THE DISTRIBUTION OF THE PRODUCTS OF FISCHER-TROPSCH SYNTHESIS WITH IRON CATALYSTS

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SUMMARY

The product distribution of Iron-catalysts of different hydrogenation hydrogen values is presented and investigated with the application of the polymerisation function. A law of distribution is found for the paraffin hydrocarbons. The volumes of C-fractions follow the reciprocal proportional ratios of the squares of the C-numbers, independent of the absolute values of the hydrogenation hydrogen. Their absolute values are obtained by multiplication with hydrogenation hydrogen values. The methane formation is an exception from the rule. The minimum value of the first methane term in the series of the paraffin distribution is being estimated, and the influence of the methane formation on the formation of the higher paraffin hydrocarbons is being discussed. The paraffin distribution for different catalysts can be calculated with the help of simple data, obtained from gas analyses.

A similar law of distribution is stated for olefines. This distribution decreases for the higher olefines in a higher order, than in the reciprocal square ratios of the C-numbers. The formation of lighter olefines is favoured against the formation or preservation of the higher olefines, probably on account of the easier hydrogenation of the higher olefines. Quantitative data are given which lead to the calculation of the olefine distribution for iron catalysts.

The formation of the olefines is found to be principally a radical polymerisation which is superimposed by a lesser active ethylene polymerisation. According to the amount of hydrogenation hydrogen, activated by a catalyst, smaller or larger parts of the polymerisation olefines are being hydrogenated. The methane formation occurs at least to somewhat more than $\frac{1}{3}$ of the hydrogenation hydrogen value. The change in the formation of the higher paraffins with increasing methane formation is discussed in detail. A method is indicated according to which the total olefine volume and the division of CO-volumes, converted into paraffin and olefine hydrocarbons, can be calculated.

INTRODUCTION

In our earlier publication,[1] we have given the derivation for that part of hydrogen, which is used for the hydrogenation in the synthesis reactions, and we have also discussed the importance of it. In the following article, the influence of the hydrogenation hydrogen on the distribution of the different products of the synthesis is discussed.

EXPERIMENTAL

With our present knowledge we can calculate only that part of hydrogenation hydrogen, activated by a catalyst, which has served for the formation of methane, as it is usually known from gas analysis. With this we can obtain the remaining hydrogenation hydrogen, which has been used for [illegible] higher olefines into paraffins, but we cannot subdivide it any further. In those cases, where all the hydrogenation hydrogen has been utilized for the methane formation, it can be shown that the remaining amount of total carbon monoxide, which has been converted, appears as olefines, oxygenated compounds and [illegible] carbon deposit.

It is essential to have the product composition according to C-No. fractions in order to obtain further information about the distribution of the hydrogenation hydrogen on the higher paraffins, and thereby to obtain the information of the distribution of these paraffins. In 1943, under the title "Reichsamtsversuche", synthesis runs with 6 different iron catalysts under uniform conditions have been carried out, and all the products have been completely separated and [illegible] of. The published results of these investigations[2] have been used in our studies of the influence of hydrogenation hydrogen on the distribution of the products, as these happen to be the most complete available data.

The catalysts used in the "Reichsamtsversuche" had been developed and manufactured by 6 different firms, and they were used for the tests in the works "Schwarzheide" of Messrs. Braunkohle-Benzin, A. G., during 1943 44. Along with studies of purely technical and economical nature, all the products had been completely separated into C-fractions, and percentage amounts of paraffins, olefines, and oxygenated compounds of these fractions had been estimated. The data published so far are rather incomplete. As far as we are aware, a complete evaluation of these investigations has never been published. The F.I.A.T. Report No. 276 contains the composition and the absolute quantities produced of the products, from 6 different iron catalysts. The gas quantities and composition, however, are not given. The product composition as well as the gas quantities and gas composition, for 2 of these 6 catalysts (Rheinpreussen and Brabag Catalysts) over specific experimental periods, are at our disposal.[3] These examples enable us to carry out a complete comparison, with the aid of our earlier deductions from gas analytical data. It is, however, possible to indicate the connections of the built-up of the products, in the case of other examples, with these data, and it can

C. No. N.	Paraffins				Olefines				A	
	22·4 / Mol. wt.	Product in g.	Vol. liter $(X'-F')_N$	CO vol. col. $4\times N$ $(A'+B')_P$	22·4 / Mol. wt.	Product in g.	Vol. liter $(F')_N$	CO vol. col. $8\times N$ $(A'+B')_O$	22·4 / Mol. wt.	Produc in g.
I	2	3	4	5	6	7	8	9	10	11
1	1·400	191·80	268·52	268·52	..	..	..	..	..	..
2	0·747	199·10	148·73	297·46	0·800	18·20	14·56	29·12	0·487	74·15
3	0·509	130·80	66·58	199·74	0·533	173·40	92·42	277·26	0·373	33·25
4	0·386	120·20	46·40	185·60	0·400	125·00	60·00	240·00	0·303	23·20
5	0·311	81·45	25·33	126·65	0·320	114·70	36·70	183·50	0·254	0·90
6	0·261	67·91	17·72	106·32	0·267	76·00	20·29	121·74	0·229	1·69
7	0·224	64·51	14·45	101·25	0·229	64·40	14·73	103·11	0·193	4·60
8	0·197	54·54	10·74	85·92	0·200	50·10	10·02	80·16	0·172	6·04
9	0·175	44·15	7·73	69·57	0·178	37·00	6·58	59·22	0·155	4·32
10	0·157	49·85	7·83	78·30	0·160	33·00	5·28	52·80	0·142	3·55
11·5	0·137	64·93	8·90	102·35	0·139	35·30	4·91	56·47	0·130	3·17
13·5	0·117	..	..	..	0·119	..	..	..	0·116	2·60
14·5	0·109	142·91	15·58	225·91	0·110	44·70	4·92	69·49	0·099	..
15·5	0·102	..	..	..	0·103	..	..	..	0·101	2·87
17·5	0·090	44·92	4·04	71·34	0·091	6·15	0·56	9·80	0·089	1·17
19–27	0·069	143·10	9·87	227·01	0·070	9·30	0·65	14·95	0·066	0·00
28–43	0·0399	202·00	8·06	286·13	..	0·00	0·00	00·00	0·039	0·00
Sum ..	..	1602·15	660·48	2432·07	..	787·25	271·62	1297·62	..	161·51
Loss ..	0·102	37·01	3·78	58·59	0·103	18·19	1·87	28·98	0·101	3·74
Sum .. Total	..	1639·16	664·26	2490·66	..	805·44	273·49	1326·60	..	165·25

