

Use of basic alumina in fractionation of fossil fuels

Jaroslav Černý

Institute of Geotechnics, Czech Academy of Sciences, V Holešovičkách 41, 182 09 Prague 8 (Czechoslovakia)

Gustav Šebor* and Josef Blažek

Department of Petroleum Technology and Petrochemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6 (Czechoslovakia)

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ABSTRACT

The use and efficiency of extrographic fractionation are reported for a number of fossil fuels and their processing products. The influence of basic alumina, which is a constituent of the column packing, on the fractionation selectivity is discussed. This fractionation is capable of an efficient separation of non-polar hydrocarbons, pyrrolic-type nitrogen compounds, and phenolic compounds. The hydrocarbon fraction also includes highly condensed polyaromatics. In the chromatographic fractionation these polyaromatics are eluted along with heteroatom-rich compounds. The extrographic fractionation has been found to be independent of column loading on going from a sample-to-sorbent ratio of 1:15 to 1:8 (w/w). However, it is not possible to separate aromatic hydrocarbons according to the ring number, and therefore the extrography is a suitable method for the fractionation of coal-derived liquids containing large amounts of heteroatom compounds of different polarity.

INTRODUCTION

The elucidation of the compound class composition of fossil fuels and their processing products is a prerequisite for process control work and for obtaining valuable fundamental information on cracking, hydrotreating and refining processes. A substantial amount of work has been done on developing appropriate fractionation procedures, which meet most of the generally desired capabilities, *e.g.*, separation of saturated compounds, mono-, di- and polyaromatics, basic and neutral nitrogen compounds, sulphur compounds and phenols. Unfortunately, no simple procedure exists, and a complex separation scheme, which involves a number of separation steps, is commonly needed for a detailed fractionation [1–13].

Basic alumina has not often been used for the fractionation of petroleum- and coal-derived liquids. Nevertheless, it possesses the potential for an excellent separation of nitrogen compounds

[7,14–17]. As opposed to neutral alumina [5,18,19], its basic properties are responsible for the strong retention of compounds with hydrogen-donating capability on a chromatographic column [7,15]. On the other hand, the retention of basic nitrogen compounds may be lowered, and some of these elute together with aromatic hydrocarbons [7,14]. The spreading of basic nitrogen compounds over several fractions has been overcome by using a combination of basic alumina and silica gel in the fractionation column [15,16]. The basic compounds can thus be eluted together with phenolic compounds, allowing fractions of nitrogen-free aromatics and pyrrolic-type compounds to be obtained. Further, some highly condensed polyaromatics can be present in the nitrogen fraction as significant contaminants because of the strong retention of highly condensed polyaromatics on basic alumina [20]. On the other hand, a clean cut is obtained between the fractions of nitrogen and phenolic compounds [21,22].

However, as a result of an electron donor–accept-

or interaction between the sorbent and solute, the extent of irreversible adsorption of the more polar and acidic compounds on the sorbent surface is higher for basic than for neutral alumina. It is almost impossible to release dihydric phenols and related compounds from the fractionation column [7]. Hence basic alumina fractionation is a valuable method particularly for the separation of nitrogen compounds from middle distillates [14,17]. Nonetheless, it has also been used for the extensive fractionation of coal liquids from a solvent-refined coal process [23–27].

The results presented in this paper are based on extrographic fractionation with the combined use of silica gel and basic alumina in the column [15]. This fractionation has been utilized in our laboratory for 3 years. A number of materials have been fractionated and analysed by spectroscopic methods to give compositional and average structural characteristics of the samples. The aim of this work was to evaluate the separation efficiency of the silica gel–basic alumina-based extrographic method relative to the material fractionated.

EXPERIMENTAL

Materials studied

The materials fractionated in our laboratory by using the extrographic technique [15] have so far involved the following coal-derived liquids: a distillation residue from the hydroliquefaction of bituminous coal, a coal-tar pitch, a laboratory pyrolysis tar from the carbonization of bituminous coal (samples F and S), commercial phenols from gasification of tar and a chloroform extract of a sub-bituminous coal. Other fractionated liquids were shale oil and maltenes derived from petroleum vacuum residue. The fractionation and analysis of some of these material have been described elsewhere [15,16,28].

Sorbents

Silica gel 60 (Merck) (particle size 0.063–0.200 mm) was activated in a vacuum oven for 16 h at 130°C. Its activity was then adjusted by addition of 4% (w/w) of water.

