STUDY OF HYDROGENATION OF PETROLEUM ASPHALTENES

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Dedicated to Professor V. Veselý on the occasion of his 70th birthday.

Isolated petroleum asphaltenes were subjected to model thermal and catalytic hydrogenation experiments in the temperature region 300—450°C. The course of hydrogenation of the asphaltenes studied is discussed based on ^{1}H-NMR type analysis of the starting material and the hydrogenation products.

In addition to heavy fractions, which lend themselves to distillation without decomposition, crude oil involves a large proportion of high-molecular fractions, which are dissolved or peptized in the oil substrate and form a stable colloidal system. Among these substances are — in accordance with the classical Richardson's classification[1] — maltenes (composed of resins and residual oil fraction), asphaltenes, and — after heat treatment — carbenes and carboids. Resins, asphaltenes, carbenes, and carboids are sometimes collectively referred to as petroleum pitch. Of these, the two former are most important. They occur in a vast majority of crude oils and in oil fractions from fossil fuels (coal tar, oils from bitumenous shales, oil sands, *etc.*), their content, however, is variable, from minimal amounts up to about 40%. This is demonstrated by Table I. Apparently, maltenes and asphaltenes are present in significant amounts in many cases (in Romashkino crude oil, for instance, the total amount of these substances is about 15%).

The high-molecular components are utilized essentially in three ways: *a*) the oil fraction is separated by vacuum distillation, and the remaining so-called distillation asphalts are further industrially used; *b*) the crude oil residues are treated (partially desulphurized, thermally cracked) to serve as fuel oils of different quality; *c*) mazut and other petroleum residues are gasified.

The petroleum residues represent, however, a significant reserve for further intensification in chemical utilization of petroleum raw material, particularly by application of cleavage processes which can be employed to substantially raise the yield of light products. Since these processes (cracking, hydrocracking) are catalytic by nature, the main problem is elimination or suppression of the deactivating effect of resins and, particularly, asphaltenic fractions on the catalysts used[2,3].

Of importance is particularly the presence of asphaltenes, especially during catalytic treatment of residual fractions, because their conversions affect essentially the technological process applied. These conversions can be understood in terms of the dynamic equilibrium

$$\text{oils} \rightleftharpoons \text{resins} \rightleftharpoons \text{asphaltenes} \rightleftharpoons \text{carbenes} \rightleftharpoons \text{carboids}$$

in which asphaltenes play a dominant role, since the kinetics of their conversion controls the formation of the oil fractions (especially for raw materials with high asphaltene contents) as well as of carbenes and carboids as precursors of the irreversibly formed coke deposits on the walls of the technological equipment and, especially, on the surface of the catalysts employed[4].

In asphaltenic fractions containing hetero atoms (S, O, N) to a high degree, organometallic components concentrate, complicating the conversion of the asphaltenic matter to the desired products (fuel oils, material to be cracked, *etc.*), particularly during the catalytic hydrogenation and hydrocracking.

Asphaltenes are very difficult to desulphurize and denitrogenize during the hydrogenation treatment. Asphaltenic micelles, formed by agglomerates of the asphaltene molecules, are in normal circumstances colloidally stabilized by the presence of the other constituents of the petroleum residue[5]. In the conditions of hydrocracking, however, the asphaltenic micelles break down, the most important changes in the residual petroleum fraction being as follows: *a*) the proportion of the asphaltenic fractions decreases; *b*) partial desulphurization takes place; *c*) the aromatic nature of the residual asphaltenic fractions becomes more pronounced; *d*) the metal content in the asphaltenic fractions lowers; *e*) the nickel-to-vanadium ratio in these fractions rises[6].

Under mild reaction conditions the desulphurization only occurs in the surface layers of the asphaltenic micelles; the sulphur bonded inside them is hydrogenolytically accessible only under severe reaction conditions. The amenability of asphaltenes to desulphurization and denitrogenation will, of course, depend first of all on their structure and origin (high differences are observed in the resistance of asphaltenes from crude oil, coal tar, shales, *etc.*, during treatment of heavy hydrocarbon mixtures)[4].