U-Factor calculations:—

$(x-f) = 100 - 3(a+b)$.
$(x'-f') = A - 3(a'+b')$.
$A = (x'-f') + 3(a'+b') = 664{\cdot}26 + 3(4011{\cdot}53) = 12698{\cdot}85$.
$U = 100/A = 100/12698{\cdot}85 = 0{\cdot}007874722$.

General produ
Paraffins-C
Methane-C

Total Para
Olefins-C
Alcohols
Esters-C

Total CO
converte
hydroca

* E. Sauter, "Report on the Works of the Department of Research and Development of the Works Schwarzheide of Messrs. Braunkohle-Benzin, A. G.," 1938–45.

TABLE I

Distribution of the products of an Iron Catalyst of Rheinpreussen. A. G. Homberg.

Alcohols			Esters				Sum Paraffins+ Olefins+ Alcohols+ Esters-CO Vol. liter	Sum Paraffins+ Olefins+ Alcohols+ Esters-CO Vol. liter	Mol. volumes on $CO+H_2=100$			
Product in g.	Vol. liter (G_1')	CO vol. col. $12\times N$ $(A'+B')_{A1}$	22·4 Mol. wt.	Product in g.	Vol. liter (G_2')	CO vol. col. $16\times N$ $(A'+B')_{ES'}$			Paraffins $(X-F)_N$	Olefines F_N	Alcohols G_1	E
11	12	13	14	15	16	17	18	19	20	21	22	
..	..	..	..	..	..	..	268·52	268·52	2·114	..	..	
74·15	36·11	72·22	..	..	..	..	199·40	308·80	1·171	0·115	0·284	
33·25	12·40	37·20	..	..	..	..	171·40	453·72	0·524	0·728	0·098	
23·20	7·63	28·12	..	..	..	..	113·43	458·72	0·365	0·472	0·055	
0·90	0·23	1·15	0·220	0·850	0·14	0·70	62·40	312·00	0·199	0·289	0·002	
1·69	0·37	2·22	0·193	0·597	0·11	0·66	38·49	230·94	0·139	0·160	0·003	
4·60	0·89	6·23	0·172	0·690	0·12	0·54	30·19	211·43	0·114	0·116	0·007	
6·04	1·04	8·32	0·153	0·722	0·11	0·88	21·91	175·28	0·084	0·079	0·008	
4·32	0·67	6·03	0·142	0·530	0·07	0·63	15·05	135·45	0·061	0·052	0·005	
3·55	0·50	5·00	0·130	0·400	0·05	0·50	13·66	136·60	0·062	0·041	0·004	
3·17	0·41	4·71	0·116	0·400	0·05	0·57	14·27	164·10	0·070	0·039	0·003	
2·60	0·30	4·05	0·101	0·530	0·05	0·67	0·35	4·72	..	..	0·002	
..	..	..	..	..	..	..	20·50	295·40	0·123	0·039	..	
2·87	0·29	4·49	0·089	0·590	0·05	0·77	0·34	5·26	..	..	0·002	
1·17	0·10	1·75	0·080	0·360	0·03	0·52	4·73	33·41	0·032	0·004	0·001	
0·00	0·00	0·00	..	0·000	0·00	0·00	10·52	241·96	0·078	0·005	0·000	
0·00	0·00	0·00	..	0·000	0·00	0·00	8·06	286·13	0·063	0·000	0·000	
161·51	60·34	181·49	..	5·469	0·78	6·74	993·22	3977·92	5·199	2·139	0·474	
3·74	0·38	5·89	0·089	0·130	0·01	0·15	6·04	93·61	0·030	0·015	0·003	
165·25	60·72	187·38	..	5·599	0·79	6·89	999·26	4011·53	5·229	2·154	0·477	