Neutral and basic alumina 90 (Merck) (particle size 0.063–0.200 mm, activity I) were reactivated for 8 h at 400°C.

Fractionation procedures

All extrographic fractionations were performed as described [15]. Briefly, a column (450 mm × 13.5 mm I.D.) was dry packed successively with silica gel (75 mm), a sample precoated on silica gel in a ratio of 1:15 (w/w) (300 mm) and basic alumina (75 mm). Two hydrocarbon fractions and a pyrrolic-type compounds fraction were eluted through basic alumina with *n*-hexane, toluene and chloroform. Polar fractions were eluted by reversing the solvent flow through the silica gel filter section with chloroform–diethyl ether (9:1, v/v) and tetrahydrofuran–methanol (17:3, v/v).

Additionally, the compound-class composition of petroleum-derived maltenes was determined according to the chromatographic method of Sawatzky *et al.* [4]. The purity of the individual hydrocarbon classes was carefully controlled by UV spectrophotometry through the determination of the molar absorptivities and by ¹H NMR spectroscopy [29]. The elution solvents of Sawatzky *et al.* [4], including chloroform to yield the pyrrolic nitrogen fraction, were also applied in the extrographic fractionation of petroleum maltenes in addition to the solvents mentioned above. The separation procedure on neutral alumina with the elution order of Sawatzky *et al.* [4] was also used for the fractionation of the aromatic extrographic fractions of the pyrolysis tars.

Analytical methods

Infrared spectra were acquired on a Bruker IFS 88 Fourier transform IR or a Specord M80 dispersive IR spectrometer at a resolution of 2 or 4 cm⁻¹. Solutions in dichloromethane were measured at a concentration of 30 or 50 mg/ml in a 0.6-mm sodium chloride cell.

Average molecular weights were measured on a Knauer vapour-pressure osmometer in benzene or tetrahydrofuran at 32 and 45°C, respectively. Four measurements were made at finite concentrations and data were extrapolated to infinite dilution.

Nitrogen contents in samples together with carbon and hydrogen percentages were determined with a Perkin-Elmer Model 240 C elemental analyzer.

RESULTS AND DISCUSSION

Separation efficiency

Details on the extrographic fractionation have been published recently [15,16]. One of the advantages of this procedure lies in obtaining a nitrogen-free aromatic fraction and a highly concentrated pyrrolic-type compounds fraction. Infrared spectra of these two fractions in the spectral region 3700–3300 cm^{-1} for a number of fractions are shown in Fig. 1.

Except for petroleum maltenes, the aromatic fractions exhibited only negligible or no absorption around 3460 cm^{-1} , which is characteristic of N–H bond vibrations. This was also revealed by the determination of the nitrogen percentage, which is presented in Table I as being below 0.2% (w/w), but the elemental analyses gave values from 0 to 0.15% (w/w). The pyrrolic-type compound fractions showed a significant absorption in the infrared spectra due to N–H bond vibrations around 3460 cm^{-1} (Fig. 1). Also, the nitrogen percentages in Table I are correspondingly high. The best concentrate of nitrogen compounds was obtained for shale oil,

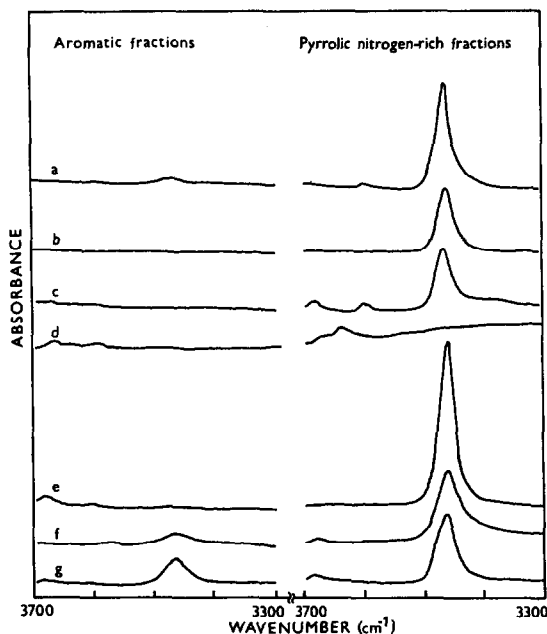


Fig. 1. Infrared spectra of aromatic and pyrrolic nitrogen-rich fractions. a = Liquefaction product; b = coal tar pitch; c = commercial phenols; d = coal extract; e = shale oil; f and g = petroleum maltenes.

