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Enhanced Feedstock Recycling of Post-Consumer Plastic Waste

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Feedstock recycling of waste plastics is becoming more crucial as a method to convert plastics back into a source of useful platform chemicals. Although thermal cracking presents easier options, the products have limited utility and present a higher energy burden than the method proposed in this paper, that of catalytic hydrocracking a mildly exothermic process. This paper reports the use of metal loaded zeolite catalysts at much reduced temperatures (200 °C - 350 °C) to convert mixed plastic waste at significantly shorter reaction times (typically 5 min), making the continuous processing of polymer waste a possibility.

1. Introduction

Around 5 million tonnes of plastic is generated annually in the UK, with bulk of this (75 %) going to landfill (Plastics Europe, 2007). 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 (Aguado and Serrano, 1999). Enhanced feedstock recycling and hydrocracking present an excellent alternative to current recycling methods, where the plastic waste is converted into a source of useful chemical feedstocks such as naphtha or short chain hydrocarbons. A life cycle analysis carried out by Perugini et al. (2005) highlighted the environmental sustainability of feedstock recycling methods including pyrolysis and hydrocracking for polymers, for which virgin and recycled material are not of equivalent market value, with the environmental burden posed by landfill and combustion also highlighted. The most widespread approach to feedstock recycling is the pyrolysis (or cracking) of plastic waste (Kaminsky and Zorriqueta, 2007). However, significant processing issues exist as high operating temperatures (typically 500 °C - 900 °C) and large adiabatic temperature drops across the reactor (fixed bed or fluidised) are combined with separation steps and catalyst deactivation (Garforth et al., 2004). HDPE cracking using a fluidised bed reactor, offered advantages in terms of heat and mass transfer, and fresh, steam deactivated and “equilibrium” catalysts (E-Cats) with different rare earth oxides and Ni and V loadings producing predominantly a propene and butene product stream (Ali et al., 2002). 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 is tolerant of the presence of heteroatoms such as bromine, chlorine and fluorine in the plastic. The hydrocracking process is found in many modern refineries and involves a complex series of reactions (mainly hydrogenation/dehydrogenation and cracking) at elevated hydrogen pressures (Robinson and Dolbear, 2006). Catalysts are bifunctional with a metal (which performs the hydrogenation/dehydrogenation function) and an acidic support (which provides the cracking function). The most commonly used metals are noble metals such as Pt, Pd and Ni, or bimetallic sulfides such as Co/MoS or Ni/MoS with the usual acidic supports being alumina, amorphous silica alumina (ASA) or zeolites. Recent research has focussed on batch reactor studies on polymers or on using polymers as a source of hydrogen for co-mingling with coal/vacuum gas oil (Table 1).

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Table 1: Comparison of Batch reactor studies on pure polymer and blend mixtures

Reference	T(°C)	H_2 P(MPa)	$t_{(min)}$	Feed/Catalyst	Gas (%)	Liquid (%)
Ding,Anderson,1995	375	6.6	60	3/2	50	50
Walendziewski, 2002	380	3.0	120	10/1	17	75
Karagöz, 2002	435	4.3	60	20/1	60	31

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 minutes) now make continuous processing of polymer waste a possibility (Garforth et al., 2012).

2. Materials and Methods

High purity High-Density Polyethylene (HDPE), Polypropylene (PP), Polystyrene (PS), Polyethylene terephthalate (PET) and Polyvinylchloride (PVC) from Goodfellows were received in powder (< 400 µm) or pellet form and were used as model polymers for the hydrocracking tests. The zeolite catalysts used in this study were 0.5 wt. % and 1 wt. % Pt on USY and acidic H form of USY. The USY catalysts were supplied by Crosfield and had an overall Si/Al_{bulk} ratio of 2.8 but with two differing Si/Al_F ratios of 6.0 and 9.0 confirmed by MASNMR. Zeolites were ion exchanged with $Pt(NH_3)_4Cl_2$ to obtain the relevant Pt loadings and were confirmed by acid digestion and ICP-ES analysis. The ion-exchanged catalysts were then pelletized and sieved to 0.3 - 0.5 mm particle size. Catalysts were calcined in a tubular reactor with a flow of air (50 mL/min) at 450 °C for 240 min and reduced with H_2 (50 mL/min) at 450 °C for 240 min, slow heating and cooling ramps (2 °C/min) were used. Hydrocracking tests were carried out in a 300 cm^3 stainless steel stirred autoclave (Parr, USA), heated by an electric band heater at SOG Ltd in Runcorn. The reactor was loaded with 18 g of the polymer and 1.8 g of catalyst (avoiding contact with air), flushed and pressurised with H_2 at room temperature to the desired pressure (between 1.5 to 5.5 MPa). Sampling of the products was achieved using an evacuated 1000 cm^3 sampling bomb placed in an ice bath. Experiments were duplicated to ensure reproducibility and provide run-to-run comparison of mass balances.

