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Influence of the Addition of Zsm-5 on the Products Obtained in Catalytic Cracking

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Abstract

Study of ZSM-5 addition on the performance of a catalytic cracking catalyst industry was achieved by determining the conversion and products yield obtained in the cracking of industrial feed. Yields of products linearly vary with increasing of the amount of ZSM-5 added. Addition of ZSM-5 significantly increases the yield of propylene, gasoline and diesel octane number, but keeps the coke level approximately constant. The study was performed using the ASPEN-HYSYS program, using a model witch reflect a real fluid catalytic cracking plant.

Key words: *catalytic cracking, ZSM-5, octane number, FCC products.*

Introduction

Although started more than 70 years, catalytic cracking process is still the main industrial process for manufacturing gasoline. Therefore there is a constant concern for improving this process. In terms of feed, cracking materials would increasingly heavier, the industrial plant underwent improvements: reactor - riser in two steps [1], separating spent catalyst into three phases [2] or regeneration of catalyst in two or more regenerators [3] were made. The catalyst was the one who has seen the most rapid and radical evolution, from the use of natural clays activated in 1936, until today, when the most catalysts used for catalytic cracking is the type USY or REY. To improve and diversify their performance, different additives were used. Their usefulness is reflected in promotation of coke on the catalyst combustion reactions, passivation of harmful action of compounds contained in feed, the reduction of SO_2 and SO_3 contained by regeneration gases, the reduction of NO_x from flue gas of coke [4].

The product's selectivity of fluid catalytic cracking (FCC) units is one of the main topics to be understood and controlled in order to increase process benefits and comply with mandatory regulations on the compositions of transportation fuels [5]. At present, there is an increasing interest in maximizing propylene yield of FCC units. In 2000, about 34% of the worldwide propylene production was from FCC units. In fact, FCC units have become an important source of light olefins. In the next decade, it is expected that worldwide propylene supply from FCC units will continuously increase. Therefore, both process changes and new catalysts need to be considered together to improve the propylene yield of FCC processes.

For a long time, zeolite ZSM-5 has been employed as a FCC catalyst additive of great industrial importance to improve propylene yield owing to its special pore structure and acidic properties. Generally, to maximize propylene yield, the content of ZSM-5 in FCC catalysts should be increased, but the costs to be paid are the loss of catalyst activity and other desirable products [6].

Positive results were obtained in catalytic cracking additive zeolite (REY and USY) with ZSM-5. The addition of this type of zeolite has the effect of increasing the octane number of gasoline, simultaneously with a decrease by 1-2% volume / unit octane due to cracking reactions that transform C_7-C_{12} paraffin and olefins to *iso*-paraffins and *iso*-olefins C_5-C_7 and product easy to C_3-C_4 olefins and *iso*-butane, used in the manufacture of octanic components such as alkylats or ethers [7].

The literature mentions as additive mordenite or other ZSM types, but the effects on the catalytic performance are minor [8].

The addition of ZSM-5 to an equilibrium catalyst allows the production of significant amounts of light olefins, in particular propene and butene.

In traditional FCC catalysts, zeolite Y provides the major surface area and active sites [9] and thus is the key component that controls catalyst activity and selectivity [10-13]. The usual way to incorporate Y into FCC catalysts is to mechanically bind it with a matrix by a binder alumina, so no chemical bonds are formed between the zeolite and the matrix.

ZSM-5 is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolite. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\bullet 16H_2O$ ($0<n<27$). Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions.

ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings. In these rings, the vertices are Al or Si and an O is assumed to be bonded between the vertices [14].

The pentasil chains are interconnected by oxygen bridges to form corrugated sheets with 10-ring holes. Like the pentasil units, each 10-ring hole has Al or Si as vertices with an O assumed to be bonded between each vertex. Each corrugated sheet is connected by oxygen bridges to form a structure with straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets [15]. Adjacent layers of the sheets are related by an inversion point.

The seats that are occupied by Al have highly acidity. The substitution of Al^{3+} for Si^{4+} site requires the addition of new positive charges. When this is H^+, acidity zeolite is very high.