G. Homberg. 1943/44 *(Reichsanttoversuche)**

in $CO+H_2$ = 100% basis			(A + B) values on 100 % = CO+H basis					Individual (X – P) values				
Alcohols G_1	Esters G_2	P+Ol+Al +Est.	Paraffins	Olefines	Alcohols	Esters	P+Ol+Al +Est.	Paraffins	Olefines	Alcohol	Esters	P+
22	23	24	25	26	27	28	29	30	31	32	33	
..	..	2·114	2·114	..	..	..	2·114	2·114	..	..	..	
0·284	..	1·570	2·342	0·229	0·569	..	3·140	1·171	0·115	0·284	..	
0·098	..	1·350	1·573	2·183	0·293	..	4·049	0·524	0·728	0·098	..	
0·055	..	0·892	1·461	1·890	0·221	..	3·572	0·365	0·472	0·055	..	
0·002	0·002	0·491	0·997	1·445	0·009	0·005	3·456	0·199	0·289	0·001	0·001	
0·003	0·001	0·303	0·837	0·959	0·017	0·005	1·818	0·139	0·160	0·001	0·001	
0·007	0·001	0·238	0·797	0·812	0·049	0·007	1·665	0·114	0·116	0·001	0·001	
0·008	0·001	0·172	0·676	0·631	0·065	0·007	1·379	0·084	0·079	0·001	0·001	
0·005	0·000	0·118	0·548	0·466	0·047	0·005	1·066	0·061	0·052	0·005	0·000	
0·004	0·000	0·107	0·616	0·416	0·039	0·004	1·075	0·062	0·041	0·004	0·000	
0·003	0·000	0·112	0·866	0·445	0·037	..	1·292	0·035	0·019	0·003	0·000	
0·002	0·000	0·002	..	..	0·032	0·004	0·037	..	..	0·001	0·000	
..	..	0·162	1·779	0·547	..	0·005	2·326	0·031	0·0097	..	..	
0·002	0·000	0·002	..	..	0·035	0·006	0·041	..	..	0·001	0·000	
0·001	0·000	0·037	0·562	0·077	0·014	0·004	0·657	0·016	0·002	0·562	0·000	
0·000	0·000	0·083	1·788	0·118	0·000	0·000	1·906	0·009	0·0095	0·000	0·000	
0·000	0·000	0·063	2·253	0·000	0·000	0·000	2·253	0·004	0·004	0·000	0·000	
0·474	0·004	7·816	19·149	10·218	1·427	0·052	30·846	4·928	2·083	0·473	0·004	
0·003	0·000	0·048	0·461	0·228	0·046	0·001	0·736	0·030	0·015	0·002	0·000	
0·477	0·004	7·864	19·610	10·466	1·473	0·053	31·582					

') values			Individual (A+B) values					Q	R
ls	Esters	Esters P+01+Al	Paraffins	Olefines	Alcohols	Est.	P+01+Al +Est.		
	33	34	35	36	37	38	39	40	41
	..	2·114	2·114	..	..	..	2·114	..	..
4	..	1·570	2·342	0·229	0·569	..	3·140	2·158	2·158
8	..	1·360	1·573	2·183	0·293	..	4·049	2·089	2·092
5	..	0·892	1·461	1·890	0·221	..	3·572	1·920	1·919
2	0·001	0·491	0·997	1·445	0·009	0·005	2·456	2·030	2·028
3	0·001	0·303	0·837	0·959	0·017	0·005	1·818	2·024	2·021
7	0·001	0·238	0·791	0·812	0·049	0·007	1·665	1·965	1·975
8	0·001	0·172	0·676	0·631	0·065	0·007	1·379	1·987	1·982
5	0·000	0·118	0·548	0·466	0·047	0·005	1·066	2·023	2·027
4	0·000	0·107	0·616	0·416	0·039	0·004	1·426	1·926	1·931
15	0·000	0·055	0·402	0·223	0·018	0·002	0·646	2·049	2·051
1	0·000	0·001	..	..	0·016	0·002	0·018	..	..
	..	0·041	0·444	0·137	..	..	0·581	1·918	1·926
1	0·000	0·001	..	..	0·018	0·003	0·021	..	..
2	0·000	0·0185	0·280	0·039	0·007	0·002	0·328	2·022	2·023
0	0·000	0·0095	0·199	0·013	0·000	0·000	0·212	2·029	2·055
0	0·000	0·004	0·141	0·000	0·000	0·000	0·141	2·010	2·015
0	0·004	7·485	13·427	9·443	1·886	0·042	24·632	..	..
3	0·000	0·048	0·461	0·228	0·046	0·001	0·736	..	..
	..	..	..	..	..	..	..	..	..

be shown thereby that the relations developed earlier are useful in explaining further the built-up of the products.

However, it should be mentioned here that further investigations in this connection are desirable in order to establish the solidarity and completeness of the relations developed by us. The results of these investigations are valid only for iron catalysts, though the conclusions drawn may be such as to appropriate them a common validity. Unfortunately, practically no adequate data are available for cobalt catalysts, for which there may exist probably much simpler relations for the distribution of the products.

The data at our disposal have been utilized in the following manner (*vide* Table I):—

1. The weights of the different C-fractions, separated as paraffins, olefines and oxygenated compounds, have been recalculated into vapour volumes. Thus we can arrive at the distribution of the products, according to Mol.-volumes and at the sum of such volumes. The latter values are identical with our earlier defined values of $(x' - f')$, f' and g'.

2. By multiplying the vapour volumes of different C-fractions by the respective C-numbers (N) we get the different CO-volumes, which have been used up for the formation of different C-fractions. The sum of these values represent the CO-volumes, converted into the different groups of products, and further, the sum of these groups of products forms the CO-volume which has been converted into the total products, which is identical with our earlier defined value of $(a' + b')$.

3. The different vapour volumes, their sums, the CO-volumes and their sums, then have been recalculated on 100% conversion basis, in order to utilise them for comparative studies. These recalculations are possible with the help of an equation

$$(x - f) = 3\,[33{\cdot}33 - (a + b)] \qquad (I)$$

which we have already formulated in our earlier publication. Here, the values of $(x' - f')$ and $(a' + b')$ are substituted for $(x - f)$ and $(a + b)$, from our examples, and the constant equivalent to 33·33 is then obtained. With the help of the thus obtained recalculation constant (*vide* Table I), each value has been recalculated to a value, valid for total $(CO + H_2)$-conversion. Depending upon whether we consider the oxygenated compounds either as paraffins or as olefines, we obtain somewhat different $(x - f)$-values or constants. Here, throughout, we have obtained $(x - f)$-values only from paraffins. Wherever the comparison between the values of $(x - f)$, obtained in this way, and such $(x - f)$-values from gas analysis is possible, they were found to be in very good agreement [*vide* Tables I and II: $(x - f) = 4{,}992$ from gas analysis and $(x - f) = 5{,}229$ from product analysis].