2.1 Analysis

Gas and liquid products separated in the sampling bomb, along with those remaining in the reactor were collected, the liquid was weighed and volume of gases at atmospheric pressure measured. Gases were analysed by a Varian 3400 GC fitted with a 50 m x 0.32 mm PLOT Al_2O_3/KCl capillary column with FID detector; liquids by a Varian 3400 GC fitted with a 50 m x 0.25 mm non polar BP-5 column with FID detector and GC-MS (Agilent Technologies 6890N Network GC fitted with a 50 m x 0.25 mm HP-5MS non polar capillary column and a FID detector coupled with an Agilent S973 inert Mass Selective Detector. Carbon residue on the catalyst was determined by elemental analysis of the spent catalyst, cleaned from the plastic residue by refluxing with xylene.
From the GC-MS analysis, the yield of a particular product was calculated using the Eq(1):

$$Yield_{Product,i} = \frac{Mass_{Product,i}}{Mass_{feed}} \times 10 \quad (1)$$

3. Results and Discussion

Key hydrocracking parameters of mixing, hydrogen pressure, temperature and platinum loading were investigated for pure and mixed polymer feeds. As polyolefins are a major constituent of post-consumer plastic waste (typically 65 %+, Plastics Europe, 2007), the initial focus was on using 1 wt. % Pt-loaded USY catalysts with Si/Al_F ratio of 9.0 to hydrocrack HDPE. Products were divided into three fractions based solely on carbon number: gas (C_1 - C_4), gasoline (C_5 - C_{12}) and diesel (C_{13} - C_{20}). Coke formed on the catalyst was indicated as wt. % of carbon on the catalyst (accuracy ± 0.3 %). Reaction time (time at selected reaction temperature) in all experiments was 5 minutes, however, as the reaction was carried out as a batch process the time required to reach reaction temperature from room temperature was typically 25 - 30 min.

3.1 Effect of Mixing

The effective conversion with a turbine agitator was found to be 55 % whilst an anchor type agitator produced almost 100 % conversion at 270 °C and 5.5 MPa H_2 pressure. In both cases the overall product distribution was similar varying from C_3 - C_{14} and the results presented here using high density polyethylene (HDPE)

showed that appropriate mixing of a suitable catalyst, polymer and reacting gas can dramatically reduce both the reaction time and the required reaction temperature. Since this mixing efficiency is dependent on a number of factors including stirrer speed, polymer melt temperature, pressure, rheological properties of the polymer, ease of diffusion and solubility of hydrogen in the melt; the shearing of the melted plastic mix using the anchor agitator results in more intimate mixing of the reacting gas, plastic and catalyst leading to thinner boundary film thickness, better mixing and thus improved reaction rates.

3.2 Effect of Temperature

As expected increasing the temperature increased lighter product yield with increasing amounts of gas (carbon number breakdown is shown in Figure 1). Negligible amounts of products heavier than C_{12} were recorded at any temperature. Total conversion was obtained at the three temperatures studied from 270 °C to 350 °C using 5.5 MPa initial H_2 pressure and 1% Pt/USY (Table 2). The product distribution showed no significant differences in the profile for any of the three different temperatures and all catalysts gave C_4 as the major product with little or no C_1 and C_2. When the reaction temperature was lowered further to 210 °C at 5.5 MPa of H_2, all HDPE was consumed resulting in total conversion.