The estimated pore size of the channel running parallel with the corrugations is 5.4 – 5.6 Å [16].

Experimental

Effect of ZSM-5 addition on the performance of an industrial catalytic cracking catalyst was revealed by determining the reaction conversions and product yields obtained in the cracking of industrial feed in precise reaction conditions. For this we used ASPEN HYSIS, a catalytic cracking process simulation program.

A model was developed to better reflect a fluidized catalytic cracking industrial unit (FCCU).

The model can predict the output variables, namely, product yields (butane, butane, propane, and propene), coke on regenerated catalyst, temperature of the regenerator, conversion and the flue gas composition, for any set of operating or decision variables, namely, feed flow rate, reactor temperature and feed preheat temperature. Table 1 gives the details of the design data of the industrial FCCU studied. The properties of the equilibrium catalyst used in this model are presented in Table 2.

Table 1. Design data for the industrial FCCU

Parameter	Value
Riser length (m)	46.09
Riser diameter (m)	1.34
Regenerator dense bed height (m)	4.583
Regenerator dense bed diameter (m)	8.534
Regenerator interface diameter (m)	8.534
Inventory of catalyst in regenerator (kg)	25000
Feed rate (m^3/h)	316
Reactor pressure (kPa)	140
Regenerator pressure (kPa)	180

Table 2. Equilibrium catalyst properties

V, ppm	297.9
Ni, ppm	344
Na, ppm	1556
Fe, ppm	8203
Cu, ppm	25.0
Catalyst inventory, kg	25000
Fresh make-up rate, kg/h	19100
MAT, %	66.5

As feed, were used vacuum distillate (230 t / h) and coker gas oil (5.75 t / h). The reactor temperature was 520 ^oC. The properties of the feed used in this study are presented in Table 3.

Table 3. Feed properties

Vacuum distillate

Properties of Selected Feed

Name	Feed-1
Feed Type	Generic Feed
API Gravity	23.99
Specific Gravity 60F/60F	0.9100
Distillation Type	D1160
Initial Point [C]	248.0 C
5% Point [C]	280.0 C
10% Point [C]	300.0 C
30% Point [C]	350.0 C
50% Point [C]	401.0 C
70% Point [C]	452.0 C
90% Point [C]	508.0 C
95% Point [C]	531.0 C
End Point [C]	550.0 C
Basic Nitrogen [ppmwt]	0.0000 ppmwt
Total Nitrogen [ppmwt]	0.0000 ppmwt
Total/Basic Nitrogen Ratio	<empty>
Sulfur Content [%]	1.80 %
Fraction of Feed S Processed	0.0000
Conradson Carbon Residue [%]	0.26 %
Ramsbottom Carbon Residue [%]	0.26 %
RI @Specifed T Meas.(Optional)	<empty>
RI Meas. Temperature (Optional) [C]	<empty>
RI @20C Calc. from Lab Data	<empty>
RI @20C Est. from Bulk Prop.	1.51123
Ca Meas.(Optional)	<empty>
Ca Est. from Total Method	16.43
Viscosity, cSt@210F Lab.(Optional)	<empty>
Viscosity, SUS@210F Lab.(Optional)	<empty>

Heavy Coker Gasoil

Properties of Selected Feed

Name	Feed-2
Feed Type	Heavy Coker Ga
Assay	Arab Light
Top Cut Point [C]	345.0 C
Bottom Cut Point [C]	495.0 C
Fraction of Feed S Processed	0.0000
Bulk Properties	
API gravity	24.15
Specific Gravity 60F/60F	0.9091
Basic Nitrogen Content [ppmwt]	197.7
Total Nitrogen Content [ppmwt]	593.0
Total/Basic Nitrogen Ratio	3.000
Sulfur Content [%]	2.27
Conradson Carbon Residue [%]	0.01
Ramsbottom Carbon Residue [%]	0.07
RI @20C Est. from Bulk Prop.	1.50987
Viscosity, cSt@210F Est.	5.895
Ca Est. from Total Method	19.39
Nickel Content [ppmwt]	4.718e-009
Vanadium Content [ppmwt]	0.0000
Iron Content [ppmwt]	0.0000
Copper Content [ppmwt]	0.0000
Sodium Content [ppmwt]	0.0000
Distillation Data	
D2887 Initial Point [C]	328.0
D2887 5% Point [C]	338.8
D2887 10% Point [C]	349.5
D2887 30% Point [C]	383.9
D2887 50% Point [C]	416.0

