INVESTIGATION OF HYDROGENATION OF AROMATIC HYDROCARBONS ON Pt/Pd/USY CATALYST

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In this paper the aromatic reduction of gas oils and the conversion of several hydrocarbon groups in the conditions of hydrodearomatization were investigated on Pt/Pd/USY catalyst. It was concluded that in case of hydrodearomatization of gas oils cycloparaffin hydrocarbons (naphthenes) were key components, i.e. the practical process parameters of hydrodearomatization in case of a defined catalytic system (catalyst, feed, etc.) is that where the concentration of naphthenes have a maximum value. In case of this the deep hydrodearomatization and further deep heteroatom reduction can be carried out with maximum yield of gas oil. It was additionally determined that in the condition of hydrodearomatization mainly isoparaffins are formed via ring opening of naphthenes, the rate of increase of n-paraffin concentration is slower, i.e. the decadence of cold flow properties of reduced aromatic containing products are less beside the high cetane number. Therefore the gas oil products can be applied as winter quality diesel fuel blending components.

Keywords: aromatic reduction, noble metal catalyst, gas oil, cetane number.

Introduction

In the last couple of years the demand for diesel fuel has increased due to the increasing number of diesel fuelled passenger cars and heavy duty vehicles [1]. Additionally the decreasing emission level of these vehicles results the continuously tightening specifications of diesel fuels [2] (*Table 1*). Since 1st January, 2009 the maximum sulphur content of diesel fuels has been 10 mg/kg, the maximum allowable polycyclic aromatic content has decreased from 11% to 8% (in the future 2–4%) and the maximum level of total aromatic content might be specified (about 15–20%) [3].

The importance of deep heteroatom and aromatic reductions technologies, which is one of the key technologies of the production of modern diesel fuel blending components, has increased beside the quality specifications and demand. In the first step of these technologies the deep heteroatom reduction and partial hydroaromatization takes place on supported transition metal catalysts (e.g. $CoMo/Al_2O_3$, $NiMo/Al_2O_3$) [4, 5]. In the second step deep hydrodearomatization and further deep heteroatom reduction occurs on supported noble metal catalysts.

Nowadays the increasing of heteroatom resistance and hydrodearomatization activity of the above mentioned supported noble metal catalysts is in the focus of research and development activities [6, 7, 8].

The particular reactions of hydrodearomatization are studied in these catalysts as well [9].

The main focus of our research activity was the investigation of hydrodearomatization of aromatic hydrocarbons and the conversion of main hydrocarbon groups in the condition of hydrodearomatization in real gas oil matrix.

Experimental

The hydrodearomatization experiment was carried out in a high pressure reactor system with 100 cm³ efficient volume tube reactor. It contains equipment and devices applied in the reactor system of hydrotreating plants.

The range of the applied process parameters – based on the results of preliminary experiments – was the following: T: 260–340 °C, P: 35–60 bar, liquid hourly space velocity (LHSV): 1.0–4.0 h⁻¹, H_2/hydrocarbon volume ratio (in further: H_2/HC) = 600 Nm^3/m^3.

Prehydrogenated gas oil fraction derived from Russian crude was used for the hydrodearomatization experiments. Its important properties are summarized in *Table 2*.

The hydrodearomatization experiments were carried out on PtPd/USY zeolite (SiO_2/Al_2O_3 molar ratio: 33.6, total and mesoporous surface area: 650 m²/g and 51 m²/g, total noble metal content: 0.9%, Pd/Pt atomic ratio: 3.7:1, metal dispersion: 55%, acidity: 0.20 mmol NH_3/g) catalyst in continuous flow operation.

