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Experimental Evaluation of Vacuum Gas Oil−Light Cycle Oil Blends as FCC Feedstock

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In this work the effect of incorporating up to 12.8 vol % of light cycle oil (LCO) in the conventional FCC feedstock was studied in a microactivity plant (MAT). The experimental work was carried out at typical operating conditions (reaction temperature of 516 °C and catalyst-to-oil ratio of 5, 6, and 7). An equilibrium catalyst taken directly from the circulating inventory of an industrial catalytic cracking plant and real feedstocks were used in this study. A reduction in conversion, gasoline and LPG yields, and an increase in dry gas and coke yields were observed with the increasing amount of LCO in the feed. Gasoline RON also increases as the LCO content is increased in the FCC feedstock. The optimum amount of LCO in the feed was found to be 7 vol %, which maximizes the valuable product production.

1. Introduction

Because of the many reactions that take place and the rapid changes in the activity of the catalyst during the reaction, the fluid catalytic cracking (FCC) is considered a very complex process.

The feedstocks used in the FCC units are commonly a mixture of heavy straight-run gas oil (HSRGO) and heavy and light vacuum gas oils (HVGO and LVGO, respectively).

A typical FCC gas oil is a complicated mixture of hydrocarbons, including paraffins, isoparaffins, naphthenes, aromatics and asphaltenes. It also contains significant quantities of multiringed molecules containing heteroatoms such as nitrogen, sulfur and metals, the composition and properties of which affects the FCC products distribution and quality.[1] Some properties and the composition of the typical streams included in an FCC feed are presented in Table 1.

Sometimes in the common operation of the catalytic cracking plants, the amount of streams (HSRGO, HVGO, and LVGO) available for preparing the FCC feedstock is limited, due mainly to problems in the operation of atmospheric or vacuum distillation columns as well as the production policies of the refineries. when these situation occur, the FCC feed rate has to be reduced and consequently the total gasoline and other valuable products production is also decreased.

One possibility to increase the feedstock rate is to feed other streams to the FCC unit. The virgin diesel (LSRGO: light straight-run gas oil, boiling range: 232−316 °C) is frequently used for this purpose, with the consequent decreasing in FCC conversion and gasoline and lighter products yields as can be seen in Table 2.[2] Another possibility is to recycle the FCC heavy cycle oil (HCO, boiling range: 316 °C+), this causes an increase in the coke and gases production and a decrease in conversion, gasoline yield, and RON and MON[2] because of the non easy-to-crack nature of the HCO.

The heavy-ends of a heavy straight-run naphtha (HHN, Boiling range: 135−191 °C) used as lift gas along with a common FCC feed is another possibility to be considered. Hsing[3] reported the catalytic cracking of an FCC feedstock containing around 14 wt % of HHN. The

Table 1. Typical Properties and Composition of FCC Feedstocks

property	HSRGO	LVGO	HVGO	FCC feed
composition, vol %	38	18	44	100
specific gravity 60/60 °F	0.904	0.932	0.940	0.930
API gravity	24.85	20.16	18.87	20.49
UOP K	11.90	11.73	11.93	11.77
sulfur, wt %	1.62	2.13	2.22	2.18
basic nitrogen, wppm	303	420	545	399
refractive index @20 °C	1.5034	1.5201	1.5274	1.5204
ASTM distillation, °C				
10 vol %	375	400	461	381
50 vol %	421	453	510	454
90 vol %	463	513	568	538

Table 2. Impact of LSRGO in FCC Feedstock on Conversion and Product Distribution[2]

LSRGO in FCC feedstock, vol %	0	15	30
conversion, wt %	81.9	79.0	77.0
dry gas, wt %	1.8	1.6	1.5
LPG, wt %	15.2	14.8	13.8
gasoline, wt %	56.5	54.9	54.9
LCO, wt %	11.2	13.6	15.9
HCO, wt %	6.9	7.4	7.1
coke, wt %	8.4	7.7	6.8

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Table 3. Feedstocks Properties

property	VGO	LCO	B-1	B-2	B-3
vol % of LCO			2.6	6.8	12.8
API gravity	25.1	27.5	24.9	24.3	24.2
UOP K	11.72	10.64	11.67	11.64	11.60
sulfur, wt %	2.05	2.91	2.07	2.11	2.16
basic nitrogen, wppm	336	51	329	315	298
carbon distribution, wt %					
paraffinics	62.94	36.04	61.82	61.32	60.57
naphthenics	12.54	10.79	12.41	12.17	11.85
aromatics	24.52	53.16	25.76	26.50	27.59
ASTM distillation, °C					
10 vol %	290	246	281	284	283
50 vol %	392	285	385	386	384
90 vol %	468	322	462	467	465

gasoline sulfur contents with HHN as lift gas were significantly lower than those without HHN present due to the dilution effect of low sulfur content of HHN. Gasoline RON and MON were also lower with HHN as lift gas.

