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Fluid Catalytic Cracking Unit Performance Improvement by Application of the Topsoe Aroshift Technology

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Application of the Topsoe Aroshift Technology in the Lukoil Neftochim, Bulgaria (LNB), fluid catalytic cracking (FCC) unit was studied in this work. The hydrotreated vacuum gas oil (HTVGO), feed for the LNB FCC unit, was treated in the Topsoe Aroshift pilot plant. The HTVGO and Aroshifted HTVGO were cracked in a laboratory fluid bed catalytic cracking unit (FCC advanced catalytic evaluation unit). The Aroshift treatment of the HTVGO increased the mononuclear aromatics content by 3%, which resulted in 3% higher FCC conversion and higher gasoline selectivity. The octane number of gasoline, produced from the Aroshifted HTVGO, was about 0.5 lower than that of gasoline, obtained by HTVGO cracking. The economic benefit of the Aroshift process application in the LNB FCC unit at a feed rate of 185 t/h was evaluated to be $6.78 million U.S./year.

Introduction

Fluid catalytic cracking (FCC) feed hydrotreatment is an excellent way for production of low-sulfur gasoline and diesel. Moreover, the FCC feed pretreatment improves process economics as it increases feed hydrogen content. That leads to higher conversion and higher yields of highly valuable products.[1] Typically, an ultralow sulfur level in FCC gasoline is achieved by increasing the severity in the FCC feed pretreater. However, this mode of operation negatively affects the FCC feed quality. As the severity increases, the feed hydrogen drops due to polynuclear aromatics (PNA) saturation reduction, which is thermodynamically limited. To alleviate the negative effect of higher severity FCC pretreater operation, Haldor Topsoe developed the proprietary “Aroshift” process. Aroshift is a simple process comprising technology and a specialty catalyst that lowers the sulfur and PNA content in the feed to the FCC unit.[2]

The Lukoil Neftochim Bourgas (LNB) fluid catalytic cracking unit consists of a feed hydrotreating section, a FCC reactor−regenerator section, and a vapor recovery section.[3] To achieve ultralow sulfur levels in cracked naphtha, the FCC pretreater has been operating at more severe conditions. This, however, decreased the FCC feed hydrogen content and FCC unit conversion.[4] To evaluate the Aroshift technology applicability to the conditions at LNB, an FCC unit hydrotreated vacuum gas oil (feed for the FCC reactor section) has been treated at Haldor Topsoe’s Aroshift process pilot unit. The product and feed of the Aroshift process have been cracked in a BASF fluid bed catalytic cracking pilot unit.

The aim of this work is to discuss the results of cracking experiments and to evaluate the effect of application of the Aroshift technology to the FCC feed pretreatment section in the Lukoil Neftochim Bourgas refinery.

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Table 1. Physical and Chemical Properties of the Hydrotreated Vacuum Gas Oil (HTVGO) and the Aroshifted Product

analysis	HTVGO	Aroshifted HTVGO
SG@60/60F	0.9022	0.8997
sulfur, wt %	0.0594	0.0510
Nitrogen, wt ppm	964	787
monoaromatics, wt %	26.7	29.7
diaromatics, wt %	7.1	6.0
polynuclear aromatics, wt %	8.5	6.6
H content, wt %	12.62	12.70
Ni, wt ppm	0.1	0.1
V, wt ppm	0.1	0.1
Fe, wt ppm	0.1	0.1
distillation ASTM-D1160, °C		
IBP	265	253
10%	404	396
30%	431	428
50%	452	451
70%	470	472
90%	500	500
95%	507	509

Experimental Section

The hydrotreated vacuum gas oil (HTVGO) from LNB FCC pretreater has been treated in the Aroshift process pilot plant using a proprietary catalyst at the following conditions: temperature = 350 °C; hydrogen partial pressure = 40 atm H_2; hydrogen/oil = 300 N L/L.

To simulate conditions without gas removal to the HTVGO, tetrabutyl disulfide (TBDS) and dibutylamine have been added to obtain sulfur and nitrogen contents equal to those of the hydrotreatment feed (heavy vacuum gas oil): S, 1.98%; N, 1165 ppm. Table 1 summarizes the physical and chemical properties of the HTVGO and the Aroshift product (Aroshifted HTVGO).

