DEAROMATIZATION OF A JET FUEL FRACTION ON A PLATINUM CATALYST

Viliam MÚČKA[a], Alica OSTRIHOŇOVÁ[b], Ivan KOPERNICKÝ[b] and Oldřich MIKULA[b]

[a] *Faculty of Nuclear and Physical Engineering,*
Czech Technical University, 115 19 Prague 1, and
[b] *Slovnaft, 823 00 Bratislava*

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Some physical and physico-chemical properties of a platinum support catalyst were determined and its application to the dearomatization of a jet fuel fraction was studied. The dearomatization proceeds more readily at lower temperatures, at which, however, the catalyst is more sensitive to poisons. A factorial experiment was designed to determine the optimum conditions for the dearomatization. A virtually complete dearomatization using the spatial flow rate 2 h^{-1} was achieved at temperatures 245–295°C and partial pressures of hydrogen 1·5–4 MPa.

By hydrogenation of aromatic hydrocarbons in aviation turbine fuel it is possible to achieve a reduction in the formation of coke-type combustion products, increase in the height of the smokeless flame, and improvement in the luminometric number and thermal stability of the fuel. For an efficient dearomatization, a highly effective and selective catalyst must be available displaying a sufficient resistance to catalyst poisons and a satisfactory service life particularly in relatively mild reaction conditions (temperature, pressure).

The aim of the present work was to examine the dearomatization of a jet fuel fraction on an industrial platinum support catalyst. For thermodynamic reasons, the degree of hydrogenization of aromatic compounds is favoured by lower temperatures and higher partial pressures of hydrogen; on the other hand, however, at lower temperatures the catalyst is more sensitive to catalyst poisons (sulphur or nitrogen compounds), and so one has to seek for compromise optimum conditions[1].

EXPERIMENTAL

Catalyst

The catalyst used was Cherox 3903 platinum support catalyst (support: alumina), produced by the Chemical Works, Litvínov, in the extrudate form with the declared platinum content 0·65% wt. The catalyst composition was determined semiquantitatively on a Zeiss PGS-2 spectrograph. The morphology of the contact surface was examined on a Jeol JSM-50 A scanning electron microscope with the resolution of 10 nm; one and the same spot was examined repeatedly applying magnifications from 10^2 to 10^4. The specific surface area of the contact was determined by the method of low-temperature adsorption of nitrogen from a N_2–H_2 mixture (2 : 3) and its subsequent desorption at room temperature; this parameter was measured for the catalyst both in its initial form (extrudates) and after its grinding in an agate mortar. The microstructure of the catalyst was studied by X-ray diffraction on a TUR M62 instrument fitted with a goniometer. An X-ray tube with a copper anode was used; the working voltage was 30 kV, the current was 10—15 mA. The size of the coherent regions of the crystal phase detected was determined based on the broadening of the selective reflections with high ϑ angles. In some cases the catalyst was thermally treated for 3 h in an electric resistance furnace under nitrogen at 600°C prior to the testing.

Fuel

The material used was the jet fuel fraction PL-6 produced by Slovnaft, with the distillation region 122—261°C and the initial concentration of aromatic substances 16·9% vol. Prior to the testing, the material was desulphurized in the conventional manner on a cobalt–molybdenum catalyst, for the content of sulphur not to exceed $5 \cdot 10^{-4}\%$ (after a typical desulphurization, $3 \cdot 10^{-4}\%$ sulphur was found in the material). Sulphur was determined by three different methods, *viz.* by combustion in an oxygen–hydrogen atmosphere, by catalytic oxidation on Raney-nickel, and by the microcoulometric method.

Apparatus and Measuring Procedure

The catalyst tests were performed on a FOL-Gyem pilot-plant testing double reactor of Metrimpex, Budapest; its layout and description have been given elsewhere[2]. The main parts of this equipment are the reactor, liquid injection pump, raw material container, cooler, high-pressure separator, circulating compressor, and measuring and recording instruments. The volume of the reactor itself, constituted by a steel tube of the inner diameter 25 mm and length 500 mm, was divided into three parts: an upper (inlet) zone packed with aluminium rollers serving for preheating the material, a middle zone, volume 100 cm^3, constituting the catalytic bed, and a bottom (outlet) zone packed with an inert material (porcelain rings). The reactor temperature, measured by means of four thermocouples located in different positions, could be adjusted with the precision of ±0·5°C. The reaction mixture leaving the reactor was fed into the water cooler and further into the high-pressure separator. After the separation of gaseous products, the aromatic substances in the liquid samples were determined spectrophotometrically at 220 nm.

