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Inverse gas chromatography for the examination of fractions separated from oil vacuum distillation residues

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Abstract

A new procedure for the separation of petroleum vacuum distillation residues is presented and discussed. This method reduces the separation time required to ca. 30 h for typical petroleum products. Three different petroleum vacuum distillation residues were processed and the separated fractions were characterized in a traditional way as well as by means of inverse gas chromatography.

Keywords: Oils; Petroleum

1. Introduction

The available literature data seldom provide information on distribution methods for petroleum vacuum distillation residues. Most often, procedures for the isolation and distribution of the components of mineral pitches (natural asphalts) are presented and discussed. Atmospheric distillation of crude oil is followed by vacuum distillation of the atmospheric residue. The products are then separated into fractions that are further used in the preparation of bright stocks. These are one of the components of mineral-based oils that are used in the manufacture of lubricants.

The purpose of these investigations was to develop a separation method for vacuum distillation residues (residues boiling above 550°C) into group components. The other task was to characterize the separated fractions by means of inverse gas chromatography (IGC) as well as by traditional methods.

Our method should allow the separation of asphaltenes and the distribution of the oleo-resinous part, i.e. the malthenes fraction. In addition to paraffinic and naphtenic hydrocarbons, the malthenes fraction also contains polyaromatic hydrocarbons (PAHs) and several substances containing sulphur, nitrogen and oxygen atoms. The presence of heteroatoms significantly affects the chemical character of the investigated residue. Determination of the composition of the malthenes (petrolenes) fraction and its structural constitution is impossible without its earlier separation into chemically homogeneous fractions.

The first step in the procedure must be the separation of asphaltenes, followed by the isolation of polar components. Methods used for the separation of asphaltenes include (i) solvent, (ii) chemical, (iii) adsorption and (iv) thermocatalytic methods

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[1]. The solvent method is the method used most often in laboratory-scale procedures because it is simple and accurate. It is based on washing vacuum residue probes with excess *n*-paraffinic hydrocarbons (*n*-pentane to *n*-heptane) or other lipophilic precipitating agents in comparison to asphaltenes. During the coagulation process, asphaltenes co-precipitate with other substances, especially those that are strongly polar, i.e. so-called "resins", in the form of supramolecular structures [1]. Therefore, the accuracy of asphaltene precipitation depends on the following process parameters: (i) the type and amount of solvent; (ii) the ratio between the amount of "resins" and asphaltenes and (iii) the temperature and chemical characteristics of the crude oil. The total separation of asphaltenes is easy in the case of paraffinic and naphtenic vacuum residues. The process is much more difficult for vacuum residues from aromatic petroleum [1–11]. The separation of the malthenes fraction into group components may be carried out using the following processes: (i) adsorption, (ii) coagulation and (iii) selective extraction. These processes should lead to a decrease in the amount being loaded on the chromatographic column in the final step of the procedure.

The use of classical gas chromatographic techniques in the examination of organic materials is limited by their thermal stability, while in the case of high molecular mass substances (e.g., polymers, petroleum products) it is also limited by their low volatility. The method of pyrolytic GC is based on the relationship between the composition of the examined substance and the chemical characteristics of the products of its thermal degradation. This method often fails for thermally non-stable polar structures. There are also additional problems in the interpretation of experimental results from the processes occurring during the pyrolysis, i.e., rearrangement, elimination and substitution reactions. Very often the only result obtained from the analysis is the "chromatographic spectrum" corresponding to the products of degradation, but these cannot be identified or interpreted further.

IGC has become an accurate, reliable and fast method for the physicochemical characterization of different substances, including polymers and their blends, fibres, the surfaces of polymers, silicas and other minerals, surfactants and others. The term "inverse" indicates that the examined material is placed in a chromatographic column and studied using test solutes. Carefully selected test solutes are injected into the flow of a carrier gas and transported over the surface of the material being examined. The retention times and peak elution profiles, influenced by the interactions between the solute and the stationary phase, are used to estimate these interactions. Due to the characteristics of the examined material, IGC may be separated into gas–liquid and gas–solid IGC. The mixed retention behaviour is most often observed for materials that are liquids at the temperature of the chromatographic experiment. Therefore, the appropriate mathematical models have to be used to describe the process and for the evaluation of parameters characterizing the examined substances.

In the early years of IGC, the technique was used mainly to determine the activity coefficients of volatile species [12–18]. This method was first used by Davis et al. [19] for the examination of heavy oil residues (asphalts) and was used later by Davis and Petersen [20,21], Petersen and Dorrence [22] and Barbour et al. [23,24]. These authors defined the so-called interaction coefficient as the difference in the retention indices of test solutes. They assumed that this difference is proportional to the magnitude of mutual interactions between the test solute and asphalt. Funk [25] showed that it might be possible to use thermodynamically valid parameters in the characterization of petroleum products. Papirer et al. [26] characterized asphalts and asphaltenes separated from atmospheric residues using IGC. This technique was also used in the examination of polymers and their mixtures. Martire and Purnell [27] and Kogan et al. [28] used this technique to determine the average molecular mass of polymer species. Other applications of IGC include the determination of the Flory–Huggins interaction parameter, solubility parameters and partial thermodynamic functions [19,29–43], although this list may be significantly extended.