Lappas et al.[4] separated an industrial gas oil sample (boiling range, 270−560 °C) in two fractions by TBP distillation: light gas oil (LGO: 270−343 °C) and heavy gas oil (HGO: 343−560 °C). They also extracted and characterized the aromatic fraction contained in both separated fractions. The cracking of the LGO aromatic fraction, consisting mainly of condensed rings, showed the following behavior:

- The unconverted fraction of the LCO increased with the higher WHSV.
- Gasoline yields were relatively low.
- Dry gases and especially coke yields were high.

It is well-known that the aromatic part of gas oils is an important refractory fraction which is hardest-to-crack.[5]

The light cycle oil (LCO), a distillate boiling range product of an FCC unit, is also a highly unsaturated product and as in the same case of LSRGO, HCO, and HHN, it is an option to be considered as FCC feed, providing that its traditional application for preparing diesel fuel is being reduced due to the new diesel specifications around the world and the adverse effect of the LCO on the quality of the resulting diesel when it is blended together with LSRGO as hydrotreating feedstocks.[6]

LCO is generally lower in API gravity and higher in sulfur than most other distillates streams. It is more aromatic and resistant to further cracking than fresh feeds because the more readily cracked components have already been removed in the first step operation.

LCO can strongly affect the cracking behavior (reduction in conversion and product yields), however, it can be cracked in an FCC system with the objective of increasing aromatic content and hence octane number in the gasoline as well as total gasoline production rather than molecular weight reduction.

With the main purpose of increasing the total feed to the FCC units when the amount of traditional FCC feedstocks is limited, in this work, experimental information about the effect of VGO-LCO blends as FCC feedstock on conversion, product yields, octane and total gasoline production is presented.

Table 4. Industrial Equilibrium Catalyst Properties

surface area, m^2/g	168
average bulk density, kg/m^3	896
pore volume, cm^3/g	0.286
average particle size, mic.	71.0
Na, wt %	0.21
Fe, wt %	0.40
Ni, ppmw	327
V, ppmw	1600
C,[a] wt %	0.08

[a] Initial coke content.

2. Experimental Section

2.1. Materials. The vacuum gas Oil (VGO) and light cycle oil (LCO) used in this study were recovered from a commercial FCC unit. The characterization of these feedstocks is reported in Table 3. Both streams were derived from a blend of the Maya and Isthmus Mexican crude oils with the following properties: 26.9°API, 2.3 wt % sulfur, 4.5 wt % asphaltenes, 5.9 wt % Conradson carbon, and 54 and 266 wppm of Ni and V, respectively.

The catalyst sample was taken from the FCC plant inventory. This sample, referred to as equilibrium catalyst, is a REUSY-based catalyst and has already reached the desired level of deactivation. Catalyst properties are presented in Table 4. The equilibrium catalyst was previously de-coked at 580 °C during 3 h.

The commercial FCC unit processes 41000 BPD of VGO, and considering that its maximum capacity is 47000 BPD, only 6000 BPD of LCO may be added to the feedstock. For this reason, three blends with VGO (41000 BPD), containing 1000, 3000, and 6000 BPD of LCO, were defined in order to study the effect of LCO as FCC feedstock. These theoretical blends correspond to the following concentration of LCO: B-1, 2.6 vol %; B-2, 6.8 vol %, and B-3, 12.8 vol %, which were used for MAT experiments. The properties of these blends are also presented in Table 3.

2.2. Microactivity Runs. The MAT (Microactivity Test) technique, a normalized ASTM procedure for a standard feedstock which allows us to change easily the reactions conditions, was used for studying the effect of LCO as FCC feedstock. The fixed-bed tubular plug flow reactor, reactor oven, oil injection, and products recovery system is described by ASTM D3907-92 method.

The microactivity tests were performed at 516 °C and WHSV of 16. To obtain different conversions, the catalyst-to-oil ratio (C/O) was varied in the range of 5−7. In each experiment, a new portion of equilibrium catalyst was used.