Table 1: The change of diesel fuel specifications

Properties	Hungary					Hungary (EU)			
	MSZ 1627 (1973)	MSZ 1627 (1974)	MSZ 1627 (1986)	MSZ 1627 (1993)	MSZ 1627 (1997)	MSZ EN 590 (1999)	MSZ EN 590 (2000)	MSZ EN 590 (2004)	MSZ EN 590 (2009)
Cetane number, minimum	48/45	48/45	42	48	48	49	51	51	51
Density (kg/m^3)	815-860	815-860	815-860	820-860	820-860	820-860	820-845	820-845	820-845
Total aromatic content (%)	-	-	-	-	-	-	-	-	- 15-20[*]
Polycyclic aromatic content (%)	-	-	-	-	-	-	11.0	11.0	8.0 (2.0-4.0[***])
Sulphur content (mg/kg)	10000/5000/2000	10000/5000/2000	5000/2000	2000/500/100	500/100	500	350	50/10[**]	10

The MSZ 1627 diesel fuel standard was overruled in 1999 and the MSZ EN 590 standard became operative. i.e. the Hungarian and EU standards of diesel fuels have been the same since 1999.
[*] It might be introduced in the near future, - No specifications
[**] The 10 mg/kg maximum sulphur containing diesel fuels have to be available in a regionally balanced manner
[***] It might be introduced in the near future

Table 2: Main specifications of feed

Properties	Value
Density at 15.6°C (g/cm^3)	0.8374
Sulphur content (mg/kg)	6
Nitrogen content (mg/kg)	<1
Aromatic content (%)	
total	25.5
mono	23.1
di- and poly	3.4
Cetane number	50
Distillation range (°C)	184–350

The properties of the feed and products were determined and calculated by standard test methods (*Table 3*). The hydrodearomatization activity of the catalysts was calculated by equation 1.

$$HAD \ (\%) = 100(A_f - A_p)/A_f \qquad (1)$$

where: HDA: hydrodearomatization activity (%),
A_f: aromatic content of feed (%),
A_p: aromatic content of product (%).

Table 3: Standard test methods

Properties	Methods
Density	EN ISO 3675
Sulphur content	EN ISO 20846
Nitrogen content	ASTM D 6366
Aromatic content	EN 12916
Distillation range	EN ISO 3405
Cetane number	EN ISO 5165

The rate of conversion of individual hydrocarbon groups in the condition of hydrodearomatization was determined by the diagram of logarithmic conversion vs. contact time (equation 2).

$$\ln \frac{C_{A0}}{C_A} = k_f t = \frac{k_f}{LHSV} \qquad (2)$$

where: c_{A0} – total aromatic content of feed,
c_A – total aromatic content of product,
k_f – pseudo reaction rate of hydrodearomatization,
LHSV – liquid-hourly-space-velocity.

The pseudo reaction rate constant of hydrodearomatization is calculated by the gradient of this curve.

The determination of the composition of feeds and products was carried out by the results of GCxGC method. The equipment was a Thermo Trace 2DGC instrument containing a FID detector. The conditions were the following:

- columns: 0.25 μm Rtx (118 m x 0.25 mmid) and 0.1 μm BPX50 (140 cm x 0.1 mmid),
- carrier gas: 6.0 purity helium with 0,1 cm^3/min flow rate,
- temperature programme: 40 °C → 280 °C 4 °C/min heating rate.

The liquid products were separated to lighter (<200 °C boiling range) and to gas oil (>200 °C boiling range) fractions and the change of the yield and quality of the products was examined as a function of the process parameters.

