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THERMAL AND CATALYTIC CRACKING OF PARAFFINS AT HIGH PRESSURE

by

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The data available in the literature on the influence of pressure on the rate of thermal cracking of individual paraffins (at a constant temperature) relate to the low-pressure range. Dintses ¹ gives data indicating that the rate of thermal decomposition of n-butane at 575°C is increased when the pressure rises from 3.9 to 10.8 atm. Dintses et al. ² noticed a retardation of the ethane decomposition when at a temperature of 635°C the pressure rose from 1 to 26 atm. However, at 750°C and 800°C the rate of ethane decomposition increases with a rise in pressure (in the pressure range to 10 atm.) ³. Thermal decomposition of n-heptane at 580°C and a pressure up to 8.7 atm. ⁴ also showed an increase in reaction velocity with pressure increase.

The investigations in the range of pressures over 1000 atm. are restricted to one article only ⁵ on the thermal decomposition of n-hexane at 1002 kg/cm², so that no conclusions can be drawn on the change in velocity with the pressure.

The influence of high pressure on catalytic cracking of individual paraffins has not yet been investigated. The data available in the literature on catalytic cracking under pressure (see for instance ⁶) relate to various temperatures and permit conclusions on the cracking rate (and destructive alkylation) at a simultaneous change in temperature and pressure.

In the present investigation the influence was studied of high pressure on the rate of thermal and catalytic cracking of n-heptane and n-hexane. The investigation was conducted in vibrating reactors. The temperature was kept constant within + 2°C. Duration of experiments 3 hours; after this period the reactor was rapidly cooled with water.

The n-heptane and n-hexane were cut in a rectifying column with 30 theoretical plates and purified by chromatographic adsorption.

Physical constants of purified n-hexane: d_4^{20} 0.6594; n_D^{20} 1.3750; according to the literature ⁷: d_4^{20} 0.65937; n_D^{20} 1.37486; b.pt 68.4-68.8°C (760 mm).

Physical constants of purified n-heptane: d_4^{20} 0.6832; n_D^{20} 1.3879; according to the literature d_4^{20} 0.68376; n_D^{20} 1.38764; b.pt 98.1-98.4°C (760 mm).

The reaction products were distilled in a rectifying column of the above-mentioned efficiency.

For the catalytic cracking experiments aluminosilicate catalyst was used, which was heated before the experiment at 500°C in a current of air for 3 hours. For the results of these experiments we refer to tables 1 and 2.

TABLE 1
Cracking of n-heptane ($\tau = 3$ hours)

No. Exp.	Quantity of n-heptane, g	Temp. °C	P, atm.	Yield of liquid products	Including				Gas and liquid products with b.pt < 48°C (by difference)	n_D^{20} res.	$\frac{> C_7}{< C_7}$ ***
					fr. 48-76°C	fr. 76-96°C	fr. 96-99°C	residue			
in % on feed*											
a) Thermal (under n-heptane pressure)											
14	35.45	420	480-760	68.3	5.2	4.2	19.7	30.1	40.8	1.4512	0.65
31	40.5	420	750-1120	78.9	4.7	3.7	28.6	32.0	31.0	1.4480	0.90
13	41.0	420	1000-1300	88.5	3.2	3.4	39.8	33.1	20.5	1.4370	1.40
12	45.0	420	1750-1980	94.2	2.1	1.9	55.6	26.5	12.9	1.4262	1.77
11	49.0	420	3100	96.7	1.4	2.1	59.3	27.0	10.2	1.4262	2.33
48	40.0	415	100-170	75.3	3.6	3.3	33.3	22.11	37.7	1.4556	0.54
b) Under hydrogen pressure											
40	40.0	415	350	94.0	1.0	2.5	71.8	4.2	20.5	1.4050	
39	40.0	415	740	87.7	1.4	3.0	65.1	3.0	27.5	1.4006	
38	40.0	415	1200	78.2	1.8	1.3	52.2	6.2	38.5	1.3920	
c) Catalytic *** (under n-heptane pressure)											
52	30.0	420	330-550	62.4	2.4	4.8	35.0	6.6	51.1	1.4725	
49	38.5	420	950-1250	47.8	2.9	4.8	20.9	6.9	64.5	1.4712	
54	30.0	410	300-400	85.7	2.4	5.7	54.5	6.6	31.8	1.4281	
57	30.0	410	300-400	82.0	1.4	4.9	49.3	11.3	33.1	1.4112	
55	35.0	410	520-850	69.0	2.9	6.5	30.6	14.9	45.1	1.4236	
56	39.4	410	650-980	70.2	2.9	6.5	37.4	7.9	45.3	1.4480	
46	40.0	415	100-190	69.3	1.8	3.5	42.8	5.3	46.6	1.4625	
d) Catalytic under hydrogen pressure											
43	40.0	415	290	72.2	1.8	4.8	45.5	3.6	44.3	1.4358	
42	40.0	415	770	57.9	2.3	5.5	29.6	7.5	55.1	1.4032	
44	40.0	415	1240	51.7	1.6	5.5	29.4	5.3	61.2	1.3937	

* Allowing for a loss of 2 g when filling the reactors.

