Upgrading of the FCC Gasoline Quality

RALUCA ELENA DRAGOMIR, PAUL ROSCA*, LIANA BOGATU
Petroleum-Gas University of Ploiesti, Faculty of Petroleum Refining and Petrochemistry, 39 Bucharest Blvd., 100680 Ploiesti, Romania

This paper presents researches which aims, to upgrade the quality of catalytic cracking gasoline, in terms of reducing the sulfur content (<10 ppm), through a deep hydrodesulphurization (HDS) process, with recovery of the octane loss due to a partial saturation of olefins, by etherification of unsaturated C_5*-*C_7 *hydrocarbons. Due to the convenient distribution of olefins in the first part and sulfur compounds in the last part of the cracked naphtha TBP curve, the FCC gasoline was separated into a light fraction (32-95°C) and heavy fraction (95-188°C), which was subjected to deep HDS over CoMo /* Al_2O_3 *and NiMo /* Al_2O_3 *catalysts. The various temperatures which may influence the selectivity in (HDS) versus olefins hydrogenation are also discussed. To recovery 2-6 octane loss by HDS, the* C_5*-*C_7 *olefins from light FCC gasoline was etherificated with methanol and ethanol over Purolite CT 275 catalyst. Etherification associated with usage of alcohols from biomass ensure the renewable component of the commercial gasoline.*

Keywords: octane number, hydrodesulfurization, FCC gasoline, etherification, alcohols

The sulfur content in the trade gasoline is a significant contributor to the air pollution directly by SOx type emissions, but mostly indirectly by disabling of catalytic converter for the exhaust gas treating unit, resulting in an excessive increase of CO, NOx and unburned hydrocarbons [1].

It was established environmental protection legislation which severely restricting the sulfur content at less than 10 ppm in the fuel, gasoline or diesel, as a quality standard. [2-4].

Commercial gasoline consists of various fractions with ASTM oil distillation limits (C5+ at 205°C) to whom is adding components and additives for correction of some characteristics required by the quality standard. The classic recipe for the formulation of a commercial gasoline contains mainly fractions from catalytic cracking (FCC), catalytic reforming, alkylation, isomerization, atmospheric distillation and oxygenated compounds like ethanol, MTBE or TAME, butane for vapor pressure corrections and other components or additives. All the commercial gasoline compounds come from hydrofinated feedstock without sulfur, except the FCC gasoline which mean 30-40% of the gasoline pool and is responsible for 98% of the sulfur content in the fuel. [5, 6]

The sulfur compounds from the catalytic cracking gasoline are: thiols, sulfides, thiophene and alkyl-thiophenes, tetrahydrothiophene, thiophenols and benzothiophene [7, 8].

Most of the sulfur compounds mentioned are not contained as such in the feedstock used for catalytic cracking. They are formed by converting of heavy sulfur components from the feedstock or by recombination of the cracking products, an example of this being the addition of H_2S to olefins and di-olefins [9].

In order to reduce sulfur from cracking gasoline three strategies are available: 1) pre-treatment of the feedstock used at catalytic cracking by hydrodesulfurization mild hydrocracking, 2) desulfurization in situ in the catalytic cracking using additives for FCC catalysts or new catalyst matrix able to generate sulfur compounds easy to remove by caustic treatments (MEROX), 3) desulphurization of FCC gasoline (posttreating). The FCC feed pre-treating has several advantages as higher yield and better quality of FCC products, lower SOx emission of FCC regenerator, lower coke formation on the catalyst, etc., but the investment costs of such a unit are too high for a low ROI (return on investment).

With the second method, the sulfur content can generally be reduced by 15-35%.The first and second strategies are mostly not effective enough to produce ultra-low sulfur gasoline. Consequently, desulphurization of the FCC gasoline is necessary.

