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Catalyst Testing in a Continuously Operated Fluid Catalytic Cracking Pilot Plant

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Abstract

A cost-effective and risk-minimizing way to test out new plant configurations for refinery operators is the pretesting of catalysts and temperature changes in pilot plants, which are essential since refineries have to be adapted to climate change regulations in the upcoming decades. In this work, a fluid catalytic cracking pilot plant was used to test out three different catalysts at two different riser temperatures each. It was shown that all tests were conducted without any hardware changes beside the catalysts and that the obtained results corresponded to the advertised benefits of each catalyst according to the manufacturer. While the heavy residue catalyst produced more gasoline making it interesting for a fuel-focused refinery, the two gas boosting catalysts promoted different compounds of the gaseous products. These gaseous products can then be used for synthesizing polymers and other high-value products.

Introduction

International treaties like the Paris Agreement have fueled the need for refineries to transform their business model to more sustainable ways due to current and future obligatory reductions of CO_2 emissions imposed by lawmakers to accomplish the 1.5 °C goal [1]. To tackle this issue different approaches are possible from the utilization of more sustainable and greener feedstocks or from a product shift from fossil fuels to more high-value products that can be reused and recycled [2] [3] [4] [5]. One process in the refinery whose product spectra can be shifted in that way is the fluid catalytic cracking (FCC) process, which is one of the main conversion processes in a refinery [6]. To achieve this shift in product spectra the FCC unit's settings and equipment must be changed, which is often done during planned plant shutdowns, so called revamps. There are different approaches to change the product spectra of an FCC unit with elevating the riser temperature being one of the most significant ones. However, often also catalyst changes are necessary to shift the product spectrum into the desired direction. Since these revamps are costly investments with risks, refineries often are keen to test out the products shifts that would occur when the new settings are put in place. One way to test this are experiments in a pilot plant in which the new and old settings are tested and the results are compared. A big advantage of experiments in a pilot plant compared to micro activity tests (MAT-tests), often used for catalyst testing, are the more comparable results with industrial plants due to their operating conditions and their larger scale. One such pilot plant is located at the institute of chemical, environmental and bioscience engineering (ICEBE) at TU Wien, Vienna. In this work three different catalysts were chosen and experiments were conducted at 2 different riser temperatures each to show the versatility of such a pilot plant and to demonstrate its use for the refinery industry when it comes to revamping industrial scale plants.

Materials and Methods

The experiments were conducted in an internally fluidized fluid catalytic cracking pilot plant. It was designed and constructed by Reichhold [7] and further developed by Bielansky [8]. A schematic of the FCC pilot plant is depicted in figure 1. Some of its key characteristics are listed in table 1.
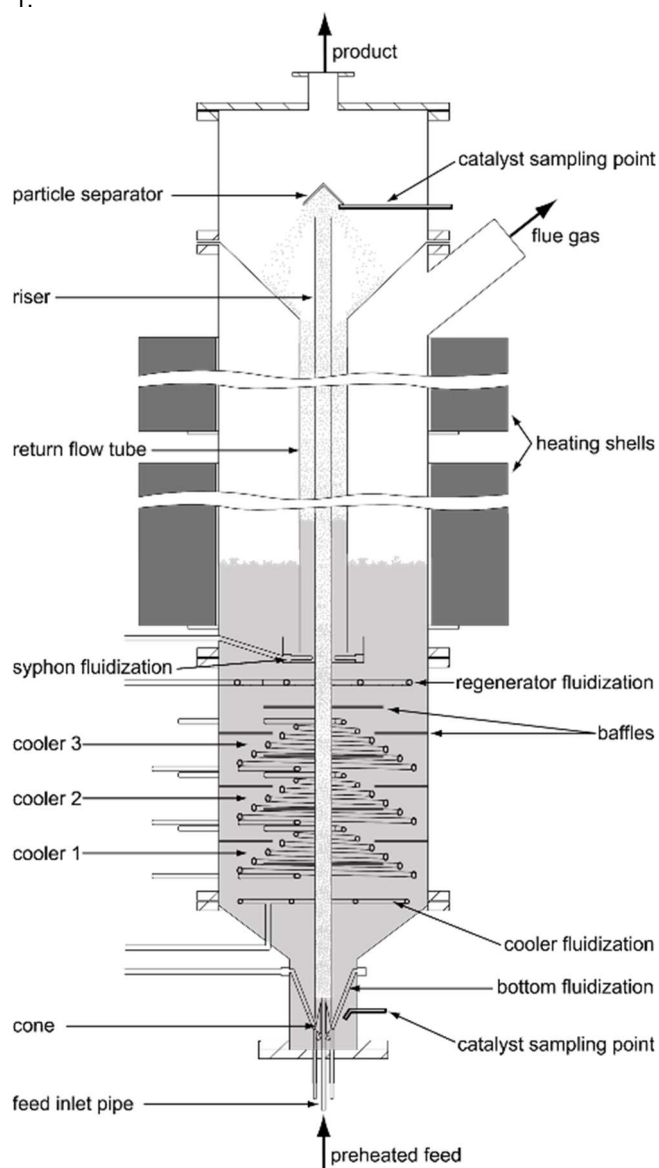

