

HYDRODEAROMATIZATION OF GAS OIL FRACTIONS ON PT-PD/USY CATALYST

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ABSTRACT

Beside the reduction of sulphur content in diesel fuels, aromatics reduction is also relevant, because it contributes to the increase of cetane number and to be abatement of exhaust gas emissions, mainly hydrocarbons (HC) and particulate matter (PM). The aim of present study was to identify and quantify the key process parameters for hydrodearomatization of prehydrogenated gas oil fractions on Pt-Pd/USY zeolite catalysts. The effect of key process parameters (temperature, pressure, LHSV, H₂-to-hydrocarbon ratio) on the yield and quality of products was investigated. Additionally, the effect of the reduction of aromatic content on the main properties of gas oils (density, refractive index, cetane number etc.) was also studied.

Keywords: Hydrodearomatization, gas oil, Pt-Pd/USY, cetane index, cetane number, nitrogen content

1. INTRODUCTION

Diesel fuel specifications are continuously tightening and its demand is also increasing, especially in Europe. Sulphur limit of diesel fuels is currently 50 ppm in the European Union that will be reduced to 10 ppm from 2009. However, ultra low sulphur (≤ 10 ppm) diesel fuels have to be already made available regionally in a geographically balanced manner^[1-3]. Not only sulphur limits but also aromatic content is expected to become stricter. A maximum specification for total aromatics is likely to be established beside the limit for polycyclic aromatics. The most important reason of aromatics reduction is that these compounds contribute to a large extent to exhaust gas emissions, especially for NO_x and PM. Removal of aromatics assists for meeting the requirements of emission standards of diesel engines introduced recently in the European Union (Table 1)^[15]. In addition to the tougher specifications, attention should also be paid to the increasing demand. Diesel fuel consumption was 140 million tons in the European Union in 2005 that is expected to raise to 170 million tons by 2020 according to the projections^[4,5] (Fig. 1.)

Increasing level of demand is not only caused by the growing consumption of diesel fuels used for transportation purpose but also by the widening application of gas oil as a feedstock for steam cracking. This is primarily the result of the growing demand on light olefins. As a result, the world's steam cracking capacity is going to increase because this is the most cost-effective technology for the production of light olefins^[3]. In several regions where the availability of light hydrocarbons is limited (e.g. European Union), the required amount of light olefins can be produced not only from naphtha but also through the pyrolysis of heavier hydrocarbon fractions for instance kerosene and gas oils.

Recent environmental legislation of diesel fuels focuses on sulphur content, aromatic content (mainly polynuclear aromatics) and cetane number. Tightening fuel requirements and higher demand

prompted the petroleum companies to proceed with research and development, mainly in the field of heterogeneous catalytic hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) [6]. To meet the regulation of cetane number, several approaches have been proposed. One approach for improving cetane number is to use cetane boosters (additive). These additives improve cold-start performance, reduce combustion noise and particulate matter emissions and improve vehicle driveability. Cetane boosters, however, increase the flammability of the fuel and degrade the storage stability. Another alternative is the blending of Fischer-Tropsch gas oil into diesel fuel results in increased cetane number and reduced concentration of aromatics, sulphur and other impurities. The third option is to reach higher cetane number while reducing the aromatics by deep hydrodearomatization. These are the most important technologies for producing environmental-friendly diesel fuels.

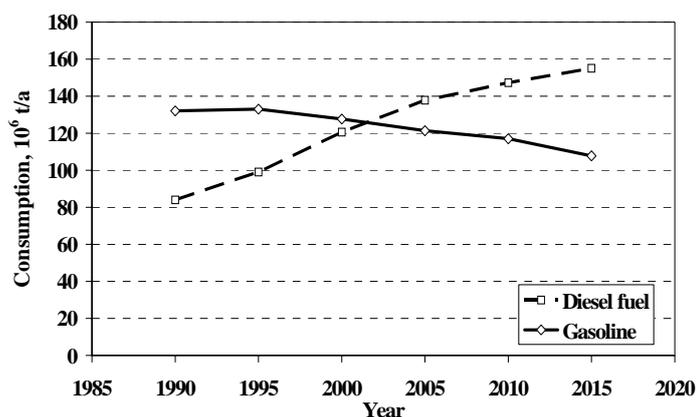


Fig. 1. Trends of diesel fuels and gasoline demands in EU

Table 1. Emission standard of passenger cars powered by diesel engines (EU)

