DETERMINATION OF FRACTIONAL COMPOSITION AND PHYSICOCHEMICAL CHARACTERISTICS OF NARROW CUTS IN UNANALYZABLE COMPONENT OF COMPLEX MIXTURES

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Researchers often find exhaustive determination of the composition of complex mixtures to be impossible for one reason or another. For example, hydrocarbons cannot be sharply fractionated by evaporation, because of thermal decomposition of high-molecular-mass hydrocarbons at temperatures above 400°C and atmospheric pressure, while the granulometric composition of a powdered catalyst cannot be precisely determined because it is impossible to use screens for sizing the smallest catalyst fractions.

The physical characteristics of crude oil cuts above 500°C are traditionally determined by extrapolation of data obtained with relatively low crude distillation temperatures, as well as in the region of high temperatures and high proportion of takeoff [1]. Procedures for obtaining reliable data in this case naturally fall within the province of probability and prediction theory.

Determination of characteristics is considerably simplified and becomes less arbitrary if the extrapolation problem is reduced to an interpolation problem. This situation is possible when graphic or tabular analysis is carried out for the dependence on proportion takeoff of the ratio between the characteristic value for the narrow cut recovered and the corresponding value for the mixture (resid and narrow cut) from which this cut was isolated (distillate). With 100% cut takeoff (or a takeoff proportion equal to one), this ratio equals one, and the problem of extrapolating individual characteristics becomes that of interpolating the characteristic-value ratio between the experimentally determined figures and unity [2].

It is also possible to analyze the experimental data in the form of the dependence on percentage distillate takeoff of the characteristic value ratio between the distillate and resid. At the limit, this ratio also tends to one. Here the connection between the characteristics of the distillate and resid is established for the takeoff region where interpolation is to be carried out: this involves one equation with two unknowns. Published functional relationships, e.g., that for the density of a petroleum-product mixture as a function of the proportion and density of each product, can be used to solve this problem.

If no sufficiently reliable, simple analytic relationship exists between the distillate and resid characteristics, crude distillation data are used to find a second relationship from the difference between the characteristics of the distillate and resid. At the limit, when the proportion of takeoff equals one, this difference tends to zero. The interpolation relationship is established between known values for the difference and zero. Partitioning the unknown takeoff region into intervals with the required steps, we define:

the characteristic ratio

$$x_{d\,i}/x_{r\,i-1} = a_i,\ x_{d\,i}/x_{r\,i} = a_i'$$

the characteristic difference

$$x_{r\,i} - x_{d\,i} = b_i$$

and solve the system of two equations in two unknowns. Here $x_{d\,i}$, $x_{r\,i}$ are the characteristics of the distillate and resid respectively in the i-th interpolation region, $x_{r\,i-1}$ is the resid characteristic in the preceding segment (i - 1), a_i, a_i' are the characteristic ratios to be interpolated in the i-th segment with the first and second data reduction variants, and b_i is the interpolated characteristic difference in the i-th segment.

This method is effective when the characteristics of the distillate and resid (density, viscosity, flash point, solidification temperature, molecular mass, sulfur content, etc.) can be determined relatively easily by experimental means.

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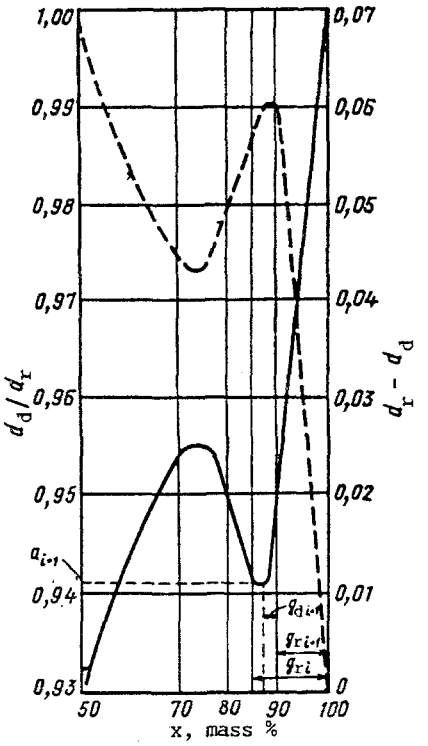

Fig. 1. Ratio d_d/d_r of relative distillate and resid densities (solid curve) and density difference $d_r - d_d$ (dash curve) as functions of proportion x of narrow-cut takeoff.

TABLE 1

Fraction No.	Catalyst granulometric composition, mm	Take off fraction x corresponding to mean granulometric composition, mass %	Specific surface, m^2/g		$\frac{n_1}{n_2}$
			cut recovered n_1	resid n_2	
1	Broad 0-0.2 cut (initial) Narrow cut	100	183	—	—
2	0,1—0,2	24,3	150	195	0,77
3	0,08—0,1	36,3	172	200	0,86
4	0,06—0,08	40,6	180	208	0,87
5	0,04—0,06	54,7	208	226	0,92
	Resid				
6	0,02—0,04	68,7	223*	230*	0,97
7	0,02	94,1	227*	231*	0,985

*Calculated figures.

Density Determination. Calculations were made for Samotlorskaya crude (mixture) with a relatively density $d_4^{20} = 0.8426$ [3]. The experimental density figures were obtained for narrow cuts boiling up to 500°C. The total density of the unanalyzed residue (15 mass %) was 0.9959 [3]. These data provided a basis for determining the ratio of the distillate and resid densities, as well as their difference (Fig. 1).

