

CATALYTIC CRACKING OF WAXES FROM POLYOLEFINS UNDER FCC OPERATING CONDITIONS

J.M. Arandes¹, I. Torre¹, M.J. Azkoiti², M. Olazar¹, J. Ereña¹ and J.Bilbao¹

¹University of the Basque Country. Chemical Engineering Department, Apdo. 644, 48080 Bilbao, Spain

²University of the Basque Country. Chemical and Environmental Engineering Department, Plaza de la Casilla 3, 48012 Bilbao, Spain

e-mail: josemaria.arandes@ehu.es

Abstract

The catalytic cracking of polyolefin pyrolysis waxes has been carried out in an FCC riser simulator in the 500-550°C range, with a catalyst/feed ratio of 5.5 and contact times between 3 and 12 s. The effect of the operating conditions on the yields and composition of products has been studied. The results have been compared with those of a vacuum gas oil (VGO) and a mixture of VGO (80 wt%) and waxes (20 wt%) catalytic cracking. The results show that the yields and composition of products are acceptable by refineries without any special modification of operating conditions. The effect of HZSM-5 incorporation on the yields and composition of product streams has also been studied.

Keywords: Waste polyolefins, catalytic cracking, FCC, waxes

1. Introduction

A way for upgrading waste plastics lies in their incorporation into refineries following different operating strategies. The most straightforward solution consists in a single-step treatment by incorporating them into a refinery process, such as the catalytic cracking unit, FCC, or the hydrocracking unit. This paper studies a two-step strategy: (1) pyrolysis at the location where the plastics are collected; (2) incorporation of the product (waxes) to a conventional FCC feed.

A study is carried out on the cracking of waxes under conditions similar to those of an FCC unit. The results are complementary to those obtained in previous papers, where polyolefins dissolved in VGO, either in pure aromatics or in LCO (light cycle oil) were cracked under FCC conditions [1].

2. Materials and Methods

The waxes have been obtained by flash pyrolysis of polypropylene (PP) at 500°C. The pyrolysis reactor is a conical spouted bed [2] that allows obtaining wax yields higher than 90 wt%. A vacuum gas oil has been used as a reference feed. The simulated distillation of VGO and of the waxes are shown in Table 1. A number average molecular weight of 363 and a weight average molecular weight of 2405 have been determined for the waxes by gel permeation chromatography. A clearly olefinic nature has been determined by FTIR.

The behaviour of two catalysts (Table 2) has been studied. CAT-1 is an equilibrated catalyst used in a Spanish FCC unit. CAT-H is a hybrid catalyst prepared by mixing CAT-1 (75 wt%) with a catalyst based on HZSM-5 zeolite (SiO₂/Al₂O₃ = 50), CAT-Z.

Table 1. Properties of the VGO and Waxes.

Properties	VGO	Waxes
Density, g cm ⁻³ (at 15°C)	0.9007	0.8902
Conradson C, wt%	0.61	---
Simulated distillation, °C		
IP	264	182
5 wt%	---	241
10 wt%	378	275
30 wt%	434	362
50 wt%	469	440
70 wt%	505	512
90 wt%	553	591
95 wt%	---	618
EP	627	---
Paraffins, wt%	6.8	---
Naphthenes, wt%	35.6	---
Aromatics, wt%	41.1	---
Sulfur compounds, wt%	16.5	---

The reaction device is a riser simulator reactor. It is an internally circulating reactor specially designed for catalytic cracking and has been previously described [3]. The runs have been carried out at 2-3 atm, in the 500-550°C range, with a catalyst/feed ratio of C/O=5.5 by weight and a value of contact time between 3-12 s. The low value of contact time minimizes the contribution of thermal cracking.

Product analysis has been carried out by means of a sampling device connected to a 6890 Agilent GC. Product identification was carried out by GC-MS (Agilent 6890 GC-MS Engine with electronic ionization). The product identification was confirmed by using PIANO standards in the C₅-C₁₂ range.

Table 2. Catalysts properties

Properties	CAT-1	CAT-Z
Zeolite percentage, wt%	14	25
BET surface area, m ² g ⁻¹	123	182
Zeolite area, m ² g ⁻¹	89	63
Micropore diameter, Å	7.8	5.5
Mesopore diameter, Å	146	103
UCS, Å	24.27	---
Ni, ppm	890	---
V, ppm	2186	---
Acidity, mmol NH ₃ g ⁻¹	0.018	0.024
Acid strength, kJ mol ⁻¹ NH ₃	125-140	<120
Bronsted/Lewis ratio	6.3	1.9

The coke deposited on the catalyst was measured by thermogravimetric analysis in a Setaram TG-DSC 111. The spent catalyst was dried at 110°C in nitrogen stream and subjected to combustion with air at a programmed temperature (5°C min⁻¹) up to 700°C.