Results and discussion

The yield of the gas oil changed according to the projection; it decreased with increasing temperature and total pressure and decreasing LHSV; i.e. the rate of hydrocracking reactions, which produce the lighter hydrocarbons, increased (*Fig. 1, 2*). Temperature has the highest effect on the yield of the gas oil. For example it increased from 85% to 94% with decreasing temperature at 45 bar and LHSV = 1.0 h^{-1} in the investigated temperature range. The gas oil yield changed between 84% and 98% in the overall range of process parameters, therefore the lowest yield of gas oil occurred at the strictest process parameter (T = 340 °C, LHSV = 1.0 h^{-1}, P = 60 bar, H$_2$/HC = 600 Nm^3/m^3).
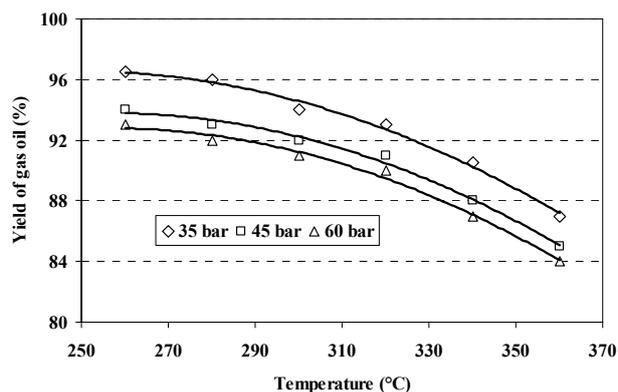
Figure 1: The effect of temperature and pressure on the yield of gas oil (LHSV = 1.0 h^{-1}, H$_2$/HC = 600 Nm^3/m^3)
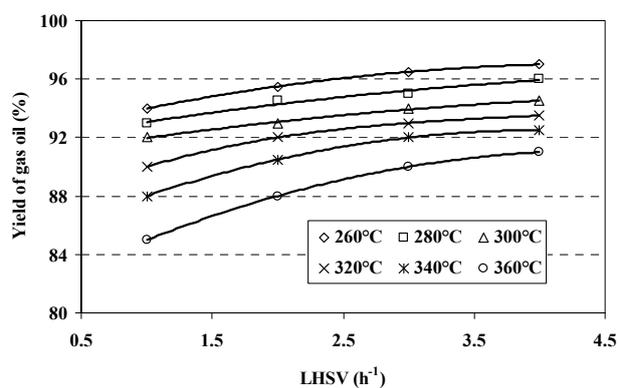
Figure 2: The effect of LHSV and temperature on the yield of gas oil (P = 45 bar, H$_2$/HC = 600 Nm^3/m^3)

Figure 3: The change of hydrodearomatization efficiency as a function of temperature and total pressure (LHSV = 2.0 h^{-1}, H$_2$/HC = 600 Nm^3/m^3)

Figure 4: The change of hydrodearomatization efficiency as a function of temperature and LHSV (P = 45 bar, H$_2$/HC = 600 Nm^3/m^3)

Figure 5: The change of hydrodearomatization efficiency as a function of total pressure and LHSV (T = 320 °C, H$_2$/HC = 600 Nm^3/m^3)

The hydrodearomatization activity of the investigated catalyst as a function of process parameters is presented in *Fig. 3, 4* and *5*. The rate of hydrodearomatization increased in the lower temperature range from 240 to 320 °C. After the optimal temperature (320 °C) it decreased, i.e. the optimal temperature of hydrodearomatization of the investigated catalyst was 320 °C. The reason of this was the exothermic reaction profile of aromatic hydrogenation. The change of hydrodearomatization as a function of LHSV and total pressure was according to the projection, i.e. it increased with decreasing LHSV and increasing total pressure. It was concluded that the hydrodearomatization efficiency of the investigated catalysts was relatively high, because the polycyclic aromatic content of the products changed in the reproducibility range of the applied test method (it was maximum 0.1%). Consequently the products did not contain polycyclic aromatic hydrocarbons. Therefore the hydrodearomatization efficiency was calculated by the monoaromatic content, which was practically the same as the total aromatic content. The hydride-aromatization efficiency was between 12% and 88% in the range of the investigated process parameters. The lowest aromatic containing product was produced (~3%, hydrodearomatization efficiency: 88%) at 320 °C, 60 bar and LHSV = 1.0 h^{-1}.