If the FCC naphtha is hydrotreated, major part of the olefins are hydrogenated, therefore its octane number becomes substantially lower with 3-4 units (even by 10 units) which are very difficult to recovery in the octane balance of gasoline pool. In addition, considerable amount of hydrogen is consumed to saturate the double bonds of the alkenes, so the operating costs are high. In order to overcome these technical and economic problems, many technologies have been proposed based on FCC gasoline fractioning into two or three fractions followed by medium and heavy fractions hydrodesulfurization. This technology is facilitated by convenient distribution of the olefins and sulfur compounds from FCC gasoline. The light gasoline fractions contain mainly olefins and have a reduced content of sulfur compounds, especially mercaptans easily to remove by caustic treatment while in the heavy fractions are concentrated the majority of sulfur's refractory compounds (alkylthiophenes or benzothiophenes) and fewer olefins [10]. The medium fraction have a lower octane number and contains mainly thiophene and light alkylthiophenes. A typical distribution of olefins and sulfur compounds in CC gasoline is shown in figure 1 [11].

Regarding hydrodesulfurization medium and heavy factions of FCC gasoline there are two strategies currently used [3, 5, 12]: 1) selective hydrodesulfurization with octane number preservation. (Prime G +, SCANfining, catalytic distillation CDHydro) and 2) deep desulfurization associated with octane number improving by isomerization

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* email: prosca@upg-ploiesti.ro

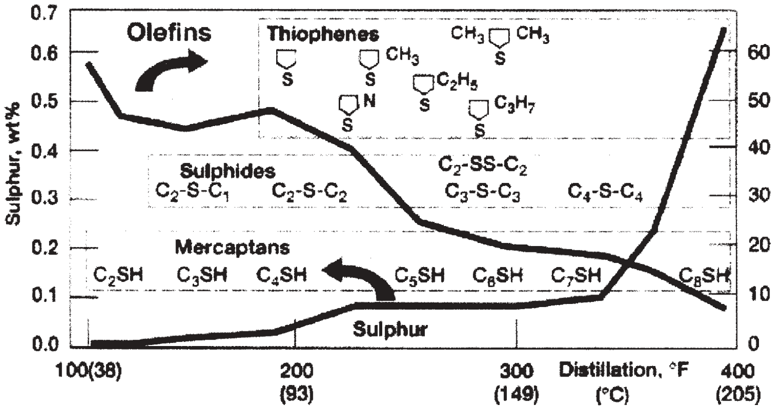

Fig. 1. Sulfur and olefins distribution in FCC gasoline

Table 1
SULFUR AND OLEFINS CONTENT DISTRIBUTION ON THE FCC GASOLINE PRF DISTILLATION CURVE

% vap.	Sulfur content [ppm]	Olefins content [%wt.]	% Cumulative vaporized	PRF Temperature
			0	32
5	16	40.6	5	62
5	22	41.4	10	73
5	30	42.6	15	80
5	38	43.8	20	85
5	44	52.6	25	88
5	76	38.0	30	90
5	153	36.4	35	92
5	200	30.8	40	95
5	248	28.6	45	100
5	264	25.2	50	104
5	322	20.6	55	111
5	370	16.8	60	119
5	546	14.1	65	130
5	608	13.6	70	142
5	710	12.4	75	151
5	782	11.2	80	160
5	804	11.2	85	168
5	825	10.9	90	175
5	1220	10.8	95	180
4	1560	9.6	99	188

(Oct-Gain and ISAL) or other subsequent processing technologies. Removal of a biggest sulfur quantity from the hydrotreated gasoline is difficult to achieve due to recombination of H_2S with olefins resulting mercaptans. Under mild processing conditions (low temperature and medium pressure), reaction is thermodynamically facilitated leading to relatively high concentrations of mercaptans, therefore can be a serious obstacle to reach the imposed objective of <10 ppm sulfur.

Catalytic distillation (CD) combines FCC gasoline separation in several fractions by distillation and catalytic hydrodesulfurization in the same process using a single reactor / vessel, actually a distillation column packed with a desulfurization catalyst [3, 4]. Catalytic distillation makes possible separate treating of the various fractions of FCC gasoline. The light fraction containing olefins and the major part of the reactive sulfur compounds will be subjected to catalytic desulfurization at a relatively low temperature on top of the column. The heavy fractions containing refractory sulfur compounds will be subjected to high temperature desulphurization at the bottom of the column. Deep hydrodesulfurization technologies (HDS) associated with significant decrease of octane Oct-Gain (ExxonMobil) and ISAL (UOP) [3] recover the octane loss by a subsequent isomerization and alkylation. The ISAL process use CoMo-P/Al_2O_3 catalyst in combination with Ga-Cr/HZSM-5 zeolite [4]. The second layer of catalyst led to octane recovery by cracking, isomerization and alkylation of the paraffins which significantly compensate the olefin saturation [13, 14]. One of the disadvantages of these processes may be some gasoline yield loss due to the cracking into light products on the catalyst acid centers. Also, another disadvantage is the consumption of hydrogen required for total olefin saturation.

