Refining Industry of Mexico

Comparative study of R&D activities and the catalysts market needs

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There are some factors that might disrupt the value chain for transferring new catalysts technology to the main processes of the refining industry. The main driving forces of the refining industry of today include the declining quality of crude and the more stringent environmental regulations. Both factors are though to play a directing role for R&D activities in the field of catalysis, and have an impact on technological and economical issues. Also, within the R&D centers both organizational and economical aspects influence the relationship between the real catalysts market needs and the specific R&D projects.

The main driving forces of the catalysts industry for refining processes in the past decades were the continuous improvement of the production volume, costs/profit ratios and catalyst activity steadiness [1-3]. However, in recent years two additional forces playing a directing role are the declining quality of crude available and the strict environmental regulations [4, 5]. The former factor brings out important technical and economical challenges to refiners, such as the transformation of heavier oil fractions having a specific density lower than 22 °Api, a high sulfur content up to about 3 to 4 wt% and metals loading up to 100-250 ppm (Ni, V).

In addition, the asphaltenes concentration in this type of crude may rise up to 3 to 5 wt%, while the carbon weight percentage remains around 10%. The second factor motivated the development of technological issues in all the processes of the refinery to comply environmental regulations, by means of the removal of precursors of the most harmful fuel emission compounds such as sulfur, nitrogen, aromatics and olefins [5]. The goals set up by the US environmental regulations for the year 2006 establish a sulfur content in gasoline of less than 30 ppm, that is an order of magnitude less than the current figure, while the total aromatics content is targeted at 10 vol.% and the benzene limits set down to less than 1% vol. In addition, the trends in Reid vapor pressure of gasoline point out to less than 7 psi (1 psi = 6894.76 Pa) [5-8]. Then, to reach these goals a twofold strategy based upon serious improvements of the refining processes and the development of new catalysts must be considered.

In this context, the refining industry of Mexico faces important challenges such as the upgrading of heavy Maya crude, the fulfillment of international standards in terms of fuels quality and post-combustion gas treatments, in order to reduce the levels of contaminants in the populated areas.

To this end, the options available include the upgrading of refinery process as well as the development of new catalysts. The latter issue is considered as a precious alternative instead of modifying the actual plants that should incur in further capital investments. For example, new hydrotreating catalysts supports having outstanding properties [9] should offer a significant performance with respect to traditional Al_2O_3-supported NiMo or CoMo catalysts, which now operate under more severe temperature and pressure conditions, which in turn accelerates the catalysts deactivation rate. Also, innovative concepts such as the deposition of active microphases into the confined space of nanoporous materials is though to give control in defining new reaction pathways for processing complex hydrocarbon molecules [10, 11].

In both cases, innovation through research must play a key role to keep abreast with the constant requirements of the refining industry. In summary, new catalysts are needed for dealing with the highly polluted crude fractions, while keeping the product quality within the stringent environmental regulations. In other industrial areas, such as the petrochemicals and chemical products industries, the monetary value of the catalysts market is even higher with respect to the oil refining industry, i.e., the market forecast for polymerization catalysts indicates a market growth rate of about 25% for the incoming years [12].

Thus, in this document we compare some of the actual needs of the refining industry of Mexico and how they compare with the recent research efforts made under both academy- and technology-driven research centers in the field of catalysis and how the researchers face the new challenges posed by the factors mentioned above.

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Types of crude oils and internal market demand

Most of Mexican crude oil originates from the coastal region off-shore around the Gulf of Mexico, where at least four types of crude prevail according to their composition and density (i.e., °Api). For example, Maya crude has a typical specific density of about 22 °Api, as illustrated in Table 1. In comparison, the typical density of crude processed in most of US refineries is close to 34 °Api [13]. Also, Table 2 indicates that Mexican Maya crude is rich in sulfur, asphaltenes, carbon and metals (Ni, V), which poses important technical challenges for their extraction, transportation and processing [14]. The latter point is particularly sensitive in terms of the yields of gasoline, intermediate distillates, gas oil feeds to FCC and residuals from Maya crude.