The rate of abatement of hydrodearomatization efficiency after the optimal temperature of aromatic hydrogenation (cause of thermodynamic properties) changed as a function of total pressure. The decrease of hydrodearomatization efficiency was high in case of low total pressure (e.g. 35 bar) and it was significantly lower at 60 bar. The reason of this phenomenon was the fact that in case of higher total pressure the rate of ring opening reactions of naphthenes increased. Therefore paraffines formed from naphthenes, which were

produced from aromatic hydrocarbons. Consequently the equilibrium reaction system of polycyclic aromatic $\rightleftharpoons$ monoaromatic $\rightleftharpoons$ naphthene changed to naphthenes, because the ring opening reactions are irreversible. It can be seen in the change of hydrocarbon composition (*Fig. 6, 7*).
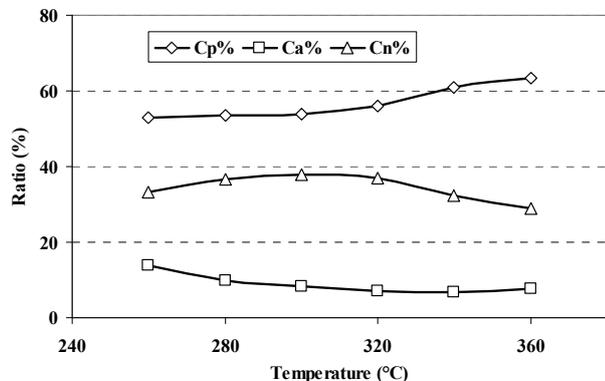
Figure 6: The change of hydrocarbon composition of the products as a function of temperature (rate of carbon atoms in C_P: paraffinic-, C_A: aromatic- and C_N: naphthenic, P = 45 bar, LHSV = 1.0 h^{-1}, H_2/HC = 600 Nm^3/m^3)
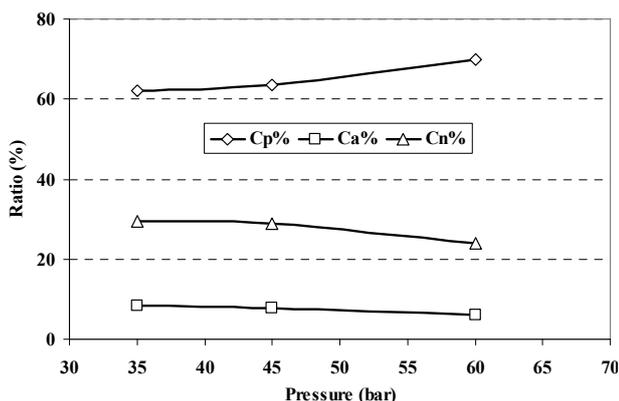
Figure 7: The change of hydrocarbon composition of the products as a function of total pressure (rate of carbon atoms in C_P: paraffinic-, C_A: aromatic- and C_N: naphthenic, T = 320 °C, LHSV = 1.0 h^{-1}, H_2/HC = 600 Nm^3/m^3)

It can be seen that the rate of ring opening and/or hydrocracking reactions increased with temperature (C_P was increased). The rate of the increase of carbon atoms in paraffinic bond increased with total pressure. The increase (about 1–2%) of carbon atoms in paraffinic bond was low in the lower temperature range (260 °C → 320 °C), but at higher temperature it was significantly higher (about 10%). I can be seen that the carbon atoms in naphthenic bond changed as a maximum curve.

It was concluded based on the yield and hydrocarbon composition of the gas oils that the yield of the gas oil significantly decreased with increasing paraffin content, i.e. in hydrodearomatization conditions the paraffinic hydrocarbons are cracked with the production of lower

boiling range hydrocarbons. Based on the above mentioned phenomenon the following inference was drawn: the hydrogenation of aromatic hydrocarbons should be done in a range of process parameters where the concentration of naphthenic hydrocarbons has a maximum value (T_{max} = 320–330 °C). In this situation deep hydro-dearomatization can be carried out with high gas oil yield. Therefore the naphthenic hydrocarbons become key components in case of hydrodearomatization.

The investigation of hydrogenation of individual hydrocarbon groups was carried out with model compounds and their mixtures in the literature. Therefore there is just a little information about the experimental results with real gas oil matrix. The reason of this is that the mono-, di- and polycyclic aromatic hydrocarbons and naphthenic molecules transform via numerous reactions to each other and to paraffines on the catalyst surface. These reactions take place in serial and parallel succession, therefore in the real gas oil matrix only the transformation of individual hydrocarbon groups can be investigated (e.g. monoaromatics, diaromatics, normal and isoparaffines).