Figure 1: schematic of the FCC pilot plant

The feed is pumped via a gear pump through a tubular oven where it is heated close to initial boiling point. The preheated feed then enters the riser through the feed inlet pipe and gets in contact with the hot catalyst. Here, it evaporates resulting

in a significant increase in volume that leads to an upward motion giving this plant section the name "riser". The cracking reactions occur, leading to a mole increase and, thus to a further volume increase. The total residence time in the riser is around 1 s. At the top of the riser, the cracking gas and the catalyst get separated. The cracking gas then leaves the plant at the top while the catalyst falls down through the return flow pipe. The particles pass through the syphon, which acts as a stripper and a gas barrier between the reactor and the regenerator section. In the regenerator the coke deposited on the catalyst due to secondary reactions gets burned of the catalyst particles providing the necessary process heat. The reactivated catalyst flows then through the cooler section ending up again at the plant bottom where it gets in contact with the feed. Therefore, a continuous plant operation is possible.

The riser section, the bottom section and the syphon use nitrogen as a fluidization gas, which is to establish an inert atmosphere. The cooler and regenerator section use air as a fluidization medium to enable the burning off of coke from the catalyst.

Table 1: key data pilot plant

Total height	3.2 m
Riser length	2.5 m
Riser diameter	0.0215 m
Regenerator diameter	0.33 m
Regenerator temperature	500 - 800 °C
Riser temperature	400 – 700 °C
pressure	atmospheric
Catalyst mass	45 - 75 kg
feed rate	1,5 - 8 kg/h
Riser residence time	~1 s
catalyst circulation rate	0.5 - 5 kg/min
C/O-ratio	10 - 50

In the refinery sector products are often mixtures of various compounds making it not feasible to analyze every single compound by itself. To tackle this issue a lump model was chosen. In this model different compounds are grouped together in lumps depending on physical state and composition and/or boiling temperature. A detailed explanation of the lump model is given in figure 2.

Three different phases (solid, liquid, gaseous) make up the FCC product. The carbon oxides are measured online via a NGA 2000 MLT from Emerson, an infrared gas analyzer. The gaseous hydrocarbons are analyzed using a gas chromatograph (GC) (for details see table 2). In this GC the hydrocarbons are measured in section I and the nitrogen is measured in section II.

The liquid products are gathered via a condensation apparatus. They are analyzed using a simulated Distillation (SimDist) and separated by boiling temperature (for temperatures see figure 2). Further details about the SimDist are listed in table 3.
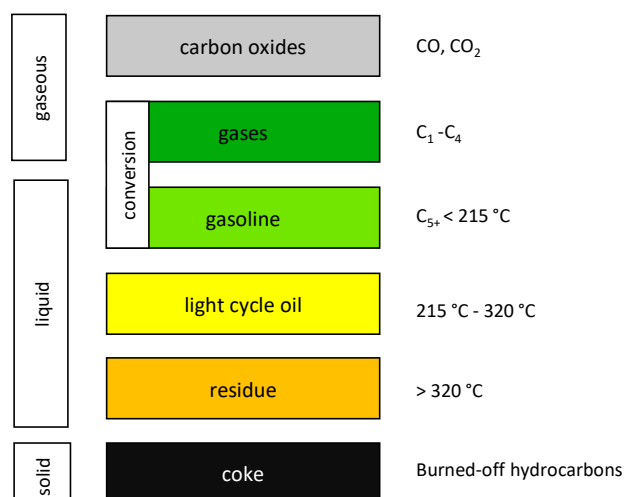