The Flory–Huggins interaction parameter, $\chi_{1,2}^{\infty}$, may be calculated from the data collected from IGC using the following expression:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \times R}{P_1^{\circ} \times V_g \times M_1}\right) - \frac{P_1^{\circ}}{RT}(B_{11} - V_1^{\circ}) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^{\circ}}{V_2^{\circ}}\right) \quad (1)$$

where M_1, P_1°, B_{11}, V_1°, ρ_1 and V_g° are the molecular mass, the saturated vapour pressure, the second virial coefficient, the molar volume, the density and the specific retention volume of the solute, respectively; ρ_2 and V_2° are the density and molar volume of the stationary phase, respectively; T is the column temperature (K) and R is the gas constant (8.314 J mol^{-1} deg^{-1}).

In our work, we present the adsorption methods used in the separation of highly boiling petroleum fractions from three vacuum distillation residues. The main problem was the use of IGC as a quick, reliable and easily accessible method for the physico-chemical characterization of technological products.

The aim was the presentation of the possibility to formally discriminate (by the use of IGC parameters) the same fractions separated from different crude oils.

2. Experimental

2.1. Separation procedure for vacuum distillation residues

The separation method for a vacuum residue that boils above 550°C is presented in Fig. 1. Vacuum residues obtained from Flotta-Blend (North Sea), Baltic Sea (B-6/II) and Russian (Pipe Oil) crude oils were taken as the starting material for this study.

The first step in the procedure was the separation of asphaltenes, followed by the isolation of polar components, i.e., "resins", using a low polar sorbent (bleaching earth) (Fig. 1). These processes should lead to a decrease in the amount of material being loaded on the chromatographic column in the final step of the procedure. Paraffinic hydrocarbons with high melting points were removed in a deparaffination process. Deparaffinate was further separated using column chromatography.

The asphaltenes precipitated from the vacuum residue sample solution as they were not soluble in n-heptane. Other substances were collected as n-heptane solutions. Bleaching earth was added to all collected n-heptane solutions (malthenes fractions). The resulting mixture was kept at room temperature for 12 h, filtered and the precipitate was extracted (Soxhlet) with n-heptane to remove the adsorbed oil.

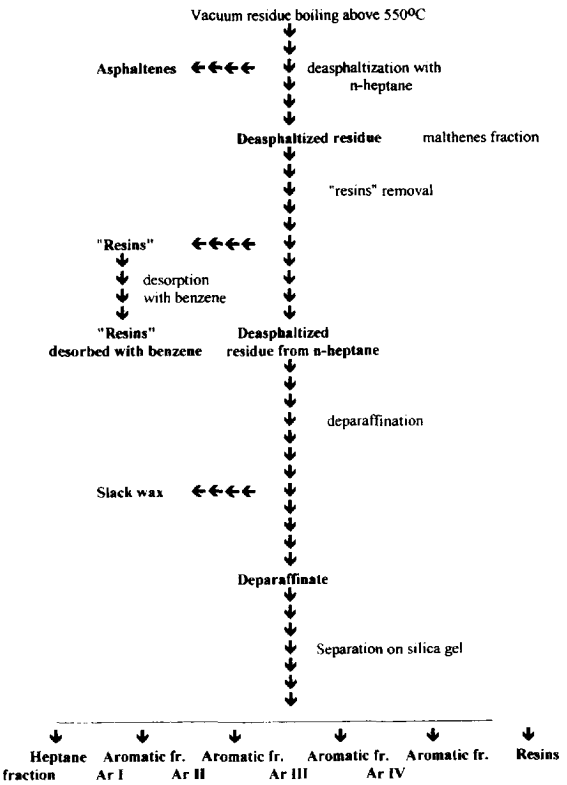

Fig. 1. Procedure for the separation of oil vacuum distillation residues.

Solutions from the extraction and filtration steps were collected, n-heptane was removed by distillation and the distillation residue was assumed to form the polar fraction, i.e. "resins desorbed with benzene". The content of the polar fraction [the content of resins-CR in (%)] was calculated. Paraffinic substances were removed by dissolving the solid residue in acetone–benzene–toluene (35:43:22 w/w) [1:3 (w/w) ratio of sample to mixture). This step was carried out at −20°C.

