Catalysis Letters 22 (1993) 135–146

Development of catalysts for the fluid catalytic cracking process: an example of CYTED-D program ☆★

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The present paper describes the development of a catalyst for the fluid catalytic cracking process of gasoils. The catalyst produced is to maximize the high octane components in the gasolines and the liquefied gases for petrochemical use. The results obtained in the riser type pilot plants of the Compañia Española de Petróleo, S.A. (CEPSA), and INTEVEP, S.A., R&D Center of Petróleos de Venezuela, S.A. are also reported. Finally, information is given on the technical–economic feasibility of a prototype plant for manufacturing this type of catalyst with an annual capacity of ten thousand tons.

Keywords: Cracking catalysts; FCC-process; zeolite synthesis

1. Introduction

The Ibero-American Science and Technology Program for Development (Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo), CYTED-D, is part of a technological and scientific cooperation plan amongst the Ibero-American countries, which includes Spain and Portugal, implemented in 1984 by the Inter-Ministerial Commission of Science and Technology of Spain (Comisión Interministerial de Ciencia y Tecnología de España) and the Institute for Ibero-American Cooperation (Instituto de Cooperación Iberoamericana) which includes 21 participating countries and support from UNESCO, the Organization of American States (OAS), and the Economic Commission for Latin America (CEPAL).

The objective of the CYTED-D Program is to encourage cooperation amongst the Ibero-American countries in order to generate innovations, developments, and technologies, transferable to productive systems with impact on the life standard and the economic development of Ibero-America.

☆ This project has been performed under the Ibero-American Science and Technology Program for Development, CYTED-D, in which 25 researchers from five Ibero-American countries have participated: Argentina, Brazil, Mexico, Spain, and Venezuela, offering an example of multinational cooperation.

★ The present work is an abstract of the final project report. The results of the different phases and activities described will be published by the authors separately.

The CYTED-D Program currently comprises 16 sub-programs including the most diverse branches of science and technology. Approximately 3000 scientists are cooperating in this program and the estimated financial resources available are in the order of 30 millions US dollars per year.

As part of this Program, Sub-Program V named "Catalysts and Adsorbents", was initiated in 1985 with the aim to develop materials for refining, petrochemistry, and fine chemicals industries, in order to manufacture and purify intermediate and final products.

This Program currently comprises to projects and a thematic network of information, which are named as follows:

- Development of Catalysts for the Fluid Catalytic Cracking Process, finalizing in 1992;
- Development of Industrial Adsorbents, initiated in 1990;
- Ibero-American Thematic Network on Molecular Sieves, initiated in 1991.

The fundamentals for the selection of these topics have been the following:

- to constitute a scientific and technological challenge;
- to gain technological know-how in a strategic area;
- to reduce foreign currency expenditures;
- to ensure that participants are able to provide the required qualified personnel and infrastructure.

The Project V.I. entitled, "Development of Catalysts for the Fluid Catalytic Cracking Process" was initiated in 1985 and finalized in 1992. Initially, a study was performed to establish the existing capacity in Ibero-America in heterogeneous catalysis and the industrial uses of catalysts in the region.

The project responds to a cooperation agreement amongst eight Ibero-American research groups, which are highly qualified in the area of heterogeneous catalysis. Approximately 25 professionals from Argentina, Brazil, Mexico, Spain, and Venezuela are participating.

The project aims at developing competitive catalysts for the process of catalytic cracking of gasoils in fluidized bed reactors with the following characteristics: high levels of conversion and selectivity to gasolines and particularly to high octane components as well as liquefied gases (LPG) for petrochemical use.

The decision to perform such a project was based on the high level of utilization of such technology in the Ibero-American refineries. This amounts to approximately 1.5 million barrels/day of installed processing capacity which requires the use of approximately 65 thousand tons/year of catalysts [1,2]. This represents a yearly expenditure of about 130 millions of US dollars. Likewise, the project was considered a scientific and technological challenge that would contribute to reinforce the technological capacity of the region in this specific area.