Results and Discussions

Increasing the amount of ZSM-5 added to catalyst produces a decrease of diesel and gasoline yield and an increase of conversion and also *n* - butane, butene, propane, propylene yields. Slightly decreases of the coke deposited on the catalyst could be considered mostly constant.

Products yields linearly vary with ZSM-5 adding.

Most pronounced increase is registered in propylene and butene yield, followed by *iso*-butane yield, conversion and *n*-butane yield.

Normal butane yield don't varies so much. So, the addition of ZSM-5 increase its yield from 1.384 to 1.402% wt that is equivalent to an increase of 1.28% (Fig. 1).

For *iso*-butane (Fig. 2), we get a fairly large increase in yield (17.78%) the addition of 0.08 mass units of ZSM-5 per unit mass of catalyst, meaning a variation of 3.7%wt. to 4.5% wt% *iso*-butane.

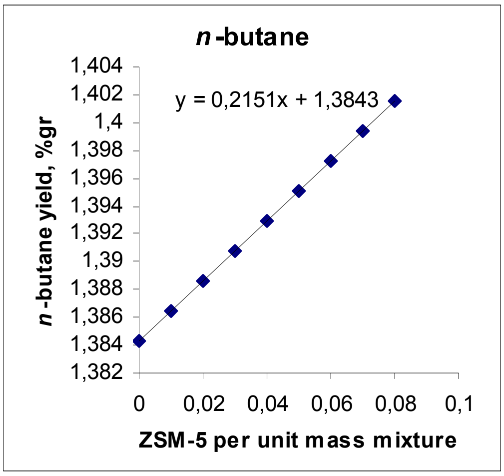

Fig. 1. Increasing *n*-butane yield at ZSM-5 adding

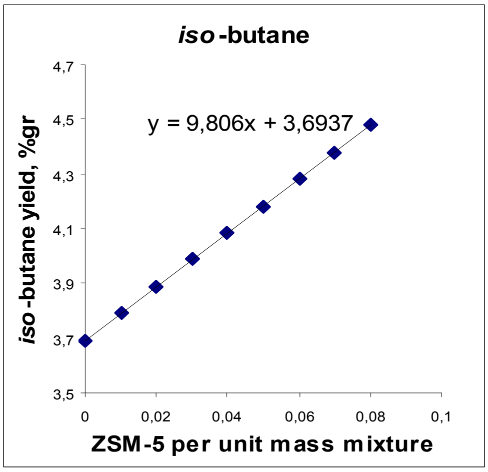

Fig. 2. Increasing *iso*-butane yield at ZSM-5 adding

A very small effect is felt on the conversion (Fig. 3). The addition of 0.08 units of ZSM-5 mass per unit mass of mixture, determine an increase in conversion of only 0.2% wt.

For propane (Fig. 4) it's observed a 13.17% increase in a variation of 0.08 ZSM-5 units of mass per unit mass of the mixed catalyst.

