Feedstock Recycling of Plastic Wastes by Hydrocracking

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Introduction

Plastic wastes are an important environmental problem due to the ever increasing production. One of the main issues of plastic wastes is their extremely slow degradability that provokes a drastic reduction of landfill capacity. Recycling is unavoidable in a global plastic waste management strategy [1].

Feedstock recycling (or chemical recycling) considers the waste as a feedstock, as a source of useful chemical products. The most widespread approach to feedstock recycling is the pyrolysis (or cracking) of the plastic waste. Thermal and catalytic cracking has been essayed with encouraging results producing a range of liquid hydrocarbons [2, 4]. However, both processes are highly endothermic and the quality of the product is varied with thermal cracking having low selectivity. In addition both processes require significant financial investment.

Hydrocracking is a novel approach to chemical recycling although a common process in modern refineries [3, 5] involving a complex series of reactions (mainly hydrogenation-dehydrogenation and cracking) at elevated hydrogen pressures. Hydrocracking catalysts consist of a metal (hydrogenation function) supported over an acidic support (cracking function). The most used metal functions are noble metals 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) and zeolites. The balance between the acidic and metal function is critical in the performance of the catalyst. Our strategy is to develop a product either in the gasoline or diesel range.

Materials and Methods

In association with Mr. Andrew Wilson at SOG Ltd at Runcorn (UK), batch slurry reactions were carried out at 40 - 70 bar using autoclaves for a range of catalysts, commercial and synthesized. ASA and Ni/ASA (66% Ni) were obtained from Aldrich (ASA is a cracking catalyst, not hydrocracking and was used as comparison), 1% Pt/ZSM5 was prepared and two commercial NiMo hydrotreating catalysts were also acquired. Other catalyst currently under development include Pt/ASA, Ni/ASA and Pt/USY. Initially, a model compound (Squalane: $C_{30}H_{62}$) was used as feed in a first step to assess catalyst behavior and optimize the reaction conditions. All products, gas, liquid, solid were analysed by GC, TG and elemental analysis obtaining mass balances of 88 + 5% typically.

Results

Early results show promising results for both the yield of gasoline and diesel fuels (Table 1). At present, the selectivity to a relevant product ranges is being optimized. However, the results shown highlight that a gasoline range product is possible with Pt/ZSM-5 when

operating at lower temperatures and a significant yield of a diesel fuel is possible when increasing the pressure of hydrogen in the case of Ni/ASA. Figure 1 shows an example of the GC analysis of the heavy liquid product showing the type and amount of hydrocarbons present. Interestingly, both Ni/ASA and Pt/ZSM-5 show high selective to methane and propane respectively.

Table 1. Early results for tests carried out using Squalane as feed. Reaction conditions are: T = 350 degC, t reaction = 60 min, P H₂ initial = 35 bar, Feed:Catalyst wt ratio = 20:1

Catalyst	None	ASA	NiMo Commercial	Ni/ASA	Pt/ZSM5
Product Yield (wt %)					
Gas HC	0.17	9.15	0.27	23.86	56.86
				C1 (91.7%)	C3 (66.7%)
Gasoline (C5-C12)	0.00	12.78	0.00	4.43	11.32
Gasoil (C13-C20)	0.00	0.59	0.00	13.51	1.28
Conversion (%)	0.45	27.75	2.70	87.65	69.32
Sample Solvent n-C6 3.4 %	n-C12 n- 4.0 %	C14 n-C16 3.8% 3.8 10 10 10 10	n-C18 n-C20 % 6.5 %	Unconve Squalan 60.2 %	rted 9 F

Figure 1. Example of the heavy liquid product analysed using a Varian 3400 GC FID fitted 50m * 0.25mm i.d. BP-5 capillary column fitted.

Real polymer streams, such as, "green dot" DSD plastic, LLDPE and HDPE are being tested. From the initial results quoted here and refinements from the results on real plastics, an initial cost estimate of commercial hydrocracking technology will be made.

Significance

A commercially profitable process to feedstock recycle plastic would successfully address the problem of plastic waste whilst providing a source of valuable liquid fuels.

References

- 1. Plastics_Europe (2004). An analysis of plastics consumption and recovery in Europe 2002-2003. Brussels. www.plasticseurope.org
- 2. Kaminsky, W., Predel, M. and Sadiki, A. (2004). Polym Degrad Stab, 85(3), 1045-1050.
- Garforth A, Ali S, Hernández-Martínez J and Akah A, Curr. Op.Solid State and Mat Sci, 8 (6) 2004, 419-425
- 4. Ali S, Garforth AA, Harris DH, et al. (2002). Catal Today, 75(1-4), 247-255.
- Aguado, J. and Serrano, D. P. (1999). Feedstock recycling of plastic wastes. Cambridge: Royal Society of Chemistry.192 pp