Catalytic cracking catalysts are currently based on type Y zeolites, that is, silica–alumina with high ratio of Si/Al and well-defined pore size, specific surface area and crystalline structure [3].

The catalytic properties of these zeolites are modified by means of ionic

exchange with elements of rare earths and certain additives which are added to improve their process behavior, as was described and illustrated in ref. [4]. They are finally deposited on a silica–alumina and/or kaolin matrix, to achieve its final form, that is, particles with a 60 micron size, which will facilitate the fluidization in the catalytic reactor.

The main project activities as well as their distribution among the participating groups was based upon the know-how and expertise of each group, with the purpose of favoring maximum cooperation among each other.

1.1. CATALYST CHARACTERISTICS

In order to be used in riser type reactors, the catalysts should comply with the following characteristics:

Composition

- active phase: hydrogen form of Y zeolite, partially exchanged with rare earth cations, with a SiO_2/Al_2O_3 ratio higher than 5.0.
- matrix: silica–alumina and kaolin.
- active phase content in the catalyst: 12–25 wt%.

Physical properties

- average particle size: 60 micron.
- specific surface area: 120–180 m^2/g.
- pore volume: 0.20–0.40 ml/g.
- resistance to attrition: 7–13 (Davison index).
- hydrothermic stability: MAT conversion (515°C, 75 s) higher than 60% after steaming (100%) at 815°C for 4 h.

1.2. ZEOLITE Y SYNTHESIS

Immediately after performing the zeolite NaY synthesis at pilot scale in CINDECA (Argentina), the same procedure was repeated at INTEVEP's premises in Venezuela. The method used was based upon a block diagram as indicated in fig. 1.

The synthesis reaction was performed in a 30 ℓ reactor and sodium silicate, sodium aluminate, sodium hydroxide and sulfuric acid, were all used as raw materials, industrial purity grade. The synthesis method includes the seeding with zeolite nucleus to initiate the crystallization, which are prepared by a combination of sodium silicate, sodium aluminate and sodium hydroxide solutions so that the final mixture (clear solution) has the following stoichiometric composition: $17.4\ Na_2O \cdot Al_2O_3 \cdot 16.5\ SiO_2 \cdot 348\ H_2O$. This clear solution is aged for 24 h at 25°C before being used as an active seed.

The sodium silicate solution is prepared by adding sodium hydroxide so that the Na_2O/SiO_2 ratio is 0.8 and then diluted in water up to 33 wt% of solids (solution 1). The sodium aluminate solution is also prepared by adding the proper quan-

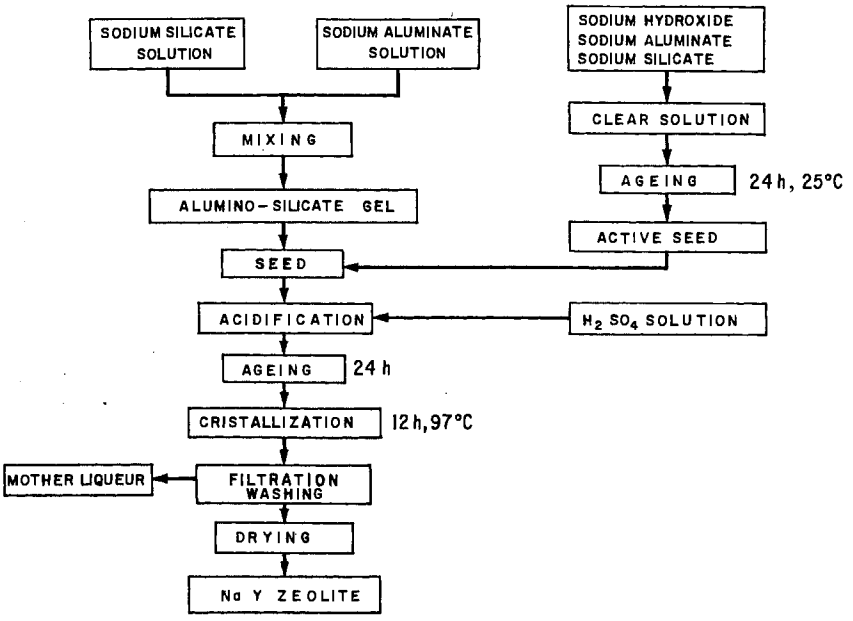

Fig. 1. Block diagram of NaY zeolite synthesis.

