THERMAL LABILITY OF LIQUID PARAFFINS

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The production of liquid paraffins is a rapidly growing branch of the national economy. By 1985, the output of these materials will be many times the 1970 production. In addition to rigid requirements on the content of n-alkanes (96–99% by mass) and aromatic hydrocarbons (0.02–0.5% by mass), the narrow cuts from the paraffin are limited in terms of the presence of unsaturated hydrocarbons; as a consequence, they must not have any odor [1].

Paraffinic hydrocarbons are comparatively unstable in the region of moderate temperatures (200–360°C). Hence, for a scientifically based selection of process conditions and flow plans for heating paraffins during the recovery of these materials from diesel fuel and subsequent distillation, the following must be known: highest allowable temperature for heating the paraffin t_{lt} (the limit of thermal lability), the degree of decomposition of the paraffin at various temperatures, and the effect of the paraffin heating method on the extent of decomposition.

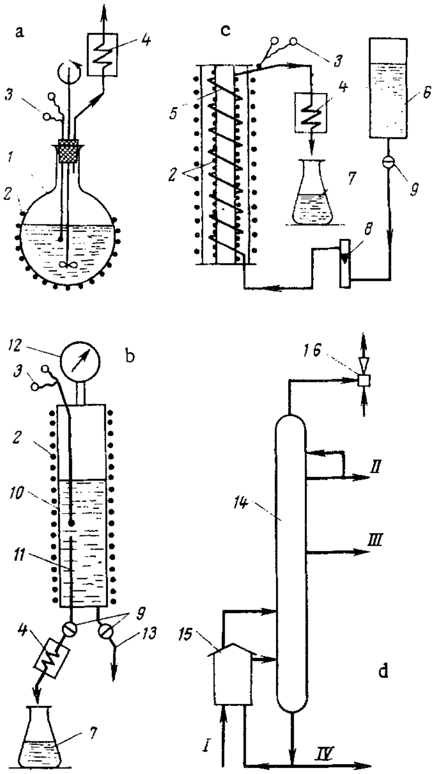

Fig. 1. Diagrams of experimental units: a) flask with stirrer; b) autoclave; c) laboratory furnace; unit for distillation of liquid paraffins; 1) flask; 2) electric heater; 3) thermocouple; 4) cooler; 5) coil; 6) feed tank; 7) receiver; 8) rotameter; 9) stopcock; 10) autoclave; 11) sampler; 12) pressure gauge; 13) drain; 14) distillation column; 15) heating furnace; 16) ejector; I) 240–350°C cut; II) IBP–200°C cut; III) 200–320°C cut; IV) 300–360°C cut; V) steam.

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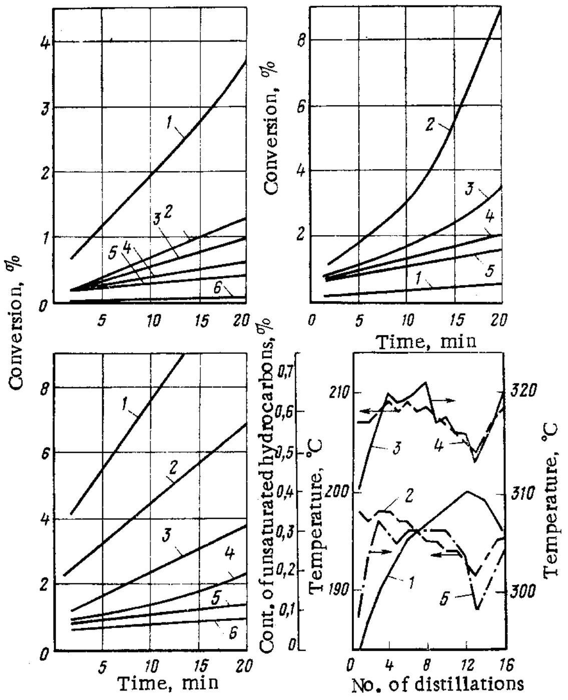

Fig. 2. Results from heating of liquid paraffins. Graphs a-c show isotherms for conversion of tridecane, octadecane, and mixed C_{10}-C_{24} n-alkanes in relation to the length of the heating period at: 1) 360°C; 2) 340°C; 3) 320°C; 4) 300°C; 5) 280°C; 6) 260°C. Graph d shows the change in content of unsaturated hydrocarbons in liquid paraffin and the characteristic temperatures on the distillation curve in relation to the number of distillations: 1) content of unsaturates in paraffin; 2, 3) IBP and EP of paraffin; 4, 5) 5% and 95% points (by volume) on distillation curve of paraffin.

