

# Upgrading FCC Light Cycle Oil

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*This paper presents options for increasing production of diesel fuel in a refinery by FCC light cycle oil (LCO) hydrotreating together with the straight run gas oil (SRGO). The experiments consist of hydrotreating mixtures of 10, 20% LCO and 90% and respectively 80% SRGO at 360, 380°C, two liquid hourly space velocity 0.9 h<sup>-1</sup>, 1.2 h<sup>-1</sup>, pressure 50 bar in the presence of two industrial catalyst type Co/Mo and NiMo. The research has focused on the influence of LCO/SRGO ratio, type of catalyst and hydrotreating conditions on diesel fuel quality compared with characteristics required by standard EN 590.*

*Keywords: straight run gas oil, hydrotreating, light cycle oil, aromatics saturation*

Global oil demand continues to grow by about 1.8% per year and is accompanied by a consumption growth of high quality transportation fuels and decrease of the heavy fuel consumption. The demand for high quality gas oil with low sulfur content has grown and will significantly grow in next few years compared to gasoline, due to the large number of vehicles with diesel engines which are more reliable and more efficient in terms of fuel consumption with 15-30% compared to gasoline engines.

To meet these challenges, refineries are looking for effective solutions to increase Heavy/Sour Crude Processing, Increase Bottoms Conversion and Conversion to Ultra-Clean Fuels Quality to satisfy the harsher restrictions imposed by the environmental legislation [1-4]. The production of Diesel fuel can be increased by introducing of the heavy and residual oil fractions (catalytic cracking, delayed coking and reducing viscosity) in the refineries processing flow in the heavy fractions, converting processes which generate products within the limits of the diesel fuel distillation [5]. Due to economic reasons and to cover the most recent demand for diesel, it is a great interest for catalytic cracking light gas oil processing (Light Cycle Oil -LCO).

The gas oil from FCC and Coker process has a lower cetane value around 15-25, considerably lower compared with 40-60 for straight run gas oil (SRGO) derived from the same crude [6]. The sulfur content in LCO is from 0.2 to 2.5 wt%. The majority of sulfur is found in alkyl-dibenzothiophenes (DBT) [7, 8], which are relatively difficult to desulfurize by hydrotreating.

Over 70% of the aromatic hydrocarbons present in LCO have two rings, while the remainder is equally split between single and three ring aromatics. Two and three ring aromatics have very low cetane values and are the main cause of the low blending LCO/SRGO ratio in diesel fuel.

Because of polynuclear aromatics (PNA) highly content the LCO processing has a negative impact on the quality of diesel fuel with an impact on achieving the right cetane number and on the density corresponding to EN 560 standard. Using of LCO for diesel fuel obtaining will negatively influence also on its color. Polycyclic aromatic hydrocarbon type anthracene, phenanthrene and their derivatives at very low concentrations, are responsible for the color green / blue of diesel [9]. Polar nitrogen compounds will also influence the color and the stability of the fuel.

Since the most compounds that change the fuel's color is concentrate in the heavy gasoil fraction with a boiling

point greater than 250 °C [10], this property correction can be done by adjusting of PNA saturation and also by adjusting the final boiling point of gasoil. To comply with the quality norms required by the EN 590 standard, all diesel fractions from which commercial diesel fuel formulates are hydrofinated.

In this regard, in order to allow the introduction in the feed stream of LCO and coking gas oil, the refineries have upgraded HDT by changing operating conditions, and choosing of an last generation catalysts able to achieve both deep desulfurization and saturation of PNA but also the reactants distribution upgrading and reactor bed configuration. Also LCO use has a negative impact on the operating conditions of the hydrotreating reactor. Adding of LCO which is less reactive than SRGO, require temperature increasing in the reactor in order to keep the desulfurization rate in the standardized limits. The reaction temperature increase proportionally with to the adding ratio LCO / SRGO increasing, but cannot exceed some high values to which saturated PNA are thermodynamic limited [11].