tities of sodium hydroxide and water in order to achieve the following ratios (solution 2): $Na_2O/Al_2O_3 = 4.8$, $H_2O/Al_2O_3 = 90$. These solutions are mixed by slowly adding the first to the second, under strong stirring at room temperature. The gel formed, is diluted in water until a mixture with the following stoichiometric relation is obtained: $7.6\ Na_2O \cdot Al_2O_3 \cdot 18\ SiO_2 \cdot 238\ H_2O$.

The active seed is then added to this solution which is afterwards acidified with sulfuric acid until obtaining a reaction mixture with the following stoichiometric relation: $7.2\ Na_2O \cdot Al_2O_3 \cdot 17.8\ SiO_2 \cdot 310\ H_2O$.

After ageing for 24 h the crystallization gel is heated up to 97°C and left to settle for 12 h at atmospheric pressure. Then the resulting mixture is filtered and washed with water in a Buchner filter. The product is then dried in an oven at 110°C and analyzed. This process achieves a highly crystalline NaY zeolite, free of NaP zeolite impurities.

Table 1 shows the physical properties of the synthesized zeolite.

1.3. MANUFACTURING OF CATALYST AT PILOT SCALE

The goal of this work was to manufacture an FCC catalyst, based on ultrastable Y zeolite, to be evaluated in a riser pilot plant.

4 kg of zeolite obtained by the Argentinean group, was activated at CSIC'S laboratories in Spain by means of the following basic stabilization procedure:

– Exchange of the sodium zeolite with an ammonium solution at 80°C, with a

Table 1
Physical properties of synthesized NaY zeolite

crystal structure	faujasite
average crystal size	0.5 μm
cell parameter	24.66 Å
SiO_2/Al_2O_3 crystal ratio (Shon-Breck)	6.37–5.00
crystallinity (XRD)	93%
specific surface area	520 m^2/g

liquid/solid ratio of 4, a 2 M ammonium solution and an exchange time of 60 min.

– Washing with deionized water using not less than 500 ml of water for each 100 g of zeolite.

– Calcination in the presence of steam. The exchanged zeolite is heated in a muffle, from room temperature up to 500°C at a heating rate of 5°C/min. At 500°C, steam is injected (90% steam in air) and the temperature increased to 630°C with a heating rate of 5°C/min, keeping this temperature for 3 h. The final product is characterized by X-ray diffraction, measuring the size of the unit cell and its crystallinity.

– Repeated exchange with ammonium solution (at the same conditions as former) until the sodium content is under 0.2% in Na_2O by weight.

– The ammonium zeolite is then exchanged with a lanthanum solution at 80°C, with a liquid/solid ratio of 4, and a lanthanum concentration between 0.2 and 0.5 M, for 60 min, at a pH = 3.

– Washing with deionized water using at least 500 ml of water for each 100 g of zeolite.

– Calcination at 350°C for 2 h.

– Measurement of the lanthanum content in the zeolite.

Once the zeolite was ultrastabilized and exchanged (USYRE) with rare earth, the Venezuelan group prepared the final catalyst. The procedure consists of the mixture of zeolite USYRE, silica–alumina, kaolin, and a binder compound in order to form the final particles with the required size to achieve a good fluidization in the riser reactor.

The silica–alumina used for the preparation of the catalyst was synthesized at the School of Chemistry, UCV, Venezuela using the mother liqueur left by the filtration and washing of the zeolite. Approximately a third of the produced silica–alumina is used in the preparation of the catalyst. The rest is considered a process subproduct.

