Development of a FCC catalyst deactivation process to simulate real operating conditions

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Abstract

The Fluidized Catalytic Cracking (FCC) is one of the most used transformation processes in petroleum refining industry, which objective it is the conversion of heavy petroleum fractions into light products with more demand in market and more added value, as is the case of gasoline. However, in last years the demand for gasoline has decreased while propylene demand has increased, a raw material of petrochemical industry. For these reasons, there is the necessity to increase the conversion of heavy hydrocarbons in light olefins, mainly in propylene and butene, which has resulted in a modification of the FCC process in refineries.

FCC process that uses zeolite catalysts to promote the molecular cracking reactions, so it is considered a heterogeneous catalytic process. The FCC catalysts have as main component the Y zeolite, which pores and crystalline structure is very well defined. This zeolite is responsible for the cracking of high weight molecules. The other type of zeolite used in FCC catalysts is ZSM-5, generally used as an additive. This one has smaller pores than Y zeolite and it is responsible for the selectivity in light olefins. It is through the increase of the concentration of ZSM-5 and through the development of the new catalysts that it will be possible to maximize the propylene production. Thus, it is necessary to study the FCC process and optimize its conditions.

Therefore, the objective of this work is to develop a FCC catalyst deactivation process, more specifically, a deactivation process of ZSM-5 additive, that is used in the catalyst composition to promote the selective cracking. This way it is intended to simulate real operating conditions of the refinery in laboratorial level. So in the future it will be possible to study the effect of different FCC variables in propylene production with the objective to maximize it.

Key-words: FCC, catalytic cracking, propylene, catalysts, zeolites, ZSM-5, deactivation.

1. State of art

1.1 Propylene global situation

Propylene is a major industrial chemical intermediate that serves as one of the building blocks for an array of chemical and plastic products, and also the first petrochemical employed on an industrial scale. Direct applications include besides the plastic polypropylene the production of important chemicals such as propylene oxide, acrylonitrile, cumene, acrylic acid and some alcohols. [1].

In 2014, about of total propylene produced for chemical uses worldwide went into the manufacture of polypropylene resins. About 8% is consumed in the production of propylene oxide, while third-largest end-use segment, acrylonitrile accounts for about 7% of total consumption. The remainder went into the manufacture of the other chemical intermediates.

The major propylene markets are China, United States, and Western Europe, which together accounted for about 55% of global consumption in 2014. As a result of a new propylene and derivative capacity schedule to
be brought on-stream during 2014-2019, the United States and especially the Chinese market will exhibit significant growth and account for about 76% of the total increase in propylene demand. Even though the Western Europe propylene market is projected to shrink in the forecast period, it will likely remain the third-largest global producer and consumer of this product. [2]

This way global consumption of propylene for chemical applications is projected to increase at an average rate of 4.6% annually over the next five years.

As if possible to see polypropylene demand currently is growing in some region of world and the currently supply cannot match the demand. A large proportion of propylene is produced by steam cracking (SC) of light naphtha and during the fluid catalytic (FCC) process. [3]

SC is an established technology for the production of light olefins, such as, ethylene and propylene. It accounts for about 55% of the world’s propylene production, with the established refinery FCC process accounting for 34% and the remainder is produced on purpose using metathesis and propane dehydrogenation. [2]

However, SC technology alone cannot satisfy the demand for propylene. So there is a need of new technology to produce additional propylene to bridge the gap between supply and demand. With one purpose propylene production technologies being touted as possible alternatives, the cost associated with these new technologies remains less competitive relative to steam crackers and FCC. It could have been easier to fill the gap by reconfiguring he steam cracker, but the SC does not provide flexibility of operation and it has high energy consumption. It is the most energy consumption process in the chemical industry and uses approximately 8% of the total global primary energy use. Being an essentially non-catalytic and non-selective process SC is energy intensive and catalysts have never been widely used in pyrolysis section in SC to optimize energy efficiency. By adopting technologies based on reconfiguration of the FCC unit maximize the production of propylene and light olefins, it is expected that energy savings and flexibility of operation will be obtained. [3]

1.2 Fluid Catalytic Cracking (FCC)

The Fluidized Catalytic Cracking (FCC) is one of the most used transformation processes in petroleum refining industry, which objective it is the conversion of heavy petroleum fractions into light products with more demand in market and more added value, as is the case of gasoline.