In all experiments, the hydrogen-to-fuel molar ratio was held at a constant value of 5 : 1 The measurements were carried out at a preselected spatial flow rate ($V = V_m/V_c$, where V_m is the flow rate of the material and V_c is the volume of the catalyst), pressure, and temperature. After testing for leaks, the reactor packing was flushed with nitrogen for approximately 30 min, and then the catalyst was activated by raising the temperaure up to 250°C applying the heating rate 40°C/h at a constant hydrogen overpressure (1·5 MPa) and a constant flow rate (10 l/h). The catalyst was dried at 250°C for 3 h, then the temperature was additionally raised to 400°C and the catalyst was reduced for 12 h. After this activation the catalyst was allowed to cool down to the temperature of the reaction, the desired partial pressure of hydrogen and the spatial flow rate of the material delivery were adjusted, and the system was allowed to reach the steady state (approximately 1 h). A sample was then withdrawn and the temperature was lowered by a preselected value, the remaining parameters being held constant. The sampling and the temperature lowering were repeated until the lowest reaction temperature chosen was attained. A long-run experiment (about 20 h), in which the reaction proceeded in the conditions chosen at a constant temperature, gave evidence that within the limits of error the catalytic activity of the contact does not change during the reaction.

Factorial Design

For establishing the optimum dearomatization conditions (temperature, pressure, and spatial flow rate), the method of a rotational three-factor design worked out by Box and Hunter[3] was employed, as used before *e.g.* in the study of hydrogenation of aromatic hydrocarbons, with the distillation region 30—205°C, on a Pd–Rh catalyst[4]. The dependence of the content of aromatic hydrocarbons in the product on the above three variables was described by the second-order regression equation

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + \\ + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 \,. \qquad (1)$$

Here x_1, x_2 and x_3 are symbols for the absolute temperature, pressure, and spatial flow rate given by the relation

$$x_{ij} = (\bar{x}_{ij} - \bar{x}_{i0})/I_i \,, \qquad (2)$$

where x_{ij} denotes the parameter x_i at the j-th level, $\bar{x}_{ij}$ is the value of the variable in the initial designation, $\bar{x}_{i0}$ is the centre of the chosen interval of the variable in the initial designation, and I_i is the chosen unit interval of the experiment.

The regression coefficients b_0, b_j, b_{jj}, and b_{jk} are given[5] by the relations

$$b_0 = 0{\cdot}1663 \sum_{i=1}^{n} y_i - 0{\cdot}05679 \sum_{j=1}^{N} \sum_{i=1}^{n} x_j^2 y_i \qquad (3)$$

$$b_j = 0{\cdot}07322 \sum_{i=1}^{n} x_j y_i \qquad (4)$$

$$b_{jj} = 0{\cdot}0625 \sum_{i=1}^{n} x_j^2 y_i + 0{\cdot}00689 \sum_{j=1}^{N} \sum_{i=1}^{n} x_j^2 y_i - 0{\cdot}05679 \sum_{i=1}^{n} y_i \qquad (5)$$

$$b_{jk} = 0{\cdot}1250 \sum_{i=1}^{n} x_j x_k y_i \,, \qquad (6)$$

where n is the number of experimental points and N is the index of the independent variable.

The scheme of the rotational three-factor design is given in Table I. The code characters $+1{\cdot}682$ and $-1{\cdot}682$ refer to the end points of the chosen interval of the variable, the character 0 refers to the centre of this interval. The use of the experimental points with the code characters $\pm 1{\cdot}682$ follows from the statistical analysis of the factorial design[5]. The experiments performed at the zero level of the three variables (Table I, points 15—20) afforded the average square deviation S^2 from the arithmetic mean of the measured values, given by the relation

$$S^2 = (1/n) \sum_{i=1}^{n} (y_i - \bar{y})^2 \,, \qquad (7)$$

where n is the number of measurements, y_i is the measured value (concentration of aromatic hydrocarbons), and $\bar{y}$ is the arithmetic mean of the measured values. In this manner the standard deviation of the factorial experiment was calculated to be $\pm 0{\cdot}053\%$.

