Standard Oil Company (Indiana)

INFORMATION DIVISION TRANSLATION T46-95

API-TOM Reel 66, Frames 494-500
Oberhausen Holten, July 11, 1944
Determination of Branched Isomers in Mixtures of Paraffin Hydrocarbons
Compare Angew. Chemie 52, 607 (1939)

The determination of branched paraffin hydrocarbons acquired practical interest as it become known that the suitability for motor purposes particularly the most important property, the knocking tendency depends upon the constitution of isomeric material. Comparative motor evaluations were carried out on a large number of paraffin bodies. The results can be generalized into a rule. The tendency to knocking is greater the longer the chain of CH_2 groups in the molecule which is undisturbed through branching. Three influences of the constitution are participating in this rule, the molecular size, the degree of branching and the position of the branching places in the molecule. The third factor can be treated as a constant in many-component mixtures commercially. Reversing the rule may give an opportunity to measure the content of branching of a paraffin fraction through motor testing. If one compares their octane numbers with those of a mixture of unbranched paraffins of the same average molecule weight, then the difference can serve as a approximate measure for the content of branching. So far as finished technical products have to be tested for their suitability as fuel material there is no reason to go beyond the octane numbers to devise values which characterize the chemical structure. But these values acquire independent value in our own processes which use the hydrocarbon not as motor fuel but with increasing importance as starting material for chemical conversions like oxidations, halogenations and polymerizations. Researches which aim at the qualitative improvement of syntheses and material improvement need not only to know the octane numbers but also information on the chemical composition. Here it is often important to notice small changes in content which cannot be detected through indirect deductions from motor tests, but which need direct and sensitive analyses. Also, each motor test requires and destroys a large amount of testing material, which can only seldom be procured from investigations which are still in the laboratory stage. Therefore, it is necessary to work out the analytical processes for small amounts of substance.

One must distinguish between mixtures of few components and multi-component mixtures. The first case can be expected in low boiling paraffin fractions including hexane, and sometimes of such products which are synthesized of larger "building stones". There exists the Raman analysis which seems to be of value among the proposed methods particularly for qualitative purposes which allow particular single materials to be recognized. The two processes which are to be described here are suitable for a summarized quantitative analysis of mixtures containing many materials.

A large part of the possible isomers were found in paraffin fractions from natural petroleum, so far as planned investigations were available. One may probably assume generally that branching, so far as it principally occurs, is distributed over a large part of the possible configurations. In a hydrogenated kogasin one found with the method described under III in the hexane fraction 0.15, the heptane 0.20, the octane 0.27, the nonane 0.35, the decane 0.40 "branching numbers". The branched molecules increased regularly with molecular weight. On this results the preliminary working hypothesis about the distribution of isomers, that there exists an equal possibility for branching in each newly-built chain member in the Fischer-Tropsch synthesis. From this one can conclude their regular distribution to all possible isomers but with the limitation, that nothing can be affirmed about the favoring of tertiary and quaternary configurations.

Distillation Analysis

The boiling diagrams of the paraffins do not show extremes in their mixtures and therefore can be separated through distillation. Also by the small differences in boiling points one obtains finally fractions which suffice for the criterion of pure material through fractionation which can be carried out as far as desired in principle. These fractions can be identified with materials through their physical properties,(melting point, boiling point, density), whose constitution is assured through synthesis. However, the difficulties of obtaining a total balance go with higher molecular weights into the practical impossibility. But one can carry out a distillation analysis for the total boiling range of the light motor fuels (up to 220°C) in products which are comparatively poor in branching like kogasin. This analysis would separate each isomeric group into the normal paraffin and the total amount of branched. The separation is on the principle that all branched paraffins have a boiling point at least 5° lower than the normal paraffin, and that only a few highly branched paraffins are in the boiling range of the normal paraffins which are 1 CH_2 group poorer.

If the Raoult relation is fulfilled one can calculate the theoretical number of plates from the relative difference of the vapor pressures of the pure components. The theoretical number of plates gives the desired enrichment. From the boiling point of the normal paraffin and the highest boiling isomers one obtains a relative difference of the vapor pressures for heptane at the boiling temperature, which amounts to 1.14 to 1 and similarly for the other groups. In order to reach the goal in one operation one must fractionate with an effectiveness of 30-40 theoretical plates. Here we shall describe a plant which is set up for 2 to 5 liters still content which assures an undisturbed operation.