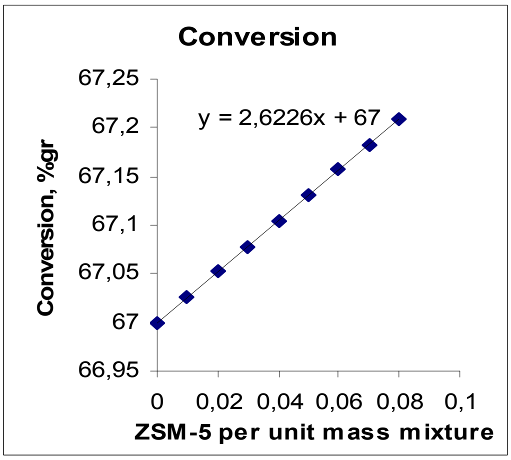

Fig. 3. ZSM-5 effect on conversion

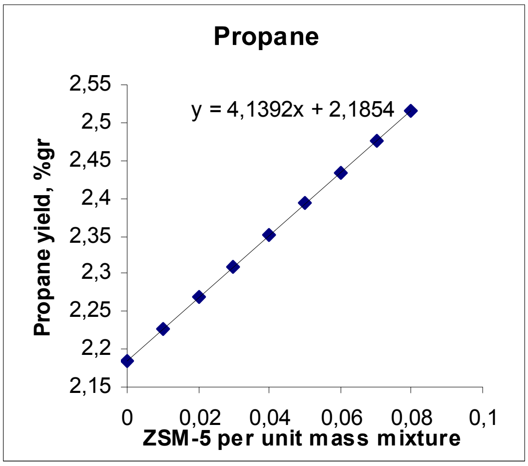

Fig. 4. ZSM-5 effect on propane yield

Strongest effect is observed on the yield of propylene (Fig. 5), which almost doubles the addition of 0.08 units per unit mass of ZSM-5 catalyst mixture mass. It is recorded as an increase from 5.12% wt properly without cracking on ZSM-5 catalyst at 8.97% wt, maximum value coresponding at ZSM-5 addition to catalytic cracking catalyst.

And the effect is obvious for butene, resulting in an increase from 6.49% wt to 8.71 % wt of yield that means an increase of 25.49% (Fig. 6).

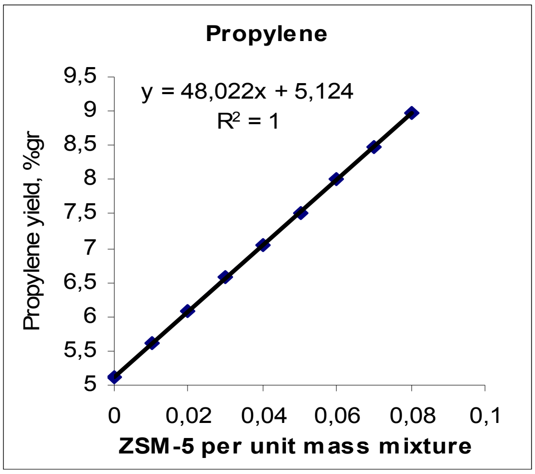

Fig. 5. ZSM-5 effect on propylene yield

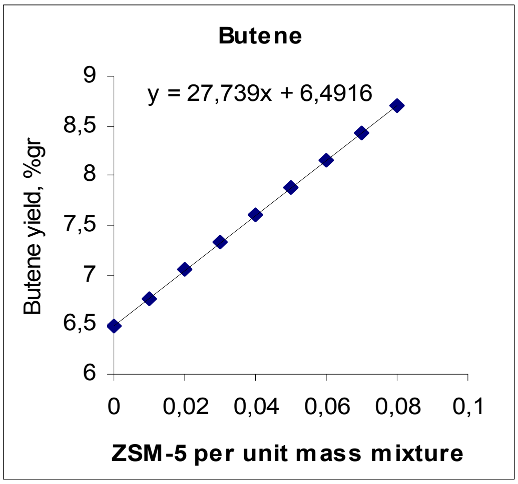

Fig. 6. ZSM-5 effect on butene yield

Yield of coke is very little affected by the addition of ZSM-5 (Fig. 7). Thus, an increase of 0.08 units of ZSM-5 mass per unit mass of mixture of catalyst is decreased from 4.02% to 4.01%, representing a difference of only 0.25%, which can be condiered that ZSM-5 has no effect on coke yield.