Deparaffinate was further separated into group components by means of column chromatography. A 200×20 mm I.D. column was filled with silica gel (Merck, 70–230 mesh) that was activated at 180°C for 5 h. The weight ratio of silica gel and separated sample was 10:1. Deparaffinate sample was separated using the following eluents: n-heptane (800 ml), 2% (v/v) benzene in n-heptane (1200 ml), 5% (v/v) benzene in n-heptane (1200 ml), 20% (v/v) benzene in n-heptane (1200 ml), benzene (480 ml), ethanol–benzene mixture (1200 ml) (i.e. with in-

creasing elution power). Eluate batches (120 ml) were collected. An UV lamp was used during collection of the *n*-heptane fractions, to facilitate the exact determination of the boundary between *n*-heptane and aromatic (Ar I) fractions. The fractions were defined according to their refractive index, as follows:

– heptane fraction	$n_D^{20} < 1.49$
– aromatic fraction I (Ar I)	$1.49 < n_D^{20} < 1.53$
– aromatic fraction II (Ar II)	$1.53 < n_D^{20} < 1.55$
– aromatic fraction III (Ar III)	$1.55 < n_D^{20} < 1.59$
– aromatic fraction IV (Ar IV)	$n_D^{20} > 1.59$

Elemental analysis (C, H, N) was performed using a Perkin-Elmer Model 240, according to the ASTM D-5291-92 standard test method. The sulphur content was determined using a Herman-Mortiz analyser and the iodometric method, according to ASTM D-1552. The oxygen content was calculated by difference to 100%. Average molecular mass was determined on a Perkin-Elmer Model 115 analyser using an isopiestic method, according to ASTM D-2503.

2.2. Inverse gas chromatography

The separated fractions were coated onto Chromosorb P AW 60/80 mesh to produce the samples of column filling 20% (w/w). The GC conditions were as follows: a Hewlett-Packard 5730A gas chromatograph with flame ionization detection (FID); stainless-steel columns (2 m length, 2 mm I.D.); column temperature, 100°C; carrier gas, argon, at a flow-rate of 17.5 cm^3/min; conditioning, 150°C, overnight; injection volume, 0.1 μl. The following compounds were used as test solutes: C_5–C_{10} *n*-alkanes, benzene, ethanol, butanol-1, 2-butanone, 2-pentanone, nitromethane, 1-nitropropane, pyridine and 1,4-dioxane.

The Flory–Huggins interaction parameter, $\chi_{1,2}^{\infty}$, was calculated from the data collected during IGC experiments according to the Eq. (1). The use of the values of the second virial coefficient B_{11} extrapolated from data presented elsewhere [43]. Vapour pressures of the test solutes ($P_1°$) at 100°C were taken from the literature [44–46]. The densities of the oil fractions were calculated by the method described in Ref. [47].

3. Results and discussion

The traditional physicochemical characteristics of vacuum distillation residues and separated fractions are presented in Table 1.

Asphaltenes isolated from the examined vacuum residues may be generally treated as intermediates between polar substances ("resins") and typical asphaltenes (e.g. those isolated from the vacuum residue of paraffinic–naphtenic crude oil). The reasons are the relatively low values of average molecular mass ($\bar{M}$), the average number of carbon atoms in aromatic rings (C_a) and the number of aromatic rings in the molecule (R_a).

Please note that in the case of the vacuum distillation residue from the Baltic Sea B-6/II Oil asphaltene and "resins from separation", fractions were not separated as well as those of the aromatic fraction, Ar IV, from the Pipe Oil.

The results from structural group analysis by densitometry show that chemical substances present in isolated fractions possess increasing aromatic character in going from the *n*-heptane fraction to asphaltenes. The aromatic character is measured by the aromaticity coefficient, f_a, the average number of carbon atoms in aromatic rings, C_a, the number of aromatic rings in molecule, R_a, and the index of ring condensation. A positive value for the index of ring condensation for an isolated fraction denotes the presence of PAHs, the amounts of which decrease in going from asphaltenes to Ar I. The relatively high index observed for slack wax indicates that co-precipitation of PAHs with paraffinic substances occurs in the deparaffination process.

Two fractions separated from B-6/II oil (Ar IV and "resins" desorbed with benzene fractions) may be treated as the exception; these fractions were characterized by significantly lower f_a, C_a and R_a values. Large differences were observed also between the characteristics for asphaltenes from Flotta-Blend and Pipe oils. Asphaltenes from Flotta-Blend oil were characterized by much lower average molecular masses, lower numbers of aromatic rings in the molecule and a higher CH_2–CH_3 ratio, in comparison to the same fraction from Pipe oil. Asphaltenes from Flotta-Blend oil may be treated as the intermediate fraction between polar compounds ("resins") and typical asphaltenes.

Table 1
Elemental analysis and structural group analysis (densitometric method) of fractions separated from a vacuum residue (550°C) from Flotta-Blend oil