TABLE I

YIELD AND NITROGEN PERCENTAGE OF AROMATIC HYDROCARBON AND PYRROLIC-TYPE COMPOUND FRACTIONS IN THE STUDIED SAMPLES

Sample	Aromatic fraction		Pyrrolic-type compounds fraction	
	Yield (% w/w)	N (% w/w)	Yield (% w/w)	N (% w/w)
Liquefaction product: distillation residue ^a	24.1	<0.2	2.5	2.0
Coal tar pitch: toluene extract	59.2	<0.2	3.2	1.3
Pyrolysis tar: maltene ^b	39.5–52.9	<0.2	—	—
Gasification tar: commercial phenols ^a	9.1	<0.2	1.0	1.9
Sub-bituminous coal: chloroform extract	9.9	<0.2	4.7	0.2
shale oil ^c	14.4	<0.2	1.9	4.2
Petroleum bottom: maltene	59.2	0.2	3.5	1.0
	17.0 ^c	0.3	4.3	1.0

^a From ref. 15.

^b From ref. 28.

^c Polyaromatics developed with benzene by separation with the elution order of Sawatzky *et al.* [4].

which is generally known to be rich in nitrogen compounds, including amines. These can also contribute to a high peak due to N–H vibrations in infrared spectra. The clean cut between pyrrolic-type and phenolic compounds is documented by the absence of a hydroxyl absorption band around 3600 cm^{-1} in the infrared spectra (Fig. 1).

Negligible amounts of nitrogen compounds were found in the pyrrolic-type compounds fraction of the coal extract. This is probably due to the low nitrogen percentage (0.3%, w/w) and/or the low abundance of purely non-basic nitrogen compounds in the chloroform-extractable material of coal. However, owing to the high oxygen content in the coal extract (10.5%, w/w), the existing nitrogen bridges between aromatic rings may be accompanied by oxygen functionalities within the molecule. This changes the chromatographic behaviour of such molecules by the superposition of moderately polar entities. Instead of the nitrogen compounds, a high abundance of carbonyl compounds (ketones, esters) was present in the "nitrogen compound fraction". The relevant regions of the infrared spectrum are shown in Fig. 2. The possibility of eluting the carbonyl species in this fraction has also been proposed in earlier work [15].

The separation of pyrrolic-type compounds from aromatics in the petroleum maltenes was not as successful as for coal-derived liquids and shale oil (Fig. 1). The nitrogen content of the total aromatics slightly exceeded 0.2% (w/w) and in the polyaromatic fraction obtained with an elution order according to Sawatzky *et al.* [4] was even 0.3% (w/w) (Table I). Taking into account the average molec-

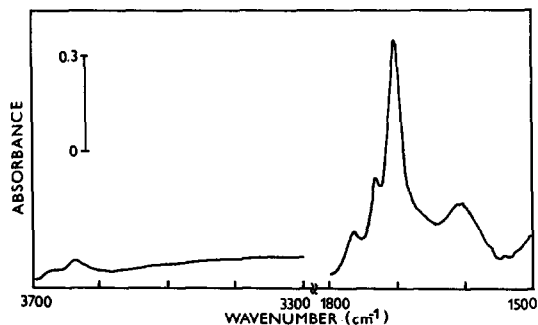


Fig. 2. Relevant part of the infrared spectrum for chloroform-extractable material of coal (measured in dichloromethane at a concentration of 50 mg/ml).

ular weights of aromatics (790) and pyrrolic-type compounds (910), the nitrogen compound content in these fractions can be as high as 15% (w/w). On the other hand, about one third of the nitrogen fraction is constituted by non-nitrogen compounds, probably polyaromatics [20]. This is probably also the case for the pyrrolic-type compounds fraction of coal-tar pitch, which exhibited a low nitrogen content of only 1.5% (w/w) (Table I), although by size-exclusion chromatography on Sephadex LH-20 a nitrogen fraction of coal-tar pitch with a nitrogen content as high as 5.5% (w/w) was obtained [30].

Both of these materials are rich in polyaromatics and the content of polar compounds is low. These aspects and possible steric shielding of nitrogen sites in the case of petroleum maltenes can lead to a poorer separation efficiency of these materials in comparison with the other fractionated liquids.

Effect of column loading

To assess the separation efficiency at higher column loadings, shale oil was fractionated at a sample-to-sorbent ratio ranging from 1:15 to 1:8 (w/w). The corresponding infrared spectra of aromatic and pyrrolic-type compound fractions are shown in Fig. 3, and integrals of the relevant spectral band together with the yield of the fractions are presented in Table II. These data lead to the following conclusions.