This silica–alumina (13 wt% alumina) is separated by filtration and is successively washed with solutions of $(NH_4)_2SO_4$, 3 wt%, NH_4OH of pH 9 and water at 60°C. Immediately after, this rinsed silica–alumina is mixed in a tank with the stabilized USYRE zeolite, ground kaolin and Ludox AS-40 as the binder compound in

the following proportions: 28% USYRE zeolite, 12% silica–alumina (13 wt% alumina), 10% sodium-free Ludox AS-40, 50% kaolin (with a particle size lower than 0.5–1 μm. This mixture, diluted with water until a 40–50% solid particles concentration is achieved, is then injected in a spray dryer where catalyst microspheres are formed. Through this procedure, a 14 kg lot of the final catalyst was obtained.

The results of the characterization by X-ray diffraction (XRD) after the main stages of zeolite activation and the preparation of the final catalyst, are shown in table 2. These results indicate that even though there is an important loss of crystallinity in the ultrastabilized zeolite (USREY) as well as of the number of aluminum atoms in the frame work, the values are in the range expected according to the initial zeolite characteristics. As expected, the steam treatment does not reduce the crystallinity significantly. Nonetheless, it is important to point out that the zeolite in the final catalyst is less stable to steam treatment than when it is pure.

A special feature of the method of catalyst preparation used can be found on the synthesis of the zeolite itself: a Y zeolite having an average crystal size of about 0.5 micron and a Si/Al ratio of about 3.0 was prepared in only 12 h of crystallization, free of zeolite P.

The high Si/Al ratio of this product joined to its submicronic crystal size makes it able to withstand severe steam-dealuminating treatment and to improve coke and gas selectivities.

The basic characteristics of the zeolites NaY, USREY, and of the final catalyst observed by an electron scanning microscopy (ESM) are shown in table 3.

2. Catalyst evaluation in the micro activity test (MAT) reactors and in riser type pilot plants

The evaluation of the CYTED-D catalyst in MAT reactors and in CEPSA's riser type pilot plant, was performed by the Spanish group. The results obtained with this catalyst are compared with those in a series of commercial catalysts. It is important to note that no additive (ZSM-5) was added to the CYTED-D catalyst

Table 2
XRD zeolite and catalyst characterization

Sample	Unit cell (Å)	No. Al/u.c.	Cryst. (%)
NaY zeolite	24.64	46	90
Y zeolite–1 exchange	24.50	30	70
Y zeolite–2 exchanges	24.52	32	70
USREY	24.52	32	65
USREY + steaming 5 h at 750°C	24.36	14	50
catalyst	–	–	20
catalyst + steaming 5 h at 750°C	–	–	13

Table 3
ESMY zeolite and catalyst characterization

Sample	Characteristics
NaY zeolite	crystal size of about 0.3 μm
USREY	analogous morphology as NaY. Apparently the treatment does not affect the external crystal structure
catalyst	the zeolite crystals in the particles of the catalyst are a little more irregular and altered than before

to increase the octane number and LPG olefins in these tests. Then, there is an open possibility to improve these basic results.

The catalyst was deactivated for 4 h by steam treatment in a fluidized bed chamber, at 815°C (severe deactivation). The specific surface area of the resulting catalyst (135 m^2 g^{-1}) indicates an excellent stability of the zeolite as well as of the matrix. This treatment reduced the size of the unit cell of the ultrastable zeolite Y (USYRE) to the foreseen value of 24.28 Å.

The feedstock used in the riser pilot plant (DCR) and in the MAT unit tests are conventional Arabian vacuum gasoils (VGO).

The tests at the MAT unit were carried out at 515°C and at a reaction time of 75 s. The catalyst/oil ratio was varied in order to obtain the product distribution at different yields.