Parameter	Fraction									
	Vacuum residue	Heptane fraction	Aromatic hydrocarbon fraction				"Resins"		Asphaltenes	Slack wax
			Ar I	Ar II	Ar III	Ar IV	Separation	Desorbed with benzene		
1. Content (% w/w)	100.0	10.9	13.4	4.8	16.3	21.1	3.7	18.1	3.9	7.8
2. Elemental analysis										
%C	85.57	85.95	85.81	85.66	85.86	85.18	83.80	84.31	85.11	86.05
%H	11.48	14.05	12.37	11.30	10.39	9.51	9.60	8.89	7.41	13.00
%N	0.37	0.00	0.19	0.13	0.34	0.69	0.65	0.78	0.99	0.00
%S	2.58	0.00	1.63	2.91	3.41	3.40	2.82	3.40	3.40	0.95
%O	0.00	0.00	0.00	0.00	0.00	1.22	3.13	2.61	4.09	0.00
3. Empirical formula for average molecule	$C_{50.6}S_{0.6}$	$C_{49}H_{96}$	$C_{51.1}S_{0.4}$	$C_{46}H_{73.2}S_{0.6}$	$C_{45.9}S_{0.7}$	$C_{52.6}S_{0.8}$	$C_{65.2}S_{0.8}$	$C_{52.1}S_{0.8}$	$C_{84.3}S_{0.9}$	$C_{51.3}S_{0.2}$
4. Average mol. weight $\bar{M}$	709	684	715	648	641	741	934	741	1189	721
5. Densitometric analysis [47]										
Density d_4^{20} [g/cm^3]	0.9730	0.8618	0.9342	0.9803	1.0195	1.0574	1.0535	1.0841	1.1479	0.9070
Aromatic fraction (f_a)	0.21	0.00	0.13	0.23	0.33	0.41	0.38	0.48	0.63	0.07
Average number of C atoms in molecule	51	49	51	46	46	53	65	52	84	52
Average number of C atoms in aromatic ring (C_a)	10.7	0.00	6.6	10.6	15.8	13.8	24.8	25.0	52.9	3.6
Number of aromatic rings in molecule (R_a)	2.2	0.0	1.2	2.2	3.5	3.0	5.7	5.7	12.7	0.3
Number of naphtenic rings per mole (R_N)	3.7	2.2	3.6	3.4	2.8	6.9	3.4	1.8	2.2	4.1
Total number of rings per mole (R)	5.9	2.2	4.8	5.6	6.3	9.9	9.1	7.5	14.9	4.4
Concentration index (C.I.)[a]	0.19	0.05	0.15	0.20	0.23	0.26	0.25	0.25	0.33	0.13

[a] C.I. $= 2 - H/C - f_a$, according to Ref. [47].

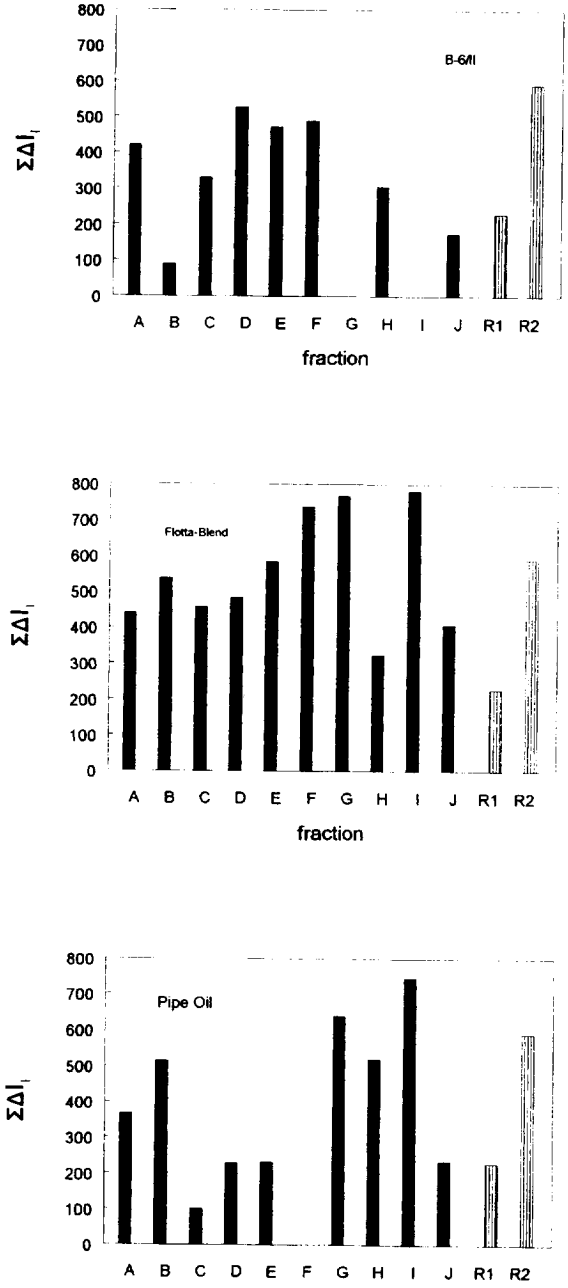

Fig. 2. McReynolds constants for fractions separated from vacuum oil distillation residues (A = vacuum residue, B = heptane fraction, C = aromatic hydrocarbon fraction Ar I, D = aromatic hydrocarbon fraction Ar II, E = aromatic hydrocarbon fraction Ar III, F = aromatic hydrocarbon fraction Ar IV, G = "resins" from separation, H = "resins" desorbed with benzene, I = asphaltenes, J = slack wax, R1 = OV-101 and R2 = OV-7).

We tried to use different systems to characterize the stationary column: Rohrschneider/McReynolds system and having strong thermodynamic meaning Flory–Huggins interaction parameter.