The variables corresponding to the code characters -1 and $+1$ were chosen as follows: temperature 533 and 593 K (260 and 320°C), pressure 1·5 and 3·5 MPa, and spatial flow rate 1 and

2 h^{-1}. The assignment of the true values of the variables to the code characters used in Table I, carried out by using Eq. (*2*), is given in Table II. The factorial experiment was performed under the condition given in Tables I and II, and from the found concentrations of aromatic compounds in the various points of the experiment (y_i) the regression coefficients in Eq. (*1*) were calculated by using Eqs (*3*)–(*6*). The evaluation was performed on a HP 9830 calculator by using the RATRE program based on the least squares method.

RESULTS

The results of the semiquantitative spectrophotometric analysis of the catalyst (Table III) indicate that the main part of the catalyst is constituted by the support

TABLE I

Scheme of the rotational three-factor design and the determined concentration of aromatic substances y_i (in % vol.)

No	Factor			y_i	No	Factor			y_i
	x_1	x_2	x_3			x_1	x_2	x_3	
1	−1	−1	−1	0·142	11	0	−1·682	0	1·520
2	+1	−1	−1	4·860	12	0	+1·682	0	0·488
3	−1	+1	−1	0·037	13	0	0	−1·682	0·495
4	+1	+1	−1	1·200	14	0	0	+1·682	0·650
5	−1	−1	+1	0·140	15	0	0	0	0·570
6	+1	−1	+1	5·140	16	0	0	0	0·440
7	−1	+1	+1	0·035	17	0	0	0	0·400
8	+1	+1	+1	2·510	18	0	0	0	0·265
9	−1·682	0	0	0·029	19	0	0	0	0·275
10	+1·682	0	0	4·795	20	0	0	0	0·303

TABLE II

Code characters of the variables

Variable	Symbol	Value for the code character					I_i
		−1·682	−1	0	+1	+1·682	
Temperature, K	x_1	512·5	533	563	593	613·5	30
Pressure, MPa	x_2	0·82	1·5	2·5	3·5	4·18	1
Spatial flow rate, h^{-1}	x_3	0·66	1·0	1·5	2·0	2·34	0·5

(alumina), the content of the active component (Pt) being low. The quantitative determination of platinum performed gravimetrically and photometrically with *p*-nitrodimethylaniline after separation of platinum[2] showed that platinum was distributed unevenly in the catalyst particles; this was confirmed also by the electron microscope investigations.

The specific surface area of the catalyst (Table IV) was found unchanged by the grinding of the contact and also by its use in the dearomatization process. Heat treatment of the catalyst did not affect appreciably its specific surface area either. However, if the catalyst thermally treated at 600°C for 3 h was used in the reaction proceeding for about 17 h, its specific surface area reduced to approximately a half of its initial value. This parameter diminishes appreciably also if the raw material

TABLE III

Results of semiquantitative analysis of the catalyst (element concentrations in %, arranged in order of decreasing intensities of the spectral lines)

>1%	1–0·1%	0·1–0·01%				<0·01%		
Al	Pt	Ti	Co	Si	Fe	Mg	Ba	Na
				Ca	Sr	Mo	Mn	
				Ni	Sn	Zr	Ga	Yb
					Pb		Li	
					Zn			

TABLE IV

Specific surface area S (m^2/g) of the catalyst

Catalyst	Catalyst form	
	initial	powder
Before the reaction	115·2	110·6
After the reaction	113·9	106·9
After heat treatment	121·0	121·1
After heat treatment and the reaction	51·4	54·4
After the reaction with the fuel with the sulphur content 0·015%	82·1	87·0

treated contains sulphur in a higher quantity (Table IV). These conclusions apply to the catalyst both in the extrudate and im the powder forms.