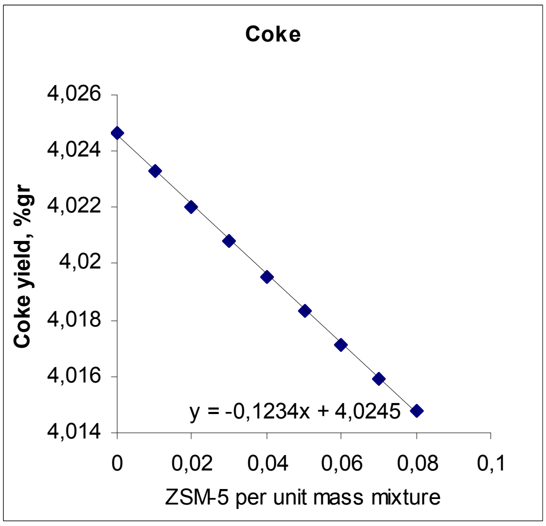

Fig.7. ZSM-5 effect on coke yield

The amount of diesel drops by 1.16% to 0.08 units of mass variation with ZSM-5 per unit mass of mixture (Fig. 8). Thus, the yield of diesel varies between 17.30%wt. and 17.10%wt.

An increase of 0.08 ZSM-5 mass units per unit mass of the mixture produces a decrease in gasoil yield from 38.38 to 31.38%wt. (Fig. 9), this being equivalent to a decrease of 18.22% in efficiency.

The most important is the increase of gasoline octane number (RON). Thus, using only the catalytic cracking catalyst free ZSM-5, would get an octane rating of 94.07 and added 8% ZSM-5 produces an increase in octane number to 96.73 (Fig. 10). The increase is linear and occurs at a rate higher gasoline (C5-265 fraction F) than light diesel oil (fraction 265-430 F).

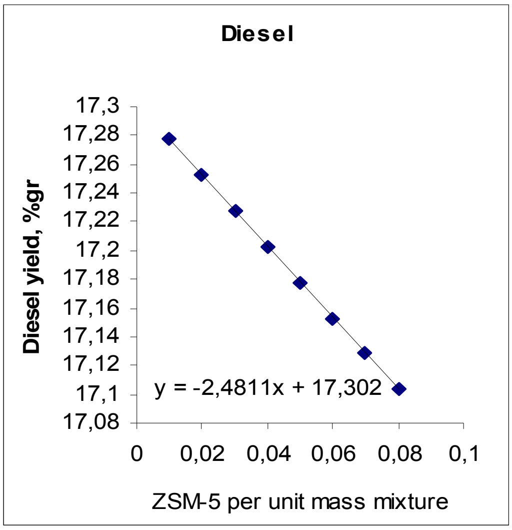

Fig .8. ZSM-5 effect on diesel yield

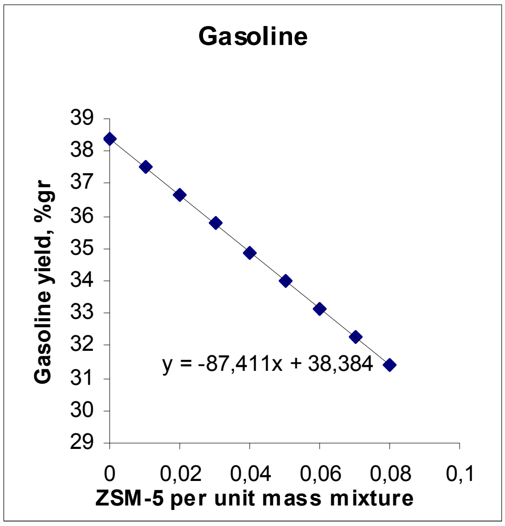

Fig. 9. ZSM-5 effect on gasoline yield

Catalytic cracking gasoline contains parrafins, olefins, naphthenes and aromatics. Addition of ZSM-5 at catalytic cracking catalyst is felt most strongly in the growth rate of aromatics than naphthenes (Fig. 11).