For example, these yields are about 15, 25.5, 22 and 37.5 vol.%, respectively, while lighter crude such as Itsmo oil yields about 23.8, 33.6, 25.3 and 17.3 vol.%, respectively. On the other hand, PEP total production is shared between internal market and exports as indicated in Table 3 and Table 4. The main trends observed here are the gradual increase of heavy oil destined to internal market (i.e., 11.3 and 24.5% in 1998 and 1999, respectively) and the step diminution of light oil (Itsmo + Olmeca) for exports (i.e., -3.3 and -10.8% for 1998 and 1999, respectively). Without a previous treatment 100% Maya feeds are not practical for processing by the actual refining plants, that is why blends containing about 70% Itsmo and 30% Maya are being more common in most of the refining system, as indicated in Table 5, where one observes a dramatic effect on the vacuum residuals derived from those feeds, which poses serious technical limits for further processing.

On the other hand, several factors influence the process configuration of most of the refineries, the main global factors being the crude quality and its composition, the market needs, the technology available and the capability for financial investment. In Latin American countries the refining scheme is variable as indicated in Figure 1, as their catalysts market structure is in consequence. Here one observes that the annual catalysts market value for the region amounts about 210 million US$, according to data corresponding to year 2000 [12], which represents about 7.6% of the total refining catalysts market on a worldwide basis. In particular, Mexico represents about 31% of the Latin American market (Table 6) or about 2% of the worldwide market (Table 7). As observed in these data, the main processes involved are hydrocracking, FCC and hydrotreating, but substantial differences occur in the market structure of each country with respect to the other. For example, in Mexico the hydrocracking process catalysts market represents about 50% on a monetary basis, while Venezuela and Brazil do not include that processes in their refining scheme. It is worthwhile mentioning the marginal importance of the reforming process in countries like Brazil and Colombia. In comparison, the specific weight of the catalyst market in the Usa, Europe, Japan, anterior Urss and Canada represents each about 42, 22, 7.2, 5.25 and 3.5% of the worldwide catalyst market for refining, respectively.

The refining capacity worldwide is indicated on Table 7. It is interesting noticing how the capacity of the refining system in Mexico compares with other countries, for example the 6 refineries of Mexico produce about 80% of the total refining capacity of Canada or Australasia, who count on 21 and 19 re-

Table 1 - Density of Mexican crude oils

*Type of crude**			
Specific density (°Api)	*Density (gr/cm³)*	*National Market*	*International Market (Types)*
10.0	> 1.0	Extra heavy	Shale oil, bitumen etc.
D≤22.3	1.0-0.92	Heavy	Maya, Altamira
22.3<D<31.1	0.92-0.87	Mean	Blends
31.1< D<39	0.87-0.83	Light	Itsmo
>39	<0.83	Super light	Olmeca

** PEP (Pemex-Exploration & Production) Annual report (2001), Vol. 3, 18.*

Table 2 - Comparison of the properties of some heavy crude oils

	Arabian		*Maya*	*Derived oil*	
	Light	*Heavy*	*Mexican*	*Coal*	*Bitumen*
Specific Density (°Api)	34.4	28.2	22	27.4	22.9
Sulfur (wt%)	1.7	2.8	3.3	0.1	0.6
Nitrogen (wt%)	0.04	0.09	0.1	0.19	1.51
Asphaltenes (wt%)	1.7	4.6	5.2	0.1	0.3
Carbon (wt%)	3.6	7.9	10.3	0.1	1.4
Ni/V (ppm)	4/13	18/56	35/174	1/1	6/1

Table 3 - Internal market distribution of oil produced by PEP in the period 1997-99*

Crude type	*1997 (10³ B/D)***	*1998 (10³ B/D)*	*1999 (10³ B/D)*
Heavy	449	500	559
Light	796	798	760
Super light	22	19	20
Total	**1,267**	**1,318**	**1,339**

** PEP (Pemex-Exploration & Production) Annual report (2001), Vol. 3, 22.*
*** B/D = Barrels per day*

Table 4 - Total annual exports of the oil produced by PEP in 1997-99* (m 10³ B/D)**

Crude Type	*1997*	*1998*	*1999*
Altamira	-	6	9
Maya	1,020	1,057	919
Itsmo	216	208	190
Olmeca	485	470	435
Total	**1,721**	**1,741**	**1,554**

** PEP (Pemex-Exploration & Production) Annual report (2001), Vol. 3.*
*** B/D = Barrels per day*

Table 5 - Properties of a typical feed blend (Maya/70/30) and vacuum residuals*

Properties	*Crude blend (70% Itsmo, 30% Maya)*	*Vacuum residuals*
Specific Density (°Api)	30.4	6.6
Sulfur (wt%)	2.07	4.6
Asphaltenes (wt% in n-C5)	6.35	22.1
Ni (ppm)	21.3	73.4
V (ppm)	127.4	439.1