Therefore the second objective of our experiments was to study the conversion of individual hydrocarbon groups on the condition of aromatic hydrogenation on the investigated catalyst.

The change of the concentration of alkyl-diaromatic hydrocarbons as a function of temperature is shown in *Fig. 8*. It can be seen that the optimal temperature of hydrogenation of alkyl-diaromatic compounds was between 280–290 °C.
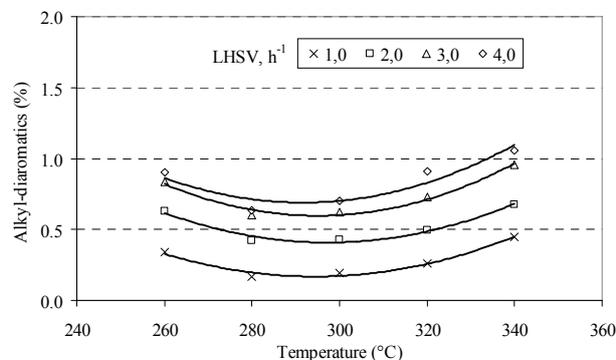
Figure 8: Change of the concentration of alkyl-diaromatic compounds as a function of temperature (P = 35 bar, H_2/HC = 600 Nm^3/m^3)

The optimal temperature of hydrogenation of cycloalkyl-aromatics was 300 °C (*Fig. 9*), but the highest optimal hydrogenation temperature was that of the alkyl-benzenes (320 °C) (*Fig. 10*).

Based on the results it was concluded that the hydrogenation rate of the different aromatic compounds from the slower to the fastest changed in the following order: alkyl-naphthalenes (condensate alkyl-diaromatics) < cycloalkyl-aromatics (decalin containing different carbon number alkyl-groupa) < alkyl-monoaromatics (alkyl-benzenes) (*Fig. 11*).
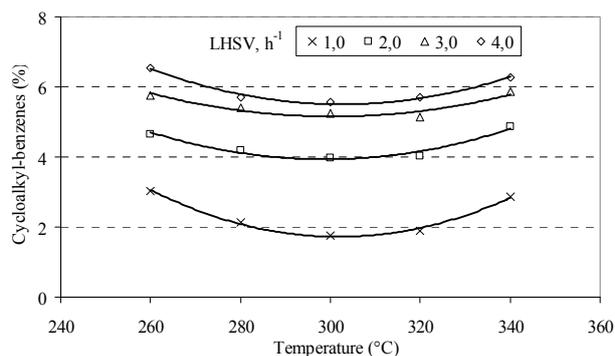
Figure 9: The change of the concentration of cycloalkyl-benzenes as a function of temperature (P = 35 bar, H_2/HC = 600 Nm^3/m^3)
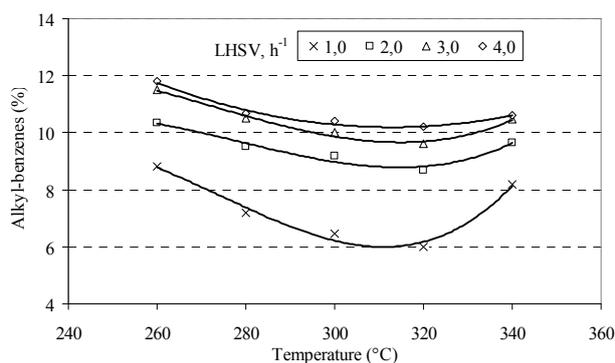
Figure 10: The change of the concentration of alkyl-benzenes as a function of temperature (P = 35 bar, H_2/HC = 600 Nm^3/m^3)
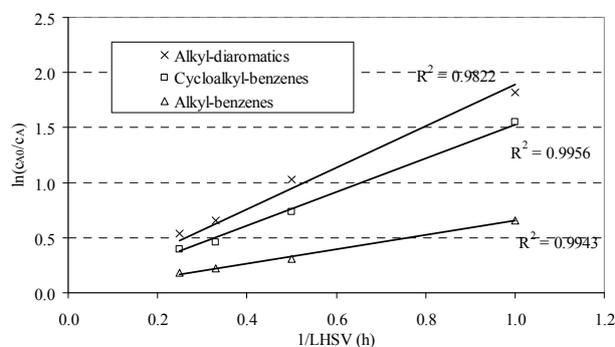
Figure 11: The hydrogenation rate of different one- and two-ring akly(cyclioalkyl)-aromatic hydrocarbons (T = 300 °C, P = 35 bar, H_2/HC = 600 Nm^3/m^3)