Many other processes, especially non-catalytic, can be considered in order to achieve a deep desulfurization of FCC gasoline [3, 4, 7]. Promising technologies involve the selective or reactive adsorption and also alkylation of sulfur compounds. The S Zorb1 a Phillips Petroleum Co. process [15] uses a solid absorbent (ZnO/NiO) reacting with sulfur to give a sulfide, which is continuously withdrawn from a fluidized bed reactor, regenerated and then recirculated. The process operates in gas phase to avoid the retention of the oil product in the pores. Olefin alkylation with thiophenic sulfur [7] is an acid catalytic process which allow switching the sulfur compounds from a lighter to a heavier gasoline fraction by increasing their molecular weight. This can be achieved by thiophene alkylation with the olefins present in the gasoline. The process can be advantageously combined with other processes such as Prime-G, for example.

As a conclusion, the majority of research studies addresses the FCC gasoline quality increasing by using combined technologies based on separation into two or three gasoline fractions, selective or deep hydro-desulfurization of the medium and heavy fraction eventually followed by isomerization and separate processing of the light fraction to convert the olefin with 5-8 carbon atoms by hydroisomerization, aromatization or etherification in higher COR components [16-18].

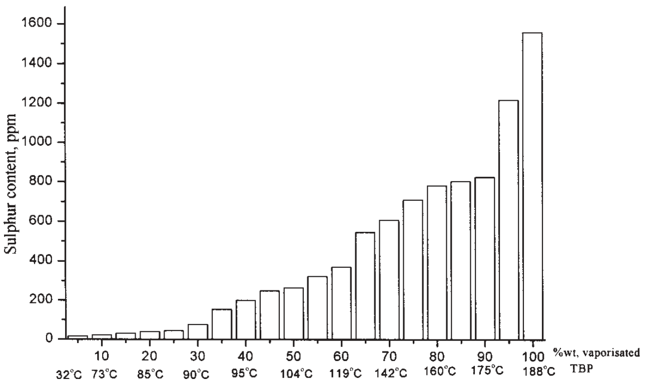

Fig. 2 Sulfur content distribution within FCC gasoline

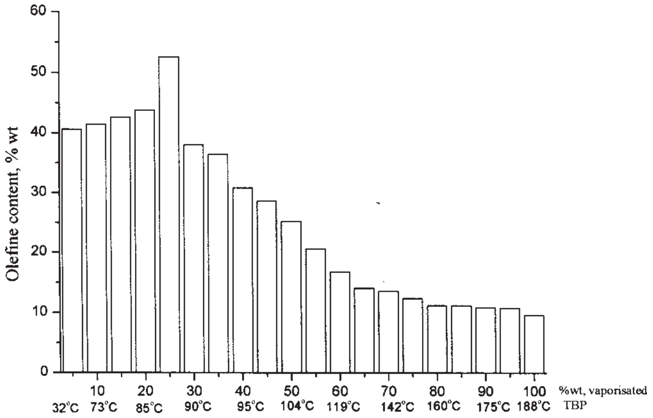

Fig. 3 Olefins content distribution within FCC gasoline

The present study is focused on upgrading of the FCC gasoline quality by deep hydrodesulfurization of the heavy gasoline fraction, associated with etherification of C_5-C_7 olefins from the light fraction. Conversion of these highly reactive olefins restore the octane deficit due heavy gasoline hydrogenation maintaining the concentration of olefins in the commercial gasoline below 18% and the vapor pressure within the range of Euro4 quality imposed limit. Etherification associated with alcohols from biomass ensure the renewable component of the commercial gasoline.