X-ray diffraction examination of the catalyst revealed that the support was the γ-modification of aluminium oxide with the cubic structure parameter $a = 791$ pm, which agrees well with the tabulated value[6] $a = 792{\cdot}6$ pm. The size of the coherent regions of the oxide is comparatively low, amounting to 17 ± 1 nm; the value did not change markedly upon using the catalyst in the reaction, but decreased slightly with the increasing content of sulphur in the fuel (15·2 and 14·0 nm for the sulphur contents 0·001 and 0·002%, respectively).

The results of the activity tests under various reaction conditions are presented in Fig. 1 in the form of the conversion curves. In dependence on temperature the curves pass a minimum, and the pressure and the spatial flow rate are seen to affect the degree of dearomatization as well: while at a higher pressure and lower spatial flow rate (Fig. 1, curve *1*) the minimum content of aromatics (0·16 ± 0·07% vol) is attained at the temperature 280°C, at a lower pressure and higher spatial flow rate (Fig. 1, curve *2*) the minimum content of aromatics is attained at lower reaction temperatures (215–240°C) and absolutely is higher (0·23 ± 0·07%).

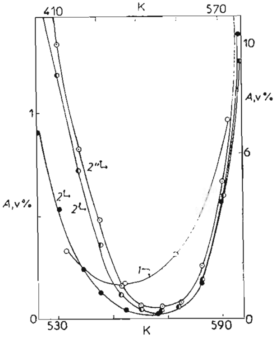

FIG. 1

Dependence of the concentration of aromatic compounds A (% vol) on the reaction temperature T (K). Reaction conditions (pressure, MPa; spatial flow rate, h^{-1}; sulphur content, %): *1* 3·0, 1·5, 0·0003; *2* 1·0, 2·5, 0·0003; *2′* 1·0, 2·5, 0·001; *2″* 1·0, 2·5, 0·002

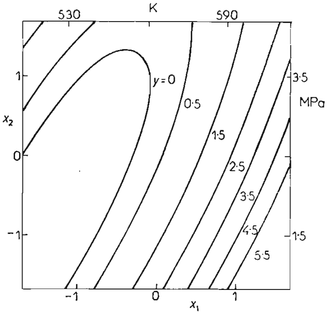

FIG. 2

Contour line diagram of the dependence of content of aromatic hydrocarbons y on temperature (T, x_1) and pressure (p, x_2) for the spatial flow rate 1 h^{-1}

The effect of the sulphur compounds present in the jet fuel fraction is apparent from the conversion curves *2'* and *2''* in Fig. 1. As the sulphur content increases, the left part of the curve shifts to higher temperatures, at which the effect of sulphur is less pronounced. As a consequence, the saddle of the conversion curve, representing the minimum of the aromatics content, becomes narrower. Still more apparent is this effect in the case of the fuel containing 0·015% S, where, however, the degree of conversion of the aromatics is very low, amounting to units or tens per cent.

The fact that the reaction conditions have a bearing on the course of the dearomatization process (Fig. 1, curves *1*, *2*) led us to seek for the optimum conditions in a systematical way, by applying the factorial design approach. The results of the chemical analysis of the aromatic substances in the various points are given in Table I. The regression equation obtained for them (Eqs (*1*)–(*6*)) is

$$y = 0{\cdot}363 + 1{\cdot}565x_1 - 0{\cdot}603x_2 + 1{\cdot}135x_3 + 0{\cdot}798x_1^2 + 0{\cdot}300x_2^2 + \\ + 0{\cdot}143x_3^2 - 0{\cdot}760x_1x_2 + 0{\cdot}119x_1x_3 + 0{\cdot}129x_2x_3\,; \qquad (8)$$

its graphical representation for the three different spatial flow rates $x_3 = 1$, 1·5, and 2 h^{-1} are the contour line diagrams shown in Figs 2–4. The optimum conditions of dearomatization, given by the zero content of aromatic substances ($y = 0$) are seen to lie within a rather broad interval of reaction temperatures and pressures.