Therefore the hydrogenation rate of the first ring of aromatic compounds increases with the increasing number of rings in the molecules. The reason of this might be the fact that the aromatic electron system of condensate diaromatic is distortional.

The change of the concentration of formed one- and two-ring naphthenes produced by hydrogenation of aromatics as a function of temperature is shown in *Fig. 12* and *13*. It can be seen that the concentration of alkyl-dycliparaffines decreased with increasing temperature. This means that these compounds are transformed to alkyl-monocycloparaffines via ring opening even in case of the mildest process conditions.
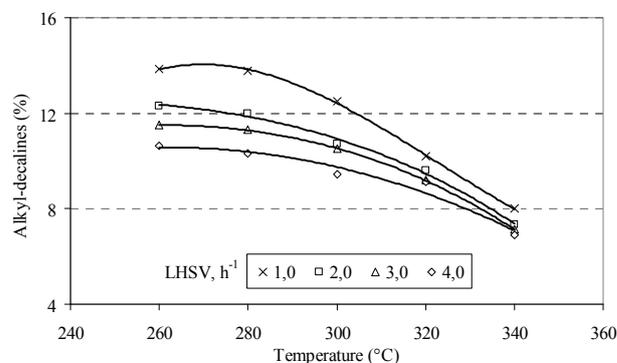
Figure 12: The change of the concentration of alkyl-dicycloparaffines as a function of temperature (P = 35 bar, H_2/HC = 600 Nm^3/m^3)
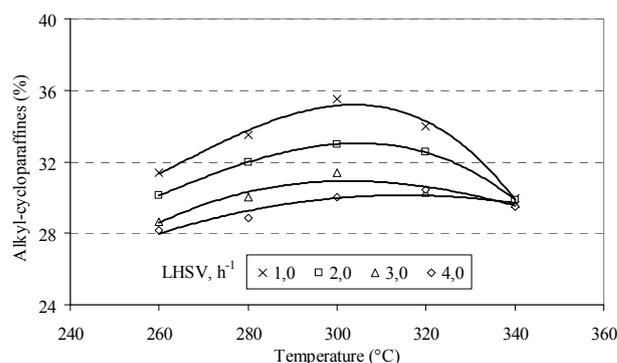
Figure 13: The change of the concentration of alkyl-cycloparaffines as a function of temperature (P = 35 bar, H_2/HC = 600 Nm^3/m^3)

The concentration of alkyl-cycloparaffines changed as a maximum curve, i.e. it first increased with temperature (alkyl-cycloparaffines are formed in the low temperature range via ring opening from alkyl-dicycloparaffines and via hydrogenation from alkyl-benzenes). After the maximum point (300 °C) it decreased with increasing temperature (the reaction rate of ring opening of alky-cycloparaffines increased, therefore the ring opening of alkyl-dicycloparaffines and hydrogenation of alkyl-benzenes could not compensate the quantity of alkyl-cycloparaffines, which were transformed to paraffines via ring opening).