The type and stability of asphaltenes affect considerably also the kinetics of formation of coke deposit on the walls of the technological equipment and on the catalysts employed for the treatment of the high-molecular hydrocarbon fractions. The kinetics is to an appreciable extent influenced also by the presence of organometallic compounds (Ni and V) in the asphaltenes[7].

Hydrocracking catalysts for treatment of residual petroleum fractions can exhibit good properties — high activity and long life time — if they possess a suitable texture, in particular the mean pore size and surface area, which must ensure that the active catalytic surface is accessible also to the bulky molecules of asphaltenes and resins present in the residual fraction[6].

TABLE I

Content of Maltenes and Asphaltenes in Crude Oils[2]

Crude oil	Content, wt.%	
	maltenes	asphaltenes
Pennsylvania (USA)	1·5	0
Groznyi (USSR) — paraffinic	4·3	0·9
Romashkino (USSR)	10·6	3·8
California (USA)	19·0	4·0
Mexico (Pánuco, Ebano, Tampico)	≦26·0	≦12·5
Iraq	15·5	1·3
Nagylengyel (Hungary)	not detd.	14·9

The maltenic fractions lend themselves to hydrogenation degradation better than asphaltenes, although during the treatment of heavy oil fractions they induce a number of analogous adverse effects too.

From the above facts it can be concluded that study of the chemical structure and behaviour of the asphaltenic-resinous fractions in conditions of thermal-catalytic treatment, especially hydrogenation, is of importance since asphaltenes (and resins) are intermediates in the formation of oil fractions as well as coke deposits, and *a*) knowledge of the asphaltene structure and genesis makes it possible to establish the optimum working conditions, in which their conversion to coke deposits is minimal; *b*) study of the structure and properties of asphaltenic and resinous fractions gives an insight into the nature of the bonding of hetero atoms (S, N, O) and metals in these materials and enables conditions to be found for their degradation in which the catalysts used in the conversion process will suffer as little as possible; and *c*) the acquired knowledge concerning the asphaltenic-resinous fractions is important for understanding the viscosity properties of heavy hydrocarbon fractions and their effect on the stability of the latter. The present work represents an introductory study of these significant theoretical and technological problems.

EXPERIMENTAL

Preparation of asphaltenes. The source of petroleum asphaltenes was a propane asphalt from Volga district crude oil; an industrial sample was taken at Paramo Works, Pardubice, in 1975. Asphaltenes were prepared from this asphalt by extraction with n-pentane[8].

Apparatus. The hydrogenations were conducted in a 50 ml shaken pressure autoclave (Andreas Hofer) with electric heating. The temperature was measured by means of an iron-constantan thermocouple and controlled with the precision of ±2°C.

Hydrogenation of decaline. The stability of decaline, used as the solvent for the asphaltenes examined, was tested by performing a series of blank hydrogenations in the working temperature range of 300—450°C. The autoclave was filled with 14 ml of decaline and, in the case of catalytic hydrogenation, 1·4 g of the catalyst, and hydrogen was delivered up to the pressure of 10 MPa. The autoclave was then heated up to the reaction temperature within 30 min and held at this temperature for 1 h. After cooling down, the liquid hydrogenation product was drawn off with a pipette, freed from the catalyst by filtration, and gas chromatographically analyzed. A Hewlett-Packard 5830 gas chromatograph was employed, equipped with a stainless steel capillary squalane column (100 m), 0·25 mm in diameter. The working temperature was 110°C, evaporator temperature 250°C, flame ionization detector temperature 300°C, divider 1 : 150, injection of 10 μl of the sample.