3. Results and Discussion

Figure 1 shows as an example the conversion of waxes and VGO at different temperatures and contact times. Wax conversion is higher at all the conditions studied, as they are more olefinic and liable to catalytic cracking than VGO, which is mainly aromatic.

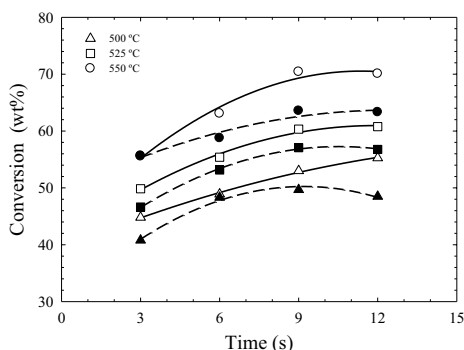


Fig. 1. Conversion of waxes (white points) and of VGO (black points).

Likewise, Figure 2 also shows as an example the results of gasoline composition obtained in the catalytic cracking of waxes, VGO and VGO+wax mixtures at severe conditions (550°C and t = 12 s).

A comparison of VGO cracking with wax cracking shows that the latter gives way to a gasoline with a higher content of olefins, naphthenes, paraffins, and isoparaffins. This is a consequence of wax composition, with olefinic linear chains, and of VGO composition, which is conditioned by its aromatic nature.

The octane number, RON, of the gasoline obtained in the cracking of waxes (between 95 and 98) is suitable for being added to the refinery gasoline pool.

The LPG obtained by cracking waxes has propene as the main component and its olefinicity increases as temperature is increased.

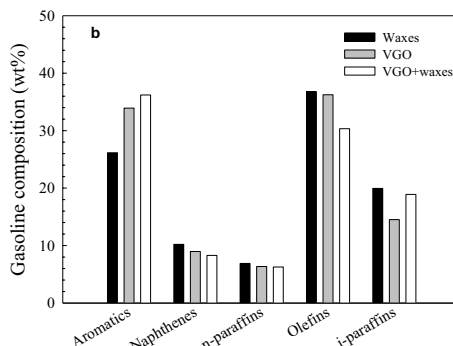


Fig. 2. Comparison of gasolines obtained by cracking different feedstocks.

The gasoline from wax cracking has a higher content of olefins, naphthenes and paraffins, with less aromatics and more isoparaffins than that obtained by cracking the VGO.

At high temperatures and contact times the mixture of VGO with waxes shows a synergistic effect, giving way to an increase in the yield of gasoline and LPG, which is probably due to the reactivity of C₂-C₄ radicals generated in the primary cracking of waxes.

A catalyst based on HZSM-5 leads to a decrease in the conversion of waxes due to the shape selectivity of the HZSM-5 zeolite. This lower conversion involves a lower yield of LPG, dry gases and coke, although the yield of gasoline is higher than using the base catalyst.

The gasoline obtained using the hybrid catalyst has a higher concentration of naphthenes, n-paraffins and olefins and a higher concentration of aromatics and of isoparaffins than the gasoline corresponding to the base catalyst.

4. Conclusions

Polyolefin pyrolysis waxes provide satisfactory results for refineries when used as an FCC feed. Given that the compounds present in the waxes are more easily cracked than those in VGO, its conversion is higher in the whole range of temperatures and contact times.

The FCC unit is sufficiently versatile for co-feeding the waxes without operational problems, which contributes to the large-scale valorisation of waste plastics and to the intensification of crude valorisation.

References

- [1] J.M. Arandes, I. Abajo, D. López-Valerio, I. Fernández, M.J. Azkoiti, M. Olazar, J. Bilbao. Transformation into Fuels of Several Plastic Wastes by Catalytic Cracking. *Ind. Eng. Chem. Res.* 36 (1997) 4523-4529.
- [2] R. Aguado, M. Olazar, B. Gaisán, R. Prieto. Kinetic Study of Polyolefins Pyrolysis in a Conical Spouted Bed Reactor. *Ind. Eng. Chem. Res.* 41 (2002) 4559-4566.
- [3] H.I. de Lasa. US Patent 5,102,628 (1992).