The HTVGO and the Aroshifted HTVGO have been cracked on a commercial equilibrium catalyst in a pilot unit with fluidized bed (advanced catalytic cracking evaluation unit) at the following conditions: reaction temperature, 532 °C; catalyst

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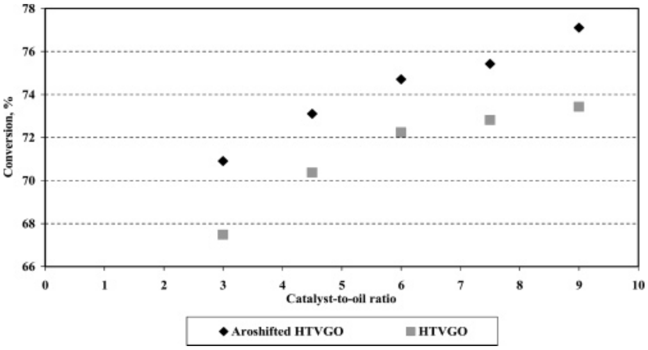

Figure 1. Dependence of the conversion of the Aroshifted HTVGO and the HTVGO on the catalyst-to-oil ratio.

Table 2. Physical and Chemical Properties of Commercial Equilibrium FCC Catalyst

chem composn		physical properties	
Al_2O_3, wt %	41.5	APS, μm	76
Na, wt %	0.17	ABD, g/cm^3	0.94
Re_2O_3, wt %	1.38	MSA, m^2/g	50
Fe, wt %	0.56	BET surface area, m^2/g	134
V, ppm	229	zeolite unit-cell size, nm	24.280
Ni, ppm	64		

contact time, 6 s; reactor catalyst quantity, 9 g. To obtain yield curves as a function of conversion, the catalyst-to-oil ratio has been varied between 3 and 9 wt/wt. The equilibrium catalyst properties are presented in Table 2.

Results and Discussion

It can be seen from the data in Table 1 that a PNA conversion of 19.2% has been obtained in the Aroshift unit. This has been accompanied by FCC feed density reduction and hydrogen content increase. Data in Figure 1 demonstrate the positive effect of the Aroshift treatment on the FCC feed crackability. It can be noted that the Aroshifted HTVGO conversion has been higher by 3% at all studied catalyst-to-oil ratios. The product yields vary as a function of conversion. Figure 2 shows that the FCC feed PNA reduction led to a lower catalyst deactivation due to lower coke generation. The lower catalyst deactivation affects catalyst selectivity by increasing primary hydrogen transfer to the β-scission cracking ratio. That results in stabilization of higher molecular weight products.[5] This may explain the higher conversion and the higher gasoline yield during Aroshifted HTVGO cracking at the expense of lower gas and coke yields.

Data in Figure 2 indicate that optimum conversion point (where gasoline yield reaches its maximum) has shifted to higher values during Aroshifted HTVGO cracking. It is well-known that the optimum conversion (conversion at which overcracking is observed) correlates with the feed gasoline precursor's content (saturated + mononuclear aromatics (MNA)).[6] In practice, the PNA transformation to MNA means that gasoline precursor's content increases in the Aroshifted HTVGO relative to that of the HTVGO. The MNA increase in the Aroshifted HTVGO by 3% led to its optimal conversion increase by about 3%.

Figure 3 shows a graph of LPG olefinicity variation as a function of conversion of both FCC feeds. These data indicate that the LPG olefinicity, obtained from Aroshifted HTVGO, was higher. It could be concluded, as a result of the lower catalyst deactivation during Aroshifted HTVGO cracking, that the reactions of secondary hydrogen transfer are suppressed. These observations confirm previous findings of the feed higher gasoline precursor's content effect on the catalytic cracking products olefinicity.[7]

Dependences of research (RON) and motor (MON) octane numbers on conversion of both FCC feeds are illustrated in Figures 4 and 5. It is evident that octane number of the gasoline obtained by HTVGO cracking was higher than that of the gasoline obtained by Aroshifted HTVGO cracking. An explanation of this observation could be found if a break down of gasoline composition is given. The gasoline hydrocarbon group composition variation as a function of both feeds' conversion is presented in Figure 6. It can be seen from these data that, similar to the LPG olefinicity, the gasoline olefinicity during the Aroshifted HTVGO cracking was higher, which resulted in higher naphthene and lower aromatic contents.

