



Common strategy to prevent the Danube's pollution technological risks with oil and oil products – CLEANDANUBE

Operation: no.2(2i)-2.2-5, code MIS-ETC 653

STUDY 3

Study on possible constructional versions, technological implications

Considerations on the chemical composition of crude oils and petroleum fractions potentially involved in the Danube river pollution.

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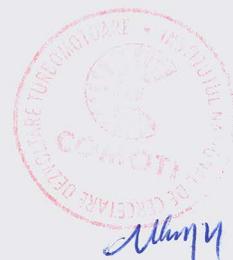
Lead partner: National Research & Development Institute for Gas Turbines COMOTI Bucharest, Romania

Puscasu Cristian
Stefanescu Mariana
Voicu Raluca
Axene Ghita
Grigorescu Mihaela
Adam Liviu
Cretu Mihaela
Precob Luminita
Toma Emilian
Teleaba Victoria
Antonescu Marilena

Partner: University of RUSE "ANGEL KANICHEV", Rouse, Bulgaria

Ivanka Mitkova Zheleva
Klimentov Kliment
Nikolaev Ivaylo
Popov Gencho
Rushev Piter
Tuzharov Krasimir
Panteleeva Yana Krалеva
Kopchev Peter

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3.1. Considerations on the chemical composition of crude oils and petroleum fractions potentially involved in the Danube river pollution.

Classes of chemical compounds present in crude oil

Hydrocarbons from crude oil are from classes: paraffin's, naphthenic, aromatic hydrocarbons with mixed structure, containing up to 100 carbon atoms in the molecule and belong to 17 homologous series, between C_nH_{2n+2} and C_nH_{2n+3} .

Crude oil does not contain unsaturated hydrocarbons (alkenes, alkadienes, alkynes).

Hydrocarbons are the major component of the oil: over 50% in the oils with aromatic naphthenic, and about 90-98% in the wax (paraffin) oils. The number of individual hydrocarbons from crude oil is very high, not known because of its high compositional complexity.

It is estimated that about ca. 500 hydrocarbons are present only in gasoline fraction, with distillation limits of 40-180 ° C.

The number of present hydrocarbons increases equally with the increasing of distillation limits of petroleum fractions, due to the growing of carbon atoms number in the molecule, respectively the number of possible isomers.

However, although the number of hydrocarbons present in crude oil is extremely high, their weight is different, which makes the oils are composed largely of a relatively small number of hydrocarbons.

Thus, for crude oil from Ponca, Oklahoma (U.S.A), approx. 50% of oil is composed of only 150 hydrocarbons from as above mentioned classes, in crude oil are present about the same hydrocarbons, but in varying proportions, leading to differences between the various oils.

The abundance of various hydrocarbons in crude oils is in a wide range, from thousandths and hundredths of a percent to several percents.

The average (200-350 ° C) and higher (over 350 ° C) fractions of crude oil, are found in high proportion hydrocarbons with mixed structure (hydroaromatics).

The relative content of individual neighbouring hydrocarbons from a class is approximately constant.

The best studied are hydrocarbons present in the light fractions of petroleum (gas, gasoline, petrol, those who distil up to 200 ° C), being identified most of the individual components.

For middle and higher fractions of crude oil, due to their great compositional complexity, only in a few cases it has succeeded separations and identifications of individual hydrocarbons, the best studied being the linear paraffin's (normal) and aromatics.

Paraffinic hydrocarbons present in oils are of the linear (normal-paraffin's) and branched (isoparaffins) types, in oil deposit being present both lower terms, components of associated gases, and higher terms, solid and liquid paraffin with up to 80 (100) carbon atoms in the molecule.

The proportion of paraffin's in crude oils and its separated fractions widely varies, as function of their chemical nature(waxy or unasked), and distilling range (distillation limits) of the fractions. Young geological age oils (60 - 80 million years) have a lower content of paraffinic hydrocarbons, compared with the old ones(160 - 180 million years), these being more advanced in terms of their chemical transformations, so more rich in paraffin's.

In waxy crude oils, normal paraffin hydrocarbons are found in greater proportion than branched ones, in which they may represent cca. 25% from oil. For unasked oil, in some of its separate fractions, the proportion of isoparaffins may exceed the normal paraffin's proportion.