Emission standard	Year	Emission, g/km			
		HC* + NOx	NOx	CO	PM**
Euro 1	1992	0.97	-	2.72	0.140
Euro 2 - IDI	1996	0.70	-	1.00	0.080
Euro 2 - DI	1999	0.90	-	1.00	0.100
Euro 3	2000	0.56	0.50	0.64	0.050
Euro 4	2005	0.30	0.25	0.50	0.025
Euro 5	2008	0.25	0.20	0.50	0.005

*HC: hydrocarbons, ** PM: particulate matter

In case of steam cracking the yield of light olefins highly depends on the properties of feedstock. The rising demand on light olefins and the growing capacity of steam cracking results in a shortage of conventional steam cracking feeds requiring an increased use of high boiling petroleum fractions (mainly kerosene and gas oil). The unfavourable cracking behaviour of gas oil resulting in low olefin yields and high rate of gum and coke formation is caused by the high aromatic (mainly polyaromatic) content of gas oils. Especially the formation of gum and coke, which is higher compared to ethane or naphtha steam cracking, renders the process more complicated and leads to more frequent shut-down of steam cracking plants. Consequently, the aromatics reduction is also important from the aspect of steam crackers' feed because aromatic hydrocarbons have negative effect on the light olefins' yield in the steam cracking process (Table 2).

Table 2. Product yields of steam cracking in case of different feeds (same steam cracking severity)

Properties	Light gasoline	Heavy gasoline	Light gas oil	Heavy gas oil
Boiling range, °C	36-110	40-164	176-343	335-515
Aromatic content, %	2.6	12.1	24.1	48.0
Yield of products, %				
Methane	17.4	13.8	11.6	8.9
Ethylene	31.0	25.5	24.1	18.9
C ₃	18.8	15.3	14.3	13.9
C ₄	10.0	8.3	8.4	9.7
Pyrolysis gasoline	14.4	16.9	18.1	19.0
Pyrolysis oil	2.0	5.1	18.9	24.4

A possible grouping of the gas oil hydrodearomatization technologies is given below:

- Hydrodearomatization and hydrodesulphurization:
 - One-stage technologies that are suitable to treat feeds with relatively high sulphur content over transition metal-sulphide ($\text{NiMo}/\text{Al}_2\text{O}_3$, or $\text{CoMo}/\text{Al}_2\text{O}_3$) catalysts [7,8].
 - Two-stage technologies that perform deep aromatics reduction with noble metal catalysts after HDS of the feed [9-11] since the hydrogenation activity of these catalysts is decreased by the sulphur compounds (e.g. by dibenzothiophenes) [12-14]. Therefore this type of catalysts can only be applied in a second reactor (aromatic reduction) after removing the heteroatom-containing compounds of the feed on a transition metal sulphide catalyst or can be applied in a one-stage process in case of feed with low sulphur and nitrogen contents.
- Hydrocracking of feeds of high aromatic, sulphur and nitrogen contents on $\text{NiW}/\text{Al}_2\text{O}_3$ catalyst in one- or two-stage processes.

Recently, two-stage processes are becoming more and more wide-spread because of the significant sulphur reduction in diesel fuels (sulphur limit 50(10) ppm). The rate of aromatic saturation is up to about 70-90% for two-stage processes in contrast with the 40-55% HDA level of one-stage processes.

The aim of our present study was to identify and quantify the key process parameters for the hydrodearomatization of prehydrogenated gas oil fractions on Pt-Pd/zeolite catalyst being under development. Effect of the key process parameters (temperature, pressure, LHSV, H_2 -to-hydrocarbon volume ratio) on the yield and the quality of products was investigated. The effect of aromatic reduction on the analytical and performance properties of products was also studied.

2. EXPERIMENTAL

2.1. Apparatus

The experiments were carried out in a high-pressure reactor system (Fig 2). This consists of a tubular down-flow reactor of 100 cm^3 efficient volume free of back-mixing; it contains equipments and devices applied in the reactor system of hydrotreating plants (pumps, separators, heat exchangers, as well as temperature, pressure and gas flow regulators). Explanation of symbols is summarized in Table 3. Under the range of the investigated reactor conditions the gas oil was present in mixed phase (both vapour and liquid).