** PEP (Pemex-Exploration & Production) Annual report (2001), Vol. 3.*

Table 6 - Catalysts market size in Latin America (monetary basis)

Catalysts market	*Mexico*	*Venezuela*	*Brazil*	*Argentina*	*Colombia*	*Other*
million US$	65	43.1	41.7	21.7	8.4	29.6
%	31	20.6	19.85	10.35	4.0	14.2

fineries, respectively. Also, the treatment of residuals by thermal coking is 41 MB/D for Mexico and 40 MB/D in Canada, while two of the major processes for obtaining automotive fuels, i.e., FCC and alkylation, are about 368 vs 417 and 62 vs 121 MB/D, for Mexico and Canada, respectively.

Research and development of catalysts

The petroleum industry of Mexico has a significant technological support in the Instituto Mexicano del Petroleo (IMP), i.e., the Mexican Petroleum Institute, which concentrates about five thousand people working on different areas of engineering, oil extraction, technical services related to production maintenance etc., and some areas of research and development. The latter are distributed in eight programs comprising about 450 people with more than a half of them holding a PhD degree. About 15% of these people work on eight catalysis research projects, which are carried out within the framework of two research programs, the “Molecular Engineering” and “Maya Crude Treatment” programs. These activities absorb about 20% of the total investment on R&D activities at IMP, that is about 4.5 million US$ (i.e., comprising manpower, utility services, equipment cost depreciation, materials, displacements etc). In addition, there is a task force of about one hundred people who are devoted to pilot plants operation and technical services required by the oil refining industry in all matters related to catalysts operation. The latter group works on a cost/benefits scheme through specific contracts with Pemex-Refinación, i.e., the national refining industry. The main topics of research are listed on Table 8.
In addition, since 1997 a special program, called FIES, is being carried out in close collaboration with academic groups from some universities and other research centers. The evaluation of the proposals is carried out by specific committees comprising academic and petroleum industry people, then a proper financing of the projects is established and taken in charge by IMP. The main partners representing the strongest groups working on catalysis research are the Metropolitan University (UAM-Iztapalapa), the National University (UNAM), the National Polytechnic Institute (IPN), the Center for Advanced Materials Research (CIMAV) and the Technological Institute of Madero City (ITCM). In terms of scientific production the catalysis community in Mexico participates in several forums where two are considered the most significant from the regional viewpoint, those are the North American Catalysis Society Meeting and the Ibero-American Catalysis Symposium. Both of these events are carried out every two years and the last ones were at Toronto (Canada) in June 2001 (NACS 2001) and Porto (Portugal) in 2000 (Simposio Iberoamericano de Catálisis 2000). If one takes these events as the most representative of the main stream of catalysis research work going on in Mexico, then a statistics emerges for