Hydrogenation of asphaltenes. 1·4 g of asphaltenes in 13·85 g of decaline was hydrogenated in the presence of 1·4 g of prior activated hydrorefining catalyst (industrial Co–Mo/Al_2O_3, catalyst 7362, product of the Czechoslovak-Soviet Friendship Chemical Works, Litvínov). The catalyst was powdered and activated at 300°C, 10 MPa H_2, for 2 h. After filling with the reaction mixture, the autoclave was multiply flushed with hydrogen and filled with it up to the pressure 10 MPa, heated up to the reaction temperature within 30 min, and held at this temperature for additional 1 h. After cooling down, the hydrogenation product was drawn off with a pipette and filtered. The solvent together with the most volatile products was distilled off under normal pressure using an oil bath at a temperature not exceeding 220°C, and the remaining liquid fractions were evaporated on a vacuum evaporator at 2·63 kPa/100C°. An analogous procedure was applied in the non-catalytic (thermal) hydrogenations.

Characterization of the hydrogenation products. The hydrogenation products obtained by the above procedure were characterized by elemental analysis and determination of the average molecular weight, by vapour pressure osmometry, and the structural parameters were calculated from the ^{1}H-NMR data.

Vapour pressure osmometry. The average molecular weight was determined in benzene at 37°C using a Knauer vapour pressure osmometer. All samples were measured at four concentrations and the results were extrapolated to infinite dilution. The apparatus was calibrated with squalane.

Nuclear magnetic resonance. The ^{1}H-NMR spectra were scanned on a Varian XL 100 NMR spectrometer at 37°C. The samples were measured in 10% solutions in CCl_4 with addition of 1% tetramethylsilane (Merck). The relative proton abundances[9] were calculated from the integrated records, which were run three times and averaged. The data of the ^{1}H-NMR spectra, elemental analysis, and average molecular weight were employed for the calculation of the structural parameters according to Brown and Ladner[9] and Williams[10], and of the structural unit weight (USW) and other structural parameters as reported previously[11].

RESULTS AND DISCUSSION

The model hydrogenation experiments were performed with isolated asphaltenes in conditions where these components were not stabilized in a colloidal system, typical of natural hydrocarbon mixtures. Conditions were chosen so as to approach those used in technological practice: temperature range 300–450°C, typical hydrorefining Co—Mo/Al_2O_3 catalyst, and pressures up to 10 MPa; analogous thermal hydrogenation experiments were performed for a comparison.

The experiments were carried out so that total destruction of the asphaltenes to low-molecular products was prevented. The solvent, decaline, which also enabled hydrogen transfer, was stable in the conditions applied up to temperatures about 400–450°C. In view of the fact that the work represented an introductory study, its main objective was characterization of the residue after removing the solvent.

The principal characteristics of the course of asphaltene hydrogenation is the degree of elimination of hetero atoms, particularly sulphur and nitrogen, associated with a decrease in the average molecular weight of the substances; the latter is in part due also to hydrogenolysis of the C—C bonds of their original skeleton. As follows from Table II, the catalytic hydrogenation is accompanied by a steady decrease in the sulphur content, from the initial 2·34% to final 0·70% at the hydrogenation temperature 450°C. In fact, hydrodesulphuration is a rather reluctantly proceeding reaction, intensive elimination of sulphur occurring mainly at temperatures above 400°C (Table II). This indicates that a predominating fraction of sulphur in the asphaltenic moiety is bonded in heterocycles, hence comparatively very strongly.

More complicated is the situation with asphaltenic denitrogenation. Although determination of nitrogen in such complex natural samples is less accurate than in pure compounds, it is noteworthy that in contrast to sulphur, the content of residual nitrogen does not exhibit a uniform decrease over the entire temperature range pursued. This also gives evidence of predominantly heterocyclic nature of nitrogen in asphaltenes; nitrogen heterocycles are known to be often considerably more resistant to hydrogenolysis than the analogous sulphur or oxygen compounds.