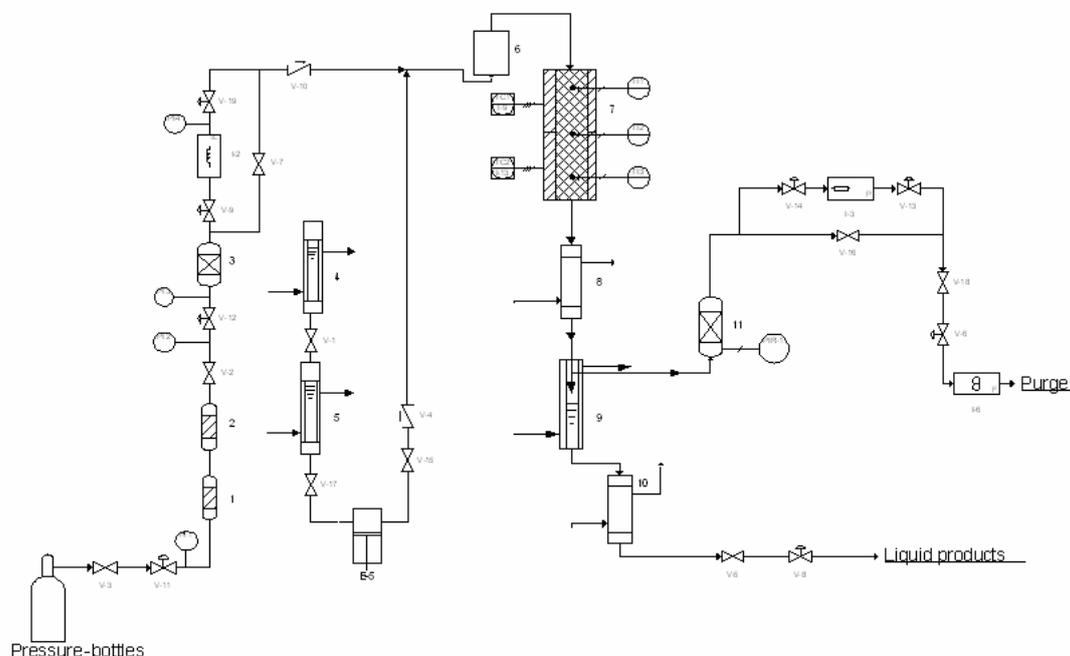


Fig. 2. High pressure reactor system

Table 3. Explanation of symbols

Symbol	Equipments	Symbol	Equipments
V-1, V-3, V-7, V-8, V-9, V-10, V-15, V-16, V-18	cut-off valve	5	feeder burette
V-2, V-4, V-5, V-6, V-13, V-14, V-17, V-19; V-20	control valve	P-1	pump
PI1, PI2, PI3, PI4	manometer	6	pre-heater
1	oxygen converter	7	reactor
2	gas dryer	8,10	cooler
3,11	gas filter	9	separator
FIC-1	gas flow meter/controller	PIR-1	pressure register
V-11, V-12	back-pressure valve	FI-1	wet gas meter
4	storage burette	PIC-1	pressure meter/controller

2.2. Catalyst

The HDA experiments were carried out on Pt-Pd/H-USY catalyst that is under development.

2.3. Feeds

The feedstocks were prehydrogenated gas oil fractions. Their important properties are summarized in Table 3.

Table 3. Main properties of feeds

Parameters	Feed "A"	Feed "B"	Feed "C"
Density, 15.6°C, kg/m ³	837.2	836.4	876.3
Sulphur content, ppm	5	8	57
Nitrogen content, ppm	< 1	30	98
Aromatic content, %			
total	24.2	33.5	51.2
mono	21.9	29.5	41.1
di	2.0	3.2	8.5
poly	0.3	0.7	1.6
Cetane index	53.1	50.3	39.9
Cetane number	51.3	50.1	43.6
Distillation, D86, °C			
Initial b. p.	184	176	200
10 vol.%	219	213	223
50 vol.%	271	265	272
90 vol.%	335	330	334
95 vol.%	349	352	340
Final b. p.	356	361	351
Pour point, °C	-15	-16	-19
CFPP, °C	-10	-12	-13
BMCi	28.2	29.2	47.4

2.4. Methods

The properties of the feeds and products were determined by standard test methods summarized in Table 4. The experiments were carried out on catalyst of steady-state activity, by continuous operation.