Experimental part

The study aims to increase the quality of catalytic cracking gasoline in terms of reducing the sulfur content (<10 ppm) through a deep hydrodesulfurization process with conservation / recovery octane due to a partial saturation of the olefins. FCC gasoline was used as a feedstock collected from an industrial catalytic cracking plant with the main characteristics presented in table 1 and figure 2 and 3. Gasoline was separated into 5% vol. fractions by PRF distillation and for each fraction, sulfur content was determined by X-ray fluorescence using PW 4025 MiniPal apparatus through the method EN ISO 2084-2004 and olefins by determining bromine number ASTM D1159 (table 1, figs. 2, .3).

The content of oxygenated compounds and RON and MON were determined by IR spectrometry using an IROX 2000 spectrometer. The measurement principle is based on the infrared measurement (FTIR) according to ASTM D 5845, in the 2.7 to 15.4μ domain. Determinations were made by linking IR spectrogram of the analyzed sample with the IR spectrum matrix of commercial gasolines with reference to oxygen content and COR, COM.

Because of the unequal distribution of sulfur and olefin the FCC gasoline was separated into a (32-95°C) light fraction which will be etherificated with methanol & ethanol and a (95-187°C) heavy fraction which will be hydrodesulphurizated. In this way will obtain a deep desulfurization accompanied by 2-6 octane loss which can be recovered by etherification of C_5-C_7 olefins from the light gasoline. Characteristics the two gasoline fractions are shown in table 2.

FCC light gasoline Etherification

The light gasoline fraction (characteristics shown in table 2), containing isoolefins with 5-7 carbon atoms are etherified with (99.5%) methanol and (99%) ethanol (Merck) on the Purolite CT 275 catalyst. Purolite CT 275 is a macro-porous polymeric catalyst, strong acid whose properties are shown in the table 3.

The etherification process was carried out in a Bergoff autoclave at 60°C temperature and a 4-6 bar pressure, under 1500-1700 rpm stirring and a 9 h reaction time. Alcohol/gasoline initial molar ratio was 4/1vol. Temperature increasing over 65°C leading to decrease of the ethers yield, and lowering the pressure under 4 bar determine conversion decreasing as a result of C_5 vaporization which obstruct diffusion of the reactants in the catalyst macro-pores.

Table 2
FCC GASOLINE CHARACTERISTICS

Characteristics	FCC gasoline	Light FCC gasoline	Heavy FCC gasoline
Density [g/cm3]	0.7564	0.7159	0.7834
Sulfur [ppm]	446	52	688
Olefins [%wt.]	25.6	40.75	15.5
Initial boiling point [°C]	32	32	95
Final boiling point [°C]	188	95	188
RON	92.6	91.2	93.9
MON	82.9	83.1	82.8

Table 3
PUROLITE CT 275 CATALYST - SPECIFIC PROPERTIES

Matrix	Macro-porous
Humidity [%]	53-57
Drying capacity [meg/g]	Min 5,2
Total pore volume [cm3/g]	0.4-0.6
Specific surface [m2/g]	20-35
Pore diameter [Å]	600-750
Particle size [μ]	Max 2%<425 Max 2%>1190
Acid strength [kJ/mol]	60

Table 4
LIGHT FCC GASOLINE
COMPARATIVE PROPERTIES

Characteristics	Light FCC gasoline	Etherified light FCC gasoline	
		with methanol	with ethanol
Density, [g/cm^3]	0.7159	0.7324	0.7388
RON	91.2	94.0	95.4
MON	83.1	85.6	86.4
Ethers [% wt.]	0	16.8	19.2
ΔRON	-	2.8	4.2
ΔMON	-	2.5	3.3

Table 5
COMPARATIVE PROPERTIES OF
HYDRODESULFURIZTED HEAVY FCC
GASOLINE OVER Co-Mo/γAl_2O_3 catalyst

Characteristics	Hydrodesulfurized heavy FCC gasoline			
	Reaction temperature [°C]			
	260	280	300	320
Sulfur content [ppm]	23	14	10	9
Olefin content [% wt.]	9.32	8.08	716	6.46
Sulfur conversion [% wt.]	96.65	98.11	98.54	9869
Olefin conversion [% wt.]	39.87	47.87	53.80	58.32
COR	90.2	89.7	87.9	88.8
ΔCOR	3.7	4.2	4.8	5.1
COM	79.9	79.6	79.4	78.8
ΔCOM	2.9	3.1	3.5	4.0

