

HYDRORREFORMING OVER Ni/h-BETA OF THE THERMAL CRACKING PRODUCTS OF LDPE, HDPE AND PP FOR FUEL PRODUCTION

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Abstract

Chemical treatments for plastic wastes deserve special attention nowadays because of the valuable products obtained, raw materials for chemical processes or fuels. For fuel production, thermal cracking of the polymers must be followed by hydrogenation or hydrotreating of the pyrolysis products in order to reduce olefin content which may cause rubber formation. In this work a two-staged process (thermal cracking / hydrotreating of the products) has been developed for the degradation of LDPE, HDPE, PP and their mixture for fuels production. A hierarchical Beta zeolite nickel-supported catalyst has been used in the second stage. Characterization of the products shows high selectivities to gasoline (C₅-C₁₂) and light diesel (C₁₃-C₁₈) as well as high RON numbers and Cetane indexes.

Keywords: polyolefins, fuels, thermal cracking, hydrotreating, Ni/hierarchical Beta.

1. Introduction

A growing plastic wastes generation and an increasingly restrictive legislation have determined new alternatives to be investigated for its recovery apart from mechanical recycling and energy-recovery incineration. Chemical treatments are a very promising alternative since they produce valuable products, useful as raw material for the Chemical Industry or as fuels.

According to new European Waste Framework Directive chemical processes leading to fuels obtaining are considered energy recovery [1]. For fuel production, thermal pyrolysis of the polymers is not the most adequate process because of the high amount of olefins obtained which may suffer oligomerization. A hydrogenation or hydrotreating of the thermal cracking products is needed in order to prevent this problem [2].

In the present work a two-stage process (thermal cracking followed by hydrotreating of the products) has been developed for the degradation of different polyolefins (LDPE, HDPE, PP and their mixture). A hierarchical Beta zeolite nickel-supported catalyst has been used in the hydrotreating stage. Nickel has been chosen because of its low cost and high capacity for olefinic double bonds hydrogenation. As for the support, hierarchical Beta zeolite combines medium-high acidity along with a bimodal micro/mesoporous structure accessible to large molecules.

The aim is to characterize the so-obtained products and test their capacity to be used as automotive fuels, both gasoline and diesel, regarding to the performance of some properties, e.g. RON number or cetane index, bromine index and total aromatic content.

2. Materials and Methods

Hierarchical Beta zeolite (h-Beta) has been synthesized by the seed silanization procedure using phenylaminopropyltrimethoxysilane (Aldrich, +97%) [3]. Nickel has been incorporated on the support by impregnation using nickel nitrate hexahydrate (Aldrich, >98.5%). Impregnated sample has been calcined at 550°C in static air and reduced under 30 ml/min hydrogen flow up to 550°C. The catalyst (Ni/h-Beta) has been characterized by X-Ray diffraction, H₂-TPR, ICP-AES, TEM, NH₃-TPD, N₂ adsorption-desorption at 77K and Ar adsorption-desorption at 87K.

Raw LDPE (MW ~ 41600), HDPE (MW ~ 188000), PP (MW ~ 450000), all provided by Repsol-YPF, and a mixture containing 45% LDPE + 27% HDPE + 28% PP have been chosen as starting raw materials. An initial charge of 30g for each single polymer or mixture is thermally cracked in a stainless steel autoclave reactor at 400°C for 90 min under nitrogen atmosphere and 700 rpm stirring. The gaseous product are vented out through an ice-cooled trap and collected into a gases bag for further analyses. Catalyst is added to the waxy products remaining in the reactor vessel which is then closed again. The hydrotreating is carried out under the following conditions: T = 310°C; t = 45 min; H₂ pressure = 20 bar; catalyst to feed ratio = 1:30. Characterization of the products includes gas chromatography (for gases and liquids), aromatics measurement by HPLC, Bromine Index determination and RON number and Cetane Index calculations.

3. Results and Discussion

Table 1 shows the main properties of the activated catalyst.

Table 1. Textural and chemical properties of the catalyst.

BET / external surface area (m²·g⁻¹)	578 / 35
Micro / mesopores volume (cm³·g⁻¹)	0.216 / 0.162
Micro / mesopores diameter (nm)	0.6 / 3.1
Si/Al molar ratio	25
Acidity (meq·g⁻¹)	0.301
Nickel content (wt %)	6.2

The hierarchical zeolite is made of aggregates 200-400 nm size. The voids between them, caused by the calcination of the silanization agent, form a secondary mesoporosity which means more than 40% of the catalyst total pore volume. This secondary porosity permits large molecules to access to acid sites and so improves the activity of the catalyst. As for the metallic phase, nickel presence diminishes BET and external surface areas and total pore volume as well as acidity regarding to the original support up to the shown values.

Regarding to the catalytic results, it is easy to see that high selectivities to products useful as automotive fuels can be achieved. Table 2 shows selectivities to gasoline (C₅-C₁₂) and light diesel (C₁₃-C₁₈) obtained in all the reactions. PP provides the higher selectivity to gasoline (67.9%) among the pure polymers, while LDPE leads to the higher amount of light diesel (26.6%). Results for the mixture are very similar to those for PP. No matter what the starting feed is, the total amount of usable fuels remains very similar, upon 83%, varying only the ratio between gasoline and light diesel in a narrow range. Taking into account the carbon atom number distributions large differences appear, as PP is more easily cracked than the polyethylenes [4] and leads to higher amounts of nonanes. For the mixture, the distribution is very similar to that of PP and much different to that expected as a mere lineal combination of the components, pointing out some synergetic effect. A reasonable explanation is that tertiary radicals formed in the PP structure could favour the cracking of the other polymers.

Table 2. Selectivities to usable fuels of the hydroreforming products (wt %).

Polymer	Gasoline	Light diesel	Total amount of usable fuels
LDPE	54.5	26.6	81.1
HDPE	63.2	21.6	84.8
PP	67.9	14.8	82.7
Mixture	68.3	15.7	84.0

Further to the properties of these fuels, figure 1 gathers some parameters related to their adaptation to automotive use. As it was expected, metallic function of the catalyst reduces olefin content in a large extent up to a minimum of 2,44 gBr₂/100g sample (95% reduction) for

LDPE. On the contrary, total aromatic content increases due to the acid function of the zeolite [5] that, besides cracking, performs secondary reactions as cyclization and aromatization, especially in a batch system. Finally, RON numbers and Cetane indexes indicate that these products could be used as automotive fuels. All Cetane indexes exceed European specifications [6] (minimum of 51) up to 87 for HDPE hydroreforming diesel. RON numbers are very close to the lower limit (95).

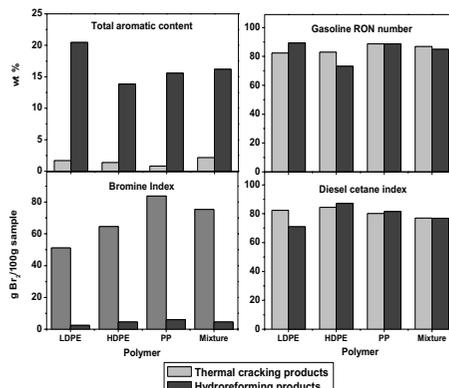


Fig. 1. Properties of the thermal cracking and hydroreforming products.

4. Conclusions

A two-stage process combining thermal cracking and further hydroreforming over Ni/h-Beta can be used for fuel production from different polyolefins. The so-obtained products are mainly gasoline and light diesel with low olefin and high aromatic contents. All gasolines present high RON number without any additive and all diesels have cetane indexes above specifications.

References

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