Let us start with the traditional (in GC) Rohrschneider/McReynolds system. The retention indices of ten McReynolds' test solutes for all separated fractions are presented in Fig. 2. The individual ΔI values for the respective test solutes are presented in Tables 2–4. For comparison, the respective values for two well known stationary phases, OV-101 and OV-7, are also given. There was significant differentiation between fractions separated from the same vacuum oil distillation as well as between the "spectrums" found for three vacuum distillation residues. The polarity of all fractions from B-6/II oil was low and no fraction was more polar than OV-7 (described as R2 in Fig. 2). The differences between the respective fractions are significant. These differences are much smaller in the case of Flotta-Blend oil. Fractions were also slightly more polar than previously found (Ar IV, "resins" from separation and asphaltene fractions are more polar than OV-7). When comparing the same fractions from different oils, one may find that their physicochemical properties are quite different (e.g. check the $\Sigma\Delta I$ values for heptane fractions, "resins" desorbed with benzene and slack wax fractions).

Separated fractions may be arranged according to their decreasing polarity (i.e. decreasing $\sum_{i=1}^{5} \Delta I_i$ values) as follows:

– B-6/II oil residue: Ar II→Ar IV→Ar III→Ar I→"resins" desorbed with benzene→slack wax→heptane fraction

– Flotta-Blend oil residue: "Resins" desorbed with benzene→"resins from separation"→Ar IV →asphaltenes→Ar III→heptane fraction→Ar II→Ar I→slack wax

– Pipe oil residue: Asphaltenes→"resins from separation"→"resins" desorbed with benzene →heptane fraction→Ar III→Ar II→slack wax→Ar I.

Once again, one may find significant differences between the three vacuum residues examined. The other problem involves the differences between the heptane and slack wax fractions. The heptane fraction is the component of the deparaffinate, i.e. the main product of the process called deparaffination.

Table 2
ΔI for McReynolds test solutes determined for vacuum distillation residues and separated fractions from B-6/II oil (373.15 K)

Test substance	Fraction							
	Vacuum residue	Heptane fraction	Aromatic hydrocarbon fraction				Resins desorbed with benzene	Slack wax
			Ar I	Ar II	Ar III	Ar IV		
Benzene	22	5	14	91	55	34	38	0
Butanol-1	118	−11	92	151	95	97	85	35
2-Pentanone	189	118	142	180	200	118	128	86
1-Nitropropane	80	−23	82	105	123	97	3	13
Pyridine	11	[a]	[a]	[a]	[a]	143	51	40
2-Methyl-2-pentanol	66	2	41	44	45	23	4	3
Jodobutane	120	23	14	177	67	15	20	12
2-Octyn	−3	−5	14	134	24	−22	18	−19
1,4-Dioxane	48	−87	34	200	45	13	−24	−20
cis-Hydrindane	30	28	−348	40	53	29	1	21

[a] Irreversible adsorption of the test solute.

Slack wax is the by-product of the same process. According to the described procedure, *n*-paraffinic and isoparaffinic hydrocarbons should be removed from the heptane fraction and they are the main components of slack wax. As the deparaffination process is carried out at a temperature of −21°C, hydrocarbons, together with other organic species, which are solids under these conditions and which have similar characteristics to the main slack wax components, are also precipitated. In our investigation we found that slack wax consists of non-polar substances (approx. 70%, paraffinic and iso-paraffinic hydrocarbons) that are eluted from the liquid chromatography (LC) column by *n*-heptane and approx. 30% polar species eluted by the alcohol–benzene (1:1) mixture. Therefore, heptane (mainly naphtenic hydrocarbons) and slack wax (*n*- and iso-hydrocarbons and polar substances) fractions are not the same fractions. One may expect that their behaviour in IGC experiments should be different from that observed. The next question if the different order of elution from LC column and the different arrangement according to their different polarities. Please note that not all fractions were eluted from the LC column. Moreover, in LC separations, these fractions act as solutes in the liquid–solid chromatographic system. In the IGC experiment, the same fractions (or residue) are the liquid stationary phases in the GC column. We determine their polarity based on the behaviour (retention data) of arbitrarily selected test solutes. The elution behaviour in LC is a result of very complex mutual interactions between solute, solid stationary phase and mobile phase, being very often the mixture with changing elution power, i.e. composition. It is almost impossible to fully compare the order of elution from a LC column and the polarity of the stationary phase in GC. Moreover, to date, there is no polarity scale in LC (HPLC) that is similar to the one that of Rohrschneider–McReynolds, which is used in GC. Both processes were carried out at different temperatures. As this parameter is important in chromatographic separation, it may cause additional problem for such a comparison.

Flory–Huggins theory is often used in the examination of mutual interactions between a test substance and a polymer and it has been presented in a number of papers [7–11]. The values of the Flory–Huggins interaction parameter for fractions separated from vacuum distillation residues have been presented earlier by us [48].