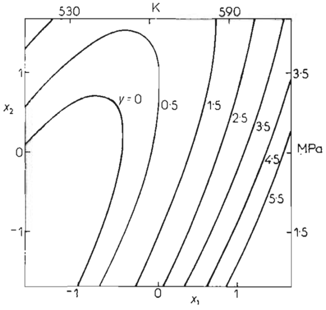

FIG. 3

Contour line diagram of the dependence of content of aromatic hydrocarbons on temperature and pressure for the spatial flow rate 1·5 h^{-1}

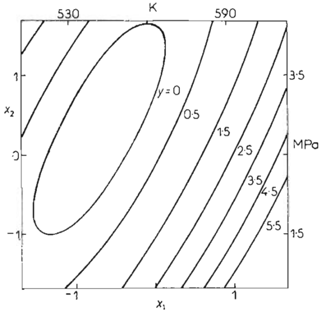

FIG. 4

Contour line diagram of the dependence of content of aromatic hydrocarbons on temperature and pressure for the spatial flow rate 2 h^{-1}

For the highest of the spatial flow rates applied, 2 h^{-1}, the dearomatization is complete over the temperature region 245–295°C and the pressure region 1·5–4 MPa; with the decreasing spatial flow rate the optimum is shifted towards lower temperatures and lower pressures (Figs 2–4).

DISCUSSION

As follows from the chemical analysis and the electron microscope examination of the catalyst, its active component is unevenly distributed over the surface. Nevertheless the surface structure of the contact seems to be stable enough, as its specific surface area changes neither on a mechanical or thermal treatment not during the reaction; still its thermal treatment obviously may bring about some latent changes in the structure that lead to a pronounced lowering of its specific surface area only in the reducing atmosphere of the activation or reaction processes (Table IV). The sulphur present in the fuel probably also plays an important part in the processes leading to a reduction in the specific surface area, as documented by the data of Table IV and by the slight decrease in the size of the coherent regions of the catalyst support.

The contact proved to be an efficient catalyst of the dearomatization. The process must be conducted at an optimum temperature given by the minima in the dependences shown in Fig. 1, obviously because of the fact that lower reaction temperatures are favourable for the process[1]. On the other hand, however, at lower temperatures the catalyst is more sensitive to catalyst poisons (particularly sulphur compounds), as demonstrated by experiments carried out using a raw material with a higher content of sulphur (Fig. 1, curves *2'*, *2''*). The presence of sulphur brings about a faster deactivation of the contact in the range of lower reaction temperatures. At higher temperatures (260–320°C) the catalyst is fairly resistant to sulphur compounds.

In order to gain an insight into the nature of the poisoning, the hydrogenation of the material with a higher content of sulphur (0·001%) was carried out so that immediately after the sampling at the lowest reaction temperature pursued the temperature was raised up again to the initial value (320°C) and after reaching the steady state, a sample was withdrawn for analysis of aromatics. The degree of aromatics conversion was found approximately 1% lower than at the same temperature at the beginning of the experiment, which indicates that the catalyst poisoning taking place at lower temperatures is irreversible.

The observed changes on the conversion curves for the sulphur-containing fuel (Fig. 1, curves *2*, *2'*, *2''*) might be attributed to the changes in the specific surface area of the contact found in experiments with the sulphur content enhanced up to 0·015% (Table IV), but this interpretation is opposed by the fact that no such reduction in the specific surface area took place when the sulphur content was

0·001%. Probably, then, the sulphur compounds attack directly the catalytic centres of the dearomatization hydrogenation.

The results of the factorial experiment show that the jet fuel fraction PL-6 can be dearomatized virtually completely on the catalyst in question if appropriate conditions are adjusted (reaction temperature 245–295°C, pressure 1·5–4 MPa for the spatial flow rate 2 h^{-1}); these conditions are practically identical with those established for the hydrogenation of 1-butylbenzene on a precious metal catalyst[7] (temperature 270°C, partial pressure of hydrogen 1·6 MPa). The optimum conditions for the dearomatization on the contact under study are even somewhat more favourable than those found for the dearomatization of the fraction with the distillation interval 30–205°C on a palladium–rhodium catalyst, where the highest degree of dearomatization (85%, *i.e.* 3·5% residual aromatics) was attained[4] at the temperature 285°C, partial pressure of hydrogen 4·1 MPa, and spatial flow rate 1 h^{-1}.

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