In fig. 2 the behavior of the CYTED-D catalyst can be observed. Although it does show the highest conversion, it is undoubtedly the one producing the highest

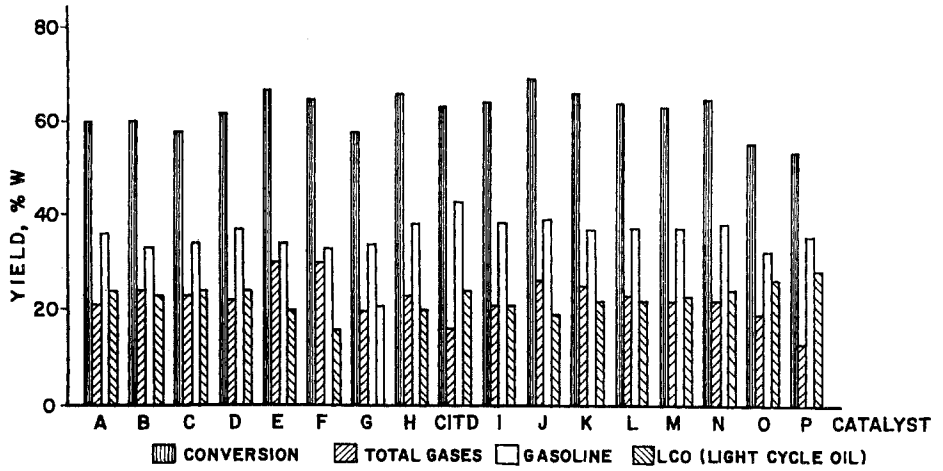

Fig. 2. MAT reactor test results.

gasoline and distillate (gasoline + diesel) yields. The catalysts behavior has been compared at constant coke yield (4%).

The commercial B and H catalysts were selected for further pilot plant testing, based on their selectivity to high octane compounds and to propylene, butenes and isobutenes. These catalysts were tested in the riser pilot plant of the Spanish Petroleum Company, CEPSA, along with catalyst CYTED-D. The obtained results at a reactor temperature of 520°C and at a 4.3% constant coke yield are shown in fig. 3. CYTED-D catalyst presents a product distribution similar to that of the other catalysts, although its conversion and gasoline yield are lower and its diesel yield is higher than those of catalyst H. On the other hand, CYTED-D catalyst produces less dry gas (methane) with high yield of propylene, *i*-butane, and total C_4 alkenes.

When the test of activity is carried out at constant conversion, the CYTED-D catalyst produces higher yield of coke, propylene, butenes, and *i*-butane than the commercial ones.

The quality of the gasoline produced by the CYTED-D catalyst is 0.5 RON (research octane number) lower than the obtained with catalyst H. However, the MON (motor octane number) level of CYTED-D catalyst is equal to that of catalyst B and higher than that shown by catalyst H. Then, the conclusion can be that the CYTED-D catalyst produces gasolines with good octane number and sensibility index.

The pilot plant tests performed at INTEVEP, Research and Development Center of Petroleos de Venezuela, S.A., were carried out in a riser type reactor (Kellog's design) with a processing capacity of 0.5 barrels/day (80 ℓ), using vacuum gasoil as feedstock with a high cracking index, high paraffins, and low metal content. The