TABLE 1. Results from Heating Liquid Paraffins under Static Conditions

Paraffin	Parameters of heating			Content of unsaturated hydrocarbons, mass %	Conversion, mass %
	temp., °C	time, min	heat flux density, MJ/(m²·h)		
	In ARN-2 apparatus				
C_9—C_{24}	275	312	16,8	0,278	2,2
	In flask with stirrer				
C_{10}—C_{18}	280	10	8,4	0,015	0,12
	In autoclave				
$C_{13}H_{28}$	260	5	13,4	0	0
	300	5	13,9	0,07	0,22
	340	5	14,3	0,24	0,45
$C_{18}H_{38}$	260	5	13,4	0,03	0,20
	300	5	13,9	0,07	0,90
	340	5	14,3	0,30	1,80
C_{10}—C_{24}	260	5	13,4	0,02	0,71
	300	5	13,9	0,03	1,05
	340	5	14,3	0,40	3,20

The thermal lability of liquid paraffins has been the subject of a combined investigation under laboratory and commercial conditions, the latter studies being carried out in a liquid paraffin distillation unit. In the first stage of this program, in view of the lack of any data on the kinetics of thermal decomposition of paraffins in the temperature range of 200-400°C, the limit of thermal lability t_{lt} was estimated on the basis of the kinetic equation for thermal cracking, $k = 1/\tau \log 100/(100 - x)$, using an extrapolated Nelson chart for the

TABLE 2. Results from Heating Liquid Paraffins under Dynamic Conditions

Paraffin	Heating parameters				Content of unsaturated hydrocarbons, mass %
	temp., °C	time, min	heat flux density, MJ/($m^2 \cdot h$)	flow velocity in coil, m/sec	
In furnace coil (l = 0.95 m)					
$C_{11}-C_{22}$	250	3,0	3,02	0,007	0
	270	0,45	14,5	0,087	0,045
	310	1,1	6,22	0,080	0,203
	350	0,28	21,2	0,410	0,153
In furnace coil (l = 10.8 m)					
C_9-C_{24}	260	1,84/13*	1,68	0,200	0,153
	280	2,0/26*	2,1	0,35	0,600
In flameless combustion furnace (l = 324 m)					
$C_{11}-C_{25}$	254	12,0	12,1	0,539	0,051
	300	19,0	9,8	0,357	0,014
	317	19,0	10,5	0,357	0,031
In flameless combustion furnace (l = 84 m)					
$C_{15}-C_{25}$	269	4,5	6,3	0,600	0,047
	276	9,0	5,0	0,350	0,056
	277	9,0	5,8	0,350	0,110

* The first value shown is the length of a single heating period (min); the second value is the number of heating cycles.

relationship between k and t [2]. It was established that t_{lt} = 260-280°C for x = 0.05%. At a higher level of x, 0.2%, the corresponding value of t is higher, in the range of 295-350°C, depending on the value of τ [3].

In the second stage of the program, the thermal lability of liquid paraffins was studied experimentally in various types of units, under static and dynamic conditions (Fig. 1). In addition to these units, use was made of the ARN-2 apparatus (GOST 11011–64) and the Engler apparatus (GOST 2177–66), as well as a continuous laboratory distillation unit and other types of apparatus. The heating conditions in the experiments were set up differently; specifically, we investigated heating in contact with air and nitrogen, under vacuum, under excess pressure, with continuous stirring, in an oil bath, with electric heating, with fired heating, etc. The experimental units and the heating conditions were selected so as to cover all possible heating methods within the particular range of temperatures investigated (240-360°C).