TABLE II

C-Balance Calculations of Iron Catalyst of Rheinpreussen, A. G. Homberg (Reichsamtsversuche, 1943–44)

No.	Gas volume %	CO_2	C_2H_4	CO	H_2	[illegible]	[illegible]	[illegible]	H_2 [illegible]	[illegible]	H_2 [illegible]
1	Inlet gas ..	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		1·[illegible]
2	Outlet gas ..	26·2[illegible]	2·41	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1·[illegible]
3	Outlet gas composition relative to inlet gas composition	15·[illegible]	1·4[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	Disappeared (−) and formed (+) [illegible]	+[illegible]	1·4[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
5	Recalculated [illegible] on 100% [illegible] basis	17·4[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Inlet gas = [illegible] liter
Outlet gas = [illegible] liter

$1 - k_{r1}$ = [illegible]

(a) − (b) [illegible] ·[illegible] + 2 [illegible] + [illegible]
4·[illegible]

(a) − 2·0[illegible]

(a) + (b) 33·[illegible]

Experimental Data:
[illegible] [illegible] Temp. [illegible]
Pressure [illegible]
[illegible]

4. All the values for different C-fractions, thus obtained, have been divided (due to reasons which will be given later) within the different product-groups, by the [illegible] (x — f), f and g-values (*vide* Tables V, VI and VII). In order to obtain this specific distribution, further evaluations have been carried out.

One [illegible] calculated through example (Rheinpreussen Catalyst) is given in Table I. Table II contains the gas analytical data for the example in Table I. Table III contains the data for the mass distribution of paraffin hydrocarbons of Fe-Catalysts, under this investigation, calculated in the manner shown in Table I. Table IV contains the respective olefine data. The tabulation of oxygenated compounds is omitted as their distribution is not known so well as that of paraffins and olefines.

The Distribution of the Paraffins

In an earlier reference,[1] an equation for the polymerisation of the (CH_2)-radicals into olefines, is given. It is of the following nature, if all the polymerised olefines of different chain-lengths are converted into paraffins:

$$(x - f) = \frac{1}{n_a}(a + b) \tag{1}$$

In this equation $(x - f)$ is the sum of the vapour volumes of all the paraffins, $(a + b)$ is the sum of all the CO-volumes which have been converted into hydrocarbons and n_a is the average chain-length of all the hydrocarbons. A similar function as equation (1) which is valid only for the sum of all the products, must also be valid for each separate fraction. We can write such an equation, by choosing the respective capital letters, for the individual fractions as follows:

$$(X - F)_N = \frac{1}{N}(A + B)_P, \tag{2}$$

and also we can write for the sum of all the separate paraffin fractions as,

$$\sum_{N=1}^{N=m}(X - F)_N = \frac{1}{n}\sum_{N=1}^{N=m}(A + B)_P = (x - f) \tag{3}$$

where N may be any C-number between 1 and m, and n is the average chain-length of all the paraffins. During the common synthesis reactions only a part of the olefines is hydrogenated, and so we can write an equation for the formation of olefines as follows:

$$F_N = \frac{1}{N} \cdot (A + B)_0, \tag{4}$$

and similarly for oxygenated compounds, as

$$G_N = \frac{1}{N} \cdot (A + B)_{A1}. \tag{5}$$

TABLE III

Distribution of Paraffins of Different Iron Catalysts

[Individual $(X-F)_N$- and $(A-B)_r$-values]

C-Nos. N	Kaiser Wilhelm Institut fuer Kohleforschung Muelheim		Rheinpreussen I Homberg		Rheinpreussen II Homberg		I. G. Farbenindustrie, Leuna		Ruhrchemie A. G. Oberhausen		Lurgi Frankfurt Main		Brabag I Berlin		Brabag II Berlin	
	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$	(X − F)	(A + B)$_r$
1	2·285	2·285	2·320	2·320	2·114	2·114	2·378	2·378	2·084	2·084	1·672	1·672	1·085	1·085	0·796	0·796
2	1·224	2·448	1·220	2·440	1·171	2·342	0·667	1·332	0·662	1·324	0·396	0·792	[illegible]	0·615	0·298	0·596
3	0·557	1·771	0·572	1·717	0·524	1·573	0·233	0·700	0·261	0·784	0·223	0·668	0·113	0·340	0·103	0·309
4	0·339	1·358	0·335	1·343	0·365	1·461	0·206	0·821	0·236	0·944	0·165	0·661	0·086	0·343	0·081	0·324
5	0·133	0·666	0·191	0·955	0·199	0·997	0·115	0·574	0·118	0·592	0·115	0·578	0·059	0·296	0·050	0·250
6	0·116	0·693	0·142	0·853	0·139	0·837	0·078	0·467	0·101	0·604	0·085	0·502	0·059	0·298	0·045	0·270
7	0·093	0·654	0·104	0·727	0·114	0·797	0·061	0·429	0·069	0·479	0·050	0·349	0·034	0·238	0·037	0·259
8	0·076	0·608	0·087	0·698	0·084	0·670	0·046	0·365	0·061	0·485	0·042	0·334	0·027	0·220	0·028	0·224
9	0·058	0·525	0·067	0·605	0·061	0·548	0·026	0·232	0·039	0·353	0·019	0·167	0·019	0·173	0·026	0·234
10	0·060	0·600	0·058	0·580	0·062	0·620	0·026	0·260	0·033	0·330	0·019	0·190	0·020	0·200	0·029	0·290
11·5	0·042	0·488	0·039	0·445	0·035	0·402	0·014	0·158	0·027	0·312	0·013	0·155	0·013	0·145	0·011	[illegible]
13·5	0·037	0·495	0·034	0·434	..	..	0·011	0·155	0·019	0·258	0·014	[illegible]	0·011	0·150	0·013	[illegible]
14·5	..	..	..	..	0·031	0·444	..	..	..	..	..	..	..	..	..	..
15·5	0·029	0·448	0·031	0·483	..	..	0·010	0·150	0·014	0·222	0·011	0·168	0·016	0·246	0·013	[illegible]
17·5	0·024	0·423	0·010	0·336	0·016	0·280	[illegible]	0·156	0·014	[illegible]	[illegible]	0·178	0·015	0·270	0·016	[illegible]
19 − 27	0·012	0·271	0·006	0·294	0·009	0·190	0·006	0·139	[illegible]	[illegible]	[illegible]	0·162	0·012	[illegible]	[illegible]	[illegible]
28 – [illegible]	0·008	0·172	0·002	0·084	0·004	0·141	0·003	0·146	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0·247	..	..
[illegible]	[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	
[illegible]	5·3[illegible]		5·4[illegible]		5·2[illegible]		4·071		[illegible]		3·11[illegible]		2·2[illegible]		1·[illegible]	
[illegible]	2·07[illegible]		1·9[illegible]		1·9[illegible]		1·8[illegible]		1·9[illegible]		1·[illegible]		1·9[illegible]		2·2[illegible]	
R	1·8[illegible]		1·922		2·0[illegible]		2·136		1·973		2·1[illegible]		2·0[illegible]		2·1[illegible]	