Wax content in oil increases with increasing of number of carbon atoms in the molecule, reaching the maximum of 2.5% of crude oil, for n-C₈ hydrocarbons, then a gradual decline occurs, so that the proportion of hydrocarbon is only approx. 0.1%.

In various successive fractions separated from oils, paraffin hydrocarbons ratio decreases with the increase of their distillation range: in lower fractions (under 200 ° C) approx. 80%, medium fractions (200-350 ° C) approx. 55-60%, and in the residual oil fractions (over 500 ° C) till 5-20%.

Normal paraffin hydrocarbons from crude oil are the best studied because they can be relatively easily separated by various methods: urea treatment, molecular sieve separation, various chromatographic techniques. Linear paraffin components were separated and identified from all oil fractions: gas, gasoline, distillate oil, diesel fuel, oils.

Branched paraffinic hydrocarbons (isoparaffins) are in higher proportion in un waxed oils (naphthenic - aromatic), many of its components being in a so low proportion that they can not be separated and identified. In average fractions of the oil, paraffinic branched hydrocarbons with isoprenoide structure have been identified, these being probably from the organic material from which oil was formed. In the oils and their fractions there are isoparaffins with few branches: one to three branches per molecule, isoparaffins with one branch being more abundant than those with two branches, which in turn are found in greater proportion than those with three branches

For isoparaffins with one branch, the components with the branch placed at the second carbon atom of the main chain are in greater proportion than those with the branch placed in the third carbon atom, etc.. The most frequently branches are methyl and ethyl groups.

The most components have methyl group branch linked at positions 2 and 3 of the main chain.

Naphthenic hydrocarbons are the main components of the most oils, whatever their chemical nature, the content of these hydrocarbons varying between 30-50%.

As chemical structure, they are alkylcyclopentans, alkylcyclohexans and polycyclic types, with up to ten cycles per molecule

The most abundant are metilcyclohexan (the most abundant naphthenic component of crude oil), followed by metilcyclopentan. The lower oil fractions contains cyclopentane derivatives in a greater proportion than cyclohexane derivates, while in the upper fractions, the cyclohexane derivates are in a significantly higher proportion.

At the same number of carbon atoms in the molecule, the alkylnaftens with three side chains are in a significantly higher proportion. The alkylnaftens with two substituent's on the same carbon atom of the cycle are in a very low proportion in oil.

Most of the mono-naphthenic from the crude oil are mono and dicyclic.

The physical characteristics of naphthenic have intermediate values between those of paraffin's and aromatics. The differences are more pronounced for lower terms, being lower with the length of side chains increasing.

It must be mentioned that the melting temperature of cyclohexane is high (+6.4 ° C) compared with other components.

It must be also highlighted the fact that monocyclic alkylnaftenes with over than 15 carbon atoms in the linear chain are solid at room temperature, such structures being components of petroleum waxes. For polycyclic naphthenes, the physical characteristics values are higher, much higher as cyclization degree is more advanced.

Regarding solubility, the naphthenic are more soluble than paraffin's in various solvents, being mentioned that at alkylnaphthenes, if the side chain length increase and at polycyclic naphthenic the solubility increases if the cyclization range decreases.

Being saturated hydrocarbons, the naphthenes have a high chemical stability, similar to that of alkanes. Among the many reactions of naphthenic that give interest to our discipline are those with sulphuric acid of 98% concentration, naphthenic non reacting with it at low temperature conditions, and catalytic dehydrogenation reaction of cyclohexane with formation of alkylbenzenes, major reaction in reforming catalytic process, as analytically, because it allows the dosage of the hydrocarbons from non-aromatic gasoline (Zelinski method)

The number of carbon atoms from the side chains attached to naphthenic cycles increases with increasing of average boiling temperature of successive fractions separated from oils, for a given degree of cyclization, and decreases with the increasing of cycles number per molecule, as seen from the data presented Table 3.2.