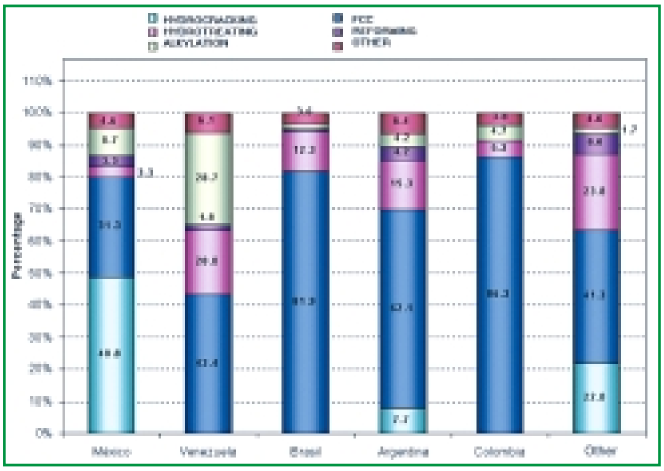

Figure 1 - Catalysts market structure of Latin America for oil refining

Table 7 - Refining capacity worldwide (MB/D)*

Country	*No. Refineries*	*Total refining*	*Vacuum distillation*	*Coker*	*TCC*	*FCC*	*Reforming*	*HDT*	*HDC*	*Alkylation*	*Other*
Usa	152	16,538	7,468	2,100	64	5,588	3,559	10,856	1,441	1,170	1,403
Canada	21	1,906	629	40	136.5	415	350	814	258	62	164
Mexico	6	1,525	757	41	-	368	226	748	68.5	121	41.3
(Rest) Latin American	70	6,676	2,816	397	435	1,115	403	1,832	162	99	175
Europe	132	16,088	5,762	413	1,662	2,424	2,385	8,629	912	241	1.010
Anterior URSS	59	8,399	2,780	217	413.5	511	1,137	3,127	68	12	205
Middle East	51	6,686	2,164	87	430	334	623	1,965	634	29	151
Asia	24	2,467	517	50	116.5	167	62	212	55.8	-	27
China	97	4,346	40	290	-	892	157	283	122	26.5	50
Japan	35	4,962	1,651	88.5	-	799	720	4,261	162	43	211
Australasia	19	1,945	470	32.6	59	331	318	461	129	35.6	72
Other Asia-Pacific	30	6,444	1,040	53	248	436	718	2,605	263	12.6	268

** MB/D = thousands of barrels per day*

Table 8 - Main catalysis R&D projects at IMP*

R&D project	*Program*
Synthesis and properties of micro- and mesoporous materials for oil refining	Molecular engineering
Development of catalysts for sulfur reduction in gasoline	Maya crude treatment
Development of catalysts for sulfur reduction in diesel	Maya crude treatment
New catalytic systems for FCC reactions	Maya crude treatment
New catalytic systems for CCR naphtha reforming	Maya crude treatment
Synthetic crude production by HDT and hydrocracking	Maya crude treatment
High octane gasoline by light olefin dimerization and I-C4 alkylation	Maya crude treatment
Catalytic monoliths for stationary emission of pollutants	Molecular engineering

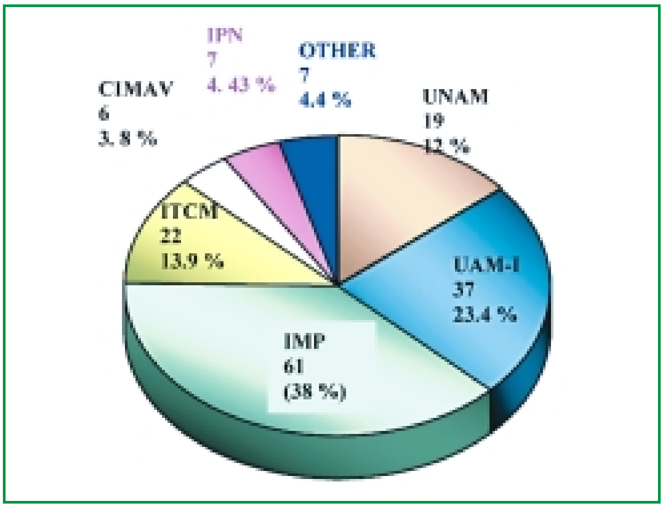

Figure 2a - Catalysis research production in Mexico (1998-2001)

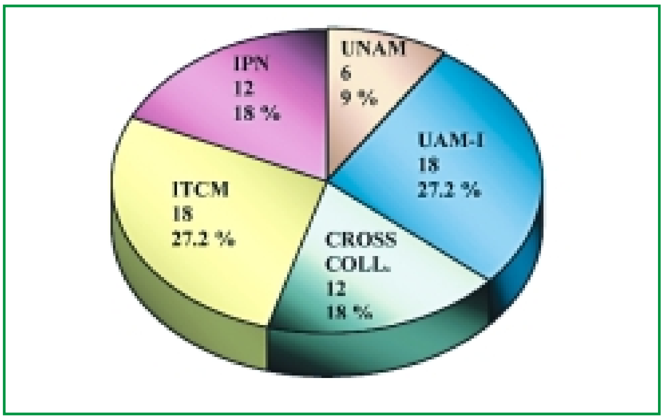

Figure 2b - Catalysis research collaboration between academic institutions with IMP [15-17]

the period 1998-2001 as shown in Figure 2a, which is the contribution of each institution to the forums mentioned above [15-18], from a total of 158 articles, where 47 belong to the Ibero-American Symposium of Porto in 2000, 40 articles were presented in the NACS Meeting in Toronto in 2001, 50 belong to the Ibero-American Symposium of Colombia in 1998 and 21 more were presented in the NACS Meeting held at Boston, Usa in 1999.
A total of 54 articles were found to include a collaboration of academic researchers with the scientific staff at IMP, that is about 34.1% with respect to the total production of the period 1998-2001 and a significant part of the 66 papers (i.e., 41% with respect to the total production) were made in cross collaboration among all the partners.
When considering the refining market needs, it arises another interesting question, that is about the main topics of research presented in the forums mentioned above. These should reflect the main focus of catalysis research, but this information could be biased by several factors such as the novelty of the topic in the international scientific journals, the main financing currently established by the FIES program itself, the particular interests of researchers on a specific topic issued from their previous PhD work and last, but not least, from the market needs. Then, Figure 3 is a summary of the main topics found in the analysis of 158 papers presented during the period 1998-2001 in the four events mentioned above [12].