TABLE IV

Distribution of Olefines of different Iron Catalysts

[Individual (F_N)- and $(A + B)_0$-values]

C-Nos. N	Kaiser Wilhelm Institut fuer Kohleforschung Muelheim		Rheinpreussen I Homberg		Rheinpreussen II Homberg		I. G. Farbenindustrie, Leuna		Ruhrchemie A. G. Oberhausen		Lurgi Frankfurt Main		Brabag I Berlin		Brabag II Berlin	
	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	$(A+B)_0$	(F)	(A+B)
1	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
2	0·146	0·292	0·145	0·291	0·115	0·229	0·457	0·993	0·398	0·797	0·478	0·957	0·345	0·690	0·424	0·848
3	0·659	0·978	0·705	2·112	0·728	2·183	0·817	2·446	0·638	1·914	0·474	1·422	0·445	1·335	0·487	1·461
4	0·352	1·406	0·442	1·769	0·472	1·890	0·392	1·582	0·276	1·104	0·333	1·330	0·334	1·335	0·281	1·124
5	0·244	1·221	0·283	1·416	0·289	1·445	0·272	1·376	0·191	0·955	0·221	1·104	0·165	0·825	0·153	0·765
6	0·151	0·903	0·171	1·023	0·160	0·959	0·155	0·927	0·136	0·818	0·111	0·664	0·137	0·825	0·135	0·810
7	0·092	0·642	0·111	0·774	0·116	0·812	0·112	0·782	0·079	0·554	0·070	0·492	0·094	0·660	0·098	0·686
8	0·061	0·487	0·085	0·681	0·079	0·631	0·082	0·659	0·052	0·420	0·064	0·510	0·057	0·453	0·078	0·624
9	0·041	0·373	0·058	0·523	0·052	0·466	0·047	0·421	0·033	0·293	0·028	0·255	0·056	0·501	0·065	0·585
10	0·029	0·290	0·041	0·410	0·041	0·410	0·049	0·490	0·031	0·310	0·033	0·330	0·058	0·580	0·071	0·710
11·5	0·014	0·169	0·018	0·207	0·019	0·223	0·022	0·261	0·017	0·203	0·023	0·267	0·023	0·360	0·025	0·287
13·5	0·007	0·102	0·008	0·108	..	..	0·016	0·218	0·009	0·129	0·020	0·283	0·030	0·413	0·029	0·330
14·5	..	..	..	..	0·009	0·137	..	..	..	..	..	..	..	..	..	..
15·5	0·004	0·063	0·005	0·079	..	..	0·011	0·147	0·006	0·101	0·013	0·200	0·016	0·257	0·019	0·302
17·5	0·001	0·022	0·002	0·038	0 002	0·039	0·007	0·123	0·004	0·081	0·007	0·124	0·013	0·232	0·013	0·236
19 – 27	0·0003	0·008	0·0007	0·015	0·0005	0·013	0·003	0·065	0·002	0·041	0·003	0·074	0·004	0·105	0·004	0·092
28 + >	0·000	0·000	0·000	0·000	0·000	0·000	0·0002	0·207	0·0003	0·013	0·0006	0·026	0·0004	0·020	0·000	0·000
F	1·832		2·098		2·154		2·532		1·936		1·993		1·933		2·018	

The distribution of the separate volumes (X – F), F and G, for the different N, appears as a hyperbolic function and results in straight lines if represented on log-log diagram. Here, two ways of graphical representation are possible. They are: (1) (X – F) or F may be plotted against N, whereby we obtain straight lines, descending from low C-numbers to high C-numbers. Similarly (A – B) values can be plotted against N. (2) (X – F) or F may be plotted against (A – B) whereby we obtain straight line descending from the right side to the left side, and each C-number, N, forming a 45 -parallel (slope equal to 1) on which lie all the possible values of the same C-number and which therefore represent isometric places for all fractions having the same C-number. These parallels cut the ordinate drawn on the (A – B)-values equal to one, at the values 1/N. This method of representation is preferred to the first as it indicates the conditions more clearly.