Adjustment of the C/O ratio in the MAT test provides a simple way to vary the severity and produce different conversions. There are two common methods of adjustment of the C/O ratio while keeping constant the amount of catalyst. One is varying the feed injection time at constant feed rate; here the activity of the catalyst is varied by coke deactivation due to an increase in catalyst time-on-stream. Another method is varying the feed rate at constant feed injection time, where the variation of conversion is achieved by changing the reactant concentration in the catalyst bed. In our case we employed the latter method.

Preheated feed was injected using a syringe pump through a 4 g bed of catalyst maintained at the required cracking temperature. Liquid product from the reactor is collected in an ice-cooled receiver.

The uncondensed gaseous products pass through the liquid products and were collected in a brine solution. The

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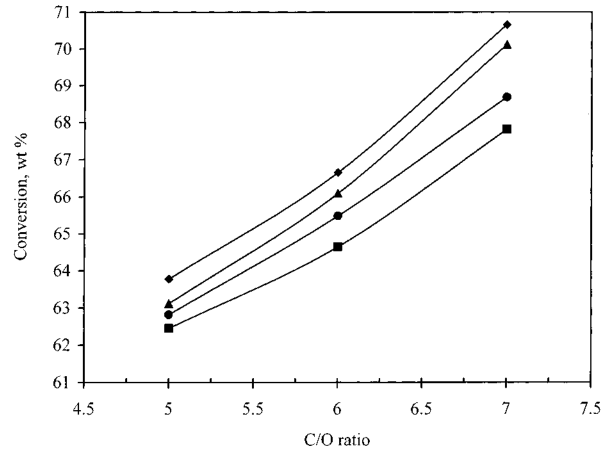

Figure 1. Impact to LCO-to-FCC admixture on conversion ((◆) 0% LCO, (▲) 2.6% LCO, (●) 6.8% LCO, (■) 12.8% LCO).

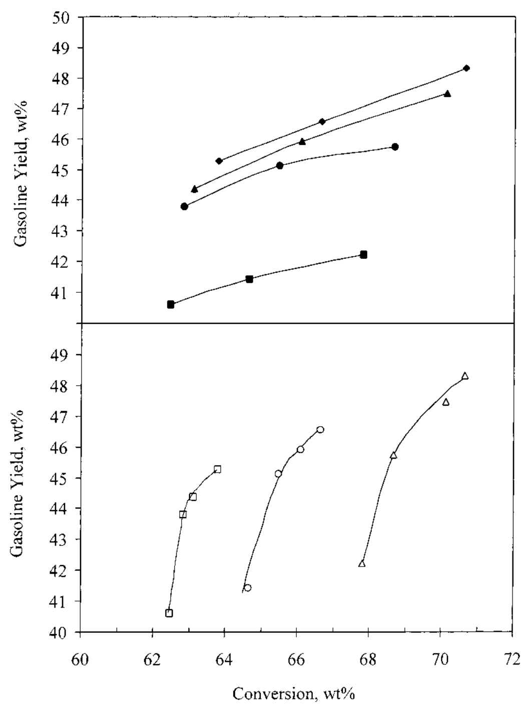

Figure 2. Impact to LCO-to-FCC admixture on gasoline selectivity ((◆) 0% LCO, (▲) 2.6% LCO, (●) 6.8% LCO, (■) 12.8% LCO; (□) C/O = 5, (○) C/O = 6, (△) C/O = 7).

gas volume is determined by displacement of the brine volume.

The liquid and gaseous products were analyzed by gas chromatography. The carbon content of the catalyst was determined after reaction by combustion using an infrared analysis of the produced CO_2.

The conversion was defined as 100% less the weight percent amount of LCO (216−342 °C) and decanted oil (342 °C+). Mass balances were performed for each run in the range 100 ± 5%.

3. Results and Discussion

3.1. Experimental Results. Prior to evaluating the VGO and the three VGO-LCO blends in the microactivity plant, a catalytic cracking experiment with the light cycle oil as feedstock was performed at 516 °C, WHSV of 16, and C/O of 6. The LCO showed a conversion level of about 30 wt %. Product distribution was not determined since it was not possible to stabilize the unit due to a high production of light gases.