It is well-known that reactions of hydrogen transfer can be represented in the following way:

$$3\ \text{Olefin} + \text{Naphthene} = 3\ \text{Paraffin} + \text{Arene}$$

It is evident that hydrogen-transfer reaction suppression leads to higher gasoline olefinicity, higher naphthene content, and

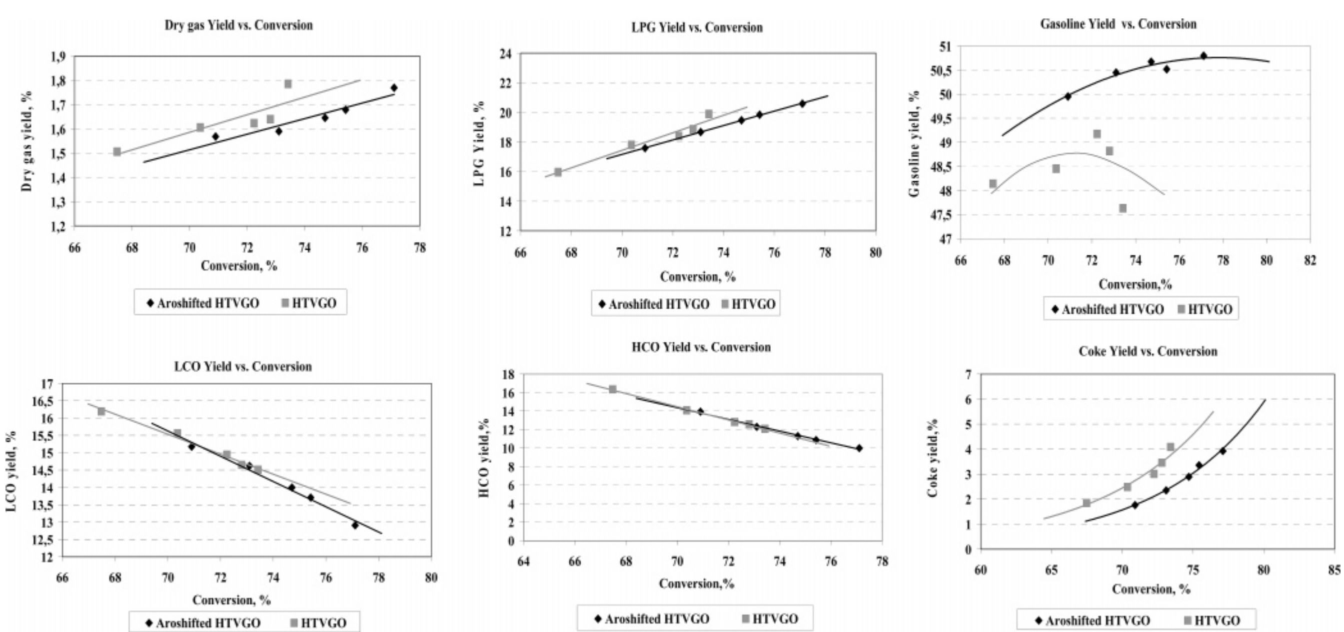

Figure 2. ACE product yields as a function of conversion of the Aroshifted HTVGO and the HTVGO.

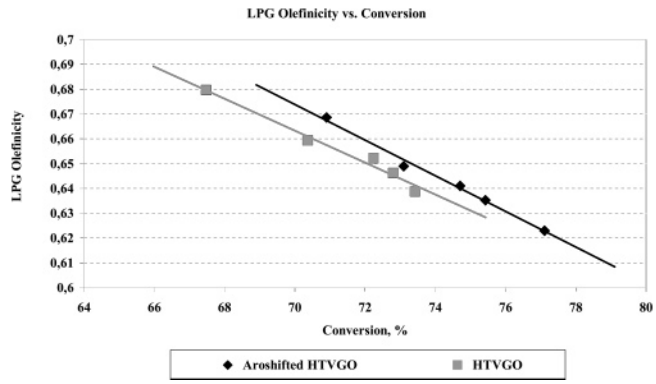

Figure 3. Dependence of the LPG olefinicity on the conversion.

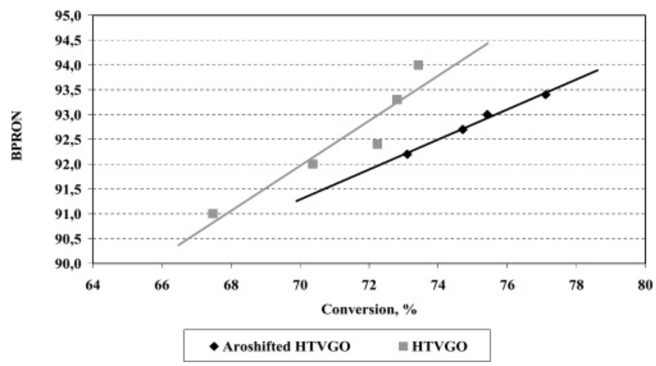

Figure 4. Dependence of the gasoline RON on the conversion.