Table 3.1 Naphthenic hydrocarbons present in high successive fractions separated from Webster crude oil

Hydrocarbons class	Hydrocarbons, % weight, in fraction(°C)		
	315-370	370 - 426	426 - 482
Total naphthenic	72,5	67,5	69,0
Monocyclic naphthenes	31,5	17,5	7,0
Dicyclic naphthenes	30,5	30,0	19,0
Tricyclic naphthenes	9,5	15,5	25,5

Tetracyclic naphthenes	1,0	5,0	8,5
Pentacyclic naphthenes		1,5	7,0
Hexacyclic naphthenes			2,0

Table 3.2. Number of carbon atoms in the side chains of naphthenic hydrocarbons

Alkilynaphthenes	Number of carbon atoms in the side chains of naphthenic hydrocarbons, fraction components (°C):		
	315-370	370-426	426 - 482
Monocyclic	14	20	28
Dicyclic	9	15	23
Tricyclic	6	12	20
Tetracyclic	3	9	17
Pentacyclic	-	5	13
Hexacyclic	-	9	9

The polycyclic naphthenic hydrocarbons contain more side chains, but shorter. In finished lubricating oils (commercial) is unlikely to exist linear chain longer than 15 carbon atoms, because such hydrocarbons have a high melting point and are removed by de waxing process.

Aromatic hydrocarbons are the third main component of hydrocarbons present in crude oil; the proportion of such hydrocarbons is less than that of paraffins and naphthenes, separately taken, and varies depending on the chemical nature of the oil, waxy (wax) or unasked (naphthenes, aromatic), between 10-50%.

In successive fractions separated from crude oil aromatic proportion increases with the average temperature of boiling, so that the upper fractions of aromatic oil proportion can exceed that of paraffin

Aromatic hydrocarbons with different structure are present in crude oil, with one to ten cycles per molecule, the highest proportion of aromatics in all fractions of crude oil being represented by alkylbenzenes with a varied numbers of side chains, of different lengths.

Polycyclic aromatic hydrocarbons are mostly of condensed type, less substituted

The values of physical characteristics (boiling point, density, refractive index) are in the most cases higher than those presented by paraffinic and naphthenic components, with the same number of carbon atoms in molecule

Lower alkylbenzenes, with one to three short alkyl substituent's, are liquid at room temperature, except β -xylene ($t_b = + 13.3$ ° C); also benzene has relatively high melting temperature (5.5 ° C); highly substituted alkylbenzenes are solid (eg, tetramethyl benzene, $t_m = 79$).

The no substituted polycyclic aromatic hydrocarbons, and some of their alkyl derivatives have high melting temperature, being solid; there are obvious differences between saturated and aromatic hydrocarbons, at the same number of carbon atoms in the

molecule, in terms of density and refractive index values, two of the most commonly characteristics, analytical used.

In terms of solubility in various solvents, the aromatic hydrocarbons are different than the saturated (para-naphthenic): the inferior aromatic hydrocarbons are totally soluble in organic solvents such as alcohols, ethyl ether, acetone, hydrocarbons; the main characteristic for all aromatic hydrocarbons with short chain is their high solubility in selective solvents, such as phenol, furfural, aniline, etc., specific behaviour which is actually used for the separation of such components from other classes of hydrocarbons, in extraction process, at both analytical and industrial level.

The aromatic hydrocarbons are involved in conducting of many chemical reactions, in particular the substitution; of particular importance are: the reaction with sulfuric acid, because it allows the separation and determination of aromatic hydrocarbon from small petroleum fractions by atmospheric distillation (sulphurimetric method), the reaction with picric acid (trinitrophenol), useful for separating aromatics (mono-and diciclice) from their mixture with other hydrocarbons and formolit reaction between aromatic hydrocarbons and formaldehyde in the presence of sulfuric acid, a reaction used to highlight the presence of aromatics in a petroleum product

Mononuclear aromatic hydrocarbons are present in the lower fractions of oil: benzene, toluene, xylene, ethyl benzene, n-and iso-propilbenzen, the most abundant being toluene, ethyl benzene and m-xylene

In the literature is mentioned the presence of indene and its derivatives, aromatic dicyclic hydrocarbons in the fractions separated from the Oklahoma Ponca crude oil; the alkylbenzenes proportion in petrol is higher than that of benzene; alkylbenzenes content decreases with increasing of carbon atoms number in the side chain, while the proportion of alkylbenzenes with the same number of carbon atoms per molecule increases with side chain increasing; in the lower fractions of crude oil were not identified alkylbenzenes with one normal chain, more than 4 carbon atoms

The aromatic hydrocarbon content of petrol is lower than that of paraffin's, respectively naphthenes, being of 10-30%, depending on the origin and nature of petroleum and fraction distillation interval.