Table 2: Product distribution as a function of T and H_2 pressure using HDPE with 1 wt.% Pt/USY

T (ºC)	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
Conversion, X (wt.%)	99	99	98	99	36

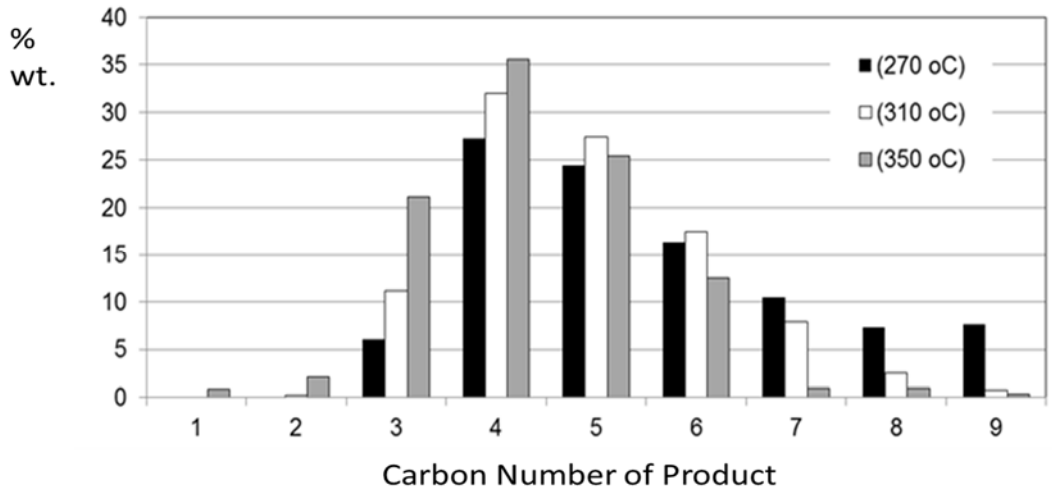

Figure 1: Product distribution (wt. %) in Carbon number as a function of T at 5.5 MPa H_2 pressure from the conversion of HDPE with 1 wt.% Pt/USY

3.3 Effect of H_2 pressure

Experiments were also carried out at three different pressures (5.5, 3.5 and 1.5 MPa initial H_2) at 270 °C using 1 wt. % Pt/USY (Table 2). When the H_2 pressure was reduced to 3.5 MPa the product distributions were virtually identical with almost total conversion, but further reduction to 1.5 MPa resulted in conversion dropping to ~ 35 %. The results suggest that high H_2 pressure was needed to avoid coking and subsequent catalyst deactivation. When the pressure was reduced from 5.5 MPa to 3.5 MPa, although coke content almost doubled, the reduction in pressure did not affect product distribution or conversion.

3.4 Effect of Platinum loading

Reduction of the amount of Pt loaded on USY by 50 % had little effect on the product slate, however, coke yield increased slightly (Table 3). Predictably HUSY coked rapidly and conversion fell to 10 wt.%.

3.5 Hydrocracking different pure polymer feedstocks and blends

A number of pure polyolefin feedstocks were studied including PE, PP and PS along with blends of these three (Table 4). Product distributions for the pure polymers are shown in Figure 2 and a predominantly C_3 - C_9 hydrocarbon yield was observed. However, different polymers and their structures yielded different product slates. For example, PP yielded a heavier product with a high yield of C_6 hydrocarbons whereas PS yielded larger amounts of C_3 and C_4 with increased amounts of C_7 - C_9s. Further hydrocracking experiments were successful with 99 ± 1 wt% conversion between 310 °C - 400 °C on additional polyolefin blends with different amounts of PET and PVC (up to 25% in both cases, Figure 3)(Garforth et al., 2012, 2013).

Table 3: Product distribution as a function of metal loading for using virgin HDPE and USY

Catalyst	1 wt.% Pt/USY	0.5 wt.% Pt/USY	HUSY
T (ºC)	270	270	310
H_2 initial P (MPa)	5.5	5.5	5.5
Gas	33.4	34.4	5.6
Gasoline	65.9	64.7	4.6
Diesel	0.3	0.3	0.0
Coke	5.0	6.0	15.6

Table 4: Product distribution for different feeds over 1 wt. % Pt/USY at 5.5 MPa H_2 pressure and T= 310 °C

Feed	Conversion (wt. %)
n-heptane	5.8
PE	99.5
PP	99.8
PS	100
PE (40%), PP (40%), PS (20%)	99.4
PE (40%), PP (40%), PS (20%)	99.2