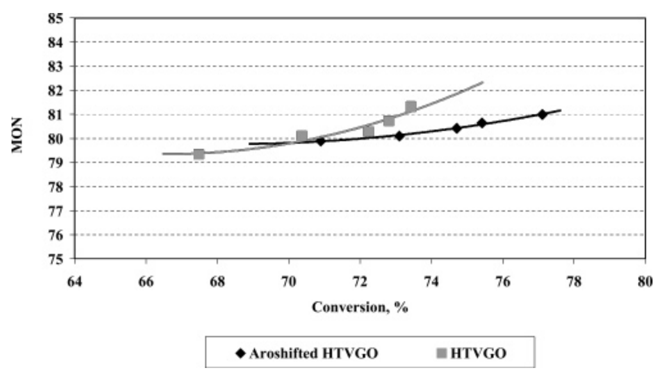

Figure 5. Dependence of the gasoline MON on the conversion.

Table 3. FCC Yields at Constant Coke Yield

	yield, wt %	
	Aroshifted HTVGO	HTVGO
fuel gas	1.62	1.58
propane	1.06	0.96
propylene	5.28	4.94
C_4 olefins	6.92	6.61
butane	5.50	4.89
gasoline	50.52	48.59
LCO	14.41	14.98
HCO	12.19	14.95
Coke	2.50	2.50
210 °C conversion	73.40	70.07

lower aromatic content. The lower gasoline octane number during cracking of Aroshifted HTVGO may be explained by higher content of high molecular weight hydrocarbons in gasoline (higher catalyst selectivity to higher molecular weight products that are known to have lower) octane[8] and higher naphthene and lower aromatic contents. With the increase in conversion, an increase of secondary reactions takes place that increases the selectivity to lower molecular weight products (higher gas and lower gasoline selectivity). Also, secondary hydrogen transfer is enhanced. This results in increased aromatic content and decreased naphthene content, which has a positive effect on gasoline octane. Due to higher reactivity of the Aroshifted HTVGO when cracked at the same catalyst-to-oil ratio, higher conversion is obtained, and the difference in octane between gasoline originating from the Aroshifted HTVGO and that from the HTVGO becomes negligible.

Table 4. Product Prices

product	price, U.S. dollars/t	product	price, U.S. dollars/t
fuel gas	292.00	gasoline	555.70
LPG	564.50	LCO	606.70
propylene	1085.90	HCO	273.00
C_4 olefins	553.30		

Table 5. Revenue Differences for FCC Unit with Aroshift Process

component	yield difference, %	yield difference, tons/day	add revenue, U.S. dollars/day
fuel gas	0.04	1.78	519.76
LPG	0.71	31.52	17 793.04
propylene	0.34	15.10	16 397.09
C_4 olefins	0.31	13.76	7 612.41
gasoline	1.93	85.69	47 617.93
LCO	−0.57	−25.31	−15 355.58
HCO	−2.76	−122.54	−33 453.42
subtotal			41 131.23
process applicability factor			0.5
net revenue increase, U.S. dollars/day			20 565.60
on-stream, days/year			330
yearly revenue increase, million U.S. dollars			6.78

Data presented in Figure 6 also show that the isoparaffin content of gasoline reached a maximum after which it started to drop as conversion increased. This can be explained by reaching the overcracking point, and at the following conversion increment, the gasoline range isoparaffins start to crack into lower molecular weight products.

To evaluate the Aroshift process application to a commercial LNB FCC unit, a comparison of the product yields at constant coke yield was made (Table 3) as the commercial FCC unit is known to be heat-balanced and operated at constant coke yield. It is evident from these data that the conversion of Aroshift product is higher by about 3%. It can be concluded that the MNA content increment by 3% corresponds to the same conversion increase in the commercial FCC unit.