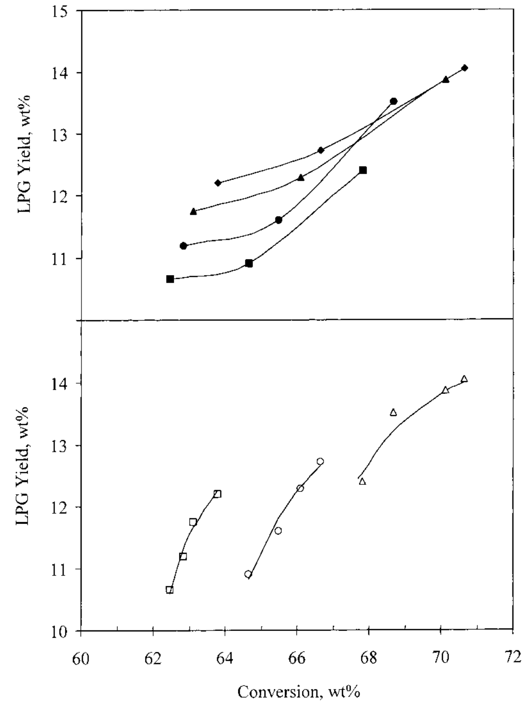

Figure 3. Impact to LCO-to-FCC admixture on LPG selectivity ((◆) 0% LCO, (▲) 2.6% LCO, (●) 6.8% LCO, (■) 12.8% LCO; (□) C/O = 5, (○) C/O = 6, (△) C/O = 7).

After confirming that LCO does exhibit a low crackeability, experiments with VGO-LCO blends were conducted in the MAT unit. The results of the catalytic cracking of these blends for conversion as a function of catalyst-to-oil ratio are presented in Figure 1.

It is obvious from this figure that as the LCO content in the feed is increased, the total conversion decreased. However, this conversion decline becomes smaller as the LCO admixture is increased, since doubling the LCO content does not double the conversion decline.

Product yields (gasoline: C_5 up to a boiling point of 216 °C; LPG: $C_3 + C_4$; Dry gas: $C_1 + C_2$, and coke) as a function of conversion for different LCO content in the feed and C/O ratio are shown in Figures 2−5.

A reduction in gasoline and LPG yields (Figures 2 and 3) is observed when conversion is increased. Dry gas and coke yields (Figures 4 and 5) exhibited an opposite behavior, it means that they increased with the increase of conversion. It should be noted that gasoline yield decreases in more than a proportional manner in the 6.8 to 12.8 vol % LCO admixture step whereas the analogous decline in conversion is less pronounced.

An increase in dry gas production is observed when LCO content in feed is increased from 0 to 12.8 vol % (Figure 4). It means that refineries may run into get gas compressor capacity problems with such an increase in dry gas.

High coke yields were found for feed B-3 (Figure 5), which has the highest amount of LCO (12.8 vol %). This high coke production is mainly due to the high amount of aromatics in this feed (27.59 wt %), since it is well-known that some of the aromatic compounds contain various rings (polynuclear aromatics), and some of these aromatics will end up on the catalyst as carbon residue (coke).

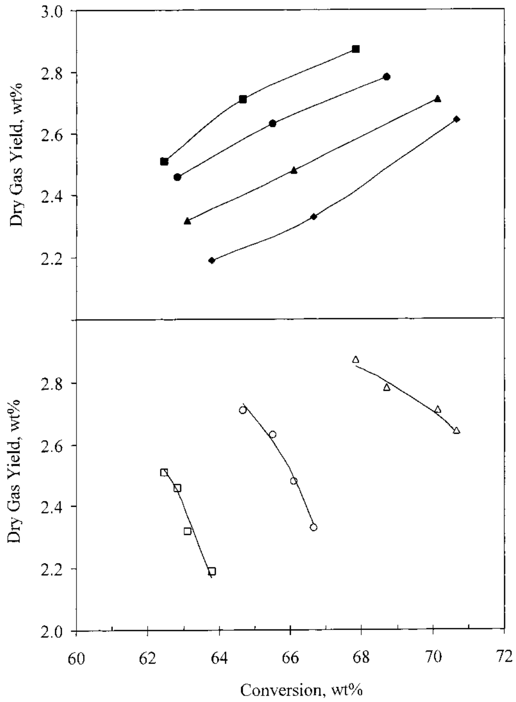

Figure 4. Impact to LCO-to-FCC admixture on dry gas selectivity ((◆) 0% LCO, (▲) 2.6% LCO, (●) 6.8% LCO, (■) 12.8% LCO; (□) C/O = 5, (○) C/O = 6, (△) C/O = 7).

