PREPARATION OF PURE HYDROCARBONS FOR MODELLING IN APPLICATION RESEARCH

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Introduction

When determining the technical application value of petroleum products usually the general properties of a distillate cut or of a refined product are tested. The underlying supposition is that there exists some correlation, say, between the carbon to hydrogen ratio and applicability, in reference to, e.g. oxidation stability in the case of lubricating oils, or to skin irritation in the case of cosmetic or pharmaceutical oils, or to soot formation in the case of fuel oils, all these characteristics tending to become more pronounced with the increase of carbon to hydrogen ratio.

Study of oxidation stability by VESELY et al. [1] has shown that the validity of such empirical rules is rather restricted. Similar uncertainties may be encountered also in other fields of application.

One way to acquire relevant, better founded knowledge would be to study first the individual hydrocarbons or types of hydrocarbons of which petroleum products are composed and then, to proceed to the study of multicomponent mixtures. To this aim, however, individual hydrocarbons, or in some respect homogeneous fractions are needed.

The composition of lubricating oils or of other high-molecular petroleum products is a very complex one. The number of components in these products is generally more than a million, of concentration percentages below one hundredth of a mole per cent, therefore separation of quantities of a single hydrocarbon sufficient for a study is practically impossible, only concentrates with uniform ring structures may be feasible. Even the study of such concentrates may yield new information.

The other way would be the synthetic preparation of model products of smaller molecules, or of concentrates of less complex mixtures; on their analogy, conclusions relevant to phenomena in high-molecular domains could be drawn. Also studies of single hydrocarbons considered as pure for a specific field of application allow to extend conclusions on more complex systems.

This paper deals with questions of the preparation of pure hydrocarbons of use for the second way of research; also some results relevant to application will be briefly given.

Preparation of n-paraffins

In the paraffin group, straight chain types from decane to octadecane have been prepared. Every one of these has been separated from a petroleum fraction. Generally, 10- to 100-litre batches of a suitable petroleum fraction were processed to yield finally about 10 to 20 ml of the individual hydrocarbon. C_{10} to C_{14} n-paraffins were separated from a light kerosene cut, previously refined by sulphuric acid treatment. From this refined product n-paraffins were produced by urea adduct formation. This process was slightly modified to suit our requirements, e.g. smaller portions of urea were used at a time, thus n-paraffins separated in a more pure form, though in worse yields, of course, but this was not an important point in this context. In this way a mixture of n-paraffins was obtained.

Calculations relevant to possible separation by distillation of n-paraffins with 10 to 15 carbon atoms showed that a column of 15 to 20 theoretical plates would be suitable for the separation of the individual compounds, at purities of 90 to 95 per cent by weight. In a column with this efficiency we really succeeded in obtaining compounds at a satisfactory grade of purity.

For pentadecane and higher homologues other initial products had to be selected. This was a reference fuel grade normal-cetane and a refined gas oil used for the manufacture of detergents. In this instance, concentration of paraffins was begun by urea treatment. However, part of the isomers entered the adducts formed, therefore the n-paraffin concentrate was further purified on a Linde (Type 5 Å) molecular sieve. The paraffin concentrate was dissolved in benzene and passed through the molecular sieve column in the vapour phase. Then the column was flushed with nitrogen, followed by elution with n-hexane, desorption temperature being kept by 60 °C above that of the adsorption cycle. The eluates were separated from n-hexane and benzene by distillation.

This procedure proved very satisfactory. Not only could the n-paraffins be well purified from other hydrocarbons but also some separation according to molecular sizes occurred. Desorption of the higher molecular weight paraffins needed temperatures at which light cracking was already taking place, therefore in the preparation of heptadecane and octadecane this was not to be resorted to.

Generally, the higher the molecular weight of the hydrocarbons, the more difficult is their separation. Not only their separation according to molecular structures, i. e. according to configurations, but also their separation according to chain-length from a hydrocarbon mixture mainly composed of straight-chain compounds is more difficult because the differences between boiling points and relative volatilities gradually diminish.

Separation according to molecular weight in the C_{16} to C_{18} range required a specifically sharp rectification and a preparative gas-chromatography technique. For rectification a rotational column equivalent to 100 theoretical plates was used; separation by gas-chromatography was carried out on a preparatory instrument, the Model P of Carlo Erba Co.

With the techniques mentioned and with their combined application the hydrocarbons were prepared at purities shown in Table 1.

Table 1

Product	Purity (% weight)
n-Decane	94.5
n-Undecane	98.8
n-Dodecane	98.5
n-Tridecane	97.5
n-Tetradecane	97.8
n-Pentadecane	98.0
n-Hexadecane (Cetane)	99.9
n-Heptadecane	99.0
n-Octadecane	90—95

After the separation of n-hexadecane by preparative gas-chromatography the concentrate was further purified by gas-chromatography, resulting in a product of much higher purity than that of a BDH standard substance.

The homogeneity of our final products was checked by conventional gas-chromatography, in some cases a capillary column was used.