The ring opening of alkyl-cycloparaffines can be seen in the increasing concentration of paraffin hydrocarbons with the temperature in the investigated temperature range (*Fig. 14, 15*).
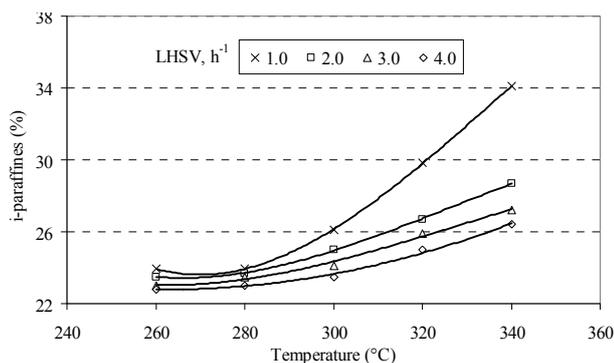
Figure 14: The change of the concentration of
i-paraffines as a function of temperature
(P = 35 bar, $H_2/HC = 600\ Nm^3/m^3$)

It can be further concluded from the change of the concentration of n- and i-paraffines that i-paraffines are formed via ring opening. The concentration of n-paraffines increased with temperature by only a few degrees in the lower temperature range (260–300 °C). After this range it set to a constant value, i.e. the curve became saturation. It means that the reaction rate of ring opening to n-paraffines was low. It was caused by the following two facts. On the one hand the shrinking of the 6-member ring to a 5-member ring branched with one alkyl-group takes place on the strong acidic catalyst. On the other hand the rate of ring opening is lower in the substituted carbon atom [15-18], due to the steric hindrance and the fact that the alkyl-groups have electron-donor properties, which lead to the increasing electron-density of the orto- and para-located carbon atoms. Therefore the ring opening reactions take place in these atoms.
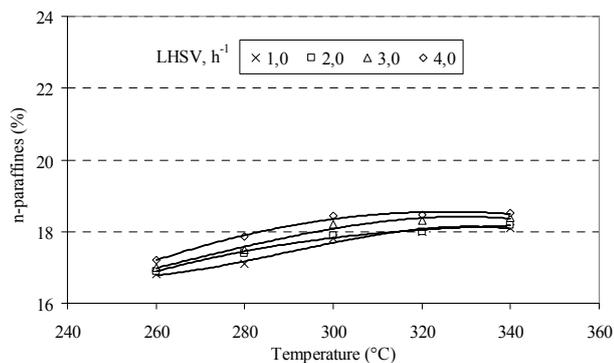
Figure 15: The change of the concentration of n-paraffines as a function of temperature
(P = 35 bar, $H_2/HC = 600\ Nm^3/m^3$)

The main advantage of the formation of a large amount of isoparaffins in case of the hydrodearomatization is the better cold flow properties of the products than in the case of n-paraffines. Therefore these products can be applied as blending components of winter quality diesel fuels.

Conclusions

The objective of our research and development work was to study the hydrogenation of aromatic compounds on PtPd/USY catalysts in case of real gas oil matrix as feedstock, and the determination of conversion of individual hydrocarbon groups in the condition of aromatic hydrogenation, respectively.

It was concluded that the cycloparaffines are key components in hydrodearomatization, i.e. the aromatic hydrogenation in extant catalytic system (feed, catalyst) should be done at process parameters where they have a maximum concentration. In case of this the hydro-dearomatization can be carried out with maximum yield of gas oils, and the hydrogen consumption can also be decreased. The reason of the latter is the fact that it does not need extra hydrogen consumption without ring opening to produce saturated hydrocarbons.

On the investigated catalysts modern diesel fuel blending components can be produced, which satisfy the future requirements (<10 mg/kg sulphur-, <1mg/kg nitrogen content, <15-20% total- and <2.0–4.0 polycyclic aromatics, at T = 320°C, P = 45 bar, LHSV = 1.0–2.0 h^{-1}, H_2/HC: 600 Nm^3/m^3 process parameters with high yield (about 90%).

It was further concluded that in case of hydrode-aromatization condition mainly isoparaffines are formed via ring opening of naphthenes on the investigated catalyst, the increase of the concentration of n-paraffins was lower. Therefore the hydrodearomatization can be done with high gas oil yield with the use of appropriate process parameters, and the decadence of cold flow properties of partially aromatic saturated products is lower.

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