One of its main characteristics is its versatility, since it presents great flexibility in the adjustment of the operative conditions thus allowing the maximization of the production in different compounds. [5]

1.2.1 Process Description

The various catalytic cracking processes using a fluidized bed are similar in many ways. Basically a FCC process consists of three sections: the reactor, the stripper, and the regenerator. The feed enters the bottom of a vertical reaction riser where it encounters a steam of hot, regenerated catalysts following downward in an inclined regenerator pipe coming from the regenerator. The hot catalysts vaporize the feed oil; the vapor carries this powder catalyst up the riser into a reactor vessel. The reactor contains the catalyst, which is retained as a fluidized bed, meaning the fine powder is held in a fluid state- This fluidized state depends on the particle size, the density of the particles, the velocity of the vapor and its density. Cracking reactions start in the reactor riser and continue through the fluidized-bed reactor. The cracked product moves on from the top of the reactor to a fractionation tower further separation.

The deactivated or spent catalyst leaves the reactor continuously through a side pipe and carried by steam into a stripper. The steam removes the remaining hydrocarbons attached to the spent catalyst. In the stripper,
the steam leaves the top and joins the product vapors leaving the reactor.

After the catalyst has been stripped from attached hydrocarbons, it moves down to the regenerator where it joins the catalytic bed. Air is distributed from bottom of the regenerator into the catalyst to burn off deposits. The flue gas leaves the top of the regenerator, and the regenerated catalysts moves down a pipe. It is then picked up by steam and the fresh feed, and it is carried into the fluidized-bed reactor. The cycle continues in this fashion.

The fraction unit further separates the product into gases, cracked gasoline, and lights and heavy gas oils. The distribution of these products depends strongly on the type of feedstock and the process operations. Light gases—normally methane, ethane and ethylene—join the refinery fuel system, or they may be further separated to become a feed for petrochemical industry. The heavier gas is separated further by distillation under pressure in order to yield propane, propylene, butane, butylene, and the desired product gasoline. [6][7]

1.2.1 Feedstocks and products

Feedstocks for the FCC process are complex mixtures of hydrocarbons of various types and size ranging from small molecules, like gasoline up to large molecules of perhaps 60 carbons atoms. These feedstocks have a relatively small content of contaminant materials such as organic sulfur, nitrogen compounds and organometallic compounds. Thus, the main FCC feedstocks are vacuum gas oil (VGO), hydro-treated VGO, hydrocracker bottom, coker gas oil (CGO), deasphalted oil (DAO), reduced crude oil (RCO) and vacuum residue (VR).

It is important to note that feedstock quality has a big impact in FCC unit operation and in the products quality.

The products of conversion from catalytic cracking are largely olefinic for light fractions and strongly aromatic for the heavy fractions. The main products are:

- Liquefied gas fractions (propane, propylene, butanes, butenes) that will be able to provide feedstocks to units of MTBE, ETBE, alklylation, dimerization, polymerization after sweetening and/or selective hydrogenation;
- A gasoline fraction of good octane number (RON 91-93, MON 79-81) which is sent to the gasoline pool after sweetening. The light C₅ fraction can be etherified (TAME); the lower quality cut (75-125°C) is sent to catalytic reforming while the heavy fraction (125-210°C), strongly aromatic with a high octane number, is sent to the gasoline pool;

- As light distillate cut (LCO) similar to gas oil but having aromatic and low cetane number.

The FCC byproducts are refinery gases, residue (slurry) and coke. [5][8][9]

1.2.2 Reactions

Catalytic cracking reactions are frequently classified into primary and secondary reactions. The primary reactions involve the initial carbon/carbon scissions and may be represented as:

Paraffin → paraffin + olefin
Alkynaphthene → naphthene + olefin
Alkyl aromatic→ aromatic+ olefin

The actual reactions are, of course, not this simple, as the initial scission proceeds through a carbon ion mechanism with several possible products other than a single olefin and a single saturated fragment. The secondary reactions are more than side reactions. They include a large number of reactions of olefins and a small number of independent reactions. The secondary reactions are a major factor in determining both product yield and product quality. The major secondary reactions are those of olefins catalyzed or promoted by the same acidic properties of the catalyst that initiate the primary reactions. The major secondary reactions are:

