

Effect of hydrotreating FCC feedstock on product distribution

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Abstract

The demand of low-sulfur fuels has been increasing during the last 20 years due to environmental concerns about SO_x emissions from processing plants and engines. Due to its high contribution to the gasoline pool, hydrotreating fluid catalytic cracking (FCC) feedstock offers several advantages, such as the increase of conversion and yields of gasoline and liquid-phase gas, meanwhile sulfur content in fuels is diminished. However, there are more important factors to be considered when hydrotreating FCC feedstock.

In this work, two FCC feedstocks, typical and hydrotreated, were converted in a microactivity test (MAT) reactor, as described by ASTM D-3907-92, at different severities and using two commercial catalysts. Feedstock conversion, product yields and selectivity to valuable products were compared against industrial-scale results predicted by using commercial FCC simulation software. Expected increment in conversion and yield to profitable products was observed when hydrotreated feedstock was used; simulation results follow acceptably MAT results. Some recommendations are given for looking closely at the overall behavior (riser–regenerator), using reliable kinetic models and simulation programs.

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Keywords: Catalytic cracking; Feedstock hydrotreatment; MAT reactor; Product selectivity; Simulation

1. Introduction

Often, fluid catalytic cracking (FCC) is the primary conversion process in an integrated refinery, playing a key role in the refinery's profitability. The successful operation of this unit determines whether or not the refiner can remain competitive in the market. An issue that has been gaining importance in the refining industry comes from the fact that the demand of low-sulfur distillates has been increasing during the last 20 years due to the environmental concern about SO_x emissions. FCC feedstock's sulfur content is becoming too high and, consequently, FCC liquid products contain excessive sulfur compounds that need to be treated prior to being used. Worldwide, about 45% of all gasoline comes from FCC and ancillary units; moreover, about 90% of the sulfur in the gasoline pool is supplied by the FCC unit.

An interesting solution is the hydrotreatment (HDT) of the FCC feedstock. There is some industrial concern about the advantages of feedstock hydrotreatment, mainly because this operation needs high investment. Nevertheless, in addition to the aggregated environmental and economic value due to the production of cleaner fuels, there are also increments in yields to valuable products. This situation is consequence of several factors, such as the higher catalytic activity, consequence of the minor amount of metallic pollutants, and the better selectivity to liquid fuels that are obtained when a hydrogen-enriched feedstock is used [1–3]. Also, sulfur oxides emission by the regenerator is diminished.

The main objective of this work is to compare, experimentally, conversion and yields during catalytic cracking of a typical and a hydrotreated feedstock in a MAT reactor. Then, some simulations are performed, using commercial software, in order to extrapolate these results to an industrial scale FCC unit.

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- The ratio (i-butane/butylenes) increases, which correlates to better selectivity to gasoline because of a diminishing of overcracking [1,6].

During HDT, difficulty in the elimination of the aforementioned pollutants depends on the operation severity, following the next sequence: metals < sulfur < nitrogen < aromatics.

It is important to note that there is an economic optimum limit to HDT severity. As severity is increased, it comes to a point where the introduction of more hydrogen to the feedstock does not improve the yield to FCC gasoline. Hence, as sulfur reduction has become essential for meeting quality specifications of fuel products, finding a point of equilibrium between feedstock hydrotreatment and profitable yields has acquired growing industrial importance.

2. Process emulation

In this work, a typical feedstock for an industrial FCC unit was hydrotreated in a hydrodesulfurization unit for gas oils; properties of the typical (TF) and the hydrotreated feedstock (HF) were measured (Table 1). As it is possible to note, the effects of hydrotreating include decrease of density, viscosity and refraction index; this is consequence of the change of hydrocarbon type distribution where aromatics diminished and paraffins and naphthenes increased. Also, microscopic coke precursors (Conradson carbon) are diminished.

TF and HF were converted using two equilibrium industrial catalyst samples, named C1 and C2. Catalysts properties and measurement methods are given in Table 2. It is important to note that the microactivity test (MAT) conversion, named MAT activity, of both catalyst differs in 11.5 wt.%. High-activity catalysts tend to increase conversion, coke and LPG, not affecting much olefins or light gas yields [1]; in contrast, low-activity catalysts tend to maintain constant gasoline yields.