Main resources and perspective of catalysts development

In 1985 the Pimentel Report presented before the US Research Council [19] a survey of the most important technologies, where catalysis was defined as "one of the five priority areas needed to keep industrial and economical leadership of the US". Then, a sustained endeavor was recommended to further develop the interaction between the basic research areas and their technological counterparts.
Nowadays, the infrastructure needed for performing world class catalysis research and development includes three main factors: the artwork needed for catalysts synthesis, the highly sophisticated machines and methods for the characterization of catalysts properties and the micro and pilot plant facilities for testing and scaling up the laboratory leads. All of this requires important economical resources for keeping up the facilities updated, as well as a sustained endeavor from qualified human resources. In this respect, the national catalysis R&D resources in Mexico comprise a variety of modern techniques located either in academic laboratories or at IMP, where most of the newer developments for industrial applications in this field come from. The main infrastructure needed for keeping up a competitive endeavor in innovative R&D projects exist at IMP and in other Mexican academic centers. Most of the modern techniques like NMR-MAS (Solid State), High Resolution Electron Microscopy and a Combinatorial Catalysis Robot (i.e. from Symyx Inc.) are available at IMP, together with sophisticated Pilot Plants for FCC, hydrocracking and HDT studies, but other techniques like XPS (X-Ray Photoelectron Spectroscopy) or Synchrotron related facilities are not available by now.
With respect to human resources (Figure 3), a significant part of the senior researchers working in the catalysis field obtained their PhD in Europe and Usa. At IMP, about one tenth of the total PhD's work on catalysis R&D programs. About 26 PhD's, 21 M.Sc.'s and 61 B.Sc.'s participate in the R&D projects and technical services, respectively, while about 49 people at IMP participate in the operation of microplants and pilot plants facilities, as well as other administrative endeavors.

Table 9 - Potential areas of opportunity in the refining industry in Mexico (period 2000-2006) [5]

Opportunity areas	*Process*
Reduction of sulfur in gasoline (i.e., 30 ppm)	Hydrotreating of FCC feeds Gas oil HDS Hydrocracking
Reduction of sulfur in diesel (i.e., 30ppm)	Hydrotreating of FCC feeds Gas oil HDS Hydrocracking
MTBE phase out	Isoparaffines alkylation with olefines C_4=dimerization
Hydrogen production	Synthesis gas reforming
Improvement of catalysts performance	Minor deactivation Higher activity and selectivity Possible regeneration Minor costs
Catalytic processing of complex feeds (3.3% S, 0.1% N,10.3% C, Ni/V=35/174 ppm, asphaltenes: 5.2 wt%)	HDS of naphtha, gas oil and residuals FCC Hydrocracking (H-OIL)
Improved gasoline: high octane number low vapor reid pressure low aromatics	 Isoparaffins alkylation with olefins Dimerization of light olefines Hydrocrabons isomerization Selective reforming Fischer-Tropsch Process
Synthetic crude	HDT Visbreaking Alternate processes (ultrasound, microwave etc.)