In Fig. 1, a typical representation of the individual hydrocarbon volumes against their C-No. is given for the products of the Rheinpreussen Catalyst according to Table I. Curves I and II of Fig. 1 indicate the distribution of the paraffins and olefines respectively, and Curve III indicates the distribution of the sums of the products according to C-No. Further, in Curves IV and V the respective CO-volumes of paraffins and olefines are plotted against N, and in Curve VI the sum of them.

In Fig. 2 the same representation is given against the respective CO-volumes. Further a distribution line, expected theoretically, is also drawn. The points where this line crosses the N-lines indicate the theoretical fraction figures $(X - F)_N$, and from this we can observe the close agreement between the theoretical and experimental values.

If we investigate more thoroughly the distribution of paraffin hydrocarbons, we notice that they follow a definite law of distribution which is indicated by the fact that all the experimental points with the exception of methane lie on a straight line which starts at the value $(x - f)$ in case this value $(x - f)$ is being used completely for methane formation. Then in such a case, the distribution line I would have to shrink on the point $(x - f)$ $(a + b)_2$ and therefore disappear. As the value e for methane formation is mostly less than $(x - f)$, the formation of higher paraffins is possible.

We further find that the slope of the paraffin distribution line is practically equal to 2·0 (*vide* Table I). It can be seen that this slope or exponent is nearly the same for all iron catalysts under investigation (*vide* Table III). We will call these values as Q and R, and they will be the average values arrived from all different points. This observation is of fundamental importance as it indicates the existence of a general mechanism of the formation of the products. The catalysts with low $(x - f)$-values are observed to deviate towards smaller slope values, theoretically on the lower product side. On the higher product side however, deviations towards higher slope values are found. But here also, the average

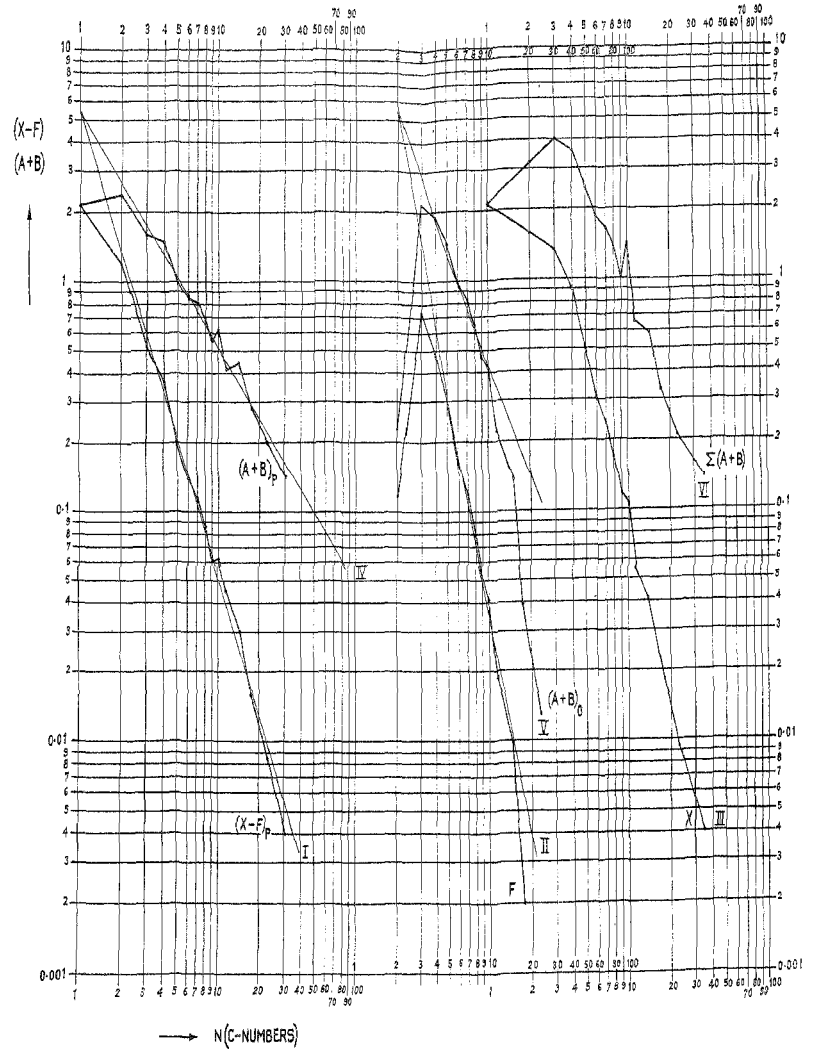


FIG. 1. DISTRIBUTION OF VOLUMES OF PARAFFINS, OLEFINES AND SUM OF ALL THE PRODUCTS INCLUDING OXYGENATED COMPOUNDS ACCORDING TO C-NO. (N), (IRON CATALYST OF MESSRS. RHEINPREUSSEN A.G. HOMBERG).