A next quantity characterizing the course of asphaltene hydrocracking is the average molecular weight. As can be seen from Table II, it decreases gradually, from the initial 1300, down to 20% at 450°C. Another evidence that during the asphaltene hydrogenation, deeper structural changes occur only at temperatures above 400°C is the substantial increase in the proportion of protons bonded directly to an aromatic system (Table II), resulting from the appreciable decrease in the content of carbon constituting the saturated substituents of the aromatic system.

The results of thermal hydrogenation (Table III) point to an appreciable role of catalysts in asphaltene desulphuration, as in their absence only 20% desulphuration was found at 450°C; the sulphur content decreased intensively again at temperatures exceeding 400°C.

As to the content of hydrogen in the asphaltene hydrogenation products, it increases with temperature up to 400°C, where it attains its maximum; at higher temperatures the hydrogen content decreases again, particularly in the case of thermal hydrogenations.

Appreciable are the differences in the content of hydrogen bonded directly to the aromatic system in the products of catalytic and thermal hydrogenation at over

TABLE II

Elemental Analysis, Relative Abundance of Protons, and Average Molecular Weight of Asphaltenes and Their Catalytic Hydrogenation Products

Parameter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
H (%)	8·00	8·33	8·56	9·05	8·51
C (%)	86·00	87·11	82·71	86·13	88·29
N (%)	0·66	—	0·35	—	0·73
S (%)	2·34	2·36	2·00	1·52	0·70
H^*_{ar}	0·1476	0·1142	0·0907	0·1284	0·1806
H^*_{α}	0·1994	0·2078	0·2278	0·2686	0·2504
H^*_{β}	0·4562	0·5197	0·5002	0·4870	0·4341
H^*_{γ}	0·1968	0·1583	0·1813	0·1160	0·1349
M_r	1 320	1 060	950	680	280

400°C, hence in a temperature range in which substantial structural changes take place. Thermal hydrogenation is accompanied by an essentially higher loss of carbon in saturated substituents owing to a more intensive dehydrocyclization of the aliphatic substituents, although this fact is not confirmed unambiguously by the structural parameter values (compare, *e.g.*, the σ and R_A values in Tables IV and V).

The proton magnetic resonance technique was employed for a structural characterization of asphaltenes and products of their hydrogenation. The NMR data, average molecular weight values, and results of elemental analysis (C, H) served for the cal-

TABLE III

Elemental Analysis, Relative Abundance of Protons, and Average Molecular Weight of Asphaltenes and their Thermal Hydrogenation Products

Parameter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
H (%)	8·00	8·97	8·55	8·66	7·69
C (%)	86·00	87·41	86·65	87·70	88·85
N (%)	0·66	0·63	—	—	—
S (%)	2·34	2·36	2·27	2·12	1·89
H_{ar}^*	0·1476	0·0956	0·1055	0·1448	0·2219
H_α^*	0·1994	0·2337	0·2492	0·2459	0·2530
H_β^*	0·4562	0·4852	0·5185	0·4916	0·3872
H_γ^*	0·1968	0·1855	0·1268	0·1177	0·1379
M_r	1 320	980	850	650	400

TABLE IV

Values of the Structural Parameters of the Brown-Ladner Method, USW and Its Parameters for Asphaltenes and Their Catalytic Hydrogenation Products

Paramcter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
f_a	0·52	0·49	0·43	0·45	0·53
σ	0·40	0·48	0·56	0·51	0·41
H_{aru}/C_{ar}	0·53	0·51	0·58	0·73	0·67
R_{aUSW}	6·43	7·04	4·90	2·73	3·50
C_{arUSW}	23·12	24·70	19·20	12·70	15·03
USW	616	692	641	392	389

culation of the most significant structural parameters by the Brown–Ladner and Williams methods and of the structural unit weight (USW) and its parameters, *i.e.* the number of the the aromatic rings (R_{aUSW}) and the number of the aromatic carbon atoms (C_{arUSW}) (ref.[11]). The results are given in Tables IV – VII. The simplest method for characterization of samples of this type, the Brown–Ladner method, was used