** In the presence of 30% wt aluminosilicate catalyst. In this investigation the pressure was not raised to above 1250 atm. to keep the ratio catalyst/n-heptane accurately constant when the n-heptane in the reactor is vibrated.

*** > C₇ fraction with b.pt upwards of 99°C; < C₇ products with b.pt lower than 76°C.

TABLE 2
Cracking of n-hexane ($\tau = 3$ hours)

No. Exp.	Quantity of n-hexane, g	Temp. °C	P, atm.	Yield of liquid products	Including			Gas and liquid products with b.pt < 48°C (by difference)	n_D^{20} res.	$\frac{> C_6}{< C_6}$
					fr. 48-66°	fr. 66-69°	residue			
in % on feed *										
a) Thermal (under n-hexane pressure)										
52	25.2	430	280-500	40.0	1.7	11.3				
53	30.6	430	420-700	54.3	2.4	20.0	26.3	51.3	1.4680	0.51
51	32.0	430	400-750	55.2	3.7	17.3	28.7	50.3	1.4608	0.57
45	40.0	430	750-980	71.8	2.5	32.4	29.4	35.7	1.4300	0.82
54	44.8	430	1520-1850	80.0	1.6	39.4	31.8	27.2	1.4335	1.17
35	24.0	420	140-180	78.5	3.2	52.9	16.9	27.0	1.4280	0.63
61	40.05	420	800-920	89.7	2.2	68.5	15.8	13.5	1.4150	1.17
b) Under hydrogen pressure										
57	40.0	420	380	89.7	0.9	71.7	6.7	20.7	1.3865	
58	40.0	420	560	89.8	1.5	71.9	6.1	20.5	1.3839	
56	40.0	420	900	85.3	1.6	68.2	6.3	23.9	1.3809	
55	40.0	420	1230	83.3	1.4	68.0	6.0	24.6	1.3795	
c) Catalytic, under hydrogen pressure **										
67	40.0	415	200	74.7	10.3	42.0	8.0	39.7	1.4000	
64	40.0	415	380	76.5	13.1	41.9	7.7	37.3	1.3887	
66	40.0	415	890	59.8	13.6	24.9	6.6	54.9	1.3850	
65	40.0	415	1380	48.2	10.3	21.8	6.4	61.5	1.3802	

* Allowing for a loss of 2 g when filling the reactors.

** In the presence of 30% wt of aluminosilicate catalyst.

*** > C₆ fraction with b.pt above 69°C; < C₆ products with b.pt lower than 48°C.

These results allow of the following conclusions.

1. The rate of thermal cracking of individual hydrocarbons (% reacted hydrocarbons) decreases with a rise in pressure. The yield of low-boiling, cracking products drops and the relative content of higher-boiling hydrocarbons in the cracking products rises (in comparison with the original hydrocarbons). In addition, the refractive indices of the high-boiling products drop with a rise in pressure.
2. A low hydrogen pressure retards and a high hydrogen pressure accelerates thermal cracking (cf. exp. Nos. 48 and 40, 39, 38 in table 1, and also exp. Nos. 51-53 and 55-58 in table 2). The refractive index of the residue obtained in cracking under high hydrogen pressure approaches the value for the original hydrocarbon, which indicates very insignificant formation of hydrocarbons with a large number of carbon atoms.
3. Catalytic cracking of n-heptane on an aluminosilicate catalyst is accelerated by high pressure (cf. exp. Nos. 52 and 49, Nos. 54, 57 and 55, 56 in table 1).
4. High hydrogen pressure accelerates catalytic cracking on an aluminosilicate catalyst.
5. During catalytic cracking under pressure a larger number of isomers of the original hydrocarbons is formed and fewer high-boiling products than during thermal cracking under the same conditions.

It should be stressed that the retardation of thermal cracking under high pressure cannot be attributed to a shift in the chemical equilibrium. In our experiments the equilibrium was not reached. This follows particularly from a comparison of the results of thermal and catalytic cracking at the same temperature and pressure. Thus, in thermal cracking at 420°C and a pressure of 1000-1300 atm. 39.8% of n-heptane remains unchanged (exp. No. 13), and in catalytic cracking 20.9% (exp. No. 49); in these experiments the yield of gaseous and low-boiling liquid decomposition products was 20.5 and 64.5% respectively calculated on n-heptane. Due consideration should be given to the fact that at high pressures the polymerization, hydrogenation and alkylation reactions are intensified, which reactions substantially decrease the free energy value of the total thermal cracking process under pressure.

This investigation thus shows that the acceleration in cracking of paraffins with a rise in pressure, as observed by some investigators, is restricted to the low pressure range and that at high pressure the rate of thermal decomposition decreases.

The acceleration of catalytic cracking of n-heptane by high pressure reflects a real difference between the thermal and catalytic processes. It may be assumed that in the catalytic process the slowest stage of the total process, which determines its rate, is the adsorption of hydrocarbon or another reaction with the catalyst.

The rules of thermal cracking observed at high pressure can be accounted for on the basis of an analysis of the chain mechanism. However, this problem lies beyond the scope of this investigation.

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