After finishing of the reaction, autoclave is allowed to cool and discharge the reaction products. The catalyst is separated by decanting, unreacted alcohol is removed by washing with two portions with 25% water towards the total reaction products. The content of ethers and the octane number of the etherified gasoline was determined by IR spectrometry using IROX 2000 (Grabner) a commercial gasoline dedicated analyzer/spectrometer.

FCC light gasoline characteristics after etherification are shown in table 4. The results presented in Table 4 show an increase of RON and MON for both etherification with methanol and ethanol as a result of the olefins conversion into ethers.

The literature [19] reports a conversion of 0.84, 0.64, 0.43, and 0.23 regarding olefins C_4, C_5, C_6, and C_7. With increasing molecular mass of the olefins their conversion into ethers decrease. Lower olefins with 4-5 carbon atoms give higher conversions at the etherification with methanol, while for those with 6-7 carbon atoms in the molecule a higher conversion is obtained after etherification with ethanol [20, 21].

It is reveal that etherification with ethanol produce a higher conversion of the olefins indicated by higher content of ethers and higher octane number for etherified gasolines (tab.4). Associated with usage of the bioalcohols, the etherification allow the increasing of the bioregenerable component of the commercial gasoline according to European standards.

FCC heavy gasoline hydrodesulfurization

The heavy cracked naphtha with characteristics listed in table 2 was subjected to hydrodesulfurization into a micropilot plant described in [22]. The hydrodesulphurisation experiments were carried out in continuous fixed bed reactor at 260, 280, 300 and 320°C temperatures, 50 bar pressure and weight hourly space velocity of 1.0 h^{-1}. The HDS method are presented in [22]. Reaction product was cooled, condensed and collected into a gas-liquid separator at 20°C and atmospheric pressure.

Was used: two industrial catalysts based on Co-Mo / γAl_2O_3 with a composition of 3.1% wt. CoO & 12.0 %wt. MoO_3 (specific surface of 336 m^2/g and a pore volume of 0.61 cm^3/g), and also the Ni-Mo / γAl_2O_3 with composition 4.5% NiO and 13.5% MoO_3, (specific surface of 258 m^2/g and a pore volume of 0.48 cm^3/g).

Industrial catalysts was activated by sulfurization with light naphtha fraction containing 1000 ppm sulfur in the presence of hydrogen at 280°C, 15 bar pressure and weight hourly space velocity of 2h^{-1}. Activation is considered completed after H_2S formation in the reaction gases indicated by the yellow color of cadmium acetate aqueous solution 5% used as indicator.

Molybdenum sulfide is highly active in elimination of atoms S, N, O reactions than the cobalt sulfide, as so MoS_3 is consider the basic catalyst and Ni & Co is promoter that enhances the catalytic activity of Mo.

Conversion of the desulfurization reaction and saturation reactions of the olefins is determined as follows:

$$HDS = (S_{feed}(ppm) - S_{product}(ppm))/S_{feed}*100,\ \%wt$$

$$HDO = (O_{feed}(\%) - O_{product}(\%))/Of_{eed}*100,\ \%wt\ ,$$

where: S_{feed}, O_{feed} and $S_{product}$, $O_{product}$ - indicate the sulfur and olefins concentration in feed and hydrogenated product.

Influence of the hydrodesulfurization temperature and of catalyst on the hidrodesulfurizated gasoline characteristics and are presented in table 5, 6 and figures 4-7.