Table 4. Standard test methods

Properties	Standards	Properties	Standards
Density, at 15°C	EN ISO 12185	Sulphur content, ppm	EN ISO 20846
Cetane index	EN ISO 4264	Nitrogen content, ppm	ASTM D 5762
Cetane number	EN ISO 5165	Aromatic content, wt%	EN 12916
Flash point, °C	EN ISO 2719	Distillation data, °C	EN ISO 3405

In order to determine the applicability of the products as feedstock for steam cracking the Bureau of Mines Correlation Index (BMCI, equation 1) was calculated which refers to the hydrocarbon types in the petroleum products. Polyaromatic hydrocarbons have the highest BMCI values (above 200) and paraffin hydrocarbons the smallest ones (below 20). BMCI value is thus an appropriate factor to evaluate the level of aromatic saturation of various feedstocks. This index characterizes the feedstocks and products in wide range and enables easy determination of the nature of hydrocarbon fractions. Considering blendstocks of diesel fuel, middle distillates having low BMCI value are optimal, since their paraffin content is high and thus their cetane number is high, as well. BMCI value was calculated using equation (1).

$$\text{BMCI} = \frac{48640}{\text{VABP}} + 473.7 \times d_{15.6}^{15.6} - 456.8 \quad (1)$$

where:

VABP - volume average boiling point, K

$d_{15.6}^{15.6}$ - density, g/cm³

In order to evaluate the applicability of the products as motor fuels the cetane index was calculated (equation 2).

$$\text{CI} = 454.74 - 1641.416d + 774.74d^2 - 0.554T + 97.803(\log T)^2 \quad (2)$$

where:

d – density at 15.6°C, g/cm³,

T – volume average boiling point, °C.

Hydrodearomatization efficiency of catalyst was calculated by equation (3).

$$\text{HDA, \%} = 100(A_{\text{feed}} - A_{\text{product}})/A_{\text{feed}} \quad (3)$$

where:

A_{feed} : total aromatic content of feed, %,

A_{product} : aromatic content of product, %.

2.5. Process parameters

The range of measured process parameters were as follows: temperature: 260-360°C, pressure: 35-60 bar, liquid hourly space velocity (LHSV): 1.0–4.0 h⁻¹ and H₂-to-hydrocarbon volume ratio: 600 Nm³/m³.

3. RESULTS AND DISCUSSION

The yield of liquid products was higher than 98%. Each sample was purged with nitrogen to remove dissolved H₂S and NH₃ (mainly in case of feed "B" and "C") and stabilized (separation of light products) before the analytical measurements. Figure 3 and 4 show the gas oil yield as a function of temperature, pressure and LHSV in case of feed "A". The yield of gas oil decreased with temperature, pressure, and increased with LHSV. The reason of this is the higher hydrocracking activity of catalyst at more severe process conditions. The gas oil yield decreased by about 9% when the temperature was increased from 260°C to 360°C at 35 bar (Fig. 3). The lowest gas oil yield (84.0%) was obtained at the most severe process conditions (temperature: 360°C, pressure: 60 bar, LHSV: 1.0 h⁻¹). In case of feed "B" these values were 6% and 87.5% when the temperature was increased from 260 °C to 360°C and pressures were 35 bar and 60 bar, respectively (Figs 5 and 6). The lowest gas oil yields were 84% for feed "A" and 87.5% for feed "B". The highest gas oil yield (91.6% due to the lowest reaction rate of hydrocracking) was obtained in case of feed "C" (sulphur content: 57 ppm, nitrogen content: 98 ppm, results are not displayed here). The experimental results indicate that mainly the basic nitrogen compounds (for example: pyridine, quinoline or acridine) of feed "B" (30 ppm) and feed "C" (98 ppm) are responsible for the reduced hydrocracking activity of applied Pt-Pd/zeolite catalyst attributed to the reduced acidity of catalyst support.