The increasing of the aromatic hydrocarbons proportion with the growing of the range of distillation of successive petroleum fractions, conducts to a relatively high content of aromatic hydrocarbons in fractions separated from Romanian oils. Aromatic hydrocarbons content of gasoline integral fraction, separated from different crude oils is between 7-19% weight.

A high proportion of aromatic hydrocarbons in gasoline is desirable, given their higher octane and giving the best combustion properties of gasoline in spark ignition engines (toluene is 104 octane, benzene 99, IPB, 99.3, etc.).

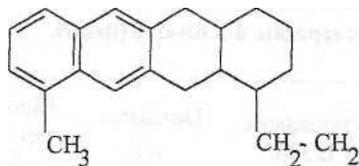
At higher fractions of oil there are more frequently aromatics like alkylbenzenes type with one or two chains, one of which being short (methyl), the other longer and branched and polycyclic aromatics with 2 to ten cycles per molecule, most frequently condensed; the

polycyclic nature of aromatic components increases with increasing the average temperature of boiling of successive fractions separated from crude oil.

Among polycyclic aromatics, are frequently found the alkyl naphthalene and its alkyl derivatives; from tricyclic derivatives, those of phenanthrene are found in higher proportion than those of anthracene. The presence of aromatic hydrocarbon in oil fractions, especially polycyclic ones, is undesirable because they have low viscosity indices, high density, high viscosity and high coke numbers, in which case they are removed, for the most part, particularly polycyclics, by selective solvent extraction.

Hydrocarbons with mixed structure (hydroaromatics) appear in distilled petroleum fractions at above 200 ° C. In their composition, in addition to those mentioned classes of hydrocarbons (paraffins, naphthenes, aromatics) are, with the percentage increasing as it grows the distillation range (average boiling temperature) of the fraction, hydrocarbons with mixed structure (hydroaromatics) whose molecule contains, in various proportions, the three structural elements: cycles aromatic condensed with naphthenic rings, with paraffinic chains attached to them, usually attached to the naphthenic cycles, on the aromatics ones being grafted short chains (methyl):

- CH₂-CH



The proportion of these structures is high in residual and heavy fractions of crude oil, according to some authors, these fractions are exclusively composed of such components. Naphthenic and aromatic rings are condensed type; paraffin chains are short, the number of carbon atoms being of around ten.

Separation modes and centrifugal types

As a result of the numerous working conditions, imposed by the raw material and the resulted products, were built many types of centrifuges.

Tabel 3.3 gives a centrifuge classification by the effectiveness factor z (see chapter 2.3.1 study No. 2) , and in fig. 3.1 a systematization of the centrifuge types from combining the different classification criteria.

Table 3.3 Centrifuge classification

Classification criteria	Classification groups
Separation power (efficiency factor z)	Normal Centrifuge ($z < 3000$) Supercentrifuge ($z > 3000$) Ultracentrifuge ($z > 5 \cdot 10^5$)
Centrifugation purpose	Filtering the granular or crystalline

	suspensions Suspensions sedimentation Emulsion separation
Function	Discontinuous (in batch) Continuous
Download (precipitate evacuation)	Manual By gravitation, at low speed With pulsed pistons With spiral conveyer With knives and scrapers By centrifugal force Hydraulics
Axis position	Vertical Horizontal Oblique
The support of the centrifuge	Suspended Supported
Operation	Upper Lower