First, we investigated the thermal lability of liquid paraffins, individual n-alkanes, and mixtures of alkanes under static conditions. The experimental data (Table 1 and Graphs a-c in Fig. 2) show that the conversion of paraffinic hydrocarbons and the content of unsaturated hydrocarbons in the paraffin test samples are proportional to the temperature and duration of heating, and also to the length of the carbon chain in the hydrocarbon. Further, the conversion is not proportional to the content of unsaturated hydrocarbons when the different paraffins are heated. For example, when $C_{13}H_{28}$ was heated to 300°C, the conversion was 0.22% by mass, and the content of unsaturated hydrocarbons was 0.07% by mass. When this same hydrocarbon was heated to 340°C, these values were higher by respective factors of 2 and 3.5. For the mixed C_{10}-C_{24} paraffins, the conversion and the content of unsaturated hydrocarbons after heating to 300°C were respectively 1.05 and 0.03%, and after heating to 340°C they were 3.2 and 0.4%.

Upon comparing the results from heating the C_{10}-C_{24} mixture and the $C_{18}H_{38}$ hydrocarbon under identical conditions, it becomes evident that the content of unsaturated hydrocarbons is lower in the mixture than in the C_{18} hydrocarbon for heating temperatures up to 300°C, whereas at higher temperatures the reverse is true. This is explained by the presence of higher n-alkanes, with lower thermal stability, in the mixed paraffins.

The 160-308°C paraffin cut was redistilled under the test conditions of GOST 2177–66, 16 times in succession, taking almost all of the material overhead each time. The results from this experiment (see Fig. 2) indicate that, with heating up to 320°C, thermal decomposition of the paraffin occurs, with the formation of unsaturated hydrocarbons and the accumulation of these hydrocarbons after each distillation. There was also a change in the paraffin distillation curve. For example, when 0.4% unsaturated hydrocarbons had appeared, the

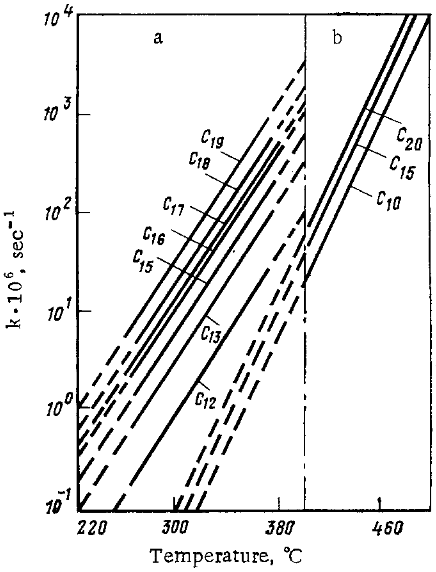

Fig. 3. Temperature dependence of thermal decomposition rate constants for n-alkanes: a) our data; b) extrapolated data of Nelson.

initial boiling point and the end point of the paraffin were lowered by 10° and 6°C, respectively. Further heating (13th distillation) led to conversion of the high-boiling fractions of the paraffin to tar, increasing its end point and lowering the content of unsaturated hydrocarbons to 0.3%.

As a result of the experiments performed under static conditions, the following values were obtained for t_{lt}: $C_{13}H_{28}$ 260°C; $D_{18}H_{38}$ 250°C; C_{10}–C_{24} mixture 240°C.

The data obtained by heating the liquid paraffins under dynamic conditions (Table 2) show that the hydraulic regime of paraffin movement in the heater has a considerable effect on the extent of paraffin decomposition and on t_{lt}, depending on the average molecular mass of the paraffin, the temperature, and the duration of the heating. With increasing rate of paraffin flow velocity in the heater, there was less decomposition, and t_{lt} was higher. For example, C_{11}–C_{22} paraffin, when heated at 250°C with a residence time of 3 min in the heater, did not decompose; the C_{11}–C_{25} paraffin, even at 300°C with a residence time of 19 min, contained about 0.014% on saturated hydrocarbons. This same paraffin, when heated at 254°C with a residence time of 12 min, decomposed to form 3.5 times the quantity of unsaturated hydrocarbons in comparison with that formed by the heating to a higher temperature. This difference is explained by the higher heat flux density, which was 12.1 MJ/(m^2 h) in the second case in comparison with 9.8 MJ/($m^2 \cdot$h) in the first case, with comparable heating rates.