Figure 7, 8 and 9 show the effect of temperature, pressure and LHSV on the total aromatic content of the products (feed "A"). The figures show that total aromatic content of the products was lower than that of the feed at every applied temperature and pressure. The degree of dearomatization linearly increased with temperature up to 300°C, then the increase was moderated and became zero at about 330°C (Fig. 7). By increasing the temperature after this point, the total aromatic content of products either increased (at 35 and 45 bar) or did not change (at 60 bar). This means that the degree of dearomatization has a temperature maximum. The thermodynamic equilibrium was probably attained for the exothermic hydrogenation of aromatics. Total aromatic content of the products decreased with LHSV (Figs. 8, 11). Similarly to the temperature, the total pressure also contributed to

the reduction of total aromatic content (Figs 7, 10). Product of lowest total aromatic content (4.0%) could be obtained at a temperature of 320°C, pressure of 60 bar and LHSV of 1.0 h⁻¹ for feed "A" (Fig. 9). Products having lower than 10% aromatic content can be obtained at the following parameters in case of feed "A": T = 320°C, P = 45 bar, LHSV = 1.0 h⁻¹. In case of feed "B" trends of decrease of total aromatic content were similar to the other feed (Figs. 10-12).

Hydrodearomatization efficiency was in the range of about 4.2% to 83.5% for feed "A" and 2.5%-61.1% for feed "B" depending on process parameters. Hydrodearomatization efficiency was a lower in case of feed "B". The results show that nitrogen and sulphur contents of feed "B" inhibited the aromatic hydrogenation activity of Pt-Pd/zeolite (mainly the basic ones: pyridine, quinoline, acridine which blocked the acid sites of the support). The hydrodearomatization efficiency by feed "C" was changed from 2.0% to 45.2%.

The previously detailed investigations of gas oils having different composition showed that the reduction of polyaromatic content was high for every feed while the conversion of mono aromatics largely depends on the nitrogen and sulphur content of the feeds. The hydrodearomatization efficiency decreased with increasing nitrogen content of feed [16,17].

HDA efficiency increased with temperature in the lower temperature range until the optimum point in case of both feeds "A" and "B". At this point the thermodynamic equilibrium of aromatics hydrogenation is established and at higher temperatures the equilibrated hydrogenation is retarded. This is supported by the change of hydrocarbon composition. Fig 13 shows the change of partition of paraffinic, naphtenic and aromatic carbon atoms as a function of temperature in case of feed "A". Above 320°C saturation of aromatic ring was followed by the ring opening reaction due to the high hydrogenation activity of applied noble metal/zeolite catalyst. Conversion of naphtenes to paraffins results in the shift of the aromatics ↔ naphtenes equilibrium towards naphtenes. The rate of naphtenic ring opening reactions was strongly influenced by temperature and pressure (Figs. 13, 14). This is the reason why higher pressure resulted in higher HDA efficiency independently of temperature (Figs. 7, 10). The results are similar in case of feed "B" and "C".

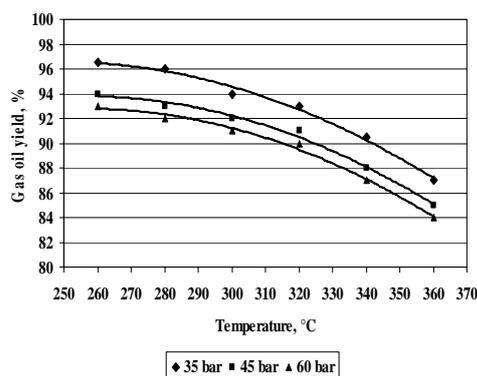


Fig. 3. Effect of temperature and pressure on gas oil yield (Feed "A", LHSV = 1.0 h⁻¹)

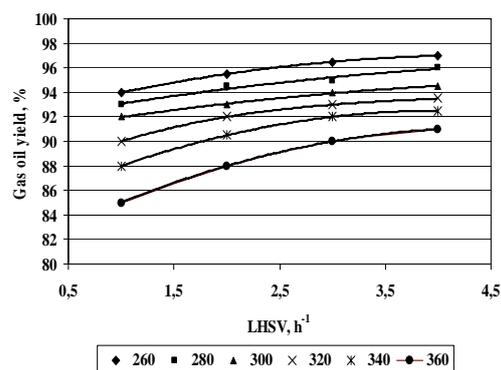


Fig. 4. Effect of LHSV and temperature on gas oil yield (Feed "A", P = 45 bar)