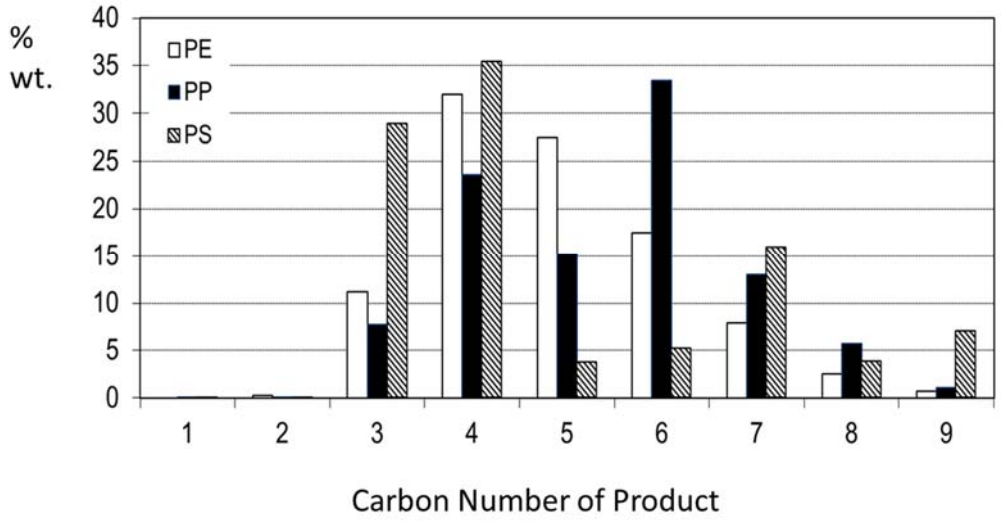

Figure 2: Product distribution (wt. %) for three pure polymers hydrocracked at 310 °C and 5.5 MPa H_2 pressure over 1 wt. % Pt/USY (Si/Al_F = 9.0, as per Table 4

4. Conclusions

Experimental results presented in this paper demonstrate the applicability of the Pt/USY to the hydrocracking process to the conversion of waste plastics into gas and naphtha fractions in the range of C_3 - C_{12}, with a high proportion of branched isomers obtained which therefore result in an increased octane number for the resultant fuel. Dependent on the polymer used or the mixture of polymer used would require a different operating temperature, high proportions of PET for example required higher processing temperatures (typically 400 °C) whereas PS was fully converted at temperatures as low as 190 °C. The key to the success

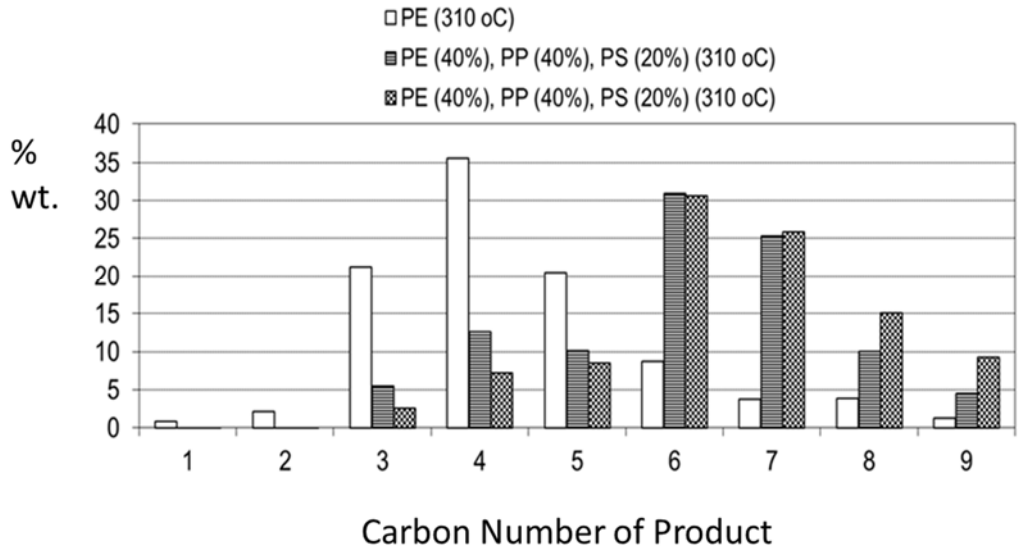

Figure 3: Product distribution (wt. %) for three pure polymers hydrocracked at 310°C and 5.5 MPa H_2 pressure over 1 wt. % Pt/USY (Si/Al_F= 9.0) as per Table 4.

of all the experiments cited here was the use of an anchor type agitator which resulted in an almost 100% conversion of the melted polymers into the resultant naphtha fractions. The results obtained demonstrate a significant improvement on the published literature, 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. Research is on-going with regards to a continuous process and the fate of legacy chemicals such as bromine-containing fire retardants in the product slate.

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