Preparation of alkyl-tetralines

Besides n-paraffins, we prepared also several alkyl-tetralines. For this purpose two methods were resorted to: 1) selective catalytic hydrogenation of alkyl-naphthalenes, or 2) alkylation of tetraline.

In both reactions mainly mixtures of isomers were obtained; these had to be separated. 1. Methyl tetralines were obtained by selective hydrogenation of 1-, or 2-methyl-naphthalene on Co-Mo catalysts. Like naphthalene, methyl-naphthalenes are hydrogenated to methyl-tetralines in the first step; exposure to more severe experimental conditions produces dekaline, or methyl-dekalines [2].

In preliminary experiments Pt, Pd, and Co-Mo-catalysts on alumina supports were tested; the last proved to be the most suitable for hydrogenation. 1-, and 2-methyl-naphthalenes, produced by the Fluka Co., were used. In a micro-reactor of 4.0 ml useful capacity, suitable for continuous operation, optimum parameters (temperature, pressure, residence time) were established first, then the compound in question was produced in a reactor of 140 ml capacity in a continuous process. About 2 kg of the parent substances were hydrogenated at parameters as follows:

temperature	390—400°C
pressure	45 atm
space velocity	0.8 to 1.0 litre litre $^{-1}$ hour $^{-1}$
gas/liquid rate	1 m^3 litre $^{-1}$

The crude hydrogenation products were distilled through a column with a "Helipack" filling equivalent to 25 theoretical plates at a reduced pressure of 10 torr, reflux ratio being 1 : 10. Owing to the closeness of the boiling points of the components, separation of isomers in pure form was not feasible, therefore preparative gas-chromatography had to be applied. Final products were analysed by gas-chromatographic methods. In this way 1-methyl-tetraline, and 5-methyl-tetraline were obtained from 1-methyl-naphthalene, and 2-, or 6-methyl-tetraline from 2-methyl-naphthalene. Exact identification of structures was achieved by NMR and IR spectrography.

2. Similarly to benzene, naphthalene and tetraline can be converted into methyl-derivates by the Friedel—Crafts reaction. From among the alkyl-halogenides mostly chlorides and bromides are chosen as alkylating agents. Lewis-acids, mainly aluminium-chloride, boron-trifluoride, or ferric-chloride are used as catalysts. Introduction of long side-chains yields inhomogeneous isomer products [3], a fact working rather against our purpose. Therefore we attempted to introduce alkyl groups through the hydrogenation of ketones. In alkylation reactions mainly the hydrogens of the aromatic ring were substituted; however, depending on the choice of parameters, chiefly on that of temperature, substitutions had also to be reckoned with.

Ethyl- and butyl-tetralines were obtained by the alkylation of tetraline. The mole-ratios were kept at 1 mole ethyl-bromide to 3 moles tetraline to 0.1 mole aluminium-chloride for ethyl-tetraline, and at 1 mole n-butyl-bromide to 4 moles of tetraline to 0.1 mole aluminium-chloride for butyl-tetraline.

Temperature above 20°C was controlled by an ultrathermostat, between 0°C and 20°C a Peltier-cell was used for this purpose. Alkylation, and the processing of the reaction product were carried out in the usual way.

In the cases of ethyl-, and of butyl-tetraline, yields as functions of temperature and reaction time were studied. The composition of the reaction products was analysed with the help of a Chrom 3 type apparatus, using a stationary phase containing 10 per cent by weight of poly-ethylene glycol-adipate on Rysorb c support. After the ethylation of tetraline, in all productdistillates two isomers were detected in ratios strongly affected by temperature. The sample obtained at 10 °C contained 6-ethyl-tetraline up to 95 per cent by weight and only about 5 per cent of 5-ethyl tetraline was found to be present. This ratio changed to 57 : 43 in a fraction produced at 50°C.

In butyl-tetralines the presence of three isomers was proven by gas-chromatography. Besides the main product 6-n-butyl-tetraline, two isomeric butyl-tetralines were formed. Change of temperature affected the ratio of the three isomers but slightly, with a tendency of reducing slightly the formation of 6-n-butyl-tetraline with increasing temperatures. Thus in a sample of product obtained at 10°C the proportion of 6-n-butyl-tetraline was 70 per cent by weight, in a sample from a product obtained at 60°C this figure was about 55 per cent.

The first step in the synthesis of n-propyl-tetraline was the preparation of propionyl-tetraline from tetraline and propionyl chloride in the presence of dehydrated aluminium chloride. The crude product prepared at 40°C yielded about 250 ml of 6-propionyl-tetraline by distillation. Reduction of this product was carried out according to the method of Kishnyer—Wolf, i. e. by the formation of the corresponding hydrazone of the propionyl-tetraline with hydrazine hydrate, and conversion of the hydrazone, in a medium of potassium-hydroxide and ethylene-glycol, into n-propyl-tetraline. This was extracted with ether from the reaction mixture and purified by distillation in a column of 25 theoretical plates. Gas chromatography of the main fraction proved this to be a homogeneous substance of about 96.4 per cent by weight purity [4].