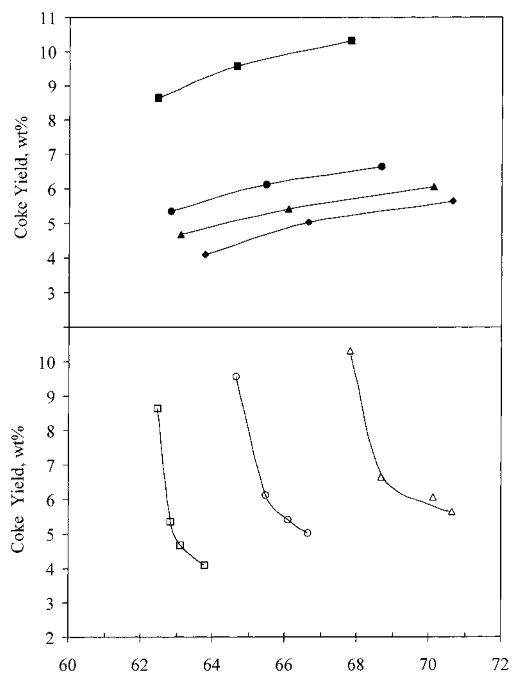

Figure 5. Impact to LCO-to-FCC admixture on coke selectivity ((◆) 0% LCO, (▲) 2.6% LCO, (●) 6.8% LCO, (■) 12.8% LCO; (□) C/O = 5, (○) C/O = 6, (△) C/O = 7).

The effect of catalyst-to-oil ratio was very similar for all feedstock, and no special behavior of this variable combined with the increasing amount of LCO in the feed was observed on conversion and product yields.

Gasoline RON showed an increase as the LCO in the feed and the catalyst-to-oil ratio were increased as can be seen in Figure 6. The major difference of this gasoline property (increase of 1.5 units with respect to gasoline RON obtained with VGO) was found at 12.8 vol % LCO

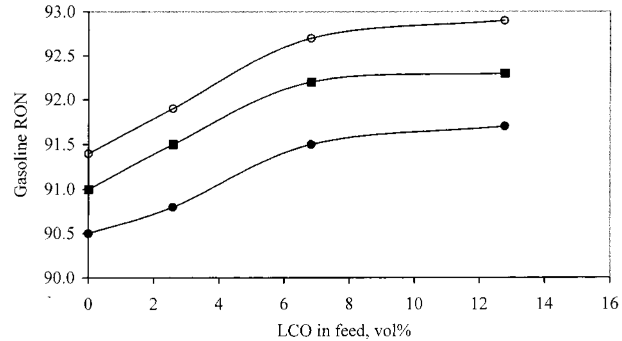

Figure 6. Variation of gasoline RON with LCO content in the feed. (●) C/O = 5, (■) C/O = 6, (○) C/O = 7.

in feed and C/O of 7. This change in gasoline RON is due to the high aromatic concentration in the feeds containing LCO.

It can also be observed from Figure 6 that after about 7 vol % of LCO in the feed, the change in gasoline RON for the three C/O ratios is minimum.

These results confirm that the composition of the feed is one of the most important factors affecting the yields and product quality in catalytic cracking.

3.2. Kinetic Point of View. An additional approach to evaluate the FCC feedstock crackability is by means of kinetic parameters. In the present work, the kinetic constants of the 3-lump kinetic model proposed by Weekman et al.[7]

$$\text{Feed} \xrightarrow{k_1} \text{Gasoline} \xrightarrow{k_2} Gas + Coke \xleftarrow{k_3} \text{Feed}$$

were estimated using correlations reported in a previous work.[8] These correlations use some feed properties (total sulfur and nitrogen, and carbon distribution by $n-d-M$ method) to calculate the 3-lump kinetic constants (k_1: gasoline formation, k_2: gasoline overcracking, and k_3: cracking of feed to gases plus coke).

The $n-d-M$ correlation is an ASTM (D-3238) method that use refractive index (n), density (d), average molecular weight (M), and sulfur (S) to estimate the percentage of total carbon distribution in aromatic ring structure, naphthenic ring structure, and paraffins chains. Both refractive index and density are either measured or estimated at 20 °C. Molecular weight is calculated by ASTM D-2502 method.