There are two important ways to infer the results of industrial operation at limited range of operating conditions. The first one is the emulation of the contact time for a given

Table 2
Catalysts properties

Property	C1	C2
Density (g/cm ³)	1.0531	0.9852
Specific area (BET) (m ² /g)	88	128
Average particle size (μm)	65	53
Equilibrium MAT activity (ASTM-D3907-92) (wt.%)	55.6	67.1
Metals content (AA, IMP-QA-031)		
Cu (ppm)	18.02	23.23
Fe (wt.%)	0.62	0.56
Na (wt.%)	0.72	0.74
Ni (ppm)	372.05	473.28
V (wt.%)	0.12	0.26

catalyst-to-oil (C/O) ratio [5]. One of the most popular ways to perform this emulation is the microactivity test (MAT) reactor (ASTM D-3907-92).

TF and HF (Table 1), which are obtained from the refining of a mixture of Mexican crude oils, were tested in a standard MAT reactor. For both feedstocks, experiments were carried out at two different temperatures (520 and 550 °C), and three different C/O ratios (3, 4 and 6). Each experiment was carried out with catalysts C1 and C2. Catalyst amount in the reactor was 4 g, feedstock injection rate was 1.3 g/min and its injected amount was varied in order to emulate different C/O ratios. Liquid products were quantified by simulated distillation according to the ASTM procedure D-2887, gaseous products were analyzed using an on-line gas chromatograph and coke on catalyst surface was quantified on an elemental carbon analyzer.

3. Process simulation

Another option to predict the behavior of an industrial unit under different operating conditions is computer simulation. In this work, a commercial simulator (FCC-Sim [9]) was used to predict the performance of a commercial FCC unit. FCC-Sim is a steady-state simulation tool, widely used around the world, based on engineering framework. It simulates the riser–regenerator system, following heat and mass balances at the required operating conditions. Among its features there are kinetic models for riser and regenerator, as well as a catalyst deactivation function.

After a careful chosen, operating test run from an industrial unit provides data that are used to adjust (*calibrate*) the theoretical model. Then, simulator correlation parameters are automatically fitted to these operating points allowing predictions to changes in operating conditions, catalyst and/or feedstock.

The simulator FCC-Sim is based in consistent mass and energy balances, and extrapolations come from sound correlations. Nevertheless, predictions accuracy degrades as the new operating conditions are far from the original operating point.

An industrial operating point was used as test run data for the calibration of FCC-Sim using TF and catalyst C2. Some

Table 1
Feedstock properties

Property/feedstock	TF	HF
Density (g/cm ³ , 20 °C, ASTM D-1298)	0.9071	0.8887
Viscosity (cSt, 40 °C, ASTM D-88)	37.57	58.46
RI (20 °C, ASTM D-1218)	1.505	1.496
Conradson carbon (wt.%, ASTM D-524)	0.14	0.05
Sulfur (wt.%, ASTM D-2622)	1.452	0.14
Basic nitrogen (ppm, ASTM D-4629)	233	67
Composition (P/N/A)	62/20/18	65/21/15
H ₂ content (wt.%)	13.07	13.83
Distillation data (ASTM D-2887)		
10 vol.% (°C)	367	366
50 vol.% (°C)	449	463
90 vol.% (°C)	528	541

Table 3
Characteristics of the FCC unit and operative parameters

Type	Riser reactor/adiabatic regenerator
Regenerator-operating mode	Complete combustion
Feedstock capacity (BPD)	25000
Outlet riser temperature (°C)	519
Preheat temperature (°C)	183
Regenerator dense-phase temperature (°C)	663
Regenerator dilute-phase temperature (°C)	689

important characteristics of this industrial unit are given (Table 3), along with operating data used for calibration. Once calibration was performed, predictions were carried out at three riser outlet temperatures (520, 535 and 550 °C), two of them used in MAT experiments, using TF and HF as well as C1 and C2.

4. Results and discussion

Conversion and product yields from MAT experiments were compared against results obtained using the simulation software for TF and HF. As expected, conversion of feedstock is improved by feedstock hydrotreating; this effect can be noticed with both catalysts. In the case of catalyst C1, there is a conversion improvement of 9 wt.% at 520 °C, and C/O of 6, and an even higher increment of 16 wt.% units at 550 °C and C/O of 3 (Fig. 2). These differences in conversion are also predicted by simulation results that follow almost the same trend for C/O = 6. It is evident that

simulated conversion reports a shift that is similar to the laboratory ones, when changing from TF to HF. The simulated temperature effect is also similar to average MAT results. Due to the lack of industrial reference data, the simulated results should be taken with care, considering that they depend on the software extrapolation capabilities.