The glass exchange column is 4.2 meters long and has a 30 mm inner diameter. The distillation retort is lifted by a wire spring to the end joint of the exchange column. The heating is done electrically through a cone-shaped heating mantle. Raschig rings 4 by 4 mm are used as filling bodies. 80 mm was determined as the effective height of a theoretical plate of this column, in all therefore somewhat over 50 theoretical plates.

In order to produce the effect which is required above, one must choose 1) the retort content large enough that the fractions that are to be separated are larger than the material amount which is circulating in the exchanger. 2) One must distill with a reflux ratio of 1:30 to 1:50. The plant works without trouble and most rationally when no interruption in the operation occurs. These conditions can be fulfilled if one does not condense in the descending cooler, instead one entirely condenses the vapor which streams out of the exchanger in a reflux cooler, and the portion which is determined for the distillate is branched off from the condensate. A 25 mm glass fiber insulation is enough for heat protection up to 150°C boiling temperature. With higher temperatures, the heat loss is compensated for by a heating coil which is installed under a mantle on the pipe of the exchange column.

In order to separate only approximately into impure normal paraffins and isomer-rich intermediate fraction, one can construct a similar smaller fractionation column of 1.2 meter height and an equivalent action of 15 theoretical plates. The spiral column with vacuum mantle is suitable for amounts below 100 grams, according to Jantzen.

One can proceed schematically in the carrying out of the distillation by separating into normal paraffins and intermediate fractions according to proportions of the transition temperature. Table 1 is an excerpt of the records of the distillation in which one separated in many small fractions in order to show the course of the separation. The fractions 10 to 13 together yielded a normal octane preparation which was proven to be pure on basis of the melting point and the cooling curve at freezing. In the same manner fractions 20 to 22 yielded a pure normal nonane. The fractions 9, 14, 15 and 23 have to be added to the normal paraffins in a balance. On the other hand, it is obvious from the course of the boiling points and densities that 16 to 19 do not represent the transition fractions from n-octane to n-nonane but contain almost only isomeric nonane. The same can be learned from accurate measurement of molecular weight. The quantitative ratio of n-octane:isomeric nonane:normal nonane which is represented in the case in Table 1 can be estimated at 53:20:27 in percentages of their sum.

Measuring of the Branching Numbers

The distillation analysis only gives indications about the amounts but not the type of isomers.

Table 1

Fractionation of a Kogasin which has been freed of olefins in a 4.2 meter packed column.

Fractions	Amount in Grams	Boiling Pt. 760 mm	Density $d^{20}/_4$
8	105	119.1	0.7041
9	102	125.3	.7026
10	190	126.0	.7023
11	175	"	.7024
12	112	"	.7022
13	128	"	.7024
14	80	"	.7037
15	67	127.4	.7062
16	46	141.2	.7196
17	76	143.5	.7197
18	105	143.9	.7196
19	87	146.2	.7196
20	58	151.3	.7178
21	107	151.3	.7179
22	158	151.3	.7176
23	103	151.4	.7181

Since the knocking tendency of isomeric materials depends upon the branching (the larger, the stronger the branching) it may be practical to determine the branching instead of the amount of isomers since one must forego the determination of single materials. The branching number Z is defined as the molecular fraction of the branching. For instance, normal heptane has a Z =0, 2,4,4 tri-methylpentane a Z=3, a mixture of each 50 mole percent of the two materials Z=1.5. The indication in the molecular ratio which declares how many branchings come to each molecule on the average in any mixture is chemically obvious and corresponds to the practice which has to be used practically in which one must reckon with molecular fragments. One must look for a measurable magnitude which would yield the same contribution in each branching. The method that was worked out here was based first on a physical property of pure materials which is rather parallel to branching. Namely, it has been known for a long time that the branching lowers the boiling point compared with the isomeric normal paraffins. The qualitative relation can be seen from Table 2 in which there are summarized the average values for lowering of the boiling points for all paraffins that are described in the literature, according to isomeric groups separated for the branching numbers 1, 2, 3 and 4. The number of materials considered is added in round brackets, the number of possible isomers are in cornered brackets. In the nonanes and decanes not only the relative portion of known materials but also the reliability of the physical data decreases much. One can learn from the table that the lowering of the boiling points occurs in all molecular weight classes and attains approximately the same value. It is about twice as large for the twice-branched materials than for the once-branched