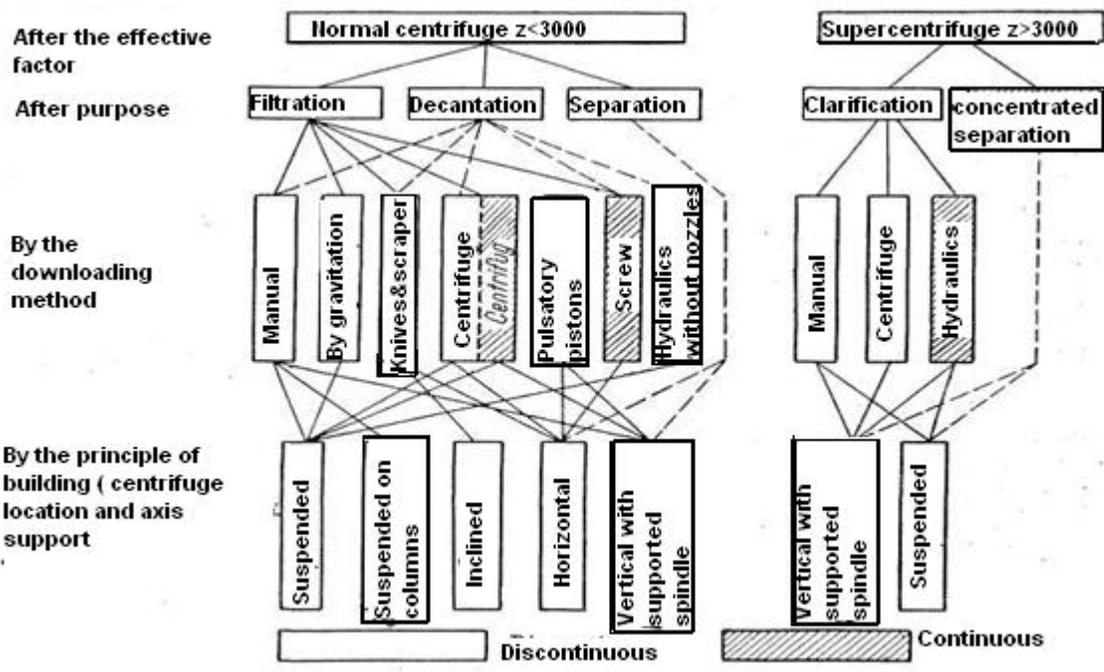


Figure.3.1 Filtrating Centrifuges

These centrifuges are characterized by a perforated brake drum, lining with mesh or cloth. They serve to filter suspensions, separation of crystals from initial solution, drying the

textiles.

Filtering Centrifuge with discontinuous function

With these centrifuges are working in batches. They are built usually with vertical axis.

Batch filtering centrifuges with manual discharge

The cycle of these centrifuges has the following phases: load; start and acceleration up to speed regime, centrifugation itself, washing of the precipitate, discharge, braking till stop, unload.

The brake drum of these centrifuges is fixed on the vertical shaft, rotated through a belt or by a electrical drive. The brake drum is perforated and reinforced with resistances circles. The bottom of the brake drum has a small declination to the periphery.

An annular cap covers the portion where the precipitate layer is formed. The brake drum is surrounded by a cylindrical cover, to capture the filtrate and prevent accidents. A pipe with sprinkler serves for washing the precipitate (crystals). The precipitate's discharge is done manually after the centrifuge stops and the cover is opened.

These centrifuge are indicated for separating suspensions that needs o long period for centrifugation and washing. The optimum efficiency factor – z is determined experimental, taking account the inconveniencias of a to big z: the decrease of the precipitate's permeability; slow discharge of the to much compacted precipitate.

Sedimentation centrifuge with horizontal screw.

The brake drum, with a ratio $L/D = 1,5 \dots 4$, is built: a) conical or cylinder-conical, with long cone and short cylinder, for heavy particles suspensions, leading to a low humidity sedimentation; b) cylinder-conical, with long cylinder and short cone, for fine particles; c) cylinder-conical with the cylinder equal to the cone

In general it is used the $L/D > 2,2$ to separate suspensions with average and high concentrations (L – total length of the brake drum; D – it's maximum diameter). to separate the components from the residual waters it is used $L/D = 4$, with the length of the cone portion equal to $1/3$ from total length.

The tip cone angle is generally $10 \dots 15^\circ$. The screw is done with one or two begins. There is a speed difference of 0,6-4% between screw and brake drum. The relative speed must be tuned with the solid phase content of the suspension.

For the centrifuge used to separate the components of the waste waters, good results were obtained with relative peripheral speed of the screw, in relation to brake drum of 0,15...0,18m/s. In general, the directions of rotation for screw and brake drum are the same.

There are built centrifuges with fast screw or with slow screw. The fast ones have smaller relative diameters (160...180mm) and big separation factors (1800...3500), where

the slower ones have bigger relative diameters (900...1800mm) and average separation factor (350.. 600).