TABLE V

Values of the Structural Parameters of the Brown-Ladner Method, USW and Its Parameters for Asphaltenes and Their Thermal Hydrogenation Products

Parameter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
f_a	0·52	0·44	0·47	0·49	0·60
σ	0·40	0·55	0·54	0·46	0·36
H_{aru}/C_{ar}	0·53	0·58	0·58	0·64	0·59
R_{aUSW}	6·43	4·90	5·04	3·90	4·72
C_{arUSW}	23·12	19·10	19·50	16·24	18·62
USW	616	589	573	451	420

TABLE VI

Values of the Williams' Structural Parameters for Asphaltenes and Their Catalytic Hydrogenation Products

Parameter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
n	4·28	4·26	3·99	3·25	3·28
f	5·64	5·57	5·55	5·34	5·38
r	0·23	0·17	0·18	0·10	0·12
C_S	38·45	41·12	43·24	42·14	37·55
C_A	47·55	46·00	39·47	43·99	50·74
f_a	0·55	0·53	0·48	0·51	0·57
$\# C_1$	25·48	18·60	15·95	15·26	6·99
$\% AS$	38·82	45·80	53·78	48·22	38·33
$\# C_A$	52·31	40·63	31·25	24·93	11·84
R_A	14·41	12·01	8·65	5·83	3·43
R_N	2·23	1·48	1·55	0·74	0·33
R_S	9·89	8·52	8·58	7·36	2·68

to obtain the principal structural parameters – aromaticity f_a, degree of substitution σ, and ratio of numbers of the aromatic hydrogen atoms to the aromatic carbon atoms H_{aru}/C_{ar} for a hypothetical unsubstituted polyaromatic system. In accordance with the recent findings concerning the nature of the hetero atoms bonding in asphaltenic-resinous fractions of crude oils, the original Brown–Ladner equations for calculation of σ and H_{aru}/C_{ar} were modified[11] to

$$\sigma = (\mathrm{H}_\alpha^*/x)/[(H_\alpha^*/x) + H_{ar}^*] \qquad (1)$$

and

$$H_{aru}/C_{ar} = [(H_\alpha^*/x) + H_{ar}^*]/[(C/H) - (H_\alpha^*/x) - (H_\beta^* + H_\gamma^*)/y] \,. \qquad (2)$$

A next important parameter describing heavy petroleum fractions is the structural unit weight (USW) based on the concept of a condensed polyaromatic system with saturated substituents attached in the non-bridge positions[12].

In accordance with the average molecular weight decreasing with increasing temperature, the structural unit weight of asphaltenes decreases too, both for the catalytic and thermal hydrogenations (Tables IV and V). The H_{aru}/C_{ar} ratio attains its maximum at temperatures near 400°C. This can be explained reasonably in terms of com-

TABLE VII

Values of the Williams' Structural Parameters for Asphaltenes and Their Thermal Hydrogenation Products

Parameter	Starting asphaltenes	Product at the temperature, °C			
		300	350	400	450
n	4·28	3·87	3·59	3·48	3·08
f	5·64	5·54	5·42	5·40	5·35
r	0·23	0·18	0·12	0·11	0·12
C_S	38·45	44·96	41·48	39·97	31·99
C_A	47·55	42·45	45·17	47·73	58·86
f_A	0·55	0·49	0·52	0·54	0·64
$\# C_1$	25·48	17·89	15·85	14·38	10·30
$\% AS$	38·82	53·03	51·62	43·31	33·70
$\# C_A$	52·31	34·67	32·00	25·85	19·62
R_A	14·41	9·39	9·08	6·74	5·66
R_N	2·23	1·71	0·98	0·69	0·42
R_S	9·89	9·49	8·18	6·23	3·47

petition of two principal reactions, *viz.* hydrogenolysis predominating at lower temperatures and dehydrocyclization prevaling at temperatures above 400°C.