Higher flow velocities of the paraffin in the heater gave less thermal decomposition. For example, the C_{15}–C_{25} paraffin, when heated in a flameless combustion furnace of the BB152/6 type with a flow velocity of 0.35 m/sec, formed 0.11% unsaturated hydrocarbons; with a flow velocity of 0.6 m/sec, it formed only 0.038% unsaturated, in both cases heating to a temperature of 277°C with a heat flux density of 7.2 MJ/($m^2 \cdot$h). The experimental data show that t_{lt} is a function of several parameters, relating to the heating conditions and also to the paraffin composition. With a flow velocity of 0.2 m/sec for this same paraffin in the heater, t_{lt} was found to be 260–280°C. When the velocity was increased to 0.5–0.6 m/sec with τ = const, this temperature limit was increased to 300–310°C; with still higher flow velocities, the paraffin may be heated to 330–340°C.

A computer-aided workup of the experimental data by the least-squares method gave the following regression equation for the degree of paraffin decomposition:

$$X = (1.479t - 5.01\tau - 2.778q + 6.792v + 0.132M)10^3$$

where X is the content of unsaturated hydrocarbons in the paraffin, mass %; it is the temperature to which the paraffin is heated, °C; τ is the residence time of the paraffin in the furnace in the hot zone, min; q is the heat flux density for the heater, MJ/($m^2 \cdot$h); v is the paraffin flow velocity in the heater m/sec; M is the average molecular mass of the paraffin.

We also obtained partial correlation coefficients between each of the five parameters investigated, through which we were able to rank their influence on X in the following order of decreasing influence: t, τ,

TABLE 3. Recommended Parameters for Heating Liquid Paraffins (C_{10}-C_{24})

Indices	Allowable content of unsaturated hydrocarbons, mass %					
	none	0,05	0,1	0,2	0,5	1
Temperature, °C, no higher than	250	260	280	300	320	340
Time, min, no longer than	10	12	15	20	20	30
Flow velocity in heater, m/sec	0,6—1,2	0,6—1,2	0,8—1,4	1,0—1,4	1,2—1,5	1,4—1,6
Heat flux density for heater surface, MJ/($m^2 \cdot h$)	30—35	35—40	40—45	45—52	52—60	60—65
Heating method	Intermediate heat carrier		Fired			

v, q, and M. On the basis of experimental data on the thermal lability of paraffins, plots were made of the temperature dependence of the thermal decomposition rate constant for the n-alkanes (Fig. 3). Also shown in Fig. 2 are analogous plots obtained by extrapolating the Nelson charts [2] to the moderate-temperature region, on the assumption of equality of the kinetic characteristics of petroleum products and n-alkanes with the same molecular mass. These relationships show that the experimental data cannot be described by extrapolating the Nelson relationship. Therefore, in carrying out design and research studies, use should be made of the relationship between k and t that is shown in Fig. 3.

Apart from the factors we have analyzed, the thermal lability of a paraffin is influenced to a great degree by the heating method. In commercial operations, the heating may be carried out in fired furnaces of the flameless combustion type, or by means of high-temperature heat transfer fluids (mixed biphenyl) or high-pressure steam (5.9-9.8 MPa). The selection of the method used for paraffin heating is determined by the limits placed on the content of unsaturated hydrocarbons in the paraffin. If no unsaturated hydrocarbons are allowed, the paraffin must be heated under mild conditions; this is done by supplying heat through a boiler, i.e., by the use of high-potential steam (6-10 MPa).

In the event that paraffin decomposition up to 0.05% by mass is allowed, other high-temperature heat carriers may be used [4], such as biphenyl mixture or ditolylmethane; however, there may be problems with these materials contaminating the paraffin and thus lowering its quality with respect to the content of aromatic hydrocarbons. In all other cases, if higher contents of unsaturates are allowable, fired heating of the paraffin is the simplest and most suitable method. The recommended parameters and methods for heating paraffins, depending on the allowable content of unsaturated hydrocarbons, are listed in Table 3.

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