- Cracking of olefins;
- Double bond shift, geometrical isomerization, or skeletal isomerization;
- Hydrogen transfer to an olefin from naphthenes to produce cyclic olefins and aromatics;
- Hydrogen transfer from another olefin to produce diolefins;
- Polymerization to produce higher molecular weight olefins;
- Aromatization;
- Alkylation of aromatics;

Several of the above reactions proceed further to produce carbonaceous deposits on the catalyst; these coke formation reactions include extended polymerization of diolefins or olefins, aromatization to from polycyclic aromatics, and cyclization and/or condensation of alkylated aromatics. [10][11]
1.2.4 Catalysts

1.2.4.1 Components

At the heart of FCC units are the catalysts themselves. The development of active and stable FCC catalysts went parallel with the FCC design development. It was known, that for cracking of C-C bonds, the acid catalysts are needed. The first acid catalyst, tested for cracking of heavy petroleum fraction, was aluminium chloride. However, the problems with the manipulation, corrosion and the wastes treatment were greater than its positive action.

In the 1940’s, silica-alumina catalysts were created and greatly improved over the natural clay catalysts. It was Houdry, who for the first time used acid-activated bentonite as active acid catalyst for catalytic cracking. But the most significant advance came in 1962 when zeolite catalysts were incorporated into the silica-alumina structures. Advances in catalysts have produced the greatest overall performance of FCC units over the last fifty years. [12] [7]

FCC catalysts are in form of fine powders with an average particle size diameter in a range of 75 microns. A modern catalytic cracking catalyst has five component systems: zeolite, matrix, binder and filler and an additive.

Zeolite

The zeolite, or more properly, faujasite, is the key ingredient of the FCC catalyst. Its role in catalyst is to provide product selectivity and much of the catalytic activity. The catalyst’s performance depends largely on the nature and quality of zeolite.

Typical zeolites may be viewed as crystalline, inorganic polymers comprising an anionic lattice of silica and alumina tetrahedral linked by shared oxygen. One consequence of atomic configuration in faujasite is the existence of a periodic pattern of tetrahedrally oriented large- and small-pore systems ([Error! Reference source not found.]). The former comprises the spherical super cages and the latter internal voids of sodalite cages and hexagonal prisms. Facile sorption of potential reactant molecules with critical dimensions less than those of the pores diameters in general observed. These can include some C₁₈ to C₂₅ mono-, di-, tri nuclear aromatics present in heavy gas oil, although exclusion by size/shape will of course occur in large/bulk molecules.

The small pore system is normally inaccessible to organic molecules, but permits sorption of water or ammonia and can be involved with a variety of ion sievings. [13]

Matrix

Zeolite crystals are dispersed in an active matrix of alumina or silica-alumina together with the clay particles. The active matrix contributes significantly to the
overall performance of the FCC catalyst. The zeolite pores are not suitable for cracking of the large hydrocarbon molecules generally having an end point > 900°F. They are too small to allow diffusion of the large molecules to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbon into and out of catalyst.

An active matrix provides the primary cracking sites. The acid sites located in the catalyst matrix are not selective as the zeolite site but are able to crack larger molecules that are hindered from entering the small zeolite pores. The matrix pre-cracks heavy feed molecules for further cracking in internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which activity attained by their combined effects can be greater than the sum of their individual effects. An active matrix can also serve as a trap to catch some of the vanadium and basic nitrogen. [11]

**Binder and filler**

The filler is clay incorporated into the catalyst to dilute its activity. Koaline (Al₃(OH)₉, Si₃O₉) is the most common clay used in FCC catalyst. On FCC catalyst manufacture uses koaline clay as a skeleton to grow the zeolite in situ.

The binder serves as a glue to hold the zeolite, the matrix, and the filler together. Binder may or may not catalytic activity. The importance of binder becomes more prominent with catalysts that contain high concentrations of zeolite.

The functions of the filler and the binder are to provide physical, a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated. [11]

**Additives**

Additives can be added to the catalyst, dispersed in the catalyst matrix, or as independent macroscopic particles that are added to improve the FCC unit.

Fluid catalytic cracking additives are injected into FCC units in small amounts for the purpose of improving specific yields, enhancing product quality, or for reducing emissions from the regenerator.

The main FCC additives are: CO promoter, used to catalyze combustion of CO into CO₂ inside the regenerator; SOx additive, used to SOx capture in the regenerator; ZSM-5 used to octane number improvement.