Figure 7 shows the values of the kinetic constants included in the 3-lump kinetic model. It can be observed that as the LCO content in the feed is increased, k_1 and k_3 decrease and k_2 increases. It means that the global kinetic constant for feed cracking, given by $k_1 + k_3$, also decreases.

Both, k_1 and k_3, which represent the cracking of the feed to gasoline and gases plus coke, respectively, decrease and hence feed conversion decreases. On the contrary, k_2 increases and consequently the gasoline overcracking also increases.

The behavior of the values of the kinetic parameters perfectly agrees with that found experimentally and discussed above.

3.3. Data Extrapolation to a Commercial Plant. It is clear that the inclusion of LCO in the FCC feed

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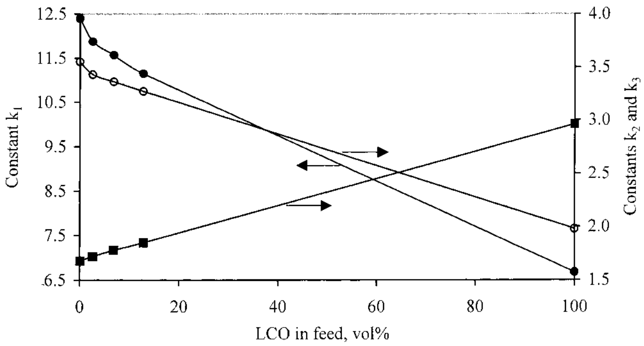

Figure 7. Variation of cracking kinetic constants with LCO content in the feed. (●) k_1, (■) k_2, (○) k_3.

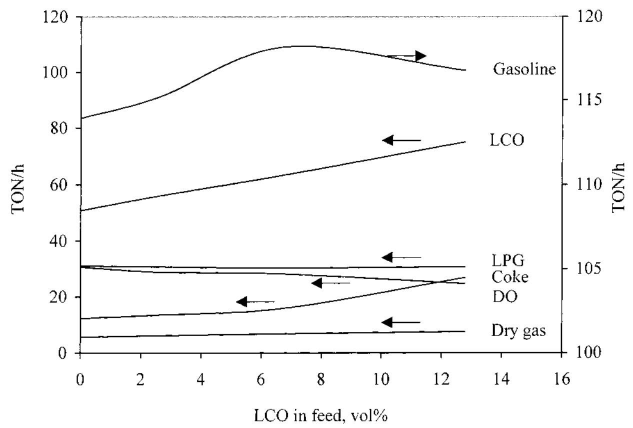

Figure 8. Production of FCC products at C/O of 6 based on MAT results.

adversely affects the conversion and valuable product yields (Figures 1−5). However, as was stated in introduction, sometimes the common components of an FCC feedstock is limited, and other noncommon streams, such as LCO, have to be used in order to operate the industrial units close to their maximum capacity.

Taking into account that the commercial FCC unit used as reference processes 41 000 BPD of VGO, and that the corresponding amounts of LCO in the feed for 2.6, 6.8, and 12.8 vol % are 1000, 3000, and 6000 BPD, respectively, the FCC products output (in ton/h) can be calculated by using the product yields given in Figures 2−5. For instance, for a C/O ratio of 6, the different products output are shown in Figure 8.

It can be seen that gases production (LPG and dry gas) is very similar for the different amounts of LCO in the feed. Coke and LCO production exhibits an increase, while decanted oil (DO) presents the opposite behavior. LCO production varies lineally with the increasing amount of this stream in the feed.

Gasoline production goes through a maximum at about 7 vol % of LCO in the feed, which also corresponds to the optimum value observed for the increase in gasoline RON. This means, that the optimum amount of LCO is around this value. It should be emphasized that the bests results in both, product yields and production, is found with the typical FCC feedstock; however, if for any reason the FCC feed cannot be completed, LCO may be added to the conventional FCC feed, but no more than 7 vol %.

Conclusions

The effect of up to 12.8 vol % of LCO in the typical FCC feed was studied in a microactivity unit.

A decrease in conversion, gasoline and LPG yields was observed when LCO is added to the conventional FCC feedstock. The opposite behavior was observed for dry gas and coke yields.

Gasoline RON increases as the LCO in the feed was also increased. This was attributed to the high aromatic contents in the feeds containing LCO.

The optimum content of LCO in the FCC was found to be 7 vol %, which maximizes both gasoline production and gasoline RON.

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