Hydrotreating of LCO to high pressure can remove sulfur to deep value, but increase modestly the cetane number due to partial saturation of tri- and higher ring aromatics led to lower aromatics.

Along with operating parameters optimization of the hydrotreating reactor, a considerable attention is given to the catalyst which must have an increased activity in the saturation reactions of PAHs. In the past 40 years, the main catalysts used in hydrotreating reactions are formulated on Co and Ni oxides with promoters of Mo and W or other metals on an alumina support, activated as sulphides [5, 12].

Co-Mo catalysts are suitable for deep desulfurization, while Ni-Mo type catalysts are more active in hydrogenation reactions of PAHs and nitrogen compounds presents in the LCO on high concentrations [3].

Some companies uses two-stage hydrotreating, using Ni-Mo catalysts in first stage and Ni-W in the second stage [13, 14]. The literature also mention Ni-W catalytic systems on zeolite support [15] used in the hydrotreating second stage in order to break naphthenic cycles which result from bi- and tri-cyclic aromatics saturation with high cetane number alkyl cyclohexanes forming.

This article provides an overview of a various options for increasing of diesel fuel production from a refinery by catalytic cracking LCO hydrotreating together with the SRGO. The article seeks to find the influence of the LCO /

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**Table 1**  
FEEDSTOCK PROPERTIES

Feed characteristics	UM	10% LCO + 90% SRGO	20% LCO + 80% SRGO
Density	kg/m <sup>3</sup>	851.4	886.4
Sulphur	ppm	5718	7876
Aromatics (HPLC)			
Total	% vol	29.44	35.28
Monoaromatics	% vol	15.27	14.84
Di-Aromatics	% vol	13.38	19.16
Tri-Aromatics	% vol	0.79	1.28
TPB			
IBP	°C	146	151
t <sub>5%vap.</sub>	°C	175	186
t <sub>10%vap.</sub>	°C	202	221
t <sub>30%vap.</sub>	°C	238	249
t <sub>50%vap.</sub>	°C	265	278
t <sub>70%vap.</sub>	°C	296	302
t <sub>90%vap.</sub>	°C	350	356
T <sub>95%vap.</sub>	°C	371	380
EBP	°C	394	400

SRGO ratio, catalyst type usage and hydrotreating conditions on the quality of obtained diesel fuel compared to EN 590 requirements.

## Experimental part

### Feedstock and catalysts

The feedstock is the mixtures of (SRGO) with 10% and 20% with (LCO). The physicochemical properties of the feedstock are presented in table 1.

Table 1 data shows that the LCO processed together with SRGO cause an excessive growth of bi- and tricyclic

aromatic content which will have a major impact on the quality of hydrotreated product. Naphthalenic type aromatics will decrease significantly the cetane number and additionally, those with three benzene rings will affect the color. Also with LCO/SRGO ratio increase, the sulfur content will also increase significantly, because it concentrates mainly in the catalytic cracking heavy gas oil fraction which has higher final boiling point.

For the hydrotreating process two industrial catalysts was used: CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>. The catalyst Co-Mo was activated by sulphurization with thiophene dissolved in gas oil at a concentration of 1000 ppm in hydrogen atmosphere, a temperature of 280°C and at a LHSV of 2h<sup>-1</sup>. The activation is considered completed after H<sub>2</sub>S formation in the reaction gases indicated by the yellow color of cadmium acetate used as indicator.

NiMo type catalyst was sulphurized with dimethyl disulfide (DMDS) solubilized in straight run gas oil at a 4%wt concentration. The reactor is heated with the sulfurization agent to 100 at a 20°C/h heating rate and a 100 mL/h flow rate. After 100°C temperature is reached, the feeding with hydrogen starts at a ratio 320 L/L H<sub>2</sub>/Mp and heating continues with a 20°C/h rate up to 250°C. The sulfurization process is kept with the same conditions for 12 h then heating continues with a 5°C/h rate up to 320°C. Catalyst activation is considered complete after maintaining the sulfurization at 320°C for 2 h time.