**1.2.4.2 ZSM-5 Additive**

One catalyst that has been incorporated into FCC catalyst formulation of light olefins is ZMS-5.

ZSM-5 is a shape selective zeolite that has a different pore structure than that of Y-zeolite. The pore size of ZSM-5 is smaller than that of Y-zeolite (5.1 Å to 5.6 Å versus 8 Å to 9 Å). In addition, the pore arrangement is different.

The shape selectivity of ZSM-5 allows preferential cracking of long-chain, low-octane normal paraffins as well some olefins in the gasoline fraction.

ZSM-5 additive is added to the unit to boost gasoline octane and to increase light olefins yields. ZSM-5 accomplishes this by upgrading low-octane components in the gasoline boiling range (C₇ to C₁₀) into light olefins (C₅, C₆, C₇). This additive inhibits paraffin hydrogenation by cracking the C₇+ olefins.

The ZSM-5 effectiveness depends on several variables. The catalytic crackers that process highly paraffinic feedstock and have lower base octane will receive the greatest benefits of using ZSM-5. This one will have little effect on improving gasoline octane in units that process naphthenic feedstock or operate at high conversion level.

When using ZSM-5, there is almost an even trade-off between FCC gasoline volume and LPG yield. For a one-number increase in the research number of FCC gasoline, there is a 1 to 1.5 vol% decrease in the gasoline and almost a corresponding increase in the LPG. This again depends on feed quality, operating parameters and base octane number.

As is possible to see the ZSM-5 additive has a strong influence in light olefins production. The increase of propylene production with additive ZSM-5 is affected by: amount of ZSM-5 used, crystal size of ZSM-5, ratio Si/Al, hydrothermal stability ofZSM-5 and coke formation. [10] [11]

**Effect of ZSM-5 amount**
Bulatov and Jirmov analysed feed conversion over varying concentrations of a component additive containing ZSM-5. The additive level was varied from 0 to 40% over a C/O ratio of about 28, a riser outlet temperature of 566°C, a riser partial pressure of 0.0793 MPa, and a contact time of 1.5 sec. From the analysis, it was observed that an increasing of the amount of ZSM-5 to very high levels had only a marginal effect on the production of propylene production. Propylene yield tends to plateau with about 10% ZSM-5 crystal concentration in the catalyst inventory. This is explained by the fact that the diminishing effectiveness of ZSM-5 at higher concentrations occurs primarily due to the depletion of the gasoline olefin precursors. ZSM-5 generates propylene by selectively cracking olefins in gasoline boiling range. As the concentration of ZSM-5 additive in catalyst inventory increases, the incremental yield of propylene produced per percentage of additive decreases. [4]

**Effect of crystal size**

The main factor allowing molecular sieving, and consequently, the shape selectivity is generally considered to be exclusively a steric effect, i.e., only molecules having critical kinetic diameter lower than the channel diameter are allowed to enter the pores and to react on an active site, or to exit them and to be recovered as a product reaction. Alternatively, transition state shape selectivity effects limit the formation of bulky transition state intermediates inside the pores and avoid the formation of some unwanted reaction products. In a heterogeneous catalytic reaction involving large molecules, diffusion of these large molecules to the catalytic active internal sites of zeolites will become a rate limiting process. More secondary products and faster deactivation were observed due to longer intra-crystalline diffusion path lengths.

One method of overcoming these functional limitations is to reduce the particle size of zeolites and shorten the diffusional paths. In ZSM-5 there is exists a remarkable molecular sieving effect for light hydrocarbons and this has been widely used as shape selective catalysts in various hydrocarbon processes. However, because the crystal sizes of ZSM-5 are usually much larger than size of micropores, the rate-limiting step of the reaction tends to be the diffusion of the reactant/product within micropores. Moreover, carbon solid (coke) readily forms near the external surface of crystal under diffusion controlled conditions, thereby, rapidly plugging the pores, leading to a short catalyst lifetime. To achieve low diffusion resistance, nano-sized zeolites are effective because the diffusion length for reactant/products hydrocarbons, which depends on the zeolite crystal size, is reduced. High propylene selectivity from cracking of naptha is favored over larger 10-membered ring zeolites having a pore index between 26 and 30. The pore index is defined as the product of the two principal dimensions, or diameter, of the pore and is in units of square Angstroms. [4]

**Effect of Si/Al**

ZSM-5 zeolite has a unique three dimensional structure with very small pores compared to the Y-zeolite in a normal FCCU catalyst. This makes ZSM-5 zeolite “shape selective” for cracking the long chain (C6-C10) olefin molecules in FCCU gasoline (it also cracks the equivalent paraffin but at a much slower rate). The products of these cracking reactions are predominantly propylene and butylene, with small amount of isobutane. Changing the Si/Al ratio in ZSM-5 translates to altering the ratio of cracking/isomerization rates.