Figure 2: lump model

Table 2: configuration of Gas-GC (Shimadzu GC-17A)

Injector	Splitless 50 µl @ 200 °C
Carrier gas	Helium 1.46 ml/min constant flow
Temperature program	50 °C to 200 °C; dwell-time 30 min
Columns	I: Varian CP-Al$_2$O$_3$/Na$_2$SO$_4$ II: CP CarboPLOT P7
Dimensions	I: 50 m x 0.25 mm ID x 4 µm II: 27.5 m x 0.53 mm ID x 25 µm
Phase	I: 100% Polydimethylsiloxan II: Carbon Porous Layer
Detectors	I: Flame Ionization Detector (FID) @ 200 °C II: Thermal Conductivity Detector (TCD) @ 105 °C

Table 3: configuration of simulated distillation (Shimadzu GC-17A)

Injector	Split 30:1 1.5 µl @ 350 °C
Carrier Gas	Hydrogen 1.68 ml/min constant flow
Temperature program	25°C to 350 °C; dwell-time 22 min
Column	Zebron ZB-1
Dimension	30m x 0.32mm ID x 0.25 µm df
Phase	100 % Polydimethylsiloxane
Detector	Flame Ionization Detector (FID) @ 350 °C

The solid product consists only of coke. The amount of carbon oxides, which are generated by burning off the coke from the catalyst is constantly measured. Through these carbon oxides, conclusions regarding the coke amount can be drawn via combustion calculation.

A commonly used term to describe the FCC process economic viability is the conversion, also called total fuel yield (TFY). It is often described as the amounts of gases (C$_1$ – C$_4$) and gasoline compared to the amount of feed. The light cycle oil (LCO) is often not considered a valuable product since it has a low quality due to its high aromatics content [9].

$$Conversion = \frac{m_{gases} + m_{gasoline}}{m_{feed}}$$

The utilized feed was vacuum gas oil (VGO). It is the top product of the vacuum distillation and a standard feed for fluid catalytic cracking units [10]. In table 4 some properties of the used batch of VGO are listed. In figure 3, a distillation curve shows the amounts of lighter and heavier compounds.

Table 4: VGO properties

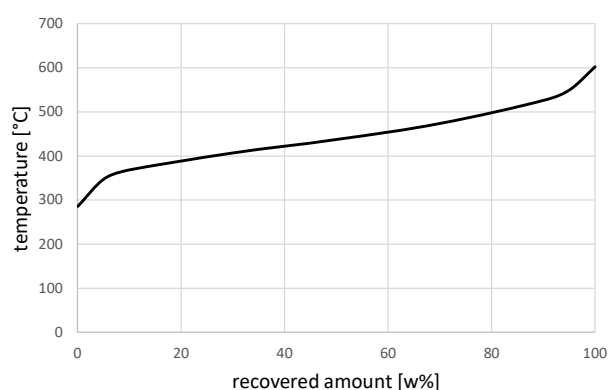|	
density @ 15 °C	890 kg/m³
sulphur	214 mg/kg
nitrogen	143 mg/kg
nickel	2 mg/kg
vanadium	2 mg/kg
aromatics	32.6 w%

Figure 3: Distillation curve of VGO

For comparison three different catalysts were chosen, which are all zeolite-based. Zeolites are alum silicates, which are minerals that constitute of mainly silicon oxide (SiO_2) and aluminum oxide (Al_2O_3). Additionally, all 3 catalysts are rare earth-doped (lanthanum oxide and cerium oxide). However, two of them enhance gas production, one C3 and the other C3 and C4, respectively. For the first one propylene is the dominant desired product while the second one promotes butene and butane production as well. The third catalyst is a heavy residue catalyst, which focuses on improved gasoline production and less on gases. To make it more resilient against impurities in residues the third catalysts outer layer acts as a trap for vanadium and nickel. This prevents those elements from reaching the inner reactive core of the catalyst particles and reduces catalyst poisoning. All utilized catalysts are equilibrium catalysts that are less reactive than fresh catalysts from the manufacturer. The catalysts used for this work are directly taken out of industrial FCC plants, therefore, enabling a higher comparability of the results from the pilot plant with industrial-sized plants. The particle size distribution of all three catalysts are depicted in figure 4. All distribution densities (q_3) show a monomodal distribution with the mode being between 80 and 90 µm for all three catalysts. The measurements have been conducted utilizing a Mastersizer 2000 particle size analyzer by Malvern Panalytical. A more detailed comparison regarding the catalyst's composition cannot be given at this point due to non-disclosure agreements with the catalyst manufacturers.
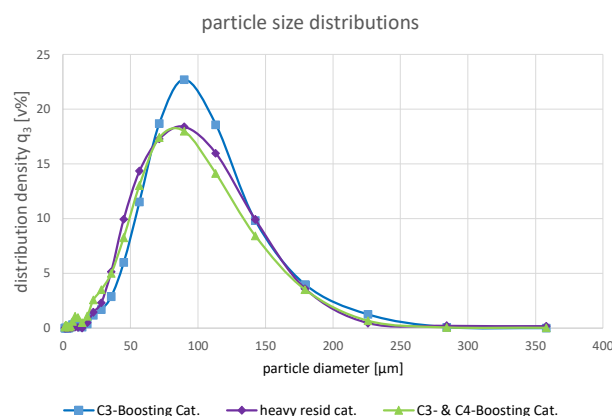