The percentage of hydrocarbon compounds is independent of the sample-to-sorbent ratio. The in-

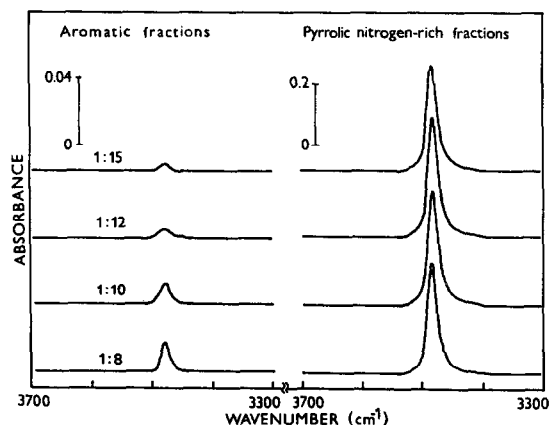


Fig. 3. Infrared spectra for aromatic and pyrrolic-nitrogen rich fractions of shale oil at different sample-to-sorbent ratios from 1:8 to 1:15 (w/w) (measured in dichloromethane at a concentration of 30 mg/ml).

TABLE II

EFFECT OF COLUMN LOADING ON THE YIELD OF FRACTIONS AND ABUNDANCE OF N-H BONDS FOR FRACTIONATION OF SHALE OIL

Elution solvent	Sample-to-sorbent ratio (w/w)							
	1:15		1:12		1:10		1:8	
	Yield (% w/w)	INT ₃₄₆₀ (A cm ⁻¹) ^a	Yield (% w/w)	INT ₃₄₆₀ (A cm ⁻¹)	Yield (% w/w)	INT ₃₄₆₀ (A cm ⁻¹)	Yield (% w/w)	INT ₃₄₆₀ (A cm ⁻¹)
Hexane	41.6	—	42.2	—	43.2	—	43.8	—
Toluene	16.5	0.1	16.6	0.2	15.4	0.3	15.0	0.3
Chloroform	1.1	9.1	1.2	10.2	1.4	9.5	1.6	9.2
Tetrahydrofuran-methanol (17:3, v/v)	25.6	—	26.5	—	25.0	—	25.1	—

^a Integral of N-H bond vibrations; see Fig. 3. A = Absorbance.

crease in the yield of fraction 1 developed with hexane is at the expense of fraction 2 developed with toluene.

The abundance of nitrogen compounds in aromatics (fraction 2) has a slightly increasing tendency with increasing column loading, but it can still be considered to be negligible.

There is an increase in the amount of the pyrrolic-type compounds fraction developed with chloroform (fraction 3) with increasing column loading. However, the abundance of nitrogen compounds in these fractions is almost constant, and consequently some of the nitrogen compounds seem to remain unrecovered in the corresponding fraction at lower loadings. Of course, quantitative elution of these compounds at higher loadings is also in question.

No phenolic compounds were eluted even at the highest sample-to-sorbent ratio in either aromatic or pyrrolic-type compound fractions. Nonetheless, the changes in the analytical results described are small, and higher loadings can successfully be used for the fractionation of coal-derived liquids with satisfactory efficiency.

Separation of aromatic hydrocarbon classes

For materials rich in aromatics, there is often a need to know the distribution of aromatics in the individual aromatic hydrocarbon classes. To evaluate the possibility of the utilization of the extrographic technique for this purpose, the petroleum maltenes were fractionated by using three methods:

(1) the chromatographic technique on dual silica gel-neutral alumina columns according to Sawatzky *et al.* [4] with careful control of the eluting material by UV and ¹H NMR spectroscopy [29]; this procedure provides the fractionation of aromatics according to ring number, at least into mono-, di- and polyaromatic fractions; (2) the extrographic technique with elution solvents as for the above method; chloroform was ordered after benzene to yield a pyrrolic nitrogen-rich fraction; (3) the extrographic technique with the originally proposed elution solvents [15].