Catalytic active sites also exist on the external surface and the pore mouth of zeolite crystals. For shape selective reactions, these sites are considered to be responsible for unwanted nonselective catalysis. Most hydrogen transfer reactions in ZSM-5 occur on the surface of the catalysts and more pronounced at low Si/Al ratios when acidity is high. These hydrogen transfer reactions lead to the production of more dry gas, such as methane and ethane, leading to a drop in the selectivity of light olefins. It is thought that a smaller crystal size in combination with high Si/Al ratio gives higher light olefins yields due to lower resistance time of primary products in the pores of the catalyst in contact with the acid sites.

The stability of the catalyst is also affected by Si/Al ratio especially in relation to the coke formation. It has been proven that the higher the Si/Al (lower acidity), the
smaller the amount of coke form, with knock-on effect being the extended catalyst lifetime. This is directly linked to the fact that coke deposition is dependent on hydrogen transfer reactions, which is turn is dependent on the catalyst acidity. If the catalyst acidity is suppressed, then the rate of coke deposition is reduced. [4]

**Hydrothermal stability of ZSM-5**

The main cause of ZSM-5 deactivation is de-alumination due to the presence of steam at high temperatures, which leads to a partial destruction of its framework. To overcome of this problem, phosphorus impregnation has been used to stabilize the ZSM-5 structure. Several studies have reported changes on the hydrothermal stability after impregnation with phosphorus not only for ZSM-5 zeolites but also for FAU and MOR zeolites. [4]

**Coke formation**

FCC processes are usually accompanied by the production of coke and all heterogeneous acid catalyzed reactions of organic compounds result in deactivation due to coking. Coke is generally formed as a result of a sequence of elementary reactions, which are affected by the type of reaction, feed composition, type of catalyst and reaction-reactor environment.

Therefore, it is very important consideration when acid zeolite catalysts are used. When deciding which process to use, it is essential to understand fully mechanisms that control coking and the effect it has on catalytic properties, such as activity and selectivity. In most industrial processes catalyst deactivation is as important a consideration as controlling the activity and selectivity, because it is extremely costly.

It is known that in zeolites, pore size, pore structure and acidity affect coke deposition. The ZSM-5 zeolite has a lower tendency to form coke, compared to the Y zeolite, due to its narrow pores that limit the formation of bulky coke intermediates. [4]

**1.2.4.3 Catalyst deactivation**

In FCC catalysts deactivation results from [12] [7]:

1- The poisoning of acid active sites by polyaromatic and the basic nitrogen-containing feed molecules and by coke molecules trapped within micropores;
2- Deposits of heavy feed components on the surface or at the micropore mouth or the formation of coke within the micropores with blockage of the access of reactant molecules to the active sites.
3- Chemical and structural alterations of the zeolite catalyst. In this case the water which is added or formed at different stages of the FCC process plays a major role because catalyst are submitted, essentially in regeneration step, in the presence of steam to very high temperatures. The severity of this step is responsible for Y zeolite dealumination and partial collapse of zeolite framework, which provokes a decrease in the concentration of active sites.

The FCC additive, ZSM-5 has a lower tendency to form coke, compared to Y zeolite, due to its narrow pores that limit the formation of bulky coke intermediates. The main cause of ZSM-5 additive deactivation is dealumination due to presence of steam at high temperatures, which leads to a partial destruction of its framework structure. [12]

**2. Methodology**

The experimental work is divided into two steps. The first one corresponds to the catalyst deactivation and the second one is related to the catalytic activity test of the previously deactivated catalyst. To make possible these two steps were used to types of pilot units:

- **Steamer Unit**
- **MAT Unit (Micro Activity Test)**

**Steamer Unit**

The Steamer Unit is designed to simulate the hydrothermal deactivation of FCC catalysts, i.e., deactivation of catalyst by destruction of the zeolite structure by the action of temperature and steam and for this reason it is done at high temperatures and under continuous water steam flow.