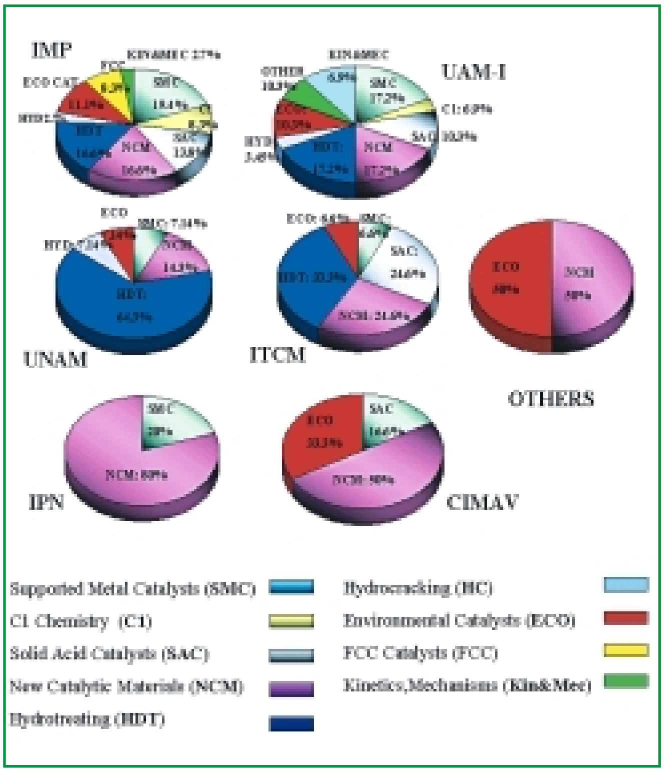

Figure 3 - Main topics of catalysis research in Mexican institutions (%) [15-17]

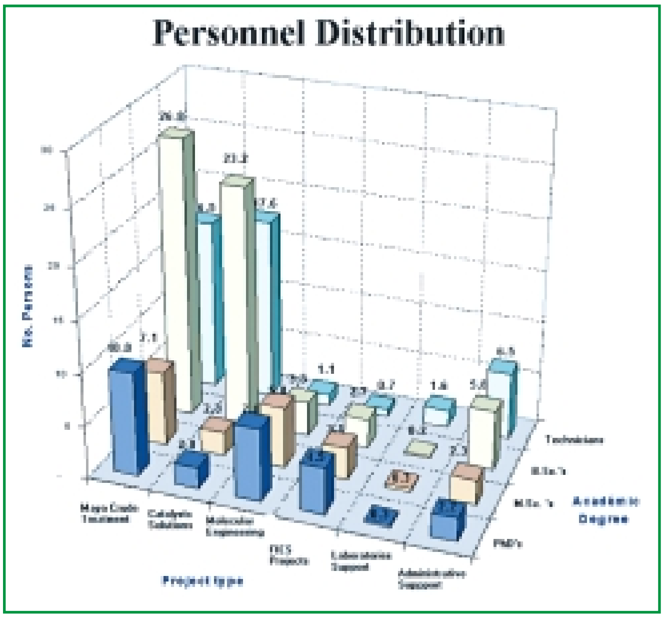

Figure 4 - Distribution of personnel working on catalysis at IMP

Conclusions

In this report a comparative study was presented between the needs existing in the refining industry of Mexico and the current R&D activities in both academic and technological centers in Mexico. The actual production of crude in Mexico comprises about 2,893 MB/D, which ranks in about 4th production place on a worldwide basis, where 1,339 MB/D are processed by the 6-Refinery Complex System of Mexico and about 1,554 MB/D are exported, mainly to the Usa. On the other hand, the annual growth in the international refining catalysts market is about 6.5%, to reach about 3,200 million US$ in 2003 [12], which is equivalent to 7,600 million pounds on a weight basis, that is about 90% of the catalysts volume in a global scale, but it only represents about 45% of the catalysts total market in a monetary basis [3, 12]. The difference of 55% comes from petrochemicals and chemicals production market, which means less volume but more value in a monetary basis. Among the main opportunities existing nowadays in the refining industry are: 1) the production of low sulfur gasoline and diesel, targeted at about 30 ppm for 2006; 2) the integral processing of heavy crude and 3) the introduction of new gasoline additives due to the probable phase out of MTBE. These trends are the basis of a forecast on major opportunities in catalytic processes and they are summarized in Table 9.

The competition factors in the refining catalysts market are based upon a clear product differentiation with a market focus in mind, the low costs leadership, a proper market positioning, the joint ventures and a combination of manufacture-distribution and technical assistance.

It is worth noticing in Figures 2a and 2b that the main catalysis R&D endeavors in Mexico are focused on three main areas, i.e. hydrotreating catalysts (HDT), new catalytic materials (NCM) and solid acid catalysts (SAC). However, according to the catalysts consumption market the main emphasis is focused on the conversion of heavy residuals by hydrocracking and FCC catalytic processes, with smaller emphasis in hydrotreating and reforming processes. The latter represent only 3% each with respect to the actual market structure (Figure 1). Then, there is an asymmetric relationship between the actual catalysts market needs and R&D efforts that must be analyzed further in the light of future R&D projects. In addition, as indicated in Figure 3, the personnel working in catalysis show a significant dispersion over three distinct platforms, which might pose organizational barriers for these groups to achieve common goals along the value chain comprising the areas from basic research to industrial applications.

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