Table III gives the yields of fractions produced by the respective methods. It can be clearly seen that the extrographic technique produced more material in the individual hydrocarbon fractions, especially in the first fraction of saturates. Therefore, the extrographic technique cannot be used to fractionate an aromatics-rich material according to ring number. Also, the cumulative yield of fractions up to benzene-toluene elution and the total material recovered are higher for the extrographic than for the chromatographic technique (Table III). These findings may be due to a larger retention of the fractionated material on alumina in chromatography. A column loading of about 1% (w/w) relative to sorbents used is commonly utilized, as opposed to extrography with a column loading more than five times higher. The short section of basic alumina in the extrographic column is overloaded and, therefore, incapable of retaining more condensed poly-

TABLE III
FRACTIONATION OF PETROLEUM MALTENES BY DIFFERENT METHODS

Elution solvent	A ^a		B ^a		C ^a	
	Yield (% w/w)	Cumulative yield (% w/w)	Yield (% w/w)	Cumulative yield (% w/w)	Yield (% w/w)	Cumulative yield (% w/w)
Hexane	8.8	8.8	19.1	19.1	19.4	19.4
Hexane-benzene (19:1, v/v)	8.0	16.8	10.6	29.7	—	—
Hexane-benzene (17:3, v/v)	8.5	25.3	10.3	40.0	—	—
Benzene or toluene	22.2 ^b	47.5	17.0 ^b	57.0	38.8 ^c	59.2
Chloroform	—	—	4.3	61.3	3.5	62.7
Chloroform-diethyl ether (9:1, v/v)	—	—	—	—	22.1	84.8
Methanol-benzene-diethyl ether (3:1:1, v/v/v)	43.6	91.1	36.6	97.9	—	—
Tetrahydrofuran-methanol (17:3, v/v)	—	—	—	—	12.9	97.7

^a A = Chromatography according to Sawatzky *et al.* [4]; B = extrography with the elution solvents of Sawatzky *et al.* [4] and chloroform; C = extrography with the solvents from ref. 15.

^b Benzene-eluted fraction.

^c Toluene-eluted fraction.

aromatics in benzene/toluene elution.

The elution of more condensed polyaromatics in the toluene fraction by extrography was revealed by using chromatographic fractionation of this extrographic aromatic fraction. The aromatic fraction obtained by extrographic fractionation of pyrolysis tars [28] contained neither nitrogen nor phenolic compounds. Results of the chromatographic fractionations on neutral alumina are given in Table IV. In both instances the entire aromatic fractions contained a material which remained on the neutral alumina after the toluene elution, although it had passed through the basic alumina in the extrographic column. Even a stronger elution solvent, toluene-methanol, did not flush all the material from alumina, as it remained slightly coloured after fractionation at the entrance to the column. However, the irreversibly adsorbed material did not account for such a percentage as may result from the total yields in Table IV. A high proportion of the losses was probably due to evaporation during the fraction treatment.

Hence it can be deduced that the extrographic procedure [15] is capable of separating the more condensed aromatics (more than approximately four rings) from pyrrolic-type nitrogen and phenolic compounds. This is probably not the case with

TABLE IV
CHROMATOGRAPHIC FRACTIONATION OF EXTROGRAPHIC AROMATIC FRACTIONS OF PYROLYSIS TARS F AND S ON NEUTRAL ALUMINA

Elution solvent	Yield of aromatics F (% w/w)	Yield of aromatics S (% w/w)
Hexane	14.5	11.6
Hexane-toluene (19:1, v/v)	27.9	17.2
Hexane-toluene (17:3, v/v)	11.1	15.6
Toluene	15.4	25.2
Toluene-methanol (17:3, v/v)	24.9	28.1
Total	93.8	97.7

chromatographic fractionation on alumina [5,7,17–19]. In this fractionation polyaromatic hydrocarbons must contribute to a significant extent to the yields of heteroatom compound fractions. The probable overlapping portion of polyaromatic hydrocarbons is represented in Table IV as the fraction eluted with toluene–methanol. This contamination of the nitrogen fraction with polyaromatics has already been described for both neutral and basic alumina [20,31].

CONCLUSIONS

Based on the compilation of fractionation results of many fossil fuel processing products and almost 10 years of experience with extrographic fractionation, the following conclusions can be drawn. Extrographic fractionation with a basic alumina section in a column [15] is capable of providing fractions of hydrocarbons including more condensed polyaromatics, pyrrolic-type nitrogen compounds, and phenolic compounds. A clean cut can be obtained between the respective fractions. Separation into the individual hydrocarbon compound classes, *i.e.*, saturated compounds and mono-, di- and polyaromatics, cannot be achieved by a simple extrographic procedure. A column loading in the sample-to-sorbent ratio range from 1:15 to 1:8 (w/w) does not have a significant effect on the fractionation efficiency. The extrographic method [15] is especially suitable for the fractionation of coal-derived liquids with a large content of heteroatom compounds with different polarities.

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