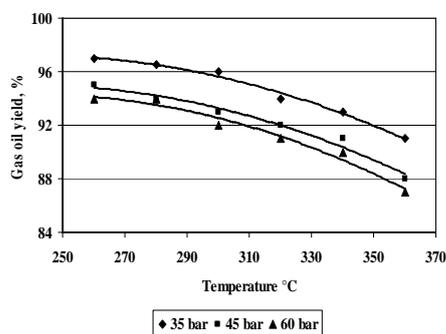


Fig. 5. Effect of temperature and pressure on gas oil yield (Feed "B", LHSV = 1.0 h⁻¹)

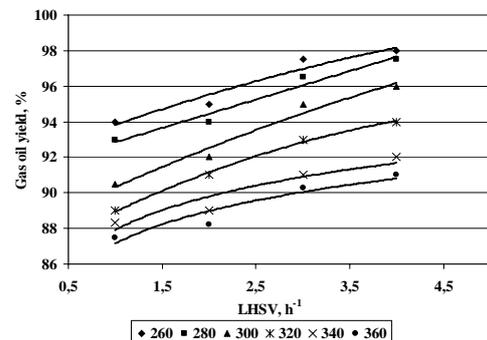


Fig. 6. Effect of LHSV and temperature on gas oil yield (Feed "B", P = 45 bar)

The formation of monoaromatics from di- and polyaromatics by consecutive ring-opening hydrogenation took place with a higher rate than their further saturation to naphtenes. The rate of saturation of mono and polyaromatics is different because saturation of polyaromatics takes place more easily [8]. Due to the excellent HDA efficiency of Pt-Pd/USY the di- and polycyclic aromatic content of products was lower than 0.4%, even under the mildest process conditions if feeds of low sulphur and nitrogen contents were investigated. This value was in the order of the reproducibility of

applied test method. Therefore change of total aromatic content was nearly the same as that of monoaromatics. However, in case of feed "C" the concentration of di- and polyaromatic hydrocarbons was changed from 5.4% to 1.6% because the hydrodearomatization efficiency was lower due to the high sulphur and nitrogen content of feed "C".

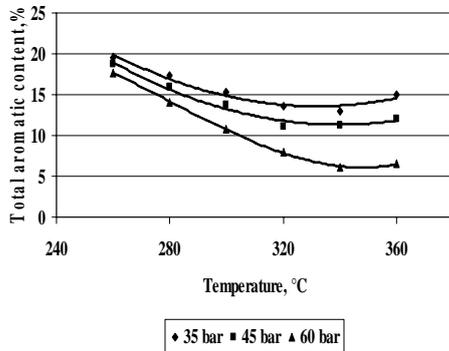


Fig. 7. Effect of temperature and pressure on total aromatic content (feed "A", LHSV=2.0 h⁻¹)

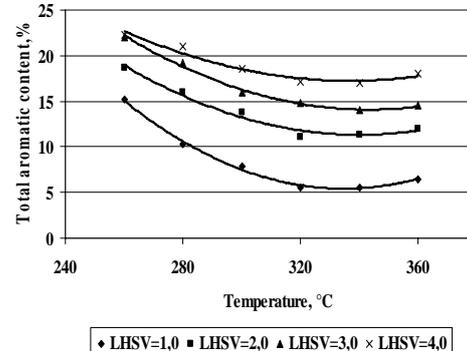


Fig. 8. Effect of temperature and LHSV on total aromatic content (feed "A", P = 45 bar)

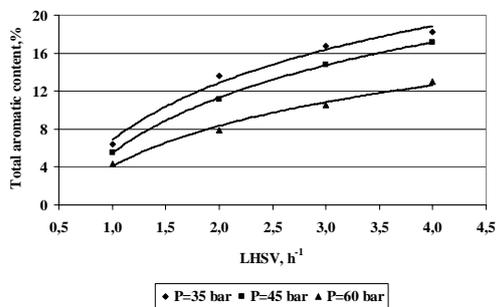


Fig. 9. Effect of LHSV and pressure on total aromatic content (feed "A", T = 320°C)