The unit consists in four quartz fluid bed reactors heated by a furnace with a bath of *carborundum*. This bath is fluidized
for an air flow that enters in its bottom. The maximum temperature in steamer unit is 865°C and its control is achieved with measurements from thermocouples in the catalyst beds and in the two phases of carborundum bath. Each reactor has a capacity to receive 200mL of catalyst and it is possible to treat one catalyst, or can be optionally delivered for testing four different catalyst samples at the same time under completely independent conditions. 

The steaming of FCC catalyst is done in the presence of 100% steam.

**Work Plan:**

1. Deactivation of FCC fresh catalyst (Base+ ZSM5) to use as a reference and to define the following deactivations. (5h; 815°C, 100 % steam);
2. Deactivation of base catalyst (zeolite Y + matrix). The deactivation conditions are the same for all the tests. (5h, 815°C, 100 % steam);
3. Deactivation of ZSM-5 additive at different conditions (5, 15, 30, 50, 75, 100 h, 815°C; 100% steam);

**MAT Unit**

The MicroActivity Test (MAT) unit used for the experiments has been designed according to the ASTM D-3907 method, with minor modification. This unit tests the catalyst activity, i.e. the MicroActivity test provides the ability of the catalyst to convert a standard feedstock into low boiling range materials.

The MAT unit it is composed by two fixed bed reactors heated by a three-zone furnace and it will be programmed to obtain until 12 samples, where it can vary different parameters without change the catalyst bed, such as: Cat/oil, reaction temperature, contact time (TOS), regeneration temperature. For each test it is used a fixed bed with approximately 5 grams of catalyst and for this reason the relation catalyst/feed changes with feed quantity. The contact time, which is actually the feed addition time (Time On Steam), can be changed with feed addition rate. Feed rate is controlled by a syringe-pump while the duration of all experiment is constant.

The vapor products are approximately cooled to -0°C at the exit of the reactor where part of it is condensed and collect in the specially designed liquid receiver. The remaining uncondensed gas products are driven to a burette where the volume of the gas is measured by water displacement at atmospheric pressure and room temperature.

To the reactor can come N₂ or air dependent of the phase of the program. There is only a moment that these gases cannot enter to the reactor that is during the reaction step. The air flow is only used during the regeneration step. The N₂ flow is used to promote catalyst fluidization and a good feed distribution.

The reaction temperature is measured by a thermocouple just above the catalyst bed. The pressure in the reactor is measured with a pressure transmitter.

The gaseous cracking products are analyzed by gas chromatography. It is equipped with three columns and two valves and is able to detect all gaseous products of the catalytic cracking reaction. The regeneration gases are analyzed by gas chromatography. In this case, the regeneration gases are driven before to a copper furnace where CO is converted into CO₂. For this reason, there is other chromatograph responsible for analyzing gases produced during regeneration step. The results are material balanced to generate a full slate of yields, with liquid product boiling range determined from the GC simulated distillation.

**Work Plan:**

1. Study the activity of the deactivated fresh catalyst;
2. Study the activity of equilibrium catalyst (E-cat) from Huelva Refinery, to use as a reference of the real operation conditions in refinery.
3. Study the activity of a mixture of deactivated base catalyst (5h; 815°C; 100% steam) deactivated ZSM-5 additive at different conditions (5, 15, 30, 50, 75, 100 h; 815°C; 100% steam)

**3. Results**

3.1影响力ZSM-5失活参数在催化剂活性
It was studied the influence of deactivation time in FCC catalysts, more specifically, in ZSM-5 additive. The ZSM-5 was deactivated during different time periods, and calculated its specific surface area because the specific surface area is a good signal of catalyst deactivation degree. Table 2 shows the specific surface area to ZSM-5 additives deactivated at different conditions.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Total surface area (m$^2$/g)</th>
<th>Zeolite surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 Additive (5h, 815°C, 100% steam)</td>
<td>120</td>
<td>86</td>
</tr>
<tr>
<td>ZSM-5 Additive (15h, 815°C, 100% steam)</td>
<td>120</td>
<td>69</td>
</tr>
<tr>
<td>ZSM-5 Additive (30h, 815°C, 100% steam)</td>
<td>116</td>
<td>56</td>
</tr>
<tr>
<td>ZSM-5 Additive (50h, 815°C, 100% steam)</td>
<td>115</td>
<td>50</td>
</tr>
<tr>
<td>ZSM-5 Additive (75h, 815°C, 100% steam)</td>
<td>114</td>
<td>46</td>
</tr>
<tr>
<td>ZSM-5 Additive (100h, 815°C, 100% steam)</td>
<td>109</td>
<td>40</td>
</tr>
</tbody>
</table>