Additionally, it is important to take into account that C/O industrial values are not shown here, as they are not comparable to MAT values. In industrial practice, this parameter is defined from heat balance with values from 6 to 14.

Catalyst C2 is more active and presents higher MAT activity, as shown in Table 2. For hydrotreated feedstock, conversion exhibits different improvement ranges but similar behavior, since the highest increase (11 wt.%) is observed at C/O of 3 and the lowest (2 wt.%) at C/O of 6 (Fig. 3). Simulation predicts also similar conversion values and temperature effect that MAT results when using TF. However, predicted industrial conversions are higher than MAT values when HF is used, even if temperature effect is closely followed.

Conversion is not the only variable to look at in FCC, the main point of interest is the production of gasoline. In the case of catalyst C1, differences in gasoline yields are about 6 wt.% for any C/O ratio at 520 °C and about 13 wt.% at 550 °C (Fig. 4), both favorable to hydrotreated feedstock, due to its higher crackability [3]. It is important to note, again, that simulator tends to estimate higher HDT benefits than MAT. Another important difference is that MAT data at 550 °C exhibit a decrease in gasoline yield for C/O = 6, which is probably due to overcracking [1]; however,

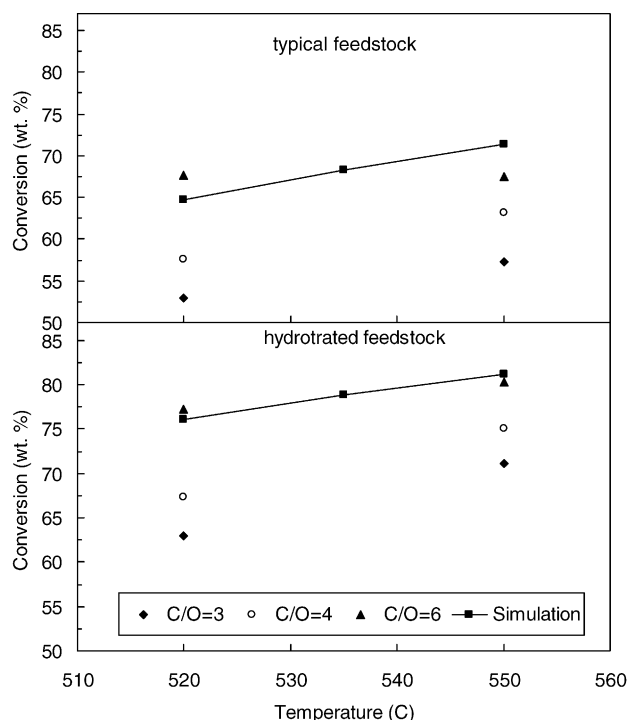


Fig. 2. Conversion of TF and HF on C1.

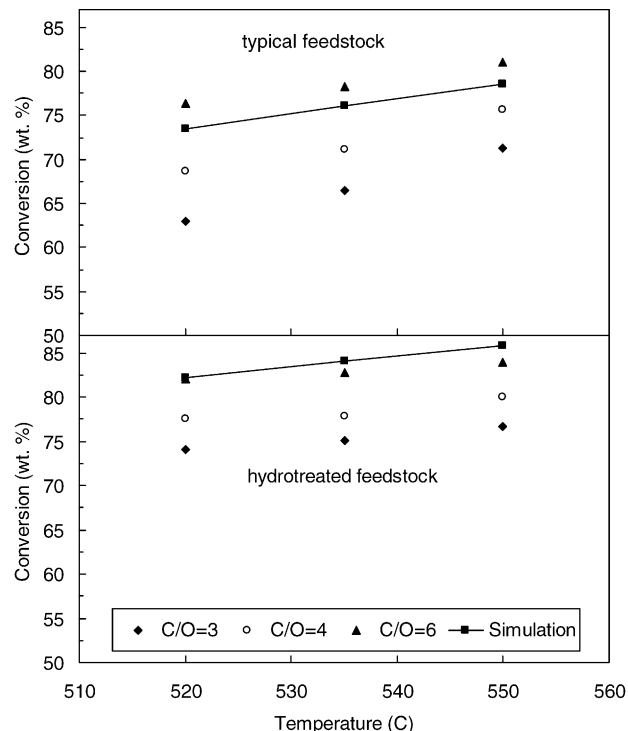


Fig. 3. Conversion of TF and HF on C2.