The Flory–Huggins interaction parameter exhibits high values for a poor solvent and low values for a good solvent. For example, high positive values of $\chi_{1,2}^{\infty}$ (>2.0) reported for *n*-decane and tetradecane indicate that these alkanes are very poor solvents for phenoxy resins. Negative values of $\chi_{1,2}^{\infty}$ indicate good solubility of the test solute in the stationary phase that is acting as a solvent. For a series of *n*-alkanes, the interaction parameter usually increases

Table 3
ΔI for McReynolds test solutes determined for vacuum distillation residues and separated fractions from Flotta-Blend oil (373.15 K)

Test substance	Fraction									
	Vacuum residue	Heptane fraction	Aromatic hydrocarbon fraction				"Resins"		Asphaltenes	Slack wax
			Ar I	Ar II	Ar III	Ar IV	Separation	Desorbed with benzene		
Benzene	−2	12	34	44	75	93	84	94	38	34
Butanol-1	60	200	144	99	108	130	133	154	114	40
2-Pentanone	183	216	193	228	224	243	252	245	186	182
1-Nitropropane	94	44	80	111	134	183	192	185	54	103
Pyridine	11	65	6	[a]	43	89	106	103	46	49
2-Methyl-2-pentanol	36	129	60	52	73	87	128	104	40	39
Jodobutane	62	15	3	60	78	107	104	103	24	56
2-Octyn	22	6	16	19	35	43	55	50	−16	19
1,4-Dioxane	20	50	43	42	47	77	73	80	46	14
cis-Hydrindane	46	20	27	37	55	66	47	61	27	21

[a] Irreversible adsorption of the test solute.

Table 4
ΔI for McReynolds test solutes determined for vacuum distillation residue and separated fractions from Pipe Oil (373.15 K)

Test substance	Fraction								
	Vacuum residue	Heptane fraction	Aromatic hydrocarbon fraction			"Resins"		Asphaltenes	Slack wax
			Ar I	Ar II	Ar III	Separation	Desorbed with benzene		
Benzene	71	25	19	48	30	82	39	83	15
Butanol-1	79	157	51	143	67	117	99	167	99
2-Pentanone	89	187	−108	−106	−37	213	195	165	130
1-Nitropropane	111	121	66	101	105	157	96	157	23
Pyridine	18	25	74	42	66	70	91	174	−32
2-Methyl-2-pentanol	41	1	123	44	21	76	150	943	
Jodobutane	63	13	41	65	59	87	81	108	29
2-Octyn	23	5	10	28	15	37	34	49	5
1,4-Dioxane	76	96	90	19	21	58	43	69	−30
cis-Hydrindane	55	24	30	40	55	53	55	35	27

with an increasing number of carbon atoms in the molecule, indicating the decreasing solubility of the *n*-alkanes in the separated fractions, which are acting as the liquid stationary phases (Fig. 3).

Very low values of $\chi^{\infty}_{1,2}$ ($\chi^{\infty}_{1,2}<0$) indicate strong inter-molecular interactions between solute and liquid stationary phases, while high, positive values characterize systems with weak interactions. Therefore, we may conclude that alcohols and nitro compounds do not interact with the various oil fractions examined (Fig. 4). Weak interactions were found for the aromatic test solute (benzene) and for 1,4-dioxane, in several fractions examined (only for B-6/II and pipe oils). Negative values of $\chi^{\infty}_{1,2}$ were found for the *n*-alkane probes on vacuum residues, the *n*-heptane fraction (except B-6/II oil), the aromatic fractions, Ar I–III (not for Ar II from pipe oil), resins desorbed with benzene (only B-6/II oil) and slack wax (only Pipe oil). This means that these fractions (stationary phases) exhibit non-polar characteristics.

Please note that $\chi^{\infty}_{1,2}$ is a measure of the magnitude of the inter-molecular interactions between solute and solvent, i.e., it is a parameter characterizing a given system. If one is looking for a parameter for a substance being examined, then the solubility parameter is a good choice. The use of the solubility parameter, its increments corresponding to different types of inter-molecular interactions, will be presented in a subsequent paper.