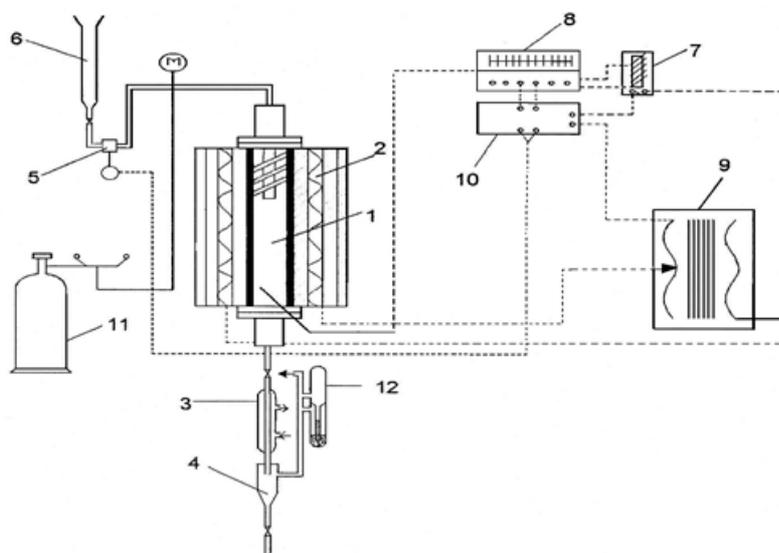
### Micropilot plant

The hydrotreating experiments were carried out into a micropilot plant (fig. 1) with fixed bed catalytic reactor (1) mounted in an electric oven (2). The total volume of the reactor is 80 cm<sup>3</sup>, out of which 40 cm<sup>3</sup> is volume filled by the catalyst, which is distributed between two layers of an inert ceramic material.

The experiments have been carried out at 50 bar pressure, at 360 and 380°C temperatures and two LHSVs 0.9 h<sup>-1</sup> and 1.2 h<sup>-1</sup>.

Feedstock supply is made with a HPLC metering pump (5) out of the burette (6) with a flow rate of 0.6 cm<sup>3</sup>/min. corresponding to a LHSV of 0.9 cm<sup>3</sup>/cm<sup>3</sup>h respectively 0.8 cm<sup>3</sup>/min. corresponding to LHSV of 1.2 cm<sup>3</sup>/cm<sup>3</sup>h. The plant is feed with hydrogen corresponding to a 400 cm<sup>3</sup>/cm<sup>3</sup> ratio H<sub>2</sub>/feedstock. The hydrogen flowrate is controlled by a flowmeter (12). The duration of an experiment was two hours. The reaction mixture is cooled in a water cooler (3)

Fig.1 The HDT Micro-pilot Plant  
(1-reactor, 2-electrical heater, 3-water cooler, 4- liquid-gas separator, 5-metering pump, 6- feedstock burette, 7-relay, temperature recorder, 9-autotransformer, 10-temperature controller, 11-hydrogen cylinder, 12-flow meter)



and then passed into phase separator (4) which separate unreacted hydrogen and small amounts of light hydrocarbons which are released into the atmosphere and a liquid phase consisting of hydrotreated gas oil. After separation, the hydrotreated product from separator vessel is stripped by nitrogen (40 L/h) for 1.5 h time for removal of hydrogen sulfide and ammonia. The liquid product obtained after stripping was separated by PRF distillation in order to remove the light fractions  $C_{3+}$ -185°C.

The products yields were determined by the material balance on each experiment, knowing the amount of raw material and weighing gasoil and gasoline separated by PRF distillation, gases were settled by difference.

After each experiment, the hydrotreated product with boiling point higher than 185°C, corresponding to gasoil, was characterized using standardized methods in order to establish the main properties: density (EN ISO 12185), pour point (SR 13552), aromatic content by HPLC on a chromatograph Varian ProStar 500 (method EN 12916/2000). Sulphur was determined by X-ray spectrometry on a PW4025 MiniPal using the EN ISO 2084-2004 method.

## Results and discussions

The results of hydrotreated mixtures of SRGO-LCO on the CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst is shown in following figures 2-8.