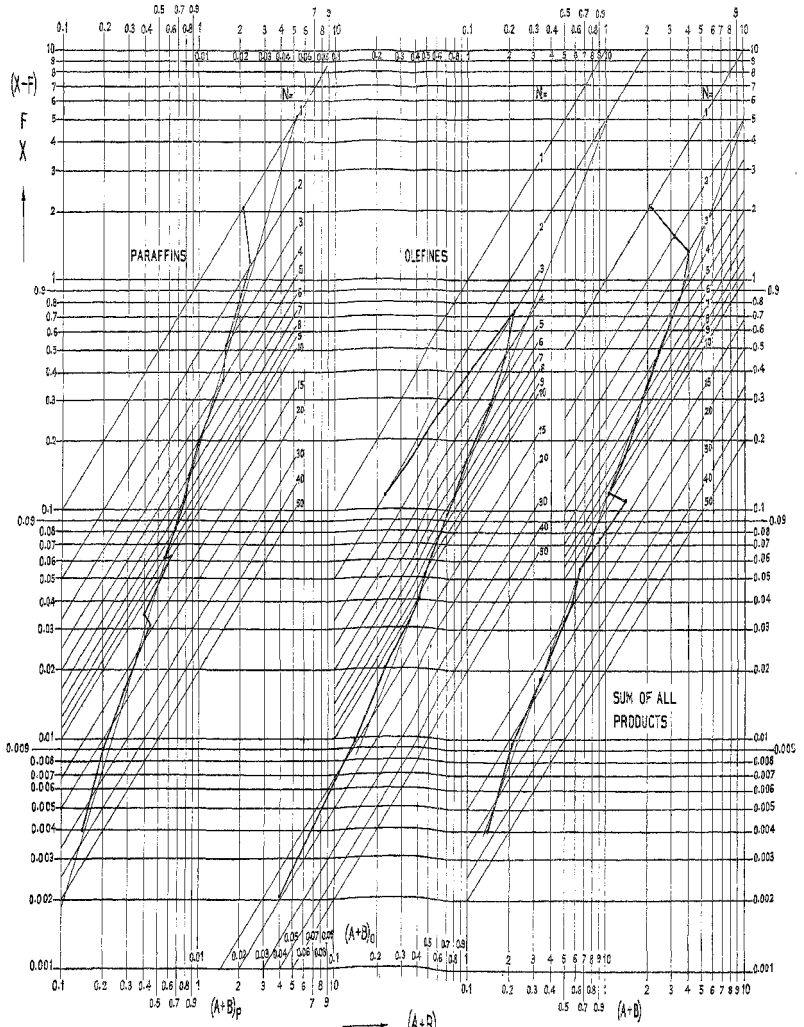


FIG. 2. DISTRIBUTION OF VOLUMES OF PARAFFINS, OLEFINES AND SUM OF ALL PRODUCTS INCLUDING OXYGENATED COMPOUNDS IN RELATION TO CO VOLUMES (A+B) (IRON CATALYST OF MESSRS. RHEINPREUSSEN A.G. HOMBERG, 1943/44).

value of slope remains nearly 2·0 and is especially maintained within medium N-range. The distribution of paraffin hydrocarbons, with the exception of the starting number methane, for the iron catalysts under investigation, therefore follows a simple quadratic function over the C-number area, which can be written as follows:

$$(X - F)_N = \frac{1}{N^2}(x - f). \tag{6}$$

If we substitute the value for $(X - F)_N$ from equation (2) in equation (6), we obtain

$$(A + B)_P = \frac{1}{N} \cdot (x - f). \tag{7}$$

This is a still simpler function which connects the amount of CO used for different paraffin fractions, with the hydrogenation hydrogen values. This equation is also satisfied by the experimental data (*vide* Fig. 1 Curve IV).

If these distribution functions are written logarithmically we get a better graphical representation. For equation (6) we can write,

$$\log (X - F)_N = \log (x - f) - 2 \log N \tag{6 a}$$

and for equation (7)

$$\log (A + B)_P = \log (x - f) - \log N. \tag{7 a}$$

Finally, for the exponent 2·0 in equation (6) we can introduce the more general term Q so that it can be applied for all the general cases and we get

$$\log (X - F)_N = \log (x - f) - Q \log N. \tag{8}$$

From equation (7) it can be observed that for each C-fraction of the paraffin series, part of the converted CO used for its formation is equal to N-th part of the hydrogenation hydrogen $(x - f)$. This means that the probability of the formation of higher hydrocarbons decreases with the increase in chain-length in logarithmic proportion. The distribution function therefore, represents itself as a rather simple function, wherein the $(x - f)$-value decides only the absolute height of the paraffin formation, while the distribution itself is more or less fixed and is the same for all the different iron catalysts under investigation.

The relations developed so far describe the representation of $(X - F)$ against N; the representation $(X - F)$ against $(A + B)_P$, then follows the following function:

$$\log (X - F)_N = 2 \log (A + B)_P - \log (x - f). \tag{9}$$

This equation is obtained by substituting the value of N from equation (2) in equation (6 *a*). Equation (9) can also be written as

$$\log (X \quad F)_N \quad \log \left({}_{(x} {}^{1} {}_{f)} \right) \quad 2 \log (A \quad B)_p \qquad (9\,a)$$

or more generally as,

$$\log (X \quad F)_N \quad \log \left({}_{(x} {}^{1} {}_{f)} \right) \quad R \log (A \quad B)_p \qquad (10)$$

where R is the slope constant, which is equal to 2·0 in this case. Values for Q and R according to equations (8) and (10) have been calculated for the distribution of paraffins of Fe-catalysts as average values of all the [illegible] points and are given in Table III. From this table we can observe that for [illegible] with $(x - f)$-values of about 5·0 these values of Q and R are close to 2·0, but for the catalysts with lower $(x - f)$ they are not so close to 2·0. In Table I, the values of Q and R, calculated for each separate paraffin fraction are given, and we find that with the natural exception of methane they are quite close to 2·0.

If these distribution laws are assumed to be followed by each type of catalyst, it then becomes very easy to calculate the distribution of the [illegible] with the aid of equation (6 *a*), as $(x - f)$-values can be easily obtained from normal gas analytical control, and it would no more be [illegible] to carry out rather complicated product analyses.