materials and it rises with further branching. But it does not lie about 3 or 4 times the amount but only about half the amount. As average value one can assume -7°C per unit of branching by simplifying it for all isomeric groups.

The analytical evaluation of the regularity of the boiling point of the pure materials in their mixtures is based on wide experience that the paraffins among themselves form ideal solutions. Thus the total vapor pressure according to the Raoult law equals the sum of the products of the vapor pressure of the components times their concentration in molecular fractions. This relation can be considered valid for all mixtures, because of the similarity of the physical properties which is always found in paraffins particularly the heat of evaporation. Now one must use the boiling temperatures which were measured at given pressures practically. The curves that are plotted for validity of Raoult's law against the molecular fractions are bent more parabolic as compared with interpolated values (straightline) the further components are from each other in boiling points. From this one can see that the boiling points can be used even more reliably the smaller the boiling intervals between the fractions that are to be investigated and the more regular the components are distributed in a given boiling interval. Each increase of the molecule by a CH_2 group raises the boiling point only by a value for which the difference in boiling points of two consecutive normal paraffins is inserted. Therefore, one must know accurately the portion of each of the various molecular sizes. Narrow boiling fractions can contain practically only two molecular sizes so that the molecular ratio can be obtained by measuring the molecular weight.

These considerations lead to the following:

Directions for Measuring of the Branching Numbers.

One fractionates the mixture of paraffin hydrocarbons which are to be tested in a column of at least 10 theoretical plates and carried out with a reflux ratio 1:10.

The gaseous materials are removed by boiling under reflux before taking off the first distillate. The fractions are cut at transition temperatures which are 5°C above the normal boiling point of the paraffins, thus at 41, 74, 103, 131, 156, 175 and 200°. Each fraction n then should contain at least 10 cu. cc. One measures their amount Hn, their molecular weight Mn and their boiling point Kpn. For the evaluation one uses a diagram in which the temperatures are plotted as the abscissa against the molecular weight as the ordinate. The points that correspond to the boiling points and molecular weight of normal paraffins are 36.0, 72.16; 86.1, 88.8; 98.4, 100.1; 125.6, 114.1; 150.7, 128.2; 173.8, 142.2; 195.8, 156.2. If one connects them linearly in series sequence, one reduces their relationship to a processional stretch which virtually represents the null curve. One finds the branching number Zn of the various fractions by subtracting their boiling point Kpn from the temperature To which belongs to the molecular weight Mn on the null curve, and one divides the difference that was found by 7.

$$Zn = \frac{To - Kpn}{7.0}$$

The branching number of the total distillate is calculated by adding all fractions. $Z = \frac{EZn \times \text{total } n \times EMn/E \text{ total } n}{Mn}$

Mixtures with small branching numbers can first be separated by the distillation process which is described under II with gain in accuracy. The measuring can be limited to intermediate fractions.

There follows the description of the apparatus in which the boiling point determination can be carried out with 10 cc.

For correction of the boiling point to normal barometric condition for the mixtures of hydrocarbons, it suffices to use the Faust rule which is derived from the rule of Pictet-Trouton. One must add to the observed boiling temperature which is recalculated into degrees Kelvin the same parts per thousand positively as the barometer state deviates negatively in percent from the normal value. On the other hand the olefins are separated from the paraffins [see Br. Chem. 10, 337, (1929)]. They can be hydrogenated on the other hand by protecting the hydrocarbon skeleton. Therefore the process to determine the branching number can also be used for olefin and their mixtures with paraffins.

Translated Oct. 30, 1946 - Rochelle H. Bondy
Checked Dec. 12, 1946 - CCM