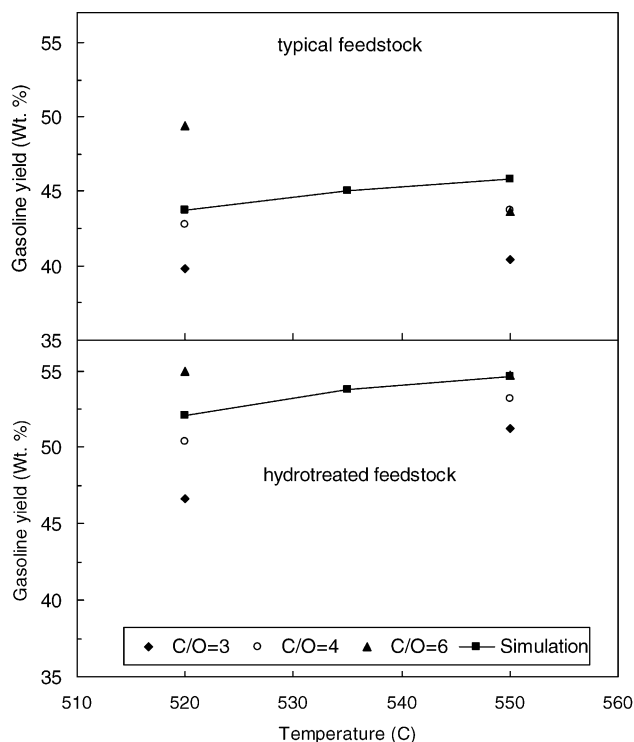


Fig. 4. Yield to gasoline of TF and HF when using C1.

simulation only exhibits a change of slope but does not reach this phenomenon.

As opposed, in the case of catalyst C2, the increase in gasoline yields is greater at 520 °C (about 8 wt.%) than at

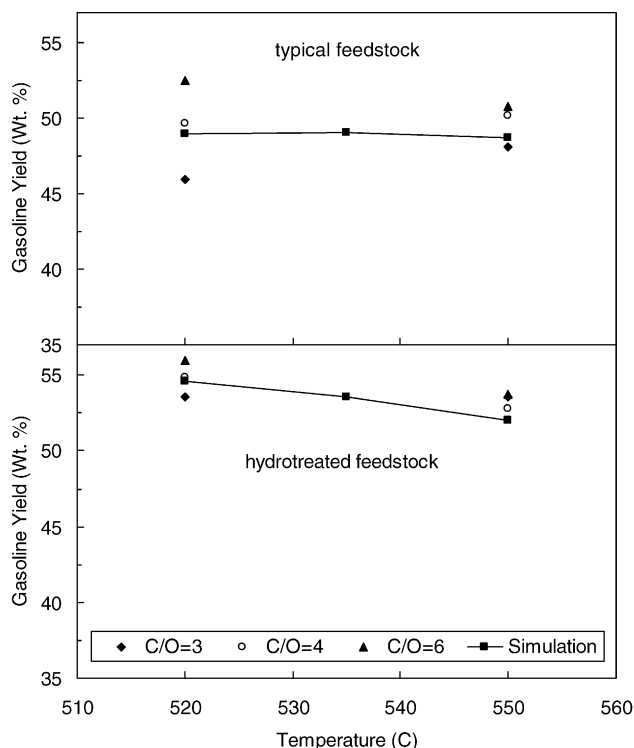


Fig. 5. Yield to gasoline of TF and HF when using C2.