The suspensions whose humid solid phase form a sticky mud, which stick to the screw spirals, is very hard to work with on these centrifuge.

At a centrifuge working in counter current (fig.3.2), the suspension feeded through pipe 1 goes through the A openings of the screw body, into the screw channel, in the passing section from cylinder to cone. Sedimentation occurs due to centrifugal force. The sediment is transported, because relative speed of the screw, to the smaller diameter evacuation end, where gets out from brake drum through the openings B, in case 7, and the filtrate goes to the opposite end (in counter current) where exit through brake drum, openings 5, in the case 6.

The discharge openings can be radial or axial, fixed on cap C. The radial position of opening 5 can be adjusted through caps: modifying the inner diameter of the liquid ring, and consequently, the length L_{sed} of the sedimentation zone. By increasing length L_{sed} shrinks the length of the drainage sedimentation zone L_d .

To wash of the sediment (when necessary) are used pipe 14, from which the washing water passes through the small diameter holes E into the screw channel. The filtrated dilutes because of the washing, and is removed through the openings.

The spire of the screw force the filtrate to move on the direction of the screw channel (prevents the direct axial flow of the liquids toward spillways), on a longer way, which favours the sedimentation. Along L_d zone the sediment is drained through filtration and compacted.

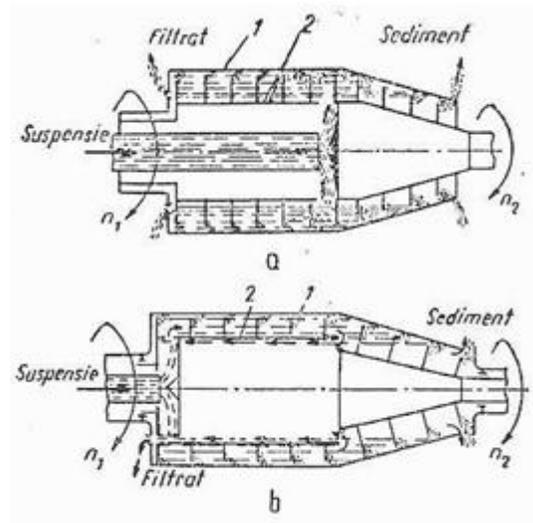


fig.3.2 Screw centrifuge functioning sketch:

- a) – in counter-current;
- b) – in echi- current.

In some builds it were achieved good results by combining the plain brake drum with a portion with holes.

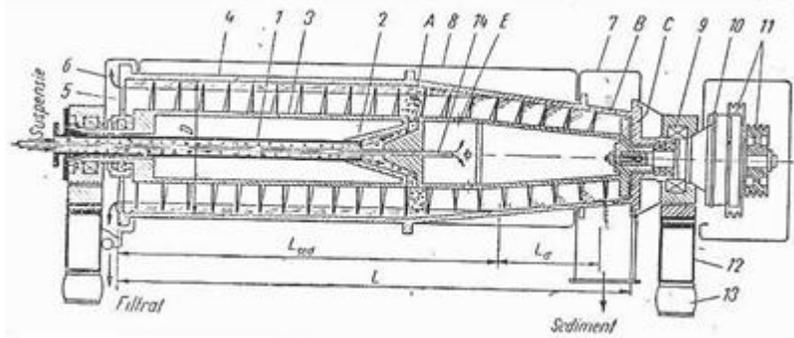


Fig. 3.3 Cross section through a sedimentation screw centrifuge.

In fig.3.3 are presented the screw, the brake drum and the case of the centrifuge, and the technical characteristics of some sedimentation screw centrifuge are given in table 3.4

Table 3.4 Technical characteristics of sedimentation screw centrifugal

Characteristics	OGS 502C-04	OGS 631C-02	OGS 501C-10	OGS 1001C-01
Rotors diameter, mm	500	630	500	1000
Relative length of the rotor L/D	1,87	3,76	3,6	3,6
Maximum speed of the rotor, rot/min	2650	2000	2650	1000
Separation factor maxim, Φ	1950	1400	2000	560
Relative peripheral speed, m/s	0,47	0,66	0,2...0,6	0,2...0,68
Circulation of suspension and filter	In counter-current		In echi-current	
Flow, m ³ /h:				
-without flocculant	8	30	<25	<80
-with flocculant	—	—	<15	<55