Figure 4: Particle size distribution of catalysts

All experiments were conducted at a constant feed rate of 2.5 kg/h. The medium riser temperatures were 550 °C and 530 °C. In total six different experimental runs were conducted (see table 5). The shown mean values consist of at least three independent measurements.

Table 5: experimental settings

feed rate [kg/h]	catalyst	Riser-temp. [°C]
2.50	C3-Boosting cat.	550
2.50	heavy resid cat.	550
2.50	C3- & C4-Boosting cat.	550
2.50	C3-Boosting cat.	530
2.50	heavy resid cat.	530
2.50	C3- & C4-Boosting cat.	530

Results

The experimental results showed a clear indication that the selection of catalysts is one of the most significant parameters to influence the products spectra of the FCC-process. In figure 5 the results of all three catalysts at a medium riser temperature of 550 °C are depicted. For graphical purposes and since they are both undesirable products the LCO and residue lump are shown together.

It can be seen that the results for the C3 boosting catalyst and the C3 & C4 boosting catalyst are very similar, while the heavy residue catalyst shows significantly different numbers. These findings were expected since the utilized catalysts are designed for different purposes. The gas and gasoline lumps for the gas boosting catalysts are around 39 and 45 w%, respectively. While the lumps for the heavy residue catalyst are around 26-27 w% for gas and 56 w% for gasoline. However, regarding the conversion the differences are much smaller with 82.6 w% for the heavy residue catalyst being the lowest and 84 w% for the C3 & C4 boosting catalyst being the highest. The LCO + residue numbers are between 10 and 12 w% with the lowest value for the heavy residue catalyst which is expected for it is designed to maximize cracking of heavier compounds like residue and LCO. The coke produced was between 4.6 and 5.7 w% with the highest value obtained for the C3 and C4 boosting catalyst.
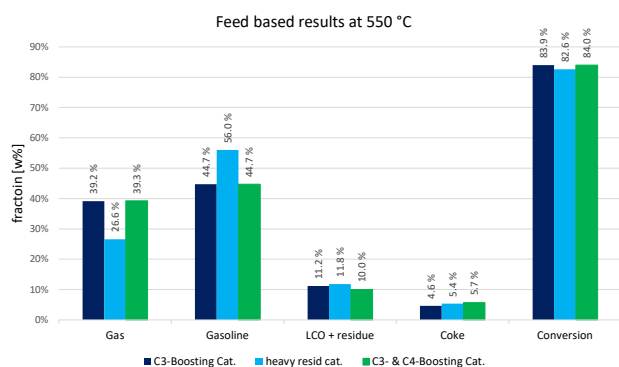
Figure 5: Produced lumps at 550°C Riser-T depending on utilized catalyst

In figure 6 the same product lumps are depicted but at a lower medium riser temperature of 530 °C. Lower riser temperatures usually lead to less cracking reactions. This leads to higher amounts of liquid products and lower amounts of coke and gas. This general assumptions were fulfilled in the experiments for all three catalysts. Additionally, the conversion with values between 81,1 and 82,6 w% declined for all catalysts since the reduction of gas was not completely compensated by the rise in gasoline.
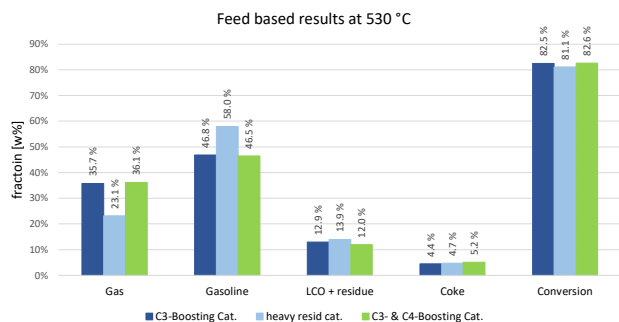