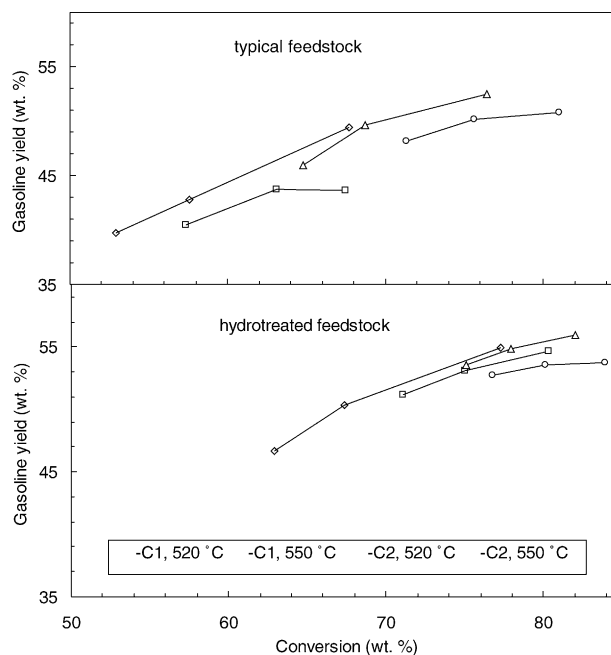


Fig. 6. Yield to gasoline as function of conversion at different C/O ratios: (◇) C1, 520 °C; (□) C1, 550 °C; (△) C2, 520 °C; (○) C2, 550 °C.

550 °C (about 3 wt.%) (Fig. 5), both favorable to hydro-treated feedstock. In this case, the more interesting behavior is that simulation predicts overcracking of gasoline for both feedstocks in the experimental temperature range. This prediction is due to the high initial MAT activity of the equilibrium catalysts, in contrast to C1 that exhibits very low MAT activity [1].

Gasoline yield is closely related to conversion, which is very dependent on catalyst selectivity, at specific reaction conditions. For hydrotreated feedstocks, catalyst selectivity may be more relevant as compared with conversion, again at otherwise specific conditions. Considering uncertainty from experimental errors, gasoline selectivity is considered similar for both catalysts (Fig. 6).

One key concern during FCC operation is coke formation. Coke attaches to the catalyst surface, blocking the catalytic sites and decreasing catalyst activity. Also, this entity regulates the energy balance of the whole unit, and as the feedstock is heavier as it is possible to form higher amounts of coke that increase regeneration temperatures [1]. Higher temperatures could mean faster catalyst deactivation, also. It is not possible to compare MAT coke yields to industrial simulation ones because

Table 4
Coke production for both catalysts at different severities (wt.%)

	C/O = 3		C/O = 4		C/O = 6	
	520 °C	550 °C	520 °C	550 °C	520 °C	550 °C
TF + C1	2.27	2.63	2.58	3.38	3.64	4.66
HF + C1	2.17	2.23	2.65	2.66	3.48	3.71
TF + C2	3.83	4.08	4.62	4.91	6.60	7.08
HF + C2	3.33	3.36	3.99	4.01	5.53	5.49

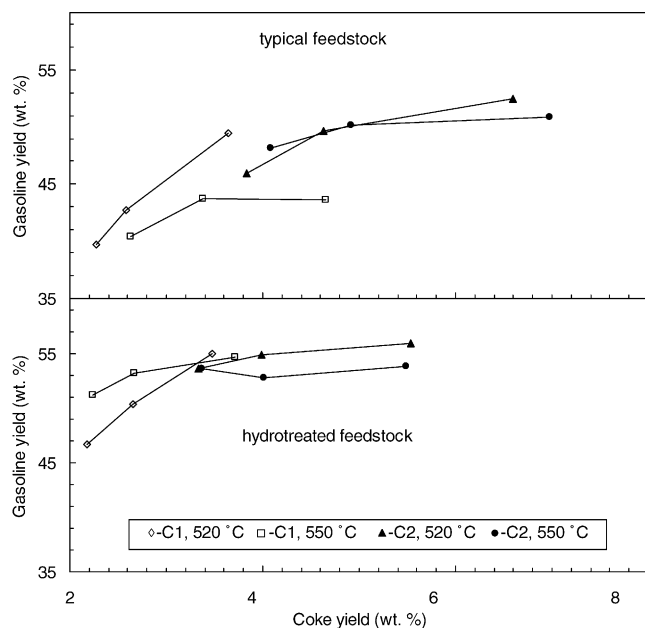


Fig. 7. Yield to gasoline as function of coke yield at different C/O ratios: (◇) C1, 520 °C; (□) C1, 550 °C; (▲) C2, 520 °C; (●) C2, 550 °C.

coke yield behaves very different in laboratory reactors [10]. After feedstock hydrotreating, coke precursors are diminished as can be noticed when catalyst C1 is used (Table 4), coke yield decreases as much as 1 wt.% at 550 °C and C/O = 6. It is important to notice that coke yield is almost proportional to C/O ratio for the typical feedstock, whereas its increase is significantly lower for the hydrotreated one. This is the consequence of the decrease of coke microscopic precursors because of HDT. As it was seen before, higher C/O ratios mean higher conversion and higher gasoline yield, at constant temperature, as long as overcracking is not attained.