On SRGO-LCO mixtures hydrotreating, high yields (over 94%) are obtained in the hydrotreated product For the same reaction conditions on the CoMo catalyst type the yields results are higher than on the NiMo type (fig. 2, 3). Lower yields on Diesel obtained on NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst is justified by its higher activity in hydrocracking side reactions. At the same reaction temperature, decreasing LHSV lead to lowering of yields in hydrotreated gasoil (fig. 2, 3) due to

growth of reaction time which favors slow hydrocracking reactions [16]. Also, due to intensification of hydrocracking side reactions, hydrotreated product yields decreases with increasing of reaction temperature at the same LHSV, for both catalysts studied.

From figures 2, 3 for all the reaction conditions, it can be noted an increase in hydrotreated product yields, with growth of the LCO content in the mixture LCO-SRGO from 10% to 20%.

The heavy components of LCO which boil in the diesel range with a 95% point of 360°C or higher, representing thermally stable cracked hydrocarbons that are not further reacted by hydrocracking reaction.

Therefore, increase of LCO content, will increase the heavier hydrocarbon content, less reactive which will be conserved in the boiling fraction corresponding to gas oil.

The data presented in figures 4 and 5 shows a higher activity of the CoMo catalyst in hydrodesulfurization reactions than of the NiMo catalyst. Thus, no matter what the hydrotreating conditions are, the CoMo/Al<sub>2</sub>O<sub>3</sub> achieve a better desulphurisation with 3-8 ppm better than NiMo/Al<sub>2</sub>O<sub>3</sub>.

It is generally accepted that the addition of LCO to the diesel feed increase the difficulties to remove the sulfur by hydrotreating; due to this fact a significant portion of the sulfur is found in alkyldibenzothiophenes (DBT), which are relatively difficult to desulfurize by hydrotreating process.

Under these circumstances in order to reduce the sulfur content, the hydrotreating reaction must be performed at a higher temperatures and lower LHSV (fig. 4, 5) which determine, on the one hand, the growth of DBT hydrodesulfurization and on the other hand increase the time of reaction leading to higher conversions for this reaction.

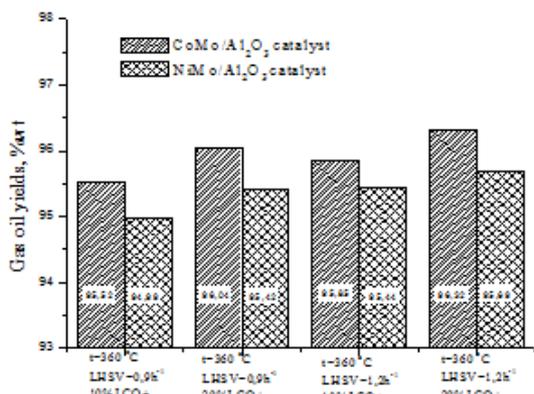


Fig. 2. Hydrotreated gas oil yields at 360°C (Pressure=50 bar, H<sub>2</sub>/feed=400 cm<sup>3</sup>/cm<sup>3</sup>mp)

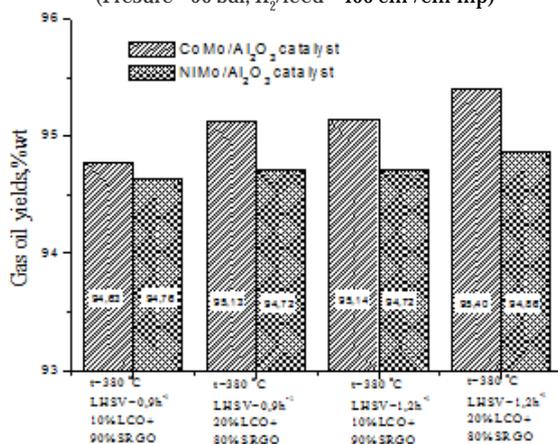


Fig. 3. Hydrotreated gas oil yields at 380°C (Pressure=50 bar, H<sub>2</sub>/feed=400 cm<sup>3</sup>/cm<sup>3</sup>mp)