The yield distribution given in Table 3 has been used to evaluate the economic benefit of the Aroshift process application at LNB FCC unit at 185 t/h FCC reactor section feed rate. The economic benefit has been estimated by using the average prices of International Markets for September 2006 (Table 4). The price of fuel gas, propane−butane, and gasoline has been accepted to be equivalent to that of the International Markets. The propylene price has been decreased by 10% because LNB produces propylene for its polymer complex needs. The price of C_4 olefins has been assumed to be valued at the gasoline price minus $2.50 U.S./t processing costs. LCO produced at the LNB FCC unit is hydrotreated and is used for the production of ultralow-sulfur diesel (ULSD). To produce ULSD ($606.80 U.S./t) from LCO, it is necessary to consider operating costs of $4.10 U.S./t for the HDS unit, and a price of $602.70 U.S./t for the LCO has been assumed. HCO is used for production of fuel

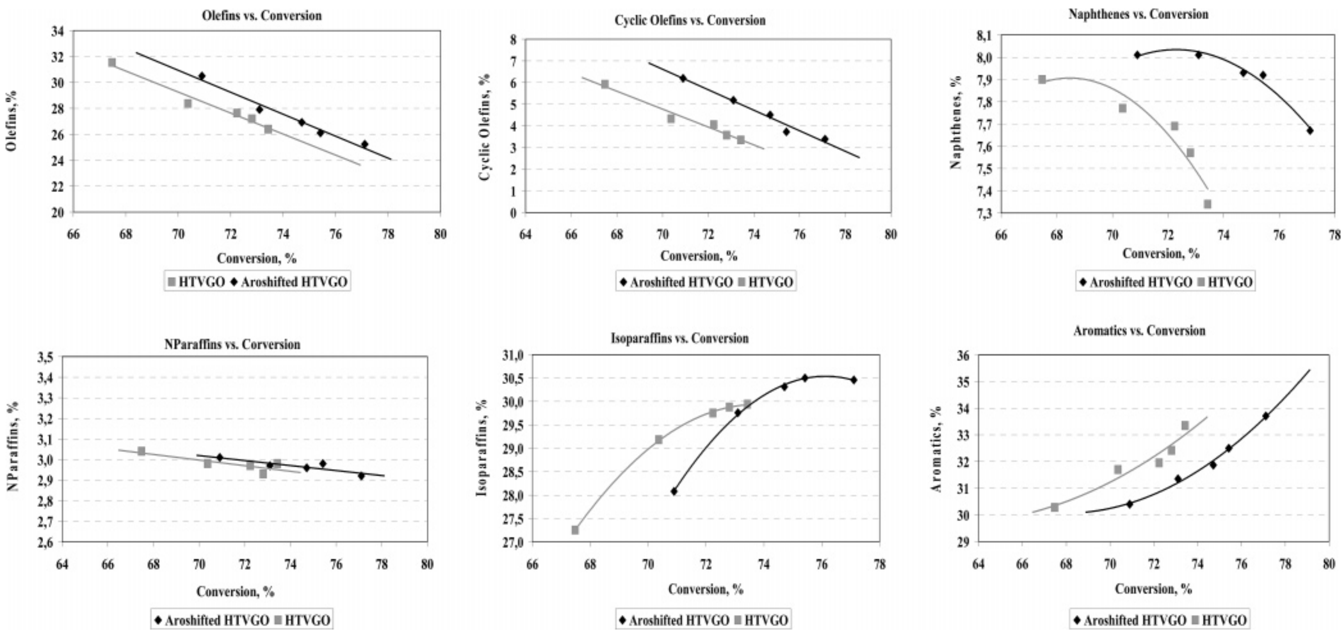

Figure 6. Distribution of compounds in the FCC gasoline obtained by cracking of HTVGO and Aroshifted HTVGO as a function of conversion.

oil, and this price has been assumed to be equivalent to that of the International Markets of $273.00/t.

The difference of the yields and product quality at the beginning and the end of the catalyst cycle is typical for the most conventional units. However, at the end of run, the product yields will be close to those shown in Table 3. To approach the real conditions, the "process applicability factor" has been used, which eliminates the difference in the quality and yield of products from the beginning to the end of the catalyst cycle. Data in Table 5 indicate that Aroshift process application to LNB FCC unit leads to an economic benefit of $6.78 million/year.

Conclusions

The treatment of hydrotreated vacuum gas oil from the LNB FCC unit by the Aroshift process leads to an MNA content increase of 3% at the expense of a PNA content decrease. The improved Aroshifted HTVGO quality results in 3% higher conversion and a higher gasoline selectivity at the expense of lower coke and gas selectivity. The octane number of the gasoline produced from the Aroshifted HTVGO is about 0.5 lower than the octane number of gasoline obtained by HTVGO cracking. The economic benefit of the Aroshift process application to the LNB FCC unit at 185 tons/h feed rate is evaluated to be $6.78 million/year.

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