Table 5
Light products yields and composition at 520 °C, using catalyst C1 (wt.%)

Feedstock	C/O = 4		C/O = 6		Simulation	
	TF	HF	TF	HF	TF	HF
Dry gas						
Hydrogen	0.11	0.08	0.14	0.12	0.08	0.09
Methane	0.30	0.24	0.43	0.48	1.03	1.27
Ethylene	0.32	0.28	0.43	0.52	0.78	0.95
Ethane	0.16	0.20	0.29	0.31	1.00	1.22
Total	0.88	0.80	1.29	1.44	2.89	3.54
LPG						
Propane	0.35	0.43	0.47	0.62	1.02	1.41
Propylene	2.91	3.61	3.80	4.83	2.70	3.72
i-Butane	2.06	2.76	2.72	4.02	2.42	3.18
n-Butane	0.36	0.46	0.50	0.73	0.98	1.29
1-Butene	0.93	1.11	1.18	1.54	0.93	1.22
i-Butylene	1.16	1.30	1.39	1.62	1.06	1.40
t-Butylene	1.18	1.41	1.51	1.98	1.00	1.31
c-Butylene	0.89	1.05	1.14	1.50	0.81	1.06
Total	11.32	13.31	13.36	17.42	10.95	14.64

It is possible to note from these data that when using hydrotreated feedstock higher C/O ratios are reachable, whereas with typical feedstock this condition produces too high amounts of coke. This is a well-known benefit coming from HDT in industrial FCC operation, which means economic profit allowing higher severities and conversion levels, as well as longer catalyst life.

In the case of catalyst C2 (Table 4), which is more active, the difference in coke yield is more evident. For the typical feedstock, yields reach 7 wt.% at 550 °C and C/O = 6, which is very high for MAT laboratory reactors. This situation, when extrapolated to the industrial unit, could translate into operating problems due to high regeneration temperatures [1]. As it is possible to note, for hydrotreated feedstock coke yield remains at constant level; this situation benefits the operation and increases profitability as stated before.

The second more important motive to avoid excessive coke production is that this entity diminishes yield to gasoline due to the decreasing of conversion. For typical feedstock there is a maximum of gasoline yield of about 54 wt.%; in contrast, hydrotreated feedstock exhibits a maximum of about 56 wt.% in gasoline yield, and lower yield to coke (Fig. 7). Lines are more separated in the case of typical feedstock than in the case of hydrotreated feedstock. This is due to the fact that activity is less decremented when coke yield changes are smaller. This is an additional advantage of feedstock hydrotreating.

Currently, there are other interesting products from FCC units, LPG, especially C₃ and C₄ olefins. Because of the partial opening of poly-nuclear hydrocarbons, production of these molecules is favored by hydrotreating also. This is an important difference, because propane is used as fuel, propylene is a feedstock for petrochemicals, i-butane is a feedstock for downstream processes and the rest of C₄ olefins are valuable products. Therefore, a change in LPG

Table 6
Light products yields and composition at 520 °C, using catalyst C2 (wt.%)

Feedstock	C/O = 4		C/O = 6		Simulation	
	TF	HF	TF	HF	TF	HF
Dry gas						
Hydrogen	0.22	0.17	0.26	0.19	0.09	0.09
Methane	0.53	0.49	0.69	0.62	1.37	1.61
Ethylene	0.50	0.48	0.64	0.62	1.03	1.21
Ethane	0.33	0.35	0.39	0.38	1.33	1.53
Total	1.58	1.49	1.98	1.80	3.81	4.47
LPG						
Propane	0.66	0.75	0.81	0.87	1.36	1.80
Propylene	4.16	4.64	4.87	5.18	3.59	4.74
i-Butane	3.38	4.38	4.16	5.00	3.28	4.13
n-Butane	0.67	0.83	0.84	0.97	1.30	1.64
1-Butene	1.24	1.39	1.40	1.49	1.23	1.55
i-Butylene	1.31	1.28	1.35	1.28	1.41	1.77
t-Butylene	1.60	1.80	1.81	1.95	1.33	1.67
c-Butylene	1.20	1.35	1.37	1.46	1.07	1.35
Total	14.84	17.63	17.16	18.74	14.62	18.69

Table 7
i-Butane/butylenes ratios

	C/O = 4		C/O = 6	
	TF	HF	TF	HF
C1	0.49	0.57	0.52	0.61
C2	0.63	0.75	0.70	0.81

yields and distribution of products means profit. Dry gases (H_2 , C_1 and C_2) also exhibit changes of weight distribution when using hydrotreated feedstock.

