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Enhanced Feedstock Recycling of Plastic Waste

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Introduction

Plastics are extremely stable and decomposition in a landfill occurs over extended periods, with the introduction of more stringent environmental regulation, rising landfill costs and the drive towards a circular economy, there is an increasing need to redirect plastic waste from landfill/energy recovery towards enhanced recovery of the raw materials. The two main routes for the recycling of plastic waste are 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 $500^{\circ}C - 900^{\circ}C$) 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}.

A more energy neutral option to catalytic cracking of plastics is that of hydrocracking, which offers the potential for the selective recovery of useful chemical fractions but is also is tolerant of the presence of heteroatoms such as bromine and chlorine.

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 μ m) 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 had an overall Si/Al_{bulk} ratio of 2.8 but were steamed with differing severity yielding two Si/Al_F ratios of 6.0 and 9.0 (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 cm³ stainless steel stirred autoclave (Parr, USA), heated by an electric band heater. 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 (between 1.5 to 5.5 MPa). Products were sampled using an evacuated 1000 cm³ sampling bomb placed in an ice bath. Gas and liquid products separated in the sampling bomb, along with those remaining in the reactor were collected, the liquid was weighed and the volume of gases 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 GC-MS (Agilent Technologies 6890N with Agilent S973 inert Mass Selective Detector) fitted with a 50 m x 0.25 mm HP-5MS non polar capillary column. Experiments were duplicated to ensure reproducibility and provide run-to-run comparison of mass balances. Catalyst carbon residue on 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):

 $[Yield]_(Product,_i) = [Mass]_(Product,_i) / [Mass]_feed \times 100$ (1)

Results and Discussion

Hydrocracking of polymers with coal or vacuum gas oil has been studied in batch reactors previously (Table 1). This research investigated key parameters of mixing, temperature, pure and mixed polymer feeds at $200^{\circ}C-350^{\circ}C$ and 500-1000 psig.

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

Reference	$T(^{\circ}C)$	$H_2P(psig)$	t (min)	F/C	Gas(%)	Liq(%)
Ding,et al 1995 ⁴	375	1000	60	3/2	50	50
Walendziewski 2002 ⁵	380	450	120	10/1	17	75
Karagoz et al 20026	435	650	60	20/1	60	31
UoM Pure Polymers ⁷	225-310	500-800	5	20/1	10-30	70-90
UoM Polymer Blends ⁷	310-400	800	5	10/1	20	80

As expected, increasing T increased lighter product yield and reducing H_2 pressure increased coke yield and decreased catalytic activity. Reduction in the amount of Pt loading on USY had little effect on conversion and the product slate but slightly increased coke yields.

The hydrocracking of mixed polymer feeds included the polyolefin blends but in addition, different amounts of PET and PVC (up to 25% in both cases). The results for some of the blends are shown in Fig. 1 typically turning the waste into naphtha fractions ($C_5 - C_{12}$), with a high proportion of branched isomers.



Fig. 1: Product distribution as a function of mixed polymer blend

Significance

This research demonstrated that mildly exothermic hydrocracking can be carried out at significantly shorter reaction times (typically 5 min.) whilst maintaining conversion comparable to the cited literature values, making continuous processing of polymer waste a possibility. The tolerance for PVC has been shown and PET helped diversify the product slate.

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