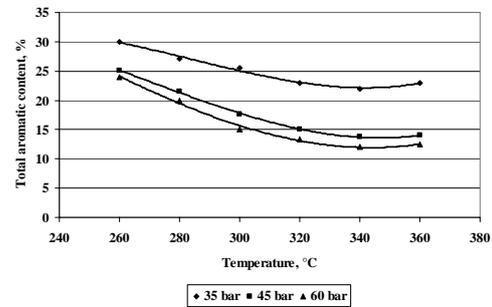


Fig. 10. Effect of temperature and pressure on total aromatic content (feed "B", LHSV=1.0 h⁻¹)

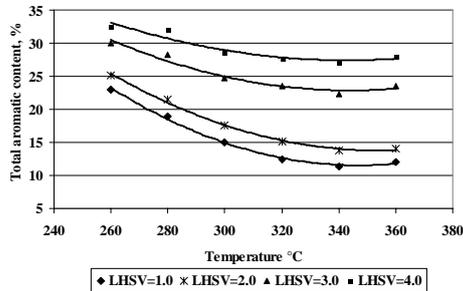


Fig. 11. Effect of temperature and LHSV on total aromatic content (feed "B", P = 45 bar)

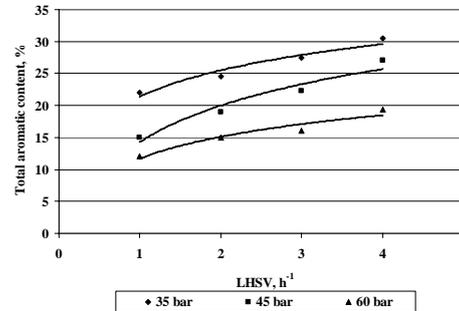


Fig. 12. Effect of LHSV and pressure on total aromatic content (feed "B", T = 320°C)

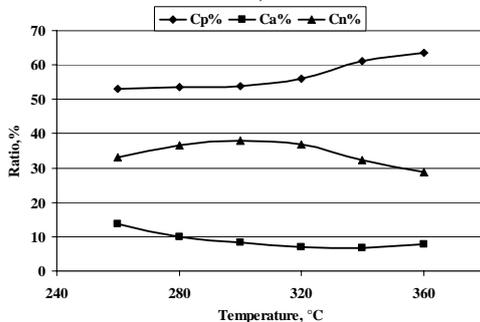


Fig. 13. The correlation between temperature and ratio of paraffinic (C_p), aromatic (C_a) and naphthenic (C_n) bonded carbon atoms (feed "A", P = 45 bar, LHSV = 1.0 h⁻¹)

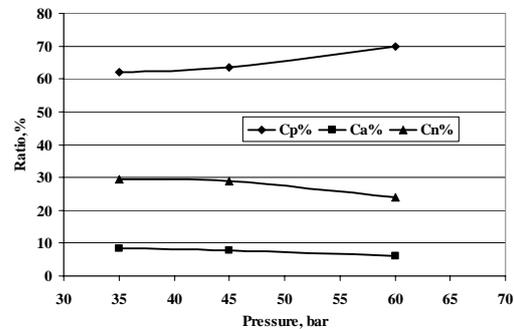


Fig. 14. The correlation between pressure and ratio of paraffinic (C_p), aromatic (C_a) and naphthenic (C_n) bonded carbon atoms (feed "A", T = 360°C, LHSV = 1.0 h⁻¹)

Beside the chemical composition, the analytical and performance properties of fuels are also important. Therefore the change of cetane index, cetane number, density and refractive index of products were also investigated. These properties are highly affected by the aromatic content of the

gas oils. Under most severe process conditions cetane index of feed "A" (53.1) was increased by 4.5 units to 57.6 and cetane number (51.3) was increased by 8.5 units to 59.8. BMCI decreased by 5.2 units to 23.0 (Figs. 15, 16). Sharp increase of cetane number with dearomatization points to ring opening of naphtene products. This is supported by the change of paraffinic bonded carbon atoms. Paraffin hydrocarbons have higher cetane number than naphthenes or aromatic hydrocarbons [6].