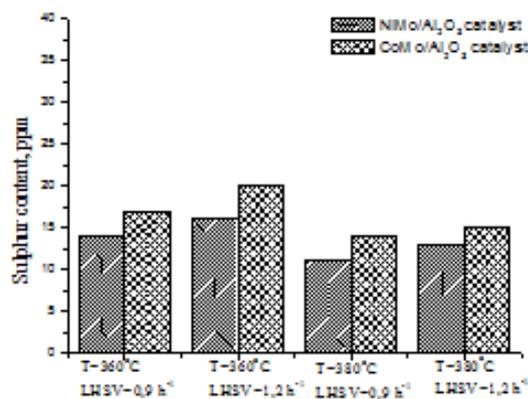


Fig. 4. Sulphur content in hydrotreated products from feed=10 %wt LCO + 90 % wt SRGO (Pressure=50 bar, H<sub>2</sub>/feed=400 cm<sup>3</sup>/cm<sup>3</sup>mp)

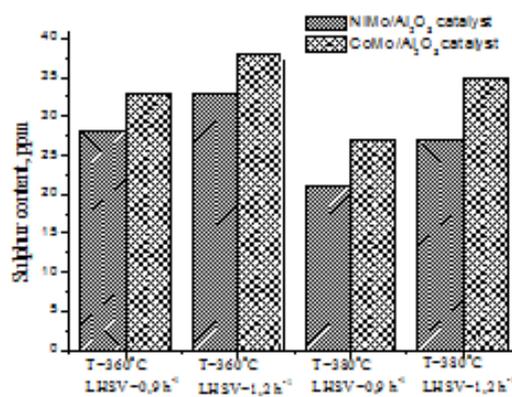


Fig. 5. Sulphur content in hydrotreated products from feed=20 %wt LCO + 80 % wt SRGO (Pressure=50 bar, H<sub>2</sub>/feed=400 cm<sup>3</sup>/cm<sup>3</sup>mp)

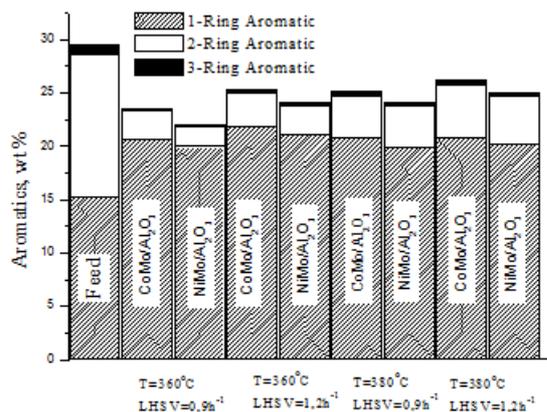


Fig. 6. Aromatics distribution in hydrotreated products (feed=10 %wt LCO + 90 % wt SRGO)

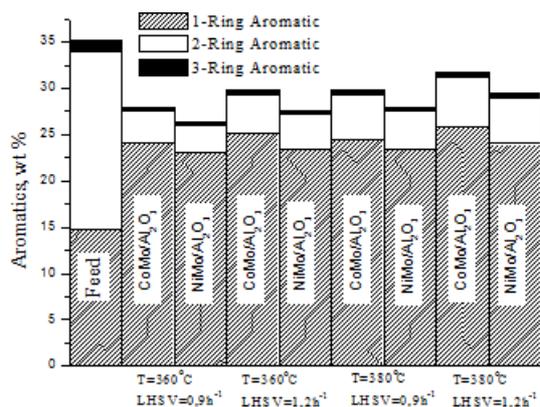


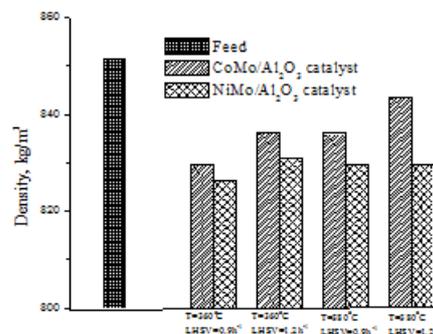
Fig. 7. Aromatics distribution in hydrotreated products (feed=20 %wt LCO + 80 % wt SRGO)