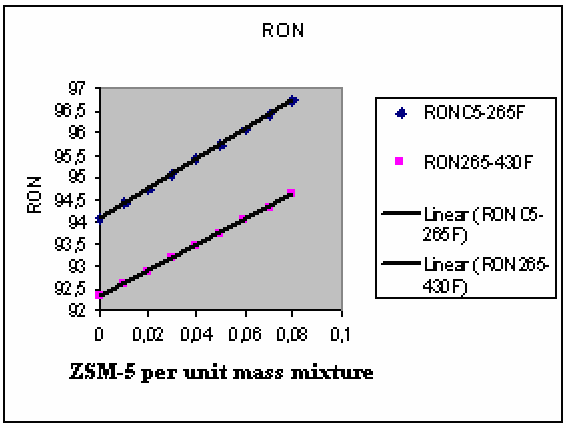

Fig.10. ZSM-5 effect on RON

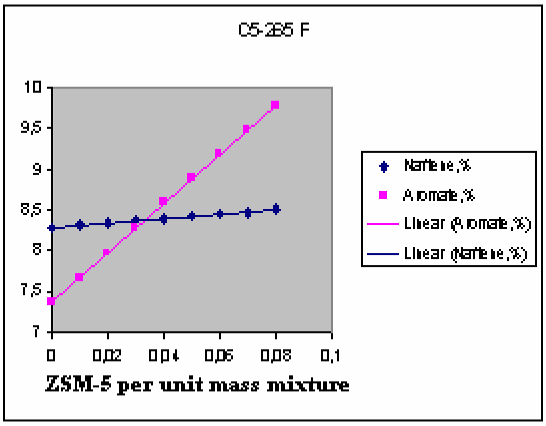

Fig.11. Increasing the percentage of aromatic and naphthenes of gasoline obtained with the amount of ZSM-5 in cracking catalyst

Simulation of catalytic cracking process using ASPEN-HYSYS program shows a 32.56% increase to the percentage of aromatics from catalytic cracking gasoline using an amount of up to 8% ZSM-5 added in mass echilibrium catalysts (Table 4).

Table 4. Effect of ZSM-5 on catalytic cracking product yields

ZSM on unit mass catalyst	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.00
Naphtenes, %	8.50	8.48	8.45	8.43	8.40	8.37	8.35	8.32	8.29
Aromatics, %	9.77	9.47	9.17	8.87	8.58	8.28	7.98	7.68	7.37
Olefins, %	53.04	53.04	53.03	53.02	53.02	53.01	53.00	53.00	52.99

Conclusions

The effect of ZSM-5 addition on the performance of an industrial catalytic cracking catalyst was revealed by determining the reaction conversions and product yields obtained in the cracking of industrial feed in precise reaction conditions. The experimental results were obtained using an ASPEN HYSIS simulation. For this we created a model to reflect better a real fluidized catalytic cracking industrial unit (FCCU).

Increasing the amount of ZSM-5 added to the mixture per unit mass of catalyst decreases the yield of diesel and gasoline, and increase the yield of butane, butene, propane, propylene and conversion. Yields of products vary linearly with the amount of ZSM-5 added.

An important effect of the ZSM-5 adding is the increase gasoline octane number. The increase is linear and occurs at a rate higher gasoline than light diesel oil.

Effect of the addition of ZSM-5 is felt most strongly in increasing the percentage of aromatics from catalytic cracking gasoline.

The major effects of the addition of ZSM-5 are:

○ increases of propylene yield;

○ gasoline octane number growth;

○ to maintaining coke constant.

We used real data for feed and for designing the fluidized catalytic cracking industrial unit. Using these data, the program allow an amount of maximum 8% ZSM-5 added per unit mass of catalyst, which is enough because the industrial units used to introduce between 2 and 5 ‰ ZSM-5 per unit mass of catalyst.

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Influența adaosului de ZSM-5 asupra produselor obținute prin cracare catalitică

Rezumat

Studiul adaosului de ZSM-5 asupra performanțelor unui catalizator industrial de cracare catalitică a fost realizat prin determinarea conversiei şi a randamentelor produselor de reacție obținute la cracarea unei materii prime industriale. Randamentele de produse variază liniar la creşterea cantității de ZSM-5 adăugate.

Adaosul de ZSM-5 creşte semnificativ randamentul de propenă, cifra octanică a benzinei şi a motorinei şi menține cocsul la nivel constant. Studiul a fost efectuat cu ajutorul programului ASPEN-HYSYS, utilizând un model care să reflecte cât mai fidel o instalație industrială de cracare catalitică.