Figure 6: Produced lumps at 530°C Riser-T depending on utilized catalyst

Beside the high-octane gasoline, olefins are the second major products of an FCC unit. So the olefins were analyzed more in detail to evaluate the catalysts influence on these economic viable products. Ethylene and Propylene were looked at separately while the different butenes were grouped together. The remaining gases, named other gases, are the alkanes. Together the alkanes and alkenes make up the gas lump. Note that, the carbon oxides are not included in this lump since they are not hydrocarbons.

In figure 7 the feed based results of the gas lump are depicted depending on the catalyst used and the riser temperature. Analogue to previous figures the amounts of gas and therefore the olefins decline at lower riser temperatures since less cracking occurs. The values for the C3-boosting catalyst for example decline for ethylene and propylene from 3.5 to 2.9 w% and from 14.5 to 13.2 w%, respectively. However, since the catalyst choice already had a bigger influence than the riser temperature regarding the gas lump, which is naturally also the case for the gas compounds. Especially for ethylene and propylene, these differences are significant since they are one of the most valuable products of an FCC. For the gas boosting catalysts the values for ethylene and propylene are at or above 3 and 13.7 w%, respectively. While for the heavy residue catalyst this numbers diminish to 1.3 and 8.8 w%. Significant differences between the C3 and C3 & C4 boosting catalyst can be seen regarding the other gases. Reason for this is that the C3 & C4 boosting catalyst also boosts butane production

which are grouped together with other alkanes in "other gases".
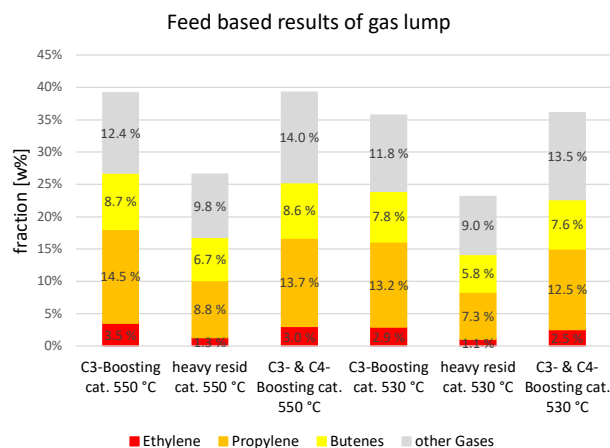

Figure 7: Feed based results of gas lump for depending on riser temperature and catalyst used

Additionally, the gas based values for the above mentioned gases were analyzed to determine the catalysts influence on the gas composition (see figure 8). For all experiments the propylene amounts are above 30 w% with 37.0 w% for the C3 boosting catalyst being the highest value for both riser temperatures. This result is as expected since this catalyst is optimized for propylene production. The least propylene was produced with the heavy residue catalyst with 31.4 w% at 530 °C riser temperature. The ethylene production showed similar results to propylene. For ethylene, the highest values were obtained with the C3 boosting catalyst, especially at 550 °C with 9.0 w%. The lowest numbers were obtained with the heavy residue catalyst, where at a temperature of 530°C 4.6 w% ethylene was obtained.

Contrary to ethylene and propylene, the butenes showed higher values for the heavy residue catalyst. Unaffected by the riser temperature the butene amount was at 25.2 w% while for the gas boosting catalysts the values varied between 21.1 and 22.3 w%. The other gases also showed the highest values for the heavy residue catalyst with a value of 38.9 w% at 530°C riser temperature. The lowest value was obtained for the C3 boosting catalyst at 31.7 w%. Note that the amount of "other gases" increased at the lower riser temperature for all three catalysts.
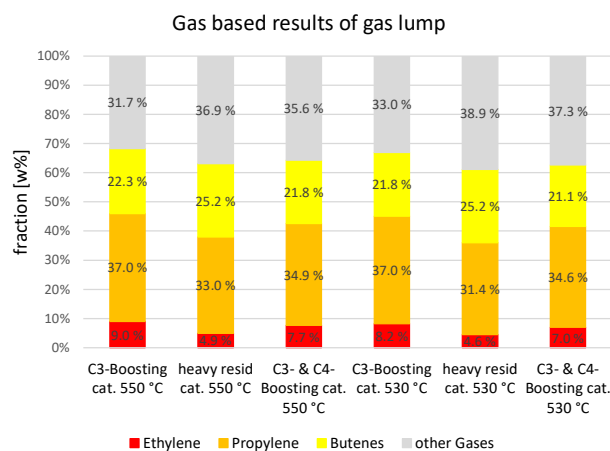