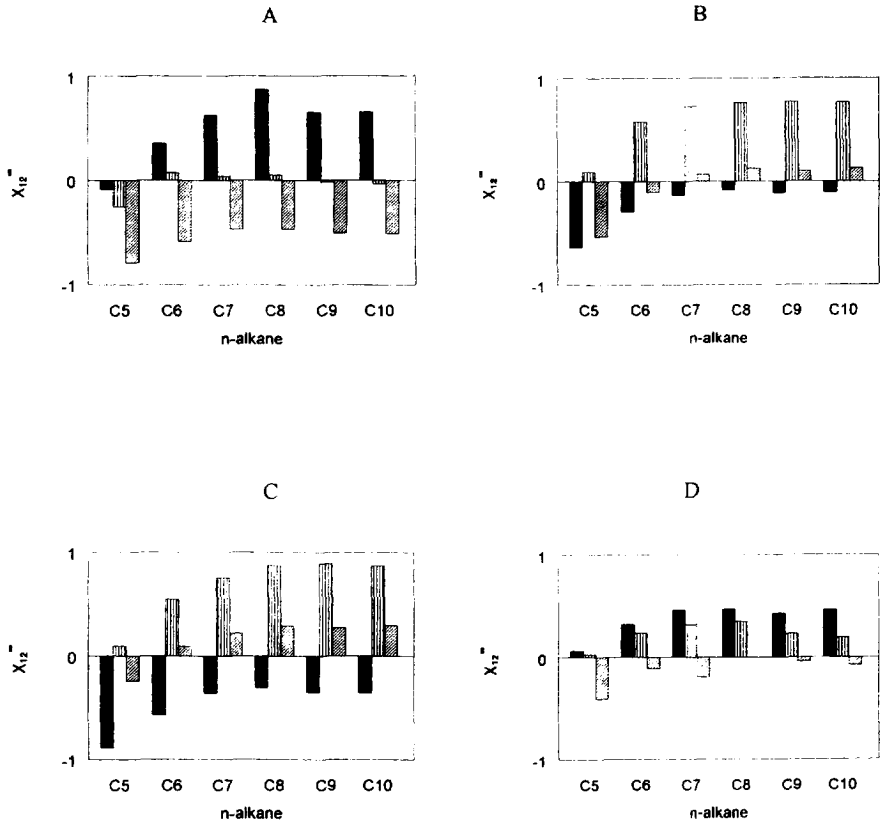

Fig. 3. Flory–Huggins interaction parameter for *n*-alkane test solutes for several fractions separated from the oil vacuum distillation residues. A = heptane fraction, B = aromatic hydrocarbon Ar II fraction, C = "resins" desorbed with benzene fraction, D = slack wax. ■ = B-6/II oil, ▥ = Flotta-Blend oil, ▨ = pipe oil.

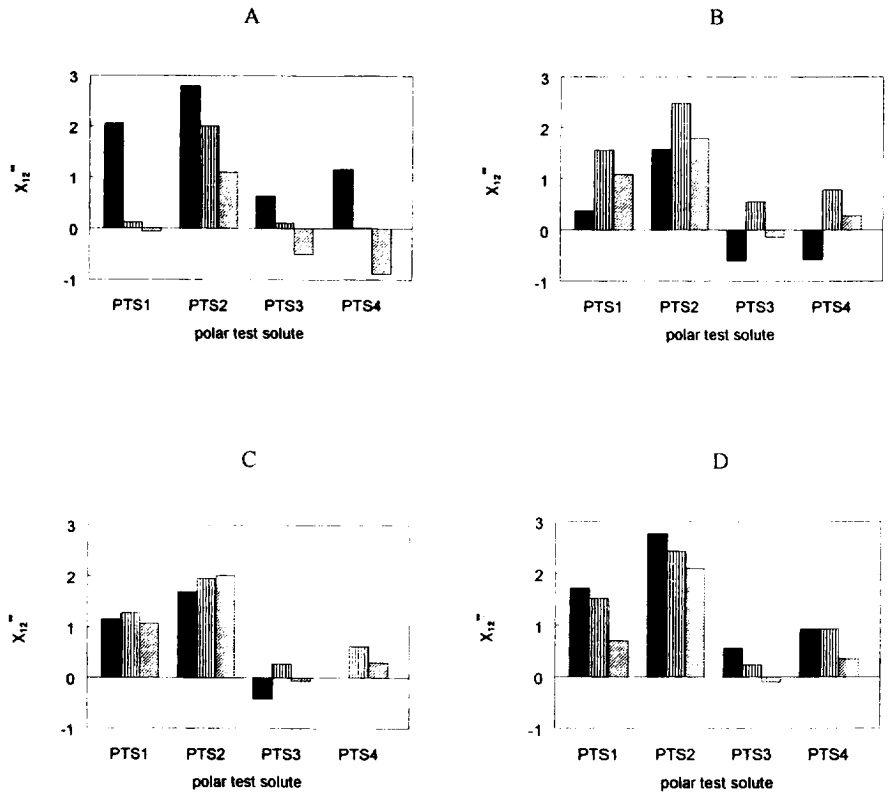

Fig. 4. Flory–Huggins interaction parameter for polar test solutes for several fractions separated From the oil vacuum distillation residues. A = heptane fraction, B = aromatic hydrocarbon Ar II fraction, C = "resins" desorbed with benzene fraction, d = slack wax. Polar test solutes, PTS: PTS1 = 1-butanol, PTS2 = nitropropane, PTS3 = benzene, PTS4 = 1,4-dioxane. ■ = B-6/II oil, ▥ = Flotta-Blend oil, ▨ = pipe oil.

4. Conclusions

Fractions separated from oil vacuum distillation residues were characterized by means of inverse gas chromatography. This method allowed us to discriminate between the same fractions separated from oils of different chemical character. Both the traditional McReynolds as well as the Flory–Huggins interaction parameters may be used to solve the problem of characterising separated fractions. However, the use of the $\chi^{\infty}_{1,2}$ parameter offers the possibility of predicting the solubility of a given fraction in a series of potential solvents.