The alkyl-tetralines obtained by the various methods were identified by the NMR method, and by IR spectrography. The former furnished the total of aliphatic and aromatic protons and their number at each position, these in turn revealed molecular structures.

However, NMR spectra do not reveal the location of the alkyl groups upon the ring. This was found by IR spectrography. Cross-checking of these

Table 2

Product	Purity % weight
1-Methyl-tetraline	96.2
2-Methyl-tetraline	99.0
5-Methyl-tetraline	95.0
6-Methyl-tetraline	98.4
5-Ethyl-tetraline	93.2
6-Ethyl-tetraline	95.6
6-n-Propyl-tetraline	96.4

two sets of information unequivocally demonstrated the structure and position of the alkyl groups on the ring. In this way the structure of our products could be identified; the work on butyl-tetralines is in progress.

The products obtained by the hydrogenation of naphthalene, or by the alkylation of tetraline, were distilled and separated into components by gas-chromatography. Table 2 lists the products and their purities.

Results of application research

Work with normal paraffins prepared in the ways just described, and with the more volatile n-heptane, shows that their biological activity causes generally acanthosis, and sometimes dermatitis. Skin-reaction increased with increasing molecular weight in the range of C_7 to C_{14} wherefrom it decreased with further increasing of the molecular weight. The greater activity of the smaller molecules is due to their easier diffusion into the skin; the greater volatility, however, of the very small molecules prevents their diffusion: they are sooner evaporated than able to irritate. The circumstances are similar with cyclo-paraffins (cyclo-hexane, decaline, medicinal white oil) but they differ somewhat with the aromatic compounds (benzene, 1-methyl-naphthalene, ethyl-naphthalenes, lubricating oils which contain aromatic compounds).

In the study of *boundary lubrication properties* the coefficient of friction and the welding limits were used as characteristics [5].

Testing of the hydrocarbons prepared in the ways described above, and comparison of the data with those referring to concentrates of higher molecular weights suggest that in the state of boundary friction the coefficients of friction and the abrased surface area, pertinent to normal and to cyclo-paraffins, respectively, do not materially differ. However, under the given set of experimental conditions the coefficient of friction and the abrased surface area is generally reduced as compared with n-paraffin hydrocarbons, if aromatics (e.g. alkyl-naphthalenes or alkyl-tetralines) are present.

Combustion experiments could not be carried out up to now with pure hydrocarbons, as the minimum volumes necessary for this work exceed the capacity of the preparative equipment to our disposition.

Studies could, however, be carried out with narrow cuts and concentrates containing mixtures of highly similar hydrocarbons. If liquid n-paraffins (C_{11} to C_{18}) were burnt in an evaporatory burner of a "Minikalor" type stove: Bacharach numbers (soot characterization factors) of 3 to 5 could be attained, in function of the excess-air factor, while 1-methyl-naphtalene (98 per cent purity) produced soot much in excess to the Bacharach-number 9, which is the extreme value on this scale [6]. For blends containing 20 to 40 per cent aromatic compounds Bacharach numbers between 8 and 9 were found.

The examples here discussed show that a study of the model-substances helps to reduce the errors of the simple empirical correlations usually considered in questions of application research.

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Summary

One way of getting information on the technical application value of petroleum products (lubricating properties, combustion behaviour, biological activity etc.) is to study the individual hydrocarbons and hydrocarbon types, constituting the petroleum products. For this purpose the C_{10}-C_{18} n-paraffins and different alkyl-tetralines (1-, 2-, 5-, 6-methyl, 5-, 6-ethyl and n-propyl) being present in petroleum products with great probability were prepared purely. The pure n-paraffins were separated from hydrocarbon mixtures by forming their urea adducts, with selective adsorption on molecular sieves and preparative gas chromatography, respectively. Of the alkyl tetralines the methyl isomers were produced by the catalytic hydrogenation of the respective methyl naphthalenes, and the other ones by alkylation. The resulting isomers were separated by means of preparative gas chromatography. All the 16 pure (93 to 99%) individual hydrocarbons have been identified by the IR spectrography and the NMR methods.

References

1. Vesely, V.: Ropa a Uhlie, **11**, No. 6, 297 (1969).
2. Kirk, R. E.—Othmer, D. F.: Encycl. of Chem. Techn. Vol. 9 (New York, 1967).
3. Petrov, A. D.—Andrejev, D. N.: Zhurn. Prikl. Chim **21**, 134 (1948).
4. Bailey, A. S.—Stoveley, C. M.: J. Inst. Petrol. **42**, 97 (1956).
5. O'Connor, J. J.—Boyd, J.: Standard Hbk. of Lubrication Engineering (McGraw-Hill, New York, 1968).
6. Reindes, H.: Die Heizölfeuerung. VDI-Verlag, Düsseldorf, 1960.

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