An increase in LCO content from 10%wt to 20%wt meet an increase of sulfur content from 5718 ppm to 7876 ppm. Due the higher end point of LCO the more of sulfur compounds are hard sulfur types (DBT), which are very difficult to hydrodesulphurisation. For all reaction condition figures 4 and 5 show a high level of sulfur in hydrotreated gas oil obtained from 20%wt LCO blends comparative with 10%wt LCO blends. The increase of reaction temperature and the decrease of HSLV are favorable to diminish the sulfur content, but the sulfur level remains high then Ultra Low Sulfur Diesel (ULSD) standard limit.

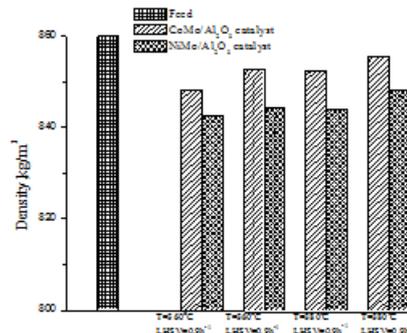
In order to convert LCO to a higher quality diesel product it is necessary to saturate and open the di and tri-aromatic rings to increase cetane number and decrease the density of the fuel. In our comparative study the NiMo catalyst behaved better than CoMo for saturation of aromatic (fig. 6, 7). By the saturation reaction the most of di- and tri-aromatic rings hydrocarbons from feed are converted in mono aromatics (fig. 6, 7).

For the two catalysts, increasing of the hydrotreating temperature at the same volume rates, decreases the saturation degree of aromatics due to thermodynamics limitations. Also at higher temperature the conversion degree of di- and tri-aromatics into mono aromatics decrease (fig. 6, 7).

To improve cetane number (CN) of diesel is not sufficient to saturate the aromatic rings. The increase of hydrotreating severity would lead to saturate and then opening di- and tri- rings resulting the alchilmonoaromatics hydrocarbons with high cetane number. The Ni promotor has a good activity in hydrocracking reaction for opening of saturate rings [17]. The difference between total aromatics in feedstock and hydrotreated gas oil show the total rings saturation and opening rings one by one.



a) 10% wt LCO+90% wt SRGO



b) 20 % wt LCO+80% wt SRGO

Fig. 8. Density of hydrotreated gas oil

At a constant temperature, decrease of LSHV will increase the reaction time which will facilitate the slow reactions of the di- and tri-rings aromatics saturation (fig. 6, 7).

The increase of LCO/SRGO ratio generate an increase in total aromatics content in the feed, with a high concentrations of naphthalenes and tri-aromatics rings compounds (table 1). The hydrotreating of feedstock with high LCO/SRGO ratio generate low cetane number gasoil due to bad saturation of aromatics with di- and tri-rings (fig. 7).

Aromatics saturation will cause density decrease of the hydrotreated product. Figure 8 shows a greater decrease of density at hydrotreating SRGO - LCO mixtures on the NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts at a higher reaction temperature and lower LHSV.

## Conclusions

To resolve the continuous demand for transportation fuels, the refiners will have to consider the investments in technology to upgrade the LCO by hydrotreating together with SRGO.

Processing LCO and SRGO blends over CoMo and NiMo catalysts has a major impact on the decreasing of total sulfur content and especially in decreasing of the di- and tri-rings aromatics hydrocarbons in the hydrotreated diesel.

The aromatics content reduction lead to an increase in cetan number.

The increase of temperature and decrease of LHSV for hydrotreating reaction generate an Ultra-Low Sulfur Diesel fuel.

The polyaromatic hydrocarbons are converted in monoaromatics by saturation and opening the rings at low LHSV and at low hydrotreating temperature.

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