For catalyst C1, a comparison of light products composition is given in Table 5 for C/O ratios of 4 and 6 at 520 °C. Simulation results are also shown for both, TF and HF. The first important point to note is that LPG production is increased in both experimental cases; similarly simulation also predicts an increase of this product when HF is used.

Dry gas is expected to decrease after hydrotreating of the feedstock [1]. For C1 catalyst this is the case at low severities, however at higher severities dry gas increases. Because of the low amounts produced in the MAT reactor, this unexpected behavior could be the consequence of experimental error. Simulation also predicts higher production of this product when using HF.

For catalyst C2, a comparison of light products composition is given in Table 6 for C/O ratios of 4 and 6 at 520 °C. Simulation results are also shown for both, TF and HF. For this catalyst, every compound in the LPG fraction is increased when HF is used, which means profit. In contrast to catalyst C1, for both laboratory-operating conditions (C/O = 4 and 6) dry gas exhibits minor production when using HF,

nevertheless simulation predictions show an increase in dry gas production when shifting from TF to HF.

In addition to the increase in LPG yield, it is possible to confirm the better yield to gasoline by the (i-butane/butylenes) ratio, as proposed in [1,6]. This index is proportional to the yield to gasoline, due to a decrease of overcracking. Table 7 shows this ratio at 520 °C for the yield to gasoline obtained in the MAT reactor (Tables 5 and 6).

As it is possible to note, for catalyst C1, the (i-butane/butylenes) ratio increases when the feedstock is changed from TF to HF. The same is true for catalyst C2, which also exhibits large values of the (i-butane/butylenes) ratio (Table 7). This ratio is proportional to the increase in yield to gasoline, and, this improve is larger for the catalysts with the higher activity.

All the improvements described (conversion and yields to valuable products) are made at cost of the production of light (LCO) and heavy (HCO) cyclic oils. Nevertheless, these products are not desirable because its incorporation to diesel or fuel oil is not as profitable as to obtain more and better gasoline. As the name indicates, these products are rich in poly-nuclear aromatics; however, if the feedstock is hydrotreated most of these compounds are partially hydrogenated, which enhance yields to gasoline and LPG [2].

As expected, for catalyst C1, product distribution improves because of the decrease of cyclic oils yield (Fig. 8). Simulation also predicts this response when HF is used. It is important to note that simulation of the industrial unit predicts some increase of coke yield, referred to MAT results. This situation cannot be validated with