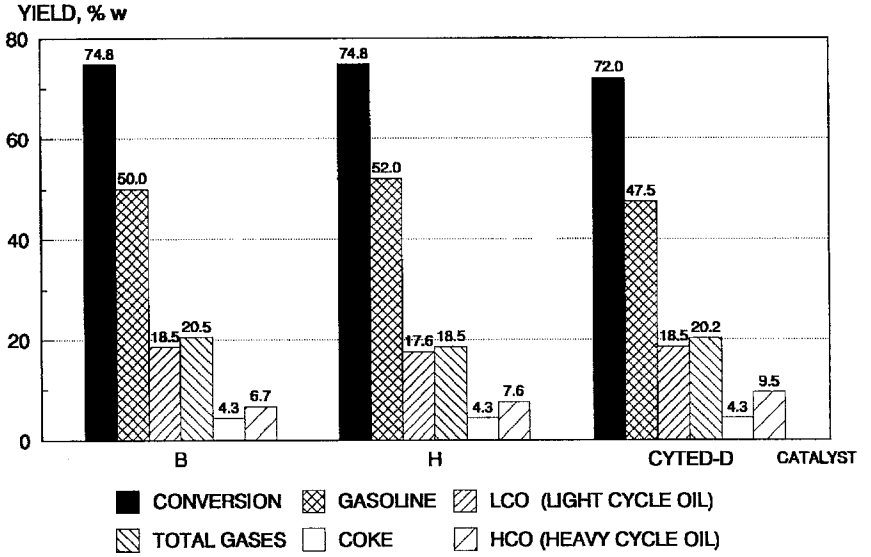

Fig. 3. Pilot plant test results (CEPSA).

catalyst was deactivated, as indicated previously, obtaining the same surface area. The operating conditions of the pilot plant are given in table 4.

The results obtained at low and high severity tests conditions are presented in table 5. As observed, the olefins yield/conversion ratio increases with the operation conditions severity. This is reflected by the potential alkylation feedstock ratio which increases from 17.8% at low severity, to 19.3% at high severity operating conditions.

The coke selectivity is good, since many commercial catalysts at the observed levels of conversion show coke yields higher than 4 wt%.

The dry gas yields are kept at reasonable levels and the gasoline yields are high. The commercial catalyst used was tested only at low severity operating conditions due to the high levels of coke formed and the low selectivity to gasoline observed.

The quality of the gasoline obtained is also shown in table 5. These results clearly indicate that CYTED-D catalyst is highly competitive since the octane numbers of the gasoline obtained at low severity are higher than those of the commercial ones.

This can be explained in terms of the crystal composition of the equilibrated samples. In fact, the cell parameter of the equilibrated USREY active phase of the CYTED-D catalyst is 24.36 Å as quoted in table 2. This is typical of a structure having less than 20 Al atoms per unit cell. At such low levels of Al loading, the hydrogen transfer reactions responsible for the transformation of olefins, are less favored than the cracking reactions (octane number of olefins are higher than their corresponding paraffins). It is well known that the lower the concentration of acid sites (associated to Al atoms), the lower the rate of bimolecular reactions such as the hydrogen transfer ones.

On the other hand, the commercial catalyst contained an active phase consisting of a conventional non-dealuminated REY zeolite, having a higher proportion of Al atoms (about 55 Al per unit cell) even after equilibration.

3. Technical and economic evaluation of a catalyst production plant

The engineering evaluation is an essential activity in the development of processes. It includes a technical and economic evaluation.

Table 4
Pilot plant test conditions (INTEVEP)

Operation conditions	Low severity	High severity
temp. feedstock (°C)	330	355
temp. reactor (°C)	510	528
catalyst circulation (K/H)	12.93	13
temp. regenerator (°C)	705	710
catalyst/oil ratio	4.3	4.3

Table 5
Results in pilot plant tests (INTEVEP) [a]

	Catalyst		
	CYTED-D		commercial L.S.
	L.S.	H.S.	
conversion (vol%)	65.70	68.09	68.50
selectivity to gasoline	85.23	82.85	70.00
coke (wt%)	2.83	3.15	4.50
residue (371+°C) (wt%)	12.30	11.60	12.40
dry gas (wt%)	3.56	4.79	4.85
	Gasoline quality		
API	53.9	54.0	53.7
S (PPM)	720.0	718.0	800.0
NBR	69.3	66.8	67.0
RON	93.0	93.6	91.0
MON	81.0	81.1	79.8
IAD	87	87.3	85.4

[a] L.S.: low severity; H.S.: high severity.

The process feasibility is considered in the technical part, meanwhile the level of investment, the production costs, and the process profitability is estimated, in the economic evaluation.

The technical and economic evaluations have different levels of accuracy which depend on the available technical and economic information.

In the present study, the evaluation of a catalytic cracking catalyst production plant has been carried out with the accuracy of the so-called "order of magnitude" [5] with a capacity of ten thousand metric tons/year (10000 MT/year). The study includes the following phases:

- conceptualization and definition of the production process;
- estimation of the mass and energy balances;
- selection and sizing of equipment;
- performing the economic analysis.