A graph representing the density ratio for the distillate and resid over the range of experimental values from the takeoff fraction to one was plotted for density interpolation. The ratio of distillate density $d_{d\,i}$ to resid density $d_{r\,i}$ was determined with 2.5 mass% steps over the segment to be interpolated:

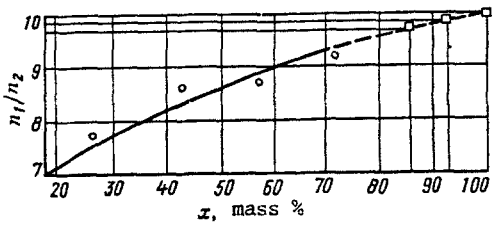

Fig. 2. Ratio n_1/n_2 for specific surfaces of narrow cut and cut from which narrow cut was recovered as function of takeoff fraction x of catalyst cut separated on screens. o) Experimental data; □) calculated data.

$$d_{d\ i}/d_{r\ i} = a_i' \tag{1}$$

The well-known additive relationship for the volumes of miscible petroleum products was used in the calculations:

$$g_{r\ i}/d_{r\ i} = g_{d\ i+1}/d_{d\ i+1} + g_{r\ i+1}/d_{r\ i+1} \tag{2}$$

where $g_{r\ i}$, $d_{r\ i}$ are the proportions by mass and density of the resid (above 500°C) in the i-th step, $g_{d\ i+1}$, $d_{d\ i+1}$ are the proportions by mass and density of the distillate in the i + 1-th step, and g_{ri+1}, d_{ri+1} are the corresponding parameters for the resid.

Solving Eqs. (1) and (2) jointly, we obtain the expressions:
for the distillate

$$d_{d\ i+1} = (d_{r\ i}/g_{r\ i})(g_{d\ i+1} + a_{i+1}g_{r\ i+1}) \tag{3}$$

for the resid

$$d_{r\ i+1} = (d_{r\ i}/g_{r\ i})[g_{d\ i+1}/a_{i+1}) + g_{r\ i+1}] \tag{4}$$

Taking the distillate density at interpolation point i + 1 and the resid density at point i in relation (1), we obtain

$$d_{d\ i+1}/d_{r\ i} = a_{i+1} \tag{5}$$

Solving Eqs. (5) and (2) jointly, we obtain the expressions:
for the distillate

$$d_{d\ i+1} = a_{i+1}d_{r\ i}$$

for the resid

$$d_{r\ i+1} = a_{i+1}g_{r\ i+1}d_{r\ i}/(a_{i+1}g_{r\ i} - g_{d\ i+1})$$

The interpolation method (utilizing the characteristics or their difference) is chosen on the basis of accuracy considerations.

We will give a fragmentary example of density calculations for narrow cuts by the method under consideration. In the first step, the density ratio $a_{i+1} = 0.941$ is found from the graph (see Fig. 1; the refractive index of 15% resid is $d_{r\ i} = 0.9959$). The amount of distillate $g_{r\ i+1} = 2.5\%$, while the amount of resid $g_{r\ i+1} = 12.5\%$, $g_{r\ i} = 15\%$

From Eqs. (3) and (4), we find

$$d_{d\ i+1} = (0.9959/15)(2.5 + 0.941 \cdot 12.5) = 0.9461$$

$$d_{r\ i+1} = (0.9959/15)[(2.5/0.941) + 12.5] = 1.0065$$

and so forth through the last cut.

Determination of Other Physical Characteristics (molecular mass, viscosity, boiling point, sulfur content, solidification temperature, coke formation capacity, etc.). Our

method for computing resid cut physical characteristics is applicable in those instances where a given characteristic can be determined experimentally or by computation. For example, the refractive index η_D^{20} of the resid cut can be calculated from the formula

$$M = 1.9778 + 0.00192\ t_b + \lg(\eta_D^{20} - d_4^{20})$$

when the molecular mass M, boiling point t_b, and density d_4^{20} are known. Refractive index determinations for narrow resid cuts are handled analogously to, e.g., density determinations.

The method under discussion makes it expedient to investigate the same physical characteristics of both distillates and resids: coke formation capacity, flash point, solidification temperature, etc. The expedience of determining all distillate and resid characteristics had not previously been clear. Our procedure makes it possible to analyze and correct experimental data, design runs, and calculate the physical characteristics of narrow resid cuts at temperatures where the characteristics of narrow petroleum cuts cannot be determined by ordinary laboratory fractionation without distorting composition.

Studies conducted at the Bashkir Scientific-Research Institute of Petroleum Refining have shown the accuracy with which the physical characteristics of heavy resid can be calculated to be equivalent to that of experimental determinations. The method under consideration provides for correction of the calculated physical characteristics of narrow resid cuts on the basis of crude characteristics: density from crude density, molecular mass from crude molecular mass, boiling point from data yielded by one-time crude vaporization, heavy resid cut viscosity from resid viscosity, etc. These crude characteristics can be determined in accordance with the additive rule. After such correction, the accuracy of the physical characteristics of narrow resid cuts calculated by our method is equivalent to that of experimental determinations.

Determination of Specific Surface of Powdered Alumosilicate Cracking Catalyst. We will consider use of our proposed methodological approach for determining the specific surface of the unseparated portion of a solid powdered cracking catalyst mixture. Table 1 gives the results yielded by 71.8 mass % catalyst separation by fractions on screens (28.2 mass % was not separated, because of the difficulty in screening the dust-sized particles). Four fractions were isolated from the broad 0-0.2 mm catalyst fraction (see Table 1, fractions 2, 3, 4, and 5), together with the residual unseparated catalyst dust (constituting the sum of fractions 6 and 7). The results obtained in investigating fractions 2-5 were used to plot the dependence of n_1/n_2 on x (Fig. 2). The ratios for determination of the specific surfaces of narrow residue fractions 6 and 7 were taken from this graph.

The method considered here is also applicable to mixtures of materials in the chemical, pharmaceutical, construction, food, and other industries.

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