution as a function of T and H₂ pressure using virgin HDPE and 1 wt% Pt/USY

Catalyst	Pt/USY	Pt/USY	Pt/USY	Pt/USY	Pt/USY
T (°C)	350	310	270	270	270
H ₂ initial P (MPa)	5.5	5.5	5.5	3.5	1.5
Gas	58.9	43.5	33.4	35.2	12.0
Gasoline	40.8	56.0	65.9	63.7	23.4
Diesel	0.0	0.0	0.3	0.2	0.2
Coke	3.9	4.9	5.0	8.8	17.4
X (%)	99	99	99	99	36

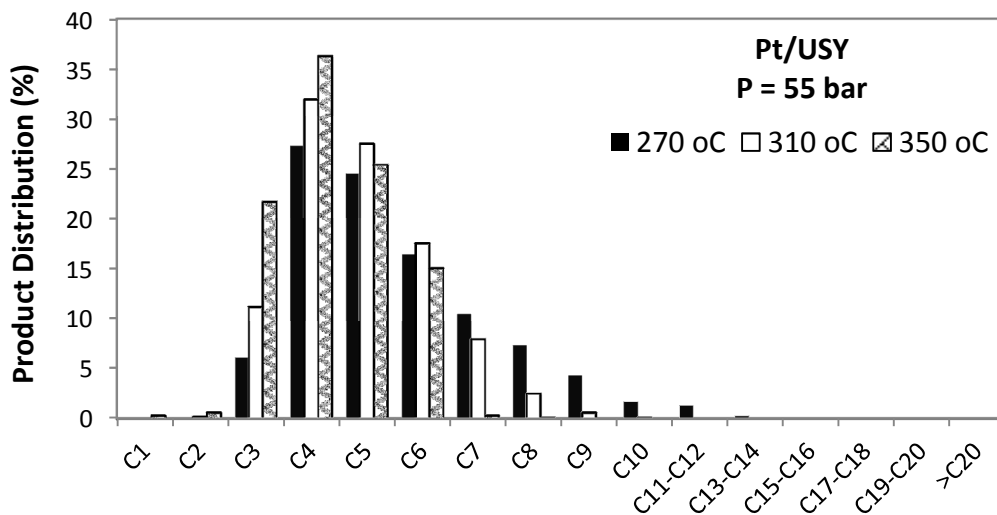


Fig. 4: Product distribution as a function of T and H₂ pressure using virgin HDPE and 1 wt% Pt/USY

Reduction in the amount of Pt loaded, although had little effect on conversion and the product slate, resulted in slightly increased coke yields (Table 5). Work on pure HDPE was extended to include different zeolite catalysts including Mordenite, ZSM-5 and Beta. More importantly, the hydrocracking of mixed polymer feeds was carried out, such as PE, PP and PS. In addition, the polyolefin blends were mixed with different amounts

Table 5: Product distribution as a function of metal loading for using virgin HDPE and USY

Catalyst	Pt/USY	0.5Pt/USY	HUSY
T (°C)	270	270	310
H ₂ initial P (MPa)	5.5	5.5	5.5
<i>Gas</i>	33.4	34.4	5.6
<i>Gasoline</i>	65.9	64.7	4.6
<i>Diesel</i>	0.3	0.3	0.0
<i>Coke</i>	5.0	6.0	15.6
X (%)	99	99	10

of PET and PVC (up to 25% in both cases). The results for some of the blends are shown in Fig. 6 and indicate that the product slate could be adjusted by changing the feed blend.

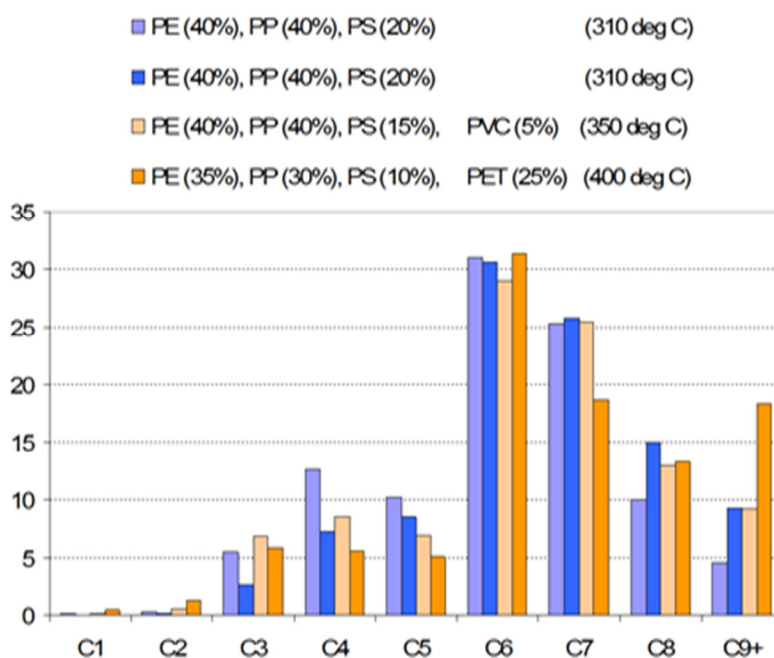


Fig. 6: Product distribution as a function of mixed polymer blend

In conclusion, the results obtained at Manchester demonstrate a significant improvement on the published literature processes, with shorter reaction times (around 10 times) indicating scope for the development of a continuous hydrocracking process at reaction conditions around 80 °C lower than typical reaction temperatures reported in the literature. The tolerance for PVC and the use of PET also diversify the product slate. The experimental results presented also demonstrate the applicability of the Pt/USY hydrocracking process to the conversion of waste plastics into naphtha fractions in the range of C₃ – C₁₂, with a high proportion of branched isomers obtained resulting in an increased octane number for fuel.

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