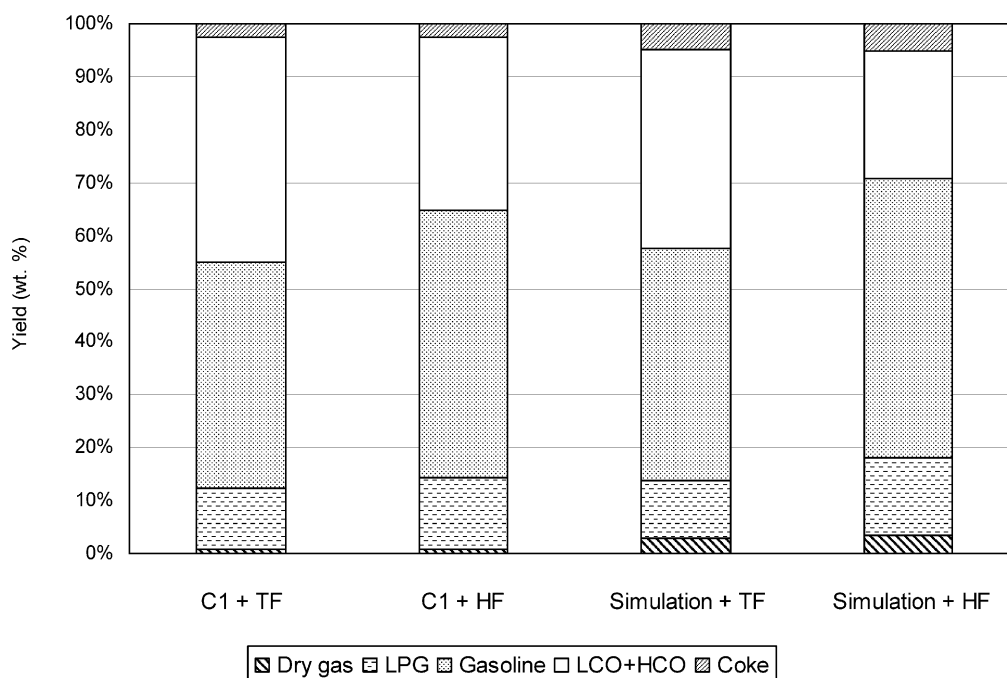


Fig. 8. Comparison in cumulative yields between MAT at C/O = 4, and simulation at 520 °C, when using C1 catalyst.

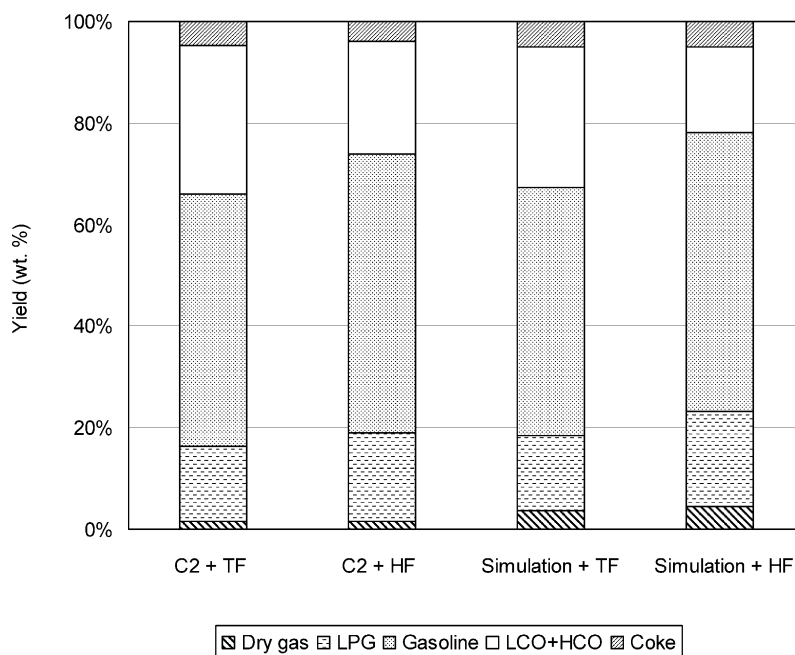


Fig. 9. Comparison in cumulative yields between MAT at C/O = 4 and simulation at 520 °C, when using C2 catalyst.

laboratory experiments because of the difference in the whole heat balance, aforementioned [10].

For catalyst C2, the same trend of improvement of valuable products because of reduction of cyclic oils yield is observed (Fig. 9). In this second case, again, simulation predicts some increase in coke yield, even if changes are minimal.

5. Conclusions

Two commercial catalysts, which exhibit different properties and production objectives, were used to convert two FCC feedstocks, typical and hydrotreated. Hydrotreating of FCC feedstock decreases heterocompounds that contain sulfur and nitrogen. However, there are other more important effects such as decreasing yield to dry gases and cyclic oils at constant conversion. The significant increase in the value of the product with increasing severity is mainly due to the increase in the gasoline production, as consequence of more efficient catalyst-to-oil interaction that leads to higher conversion. Coke yield decreases also. Due to the different behavior of MAT and industrial units, simulation results show a slight different response.

These results support the role that MAT tests could have in guiding the selection of operating conditions when hydrotreated gas oils are considered, but gives also warnings for looking closely at the overall behavior, using other tools, as simulation programs. Pilot plant experiments are scheduled for future work, in order to be able to better extrapolate MAT results to riser-regenerator units.

Acknowledgements

Authors thank the economic support from the Research Program “Tratamiento de Crudo Maya” at the Instituto Mexicano del Petróleo.

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