It is possible to see that zeolite specific surface area decreases with deactivation time, which confirms that with more severe conditions bigger is the zeolite structure destruction. To 100 h, the surface area of ZSM-5 is half of the area to the first derivation (5h).

For small zeolite surface areas are less the available acid centers for selective cracking, which has a large impact on products yield.

It is possible to see in following figures (Figures 2 and 3) that with more severe deactivation conditions, lower is the LPG yield, and consequently lower is the light olefin production. This reduction is caused by the destruction of the ZSM-5 structure responsible to crack the heavy hydrocarbon molecules in light olefins.

On the other hand, gasoline yield increases with catalyst deactivation time (Figure 4), because with the reduction of zeolite surface area, the acid centers to crack the heavy olefins in gasoline range in light olefins (propylene and butene) are less. However, the gasoline quality is lower, because of the small content in light olefins, which results in lower RON and MON values.

The RON and MON values decrease with the light olefins content, and consequently with the severity of deactivation conditions.

![Figure 2- LPG yield VS conversion for different catalysts deactivation conditions](image1)

![Figure 3- Light olefins yield VS conversion for different catalysts deactivation conditions](image2)

![Figure 4- Gasoline yield VS conversion for different catalysts deactivation conditions](image3)
Table 5 shows product yields for a constant conversion of 70%.

For a constant conversion it is possible to see that an increase of deactivation time of ZSM-5 additive results in a decrease of 4.2 % (wt.%) in LPG when compared the first and last deactivation. Light olefins yield decreases 2.4% and gasoline yield increases 4.3%. These results confirm what was previously reported, i.e., a reduction of zeolite surface area affects selective cracking that is responsible for cracking of olefins in gasoline range into light olefins. For this reason, light olefins yield decreases as the same proportion that gasoline yield increases.

3.2 Comparison of products yields for E-Cat and deactivated catalyst

It was analyzed the yield in propylene and butane obtained for all deactivated catalysts and compared its values with equilibrium catalyst. The values were analyzed to different cases:

- Constant LPG yield (24% wt.)  
- Constant conversion (70% wt.)  
- Constant Cat/Oil (5,0)

Figures 5, 6 and 7 show the “delta yields” between E-cat and deactivated catalysts, for propylene and butane yields. It is possible to see that LPG composition is independent of deactivation conditions, i.e., propylene and butane yields don't decrease with increase of deactivation time. Only LPG yield is dependent of the additive acidity. For a constant conversion, propylene yield are lower when compared with propylene yield for equilibrium catalyst, which leads us to believe that E-cat is more active than what it was supposed. It is possible that it is the result of the addition of fresh catalyst in FCC unit. However, the propylene yield decreases with deactivation time. Thus, propylene delta yield is bigger to higher deactivation times.

Butenes delta yields are smaller when compared with propylene delta yields, and its variation when compared with E-cat it is so small that will be a result of experimental errors. This way is possible to see the values obtained to a constant cat/oil.

4. Conclusion

ZSM-5 zeolite structure it is affected for deactivation time. For longer exposure times, bigger is the zeolite structure destruction and lower is the light olefins production.

A reduction in number of the active centers affects the products yields. For this reason catalysts that are exposed to more severity conditions produce a smaller LPG and light olefins yields.

Equilibrium catalyst used for comparison with deactivated catalysts were more active than what it was supposed, and so it could be interesting to test equilibrium catalysts from the refinery for other dates.
Figure 6- “Delta yields” between E-cat and deactivated catalysts at constant LPG yield.

Figure 7- “Delta yields” between E-cat and deactivated catalysts at constant conversion.

Figure 8- “Delta yields” between E-cat and deactivated catalysts for a cat/oil of 5.0.
5. Bibliography