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References

[1] Z.J. Sjunjajev, Khimija nefti, Khimija, Leningrad, 1984 (in Russian).
[2] G. O'Donnell, Anal. Chem., 3 (1951) 894.
[3] H.M. Chelton and R.W. Traxler, Proc. 5th World Petrol. Congr., Sect. V, 1959, pp. 247.
[4] T.C. Davis, J.C. Petersen and W.E. Haines, Anal. Chem., 38 (1966) 241.
[5] T.C. Davis and J.C. Petersen, Anal. Chem., 39 (1967) 1853.
[6] L.W. Corbett, Anal. Chem., 41 (1969) 576.
[7] H.B. Hayes, M. Stacey and J. Standley, Fuel, 51 (1972) 27.
[8] M. Boduszyński and L. Warzechowa, Nafta, 6 (1976) 198 (in Polish).
[9] M. Dobrowolska and S. Ligeza, Nafta, 12 (1976) 414 (in Polish).
[10] S.R. Sergiejenko, B.A. Taimova and E.I. Talalev, Vysokomolekularne Nieuglevodordnye Soedinienia Nefti, Nauka, Moscow, 1979 (in Russian).
[11] E. Papirer, J. Kuczyński and B. Siffert, Chromatographia, 23 (1987) 401.
[12] D.H. Everett and C.T.H. Stoddart, Trans. Faraday Soc., 57 (1961) 746.

[13] D.E. Martire, Anal. Chem., 33 (1961) 1143.
[14] D.H. Everett, B.W. Gainey and C.L. Young, Trans. Faraday Soc., 64 (1968) 2667.
[15] G.P. Hicks and C.L. Young, Trans. Faraday Soc., 64 (1968) 2675.
[16] B.W. Gainey and C.L. Young, Trans. Faraday Soc., 64 (1968) 349.
[17] A.J.B. Cruickshank, B.W. Gainey and C.L. Young, Trans. Faraday Soc., 64 (1968) 337.
[18] H.G. Harris and J.M. Prausnitz, I and E.C. Fundamentals, 8 (1969) 180.
[19] T.C. Davis, J.C. Petersen and W.E. Haines, Anal. Chem., 38 (1966) 241.
[20] T.C. Davis and J.C. Petersen, Anal. Chem., 38 (1966) 1938.
[21] T.C. Davis and J.C. Petersen, Proc. Assoc. Asphalt Paving Technol., 36 (1967) 1.
[22] J.C. Petersen and S.M. Dorrence, Anal. Chem., 41 (1969) 1240.
[23] F.A. Barbour, S.M. Dorrence and J.C. Petersen, Anal. Chem., 42 (1970) 668.
[24] F.A. Barbour, R.V. Barbour and J.C. Petersen, J. Appl. Chem. Biotechnol., 24 (1974) 645.
[25] E. Funk, Ind. Eng. Chem. Technol. Prod. Res. Dev., 16 (1977) 115.
[26] E. Papirer, J. Kuczynski and B. Siffert, Chromatographia, 23 (1987) 401.
[27] D.E. Martire and J.H. Purnell, Trans. Faraday Soc., 62 (1966) 710.
[28] W.B. Kogan and M.D. Fedotova, Vysok. Soed. (A) X, 8 (1968) 1704.
[29] G. DiPaola-Baranyi and J.E. Guillet, Macromolecules, 11 (1978) 228.
[30] J.E. Guillet, J. Macromol. Sci., 4 (1970) 1669.
[31] O. Smidsrod and J.E. Guillet, Macromolecules, 2 (1969) 272.
[32] G.J. Price and J.E. Guillet, J. Chromatogr., 369 (1986) 273.
[33] A.J. Hartkopf, J. Chromatogr. Sci., 10 (1972) 145.
[34] Yu-kwan Leung and B.E. Fichinger, J. Phys. Chem., 78 (1974) 60.
[35] D.E. Martire, Anal. Chem., 46 (1974) 626.
[36] J.M. Barrales-Rienda and J. Vidal Gancedo, Macromolecules, 21 (1988) 220.
[37] E. Fernandez-Sanchez, A. Fernandez-Torres, J.A. Garcia-Dominguez, J.M. Santiuste and E. Pertierra-Rimada, J. Chromatogr., 457 (1988) 55.
[38] E. Fernandez-Sanchez, A. Fernandez-Torres, J.A. Garcia-Dominguez and D. Salvador-Moya, J. Chromatogr., 556 (1991) 485.
[39] M.R. Becerra, E. Fernandez-Sanchez, A. Fernandez-Torres, J.A. Garcia-Dominguez and J.M. Santiuste, Macromolecules, 25 (1992) 4665.
[40] A. Voelkel, Wiad. Chem., 41 (1987) 269.
[41] A. Voelkel, Acta Chromatographica, 1 (1992) 69.
[42] A. Voelkel, Crit. Rev. Anal. Chem., 22 (1991) 411.
[43] A. Voelkel and J. Janas, J. Chromatogr., 645 (1993) 141.
[44] T.E. Jordan, Vapor Pressure of Organic Compounds, Interscience, New York, London, 1954.
[45] T.K. Ross and D.C. Freshwater, Chemical Engineering Data Book, Leonard Hill, London, 1962.
[46] D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, London, 1969.
[47] L.W. Corbett, Densimetric method for characterizing asphalt', Anal. Chem., 36, 10 pp 1967 (1964).
[48] A. Voelkel and J. Fall, Chromatographia, 41 (1995) 414.