By increasing of the reaction temperature, the sulfur and olefins content decrease for both catalyst Co-Mo and Ni-Mo (fig. 4 and 6). The sulfur content of <10 ppm is obtained only by hydrodesulfurization on the Co-Mo catalysts at temperatures of at least 300°C. The conversions achieved

Table 6
COMPARATIVE PROPERTIES OF HYDRODESULFURIZED HEAVY FCC GASOLINE OVER Co-Mo/γAl_2O_3 catalyst

Characteristics	Hydrodesulfurized heavy FCC gasoline			
	Reaction temperature, [°C]			
	260	280	300	320
Sulfur content, [ppm]	43	28	21	20
Olefins content, [%wt]	7.72	6.18	5.26	4.58
Sulfur conversion, [%wt]	9375	95.93	96.94	97.10
Olefins conversion, [%wt]	50.20	60.12	66.04	70.42
RON	89.1	88.5	88.1	87.9
ΔRON	4.9	5.4	5.8	6
MON	79.7	79.0	78.6	78.4
ΔMON	3.1	3.8	4.2	4.4

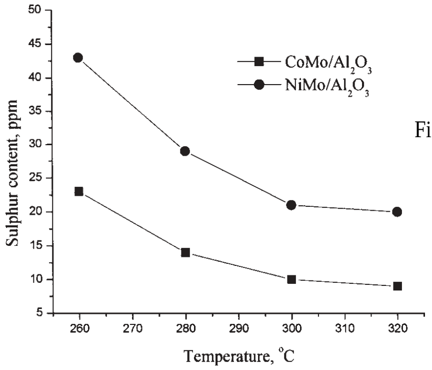

Fig. 4. Sulfur content versus reaction temperature and catalyst

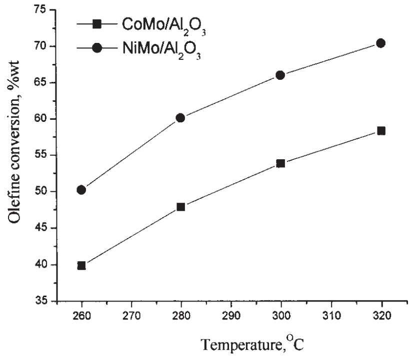

Fig. 7 Olefins conversion versus reaction temperature and catalyst

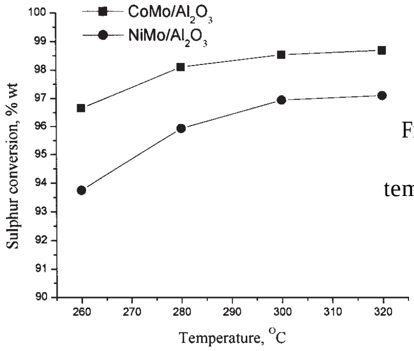

Fig. 5. Sulfur conversion versus reaction temperature and catalyst

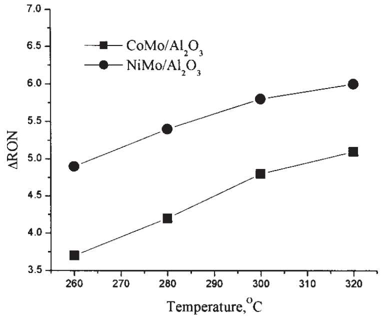

Fig. 8. Loss of RON versus reaction temperature and catalyst

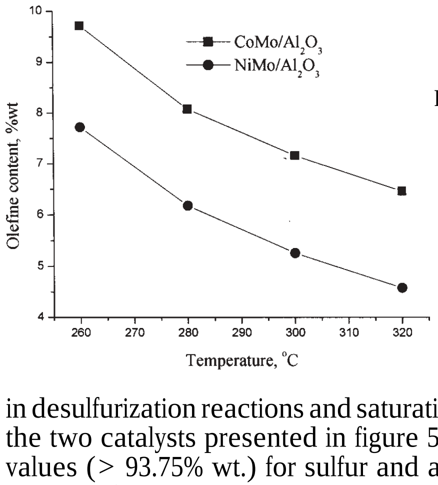

Fig. 6. Olefins content versus reaction temperature and catalyst

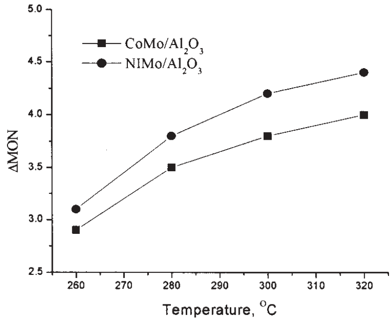

Fig. 9. Loss of MON versus reaction temperature and catalyst

in desulfurization reactions and saturation of the olefins for the two catalysts presented in figure 5 and 7 shows high values (> 93.75% wt.) for sulfur and average values (40-70% wt.) for the saturation reaction.