As to the degree of substitution (σ), its values at the highest temperatures applied (Tables IV and V) evidence a loss of carbon atoms in the saturated substituents of the aromatic system, hence they support the conclusions derived from the temperature dependence of the relative content of aromatic protons H_{ar}. The dependences discussed apply to both types of hydrogenation.

The temperature dependence of the Williams' parameters R_A and $\# C_A$ (Tables VI and VII) is in an apparent disagreement with the concept of the two competitive reactions derived from the temperature dependence of the Brown–Ladner H_{aru}/C_{ar} parameter. This discrepancy, however, is removed if the temperature dependences are examined for the H_{aru}/C_{ar} and $\# C_1/\# C_A$ ratios; both of them display maxima at temperatures about 400°C. Generally, the Williams' structural parameters that are calculated by means of the average molecular weight values, *viz.* $\# C_A$, R_A, R_N, and R_S do not enable the course of the principal reactions to be directly evaluated. The analogous quantities of the Brown–Ladner and of the Williams methods, f_a, % AS, and σ (in %), exhibit an identical trend of the temperature dependence.

The temperature dependence of the content of the saturated carbon atoms C_S (Tables VI and VII) bears out the above discussed predomination of hydrogenolytic reactions up to the temperature 400°C and of dehydrocyclization reactions at higher temperatures. In addition, the dependence of the mean number of carbon atoms in an alkyl substituent (n) gives evidence of a gradual shortening of the saturated substituents.

It can be thus concluded that during hydrogenation of asphaltenes, intensive elimination of hetero atoms proceeds at temperatures exceeding 400°C. The results of ^{1}H-NMR type analysis for asphaltenes and products of their hydrogenation indicate that up to 400°C, hydrogenolysis of the heterocyclic rings predominates, whereas above this temperature, in addition to C—C bond hydrocracking, dehydrocyclization reactions occur, resulting in an increase in the aromatic hydrogen-to-aromatic carbon ratio for a hypothetical unsubstituted polyaromatic system.

The results obtained, which are to be looked upon as a first approach to the topic in question, are important as regards the chemism of conversion of high-boiling petroleum fractions during thermal-catalytic processes, and so their application is feasible in examining routine technological processes of refining industry.

LIST OF SYMBOLS

% AS	percentrage fraction of non-bridge aromatic carbon atoms, on which saturated substituents are bonded
C/H	ratio of the number of carbon and hydrogen atoms determined by elemental analysis

C_A, C_S, C_1	fractions of the total aromatic carbon, carbon in saturated substituents on aromatic rings, and non-bridge carbon of aromatic rings, respectively
$\# C_A$, $\# C_1$	numbers of all aromatic and non-bridge carbon atoms, respectively, in an average molecule
C_{arUSW}	number of aromatic carbon atoms in a basic structural unit
H_{ar}^*, H_α^*, H_β^*, H_γ^*	relative abundances of aromatic protons and of protons in the α, β, and γ positions with respect to the aromatic rings, respectively
f	average C/H weight ratio for the alkyl groups
f_a	aromaticity (atomic ratio of aromatic carbon to total carbon)
H_{aru}/C_{ar}	ratio of the number of aromatic hydrogen atoms to the number of aromatic carbon atoms for a hypothetical unsubstituted aromatic system
M_r	average molecular weight
n	average number of carbon atoms in alkyl substituents
r	number of naphthenic rings in alkyl substituents
R_A, R_N	numbers of aromatic and naphthenic rings, respectively, in an average molecule
R_S	number of alkyl substituents in an average molecule
R_{aUSW}	number of aromatic rings in a basic structural unit
USW	structural unit weight
x	average number of protons at a carbon atom in the α position with respect to the aromatic ring
y	average number of protons at carbon atoms in positions β, γ, and more remote from the aromatic ring
σ	degree of substitution of peripheral sites of polyaromatic system

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