For this purpose, the experimental information obtained at pilot plant level has been used. The technical-economic evaluation was carried out at the School of Chemistry, UCV, Venezuela.

The performed technical evaluation indicates that the process is relatively simple in terms of equipment and operational conditions. The process is composed of well-defined unitary operations; the capacities of the equipments are standard and the temperature and pressure conditions are relatively mild.

The economic evaluation of the process leads to the following results: a total capital investment of about 20 million dollars, with a total yearly production cost between 16.34 and 17.03 million dollars, when using economic raw materials available in some Ibero-American countries.

The cash flow analysis for a catalyst sales price between US$ 1540/MT and 2000/MT, gives an estimated time of payment between 2.7 and 4 years. This is based on the following subproduct prices: silica–alumina cost of US$ 370/MT; sodium sulphate US$ 68/MT. The present net value lies between 32.8 and 58.8 million dollars and the internal rate of return ranges between 15% and 25.5%, depending on the used catalyst sales price.

When duplicating the capacity of the plant, the total capital investment is estimated to amount between 31.4 and 33.2 million dollars. The total yearly production costs lie between 29 and 30 million dollars, based on Venezuelan raw materials costs. The sales income is duplicated in these cases, achieving 49 million dollars based on the lowest selling price for the catalyst, and 58 million dollars based on the highest one.

The cash flow analysis estimates a time of payment between 2.2 and 2.7 years for this new capacity. The present net value lies between 86.8 and 132 million dollars, and the internal rate of return ranges between 24.7 and 33%, indicating a higher process profitability when the plant capacity is increased.

If production costs are based on the prices of raw materials established by Chemical Marketing Report, the profitability is so low that the capital investment could not be recovered during the lifetime of the plant.

The geographical location of the plant is a relevant factor to be considered in the economic evaluation. In this study, the estimated fixed investment was based on equipment costs in the United States. When the location of the plant changes (Spain, Argentina, or Venezuela) the costs of the equipment will have to be adjusted to the selected location. The cost of raw materials and labor strongly depends on the plant location. Once this has been defined, the economic evaluation will be estimated with greater accuracy.

4. Conclusion

The manufacturing process developed in this project for producing cracking catalysts has proved to be technically successful.

The cracking catalyst produced shows an excellent performance in the MAT and riser pilot plant tests being competitive with the commercial ones.

The results obtained in two independent riser pilot plant tests showed an acceptable level of conversion. A high selectivity to high octane components of gasoline and liquefied gases was also observed. These results were achieved without the

use of octane enhancing additives in the catalyst, thereby leaving room for further improvement.

The technical and economic evaluation of a catalyst production plant indicates the feasibility of the project. To achieve commercial level, it is considered necessary to scale up the manufacturing process, by means of integrated pilot or demonstration testing plants. This stage will be performed by means of a commercial agreement with a catalyst manufacturer. At these levels, the technical and economic aspects could be evaluated with a higher level of accuracy.

Acknowledgement

Sincere thanks and acknowledgement is given to the groups and persons who were involved in the development of the different activities leading to the successful completion of the present project. The participating institutions were the following: Argentina: Centro de Investigación y Desarrollo de Procesos, CINDECA, Universidad de La Plata, La Plata. Brasil: Universidad Federal de Rio de Janeiro, Coppe, Centro de Tecnología, Rio de Janeiro. Mexico: Universidad Autónoma Metropolitana, UAM, Division de Ciencias Basicas e Ingeníeria, Ciudad de Mexico. Spain: Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, CSIC, Madrid; Instituto de Tecnología Química, Universidad Politécnica de Valencia, Valencia. Venezuela: INTEVEP, S.A., Centro de Investigación y Desarrollo de Petróleos de Venezuela, S.A.; Universidad Central de Venezuela, UCV, Facultad de Ciencias, Escuela de Química.

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