Figure 8: Gas composition depending on riser temperature and used catalyst

To further investigate the catalysts influence on the gas lump the alkanes are depicted in figure 9. The use of the heavy residue catalyst leads to a higher amount of methane

than the other catalysts do. This can be seen for both riser temperatures. The differences in ethane production are not significant. The propane and butane values, however, show that the C3 & C4 boosting catalyst promotes the formation of n-butane and isobutene significantly. The highest amount of isobutane is with 8.1 w% at 550 °C whereas the C3 boosting catalyst only shows a value of 7.0 w% at this temperature. Also the values for n-butane are with 1.4 and 1.3 w%, for 550 °C and 530 °C respectively, slightly higher for the C3 & C4 boosting catalyst than for the other catalysts.
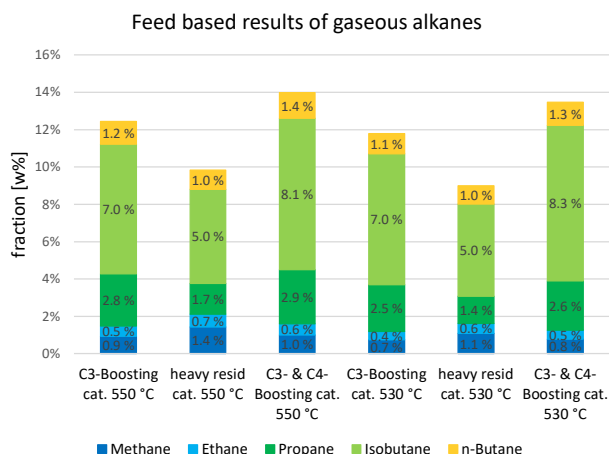

Figure 9: Alkanes in the gas lump depending on riser temperature and used catalyst

Conclusion

The experiments showed that catalyst testing in a pilot plant was possible without changing the test rig making it a test opportunity for new catalyst and temperature combinations just like MATs.

As expected, the gas boosting catalysts showed a significantly higher production of the gas lump than the heavy residue catalyst (around 38 w% compared to 26.6 w% at 550 °C). These zeolite-based catalysts have their advantages in the enhanced propylene production and the C3 & C4 production, respectively. This was observed in the gas product were the propylene enhancing catalyst showed the highest value for propene with 14.5 w% at 550 °C, the highest value for all catalyst and temperature combinations. As propylene is one of the products of the FCC-process with the highest profit margins these types of catalysts are highly in demand from refinery operators.

The heavy residue catalyst has its strength in the cracking of residual feedstocks as the name suggests and the production of higher amounts of gasoline. Consequently, the production of gases is inferior compared to the gas boosting catalysts. However, in a fuel-focused refinery the gasoline amounts of 56 and 58 w% would be favorable, especially when heavier feedstocks are used.

The C3 and C4 boosting catalyst promotes not only the propylene and butene production, although not as good as the propylene boosting catalyst, but also the butane production. The highest value for isobutane was achieved at 550 °C with 8.1 w%. So, when it comes to producing a wide variety of gaseous products that could be used for further synthesis processes, the C3 and C4 boosting catalyst showed the most promising results.

In general, it can be said that the elevation of the riser temperature leads to a higher production in gases and a lower production in gasoline, since higher temperatures lead to more cracking reactions. This basic principle together with the expected shifts on product spectra depending on used

catalysts were observed in the FCC pilot plant proving that catalyst testing in a pilot plant can be an economically sensible method to test future plant configurations and settings before they are implanted in industrial sized plants. These tests can reduce the risks for refinery operators and deliver robust test results that cannot be obtained in such quality from simple batch micro activity tests (MATs).

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