Decreasing of the sulfur content under 10 ppm for the CoMo/Al_2O_3 catalyst is accompanied by saturation of olefins with conversions greater than 53.8 wt.%. With conversion increasing in desulfurization reaction, the conversion in olefins saturation also increase, associated with reducing the octane number of the hydrofinated gasoline (fig.8 and 9). The comparison of results show a higher activity in hydrodesulfurization reaction for Co-Mo catalysts compared to Ni-Mo, which is more active in olefin saturation reactions in accordance with the data presented in the literature [23, 24]. Correlation between hydrodesulfurization reactions and the saturation of olefins for the two catalysts is shown in (fig.10 and 11).

Loss of octane number is higher when a deep hydrogenation of the FCC gasoline is make and sulfur content obtained is low. It is shown that in order to obtain a sulfur content of 20 ppm COR loss is 3.8 units for CoMo/Al2O3 and 6 units for the NiMo/Al2O3 catalysts.

After hydrodesulfurization COM decreases less than the COR and have greater reductions for catalyst Ni-Mo/Al2O3. The degree of desulfurization correlated with the loss of

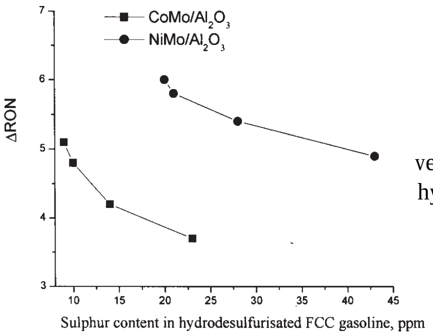

Fig. 10 Loss of RON versus sulfur content in hydrodesulfurized FCC gasoline

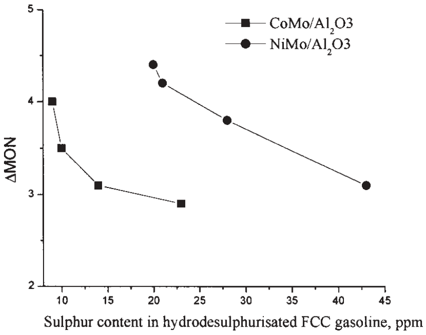

Fig. 11. Loss of MON versus sulfur content in hydrodesulfurized FCC gasoline

octane highlights the better selectivity of the Co-Mo catalyst in comparison with the Ni-Mo catalyst related to hydrodesulfurization reaction of the FCC heavy gasoline.

Conclusions

The hydrogenation is an efficient process for the deep desulfurization of the FCC gasoline, but is associated with octane number decrease as a result of the partial saturation of the olefins. Improving of the FCC gasoline quality with small losses of the octane number is possible through hydrodesulfurization of the heavy fraction separated from FCC gasoline in which the majority sulfur compounds are concentrated while the olefins are distributed in the light fraction.

The FCC heavy gasoline fraction was hydrofinated using two commercial catalysts based on Co-Mo and Ni-Mo. For the two catalysts the temperature increasing in the hydrogenation reaction (HDS) has led to increasing of desulfurization degree accompanied by partial saturation of olefins. The sulfur content of less than 10 ppm was obtained at 300°C on the Co-Mo catalyst associated with a reduction of 4.8 RON

The degree of desulfurization correlated with octane loss highlights a better selectivity for the CoMo catalyst compared with the Ni-Mo related to heavy FCC gasoline hydrodesulfurization.

Loss of the COR can be recovered by lower alcohols etherification of the C_5-C_7 olefins from the light gasoline fractions. After etherification with methanol the light gasoline COR is increased by 2.8 and MON with 2.5 respectively. For etherification with ethanol the octane increase is higher for RON with 4.2 units and 3.3 for MON.

Separation of FCC gasoline in two fractions followed by hydrodesulfurization of the heavy fraction and light fraction etherification is an efficient method of FCC gasoline quality upgrade.

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