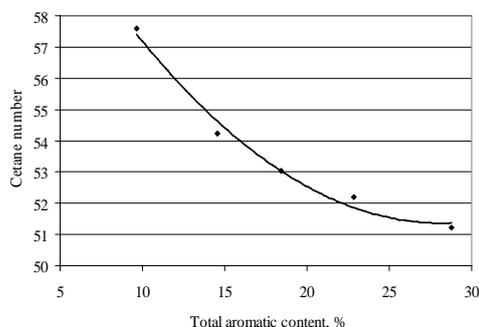


Fig. 15. Effect of total aromatic content on cetane number (feed "A")

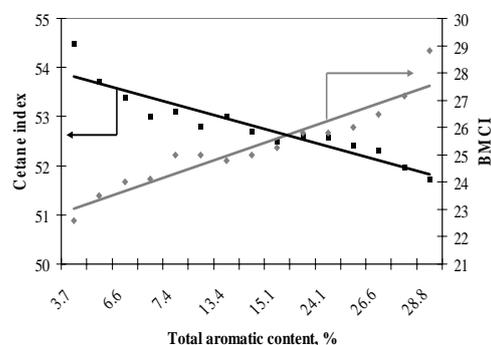


Fig. 16. Effect of total aromatic content on cetane index and BMCI values (feed "A")

Cetane index (50.3) and cetane number (50.1) of feed "B" was increased by 3.1 and 7.8 units, respectively while its BMCI (29.2) decreased by 4.2 units. The increase of cetane index and cetane number of feed "C" was 2.7 and 6.2 units. BMCI was decreased by 3.5 units. The increase of cetane number was higher than that of cetane index.

BMCI is an important property of gas oils to be applied as feed for steam cracking. Lower aromatic content or lower BMCI of gas oil results in higher yield of light olefins.

The density is also decreased from 0.837 to 0.810 g/cm³ and refractive index from 1.46 to 1.41 with total aromatic content.

4. CONCLUSIONS

Hydrodearomatization of prehydrogenated gas oil fractions (feed "A": sulphur content: 5 ppm, nitrogen content: <1 ppm, total aromatic content: 24.2%, boiling range: 184-356°C; feed "B": sulphur content: 8 ppm, nitrogen content: 30 ppm, total aromatic content: 33.5%, boiling range: 176-361°C; feed "C": sulphur content: 57 ppm, nitrogen content: 98 ppm, total aromatic content: 51.2%, boiling range: 200-351°C) on Pt-Pd/zeolite which is under development was studied. Effect of the key process parameters (temperature, pressure, LHSV) and properties of feed on the hydrodearomatization efficiency, yield and quality of products was investigated. Additionally, the effects of the reduction of aromatic content on the analytical and performance properties of products were also studied.

Pt-Pd/USY was appropriate for hydrodearomatization of prehydrogenated gas oil fractions of low sulphur (<10 ppm) and nitrogen contents (8-30 ppm). The yield of liquid products was higher than 98%. The gas oil yield was 84%-96% for feed "A", 87%-97% in case of feed "B" and 92-98% in case of feed "C". This indicates that the nitrogen content of feed inhibited hydrocracking reactions on the catalyst. Total aromatic content of the products was lower than that of the feed at every applied temperature and pressure. HDA efficiency was about 4.2% - 85.5% in case of feed "A", 2.5% - 80.2% for feed "B" and 2.0-45.2% for feed "C". Nitrogen and sulphur contents of feed "B" (S: 8 ppm, N: 30 ppm) and "C" (S: 57 ppm, N: 98 ppm) reduced the aromatic hydrogenation activity of Pt-Pd/USY.

The relevant properties of gas oils (cetane number, cetane index, density, refractive index, BMCI value) highly depend on the total aromatic content. Cetane index of feed "A" was increased by 4.5, cetane number 8.5 units and BMCI decreased by 5.2 units. The same data for feed "B" are as follows: cetane index: 3.1, cetane number: 7.8, BMCI reduction: 3.5.

By hydrodearomatization low aromatic content blendstock for diesel fuel (high cetane number and cetane index) and excellent feedstock for steam cracking (low BMCI value) could be produced. The Pt-Pd/USY catalyst under development was able to decrease the aromatic content even in case of high sulphur and nitrogen content feeds.

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