Equation (8) describes the statistical distribution of the [illegible] the sum of which can be expressed by the form of a series. The constancy of the slopes (Q or R) of the distribution curves, found in all the cases, indicates the existence of a unique mechanism of the formation of the hydrocarbons according to it, during the polymerisation and subsequent hydrogenation, for the function of a product of a certain C-Number always double as many CH_2 molecules or CH_2 molecules are required as will form simultaneously into the respective product with double the C-Number. For instance, 8 CH_2 radicals polymerise into 4 C_2H_4-molecules, which are then hydrogenated, while [illegible] only 4 (CH_2)-radicals combine to form 1 C_3H_8 molecule and so on. It means that 4 C_2H_4-molecules are hydrogenated, while simultaneously only 1 molecule of C_2H_8 is being hydrogenated. The sum of all the paraffin-volumes can be expressed as a series which is known as Riemann's Zeta functions, and it can be written according to equations (3) and (6) as follows:

$$\sum_{N=1}^{N=m} (X - F)_N = e + \frac{x - f}{2^2} + \frac{x - f}{3^2} + \frac{x - f}{4^2} + \ldots + \frac{x - f}{m^2}$$

$$(x - f), \quad (11)$$

or

$$\sum_{N=1}^{N=m} (X - F)_N = (x - f) \left[\xi + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \ldots + \frac{1}{m^2} \right] + (x - f) \times 1 \quad (12)$$

wherein the value e (in bracket of equation 11) for absolute methane formation is multiplied by $(x-f)/(x-f)$, and the term for the relative methane formation is introduced in equation (11) which is

$$\xi = \frac{e}{x-f}. \tag{13}$$

Thus we obtain equation (12) which gives the distribution independent of the changing absolute values of $(x-f)$. According to equation (3) $\Sigma(\mathrm{X}-\mathrm{F})_{\mathrm{N}}$ is identical with $(x-f)$, and thus the sum of all the terms within the bracket of equation (12) can then only become equal to 1. Therefore,

$$\left[\xi + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \ldots + \frac{1}{m^2}\right] = 1. \tag{14}$$

From this condition, we can now get a complete survey of built-up principles for the paraffins and simultaneously for all the other products.

If the first term ξ of the series given in equation (14) is equal to 1, the bracket expression converges for $m = \infty$ towards the value $\pi^2/6 = 1{\cdot}643$. The expression in bracket without the first term 1, consequently becomes,

$$\left[\frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \ldots + \frac{1}{m^2}\right] = 1{\cdot}643 - 1 = 0{\cdot}643. \tag{15}$$

This means that according to equation (14) the value for ξ must have lower as well as upper limits and that methane formation can never become zero or it can never exceed $(x-f)$. According to equation (1 and 15),

$$\left[\frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \ldots + \frac{1}{m^2}\right] = 1 - \xi = 0{\cdot}643 \tag{16}$$

and

$$\xi = 1 - 0{\cdot}643 = 0{\cdot}357 \text{ (for } m = \infty). \tag{17}$$

The relative methane formation, therefore, can never be smaller than 0·357 for which condition m becomes ∞, which means that the polymerisation should continue to indefinitely long-chained compounds. But for most of the catalysts, the polymerisation reaches only upto the chain-length of 60–100 or less, and so the effective relative methane formation should be always somewhat higher than 0·357. On the other hand for $\xi = 1$, the bracket expression in equation (16) must become zero, *i.e.*, only methane is being formed and no more any other paraffins. With increasing ξ-values, between 0·357 and 1·0, the terms in equation (16) starting from higher molecular side, must consequently disappear. It is quite interesting to state that the minimum value of the relative methane formation is just somewhat higher than $\frac{1}{3}$ of $(x-f)$-value, as already indicated earlier, and therefore nearly equal to the b_{H}-value.[1] The distribution values of the paraffins calculated on

$(x - f)$ — I, according to equation (12) for Fe-catalysts are given in Table IV and have been obtained by dividing each individual $(N \cdot P)_x$-value by the respective $(x - f)$ value belonging to the series. The [illegible] of these values against N is given in Fig. 3.

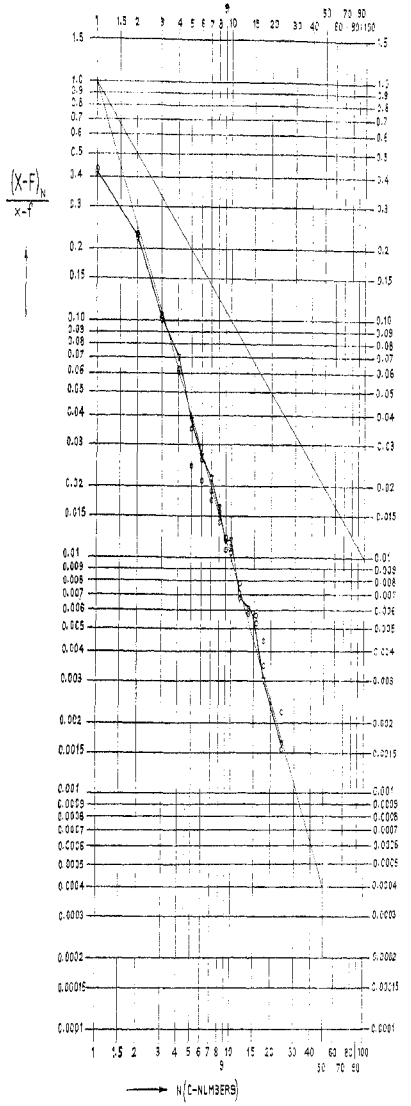
When we examine our examples of their relative methane formation, we notice that all ξ-values are higher than 0·357. Besides this, different other deviations of the exact following of the distribution law can also be noticed. For instance, on the low molecular side, the experimental values are mostly somewhat lower than the theoretical ones, which is found mostly for the catalysts with low $(x - f)$-values. On the other hand higher values are found on the high molecular side. This has been already stated. The probable explanations for such deviations may be as follows:—

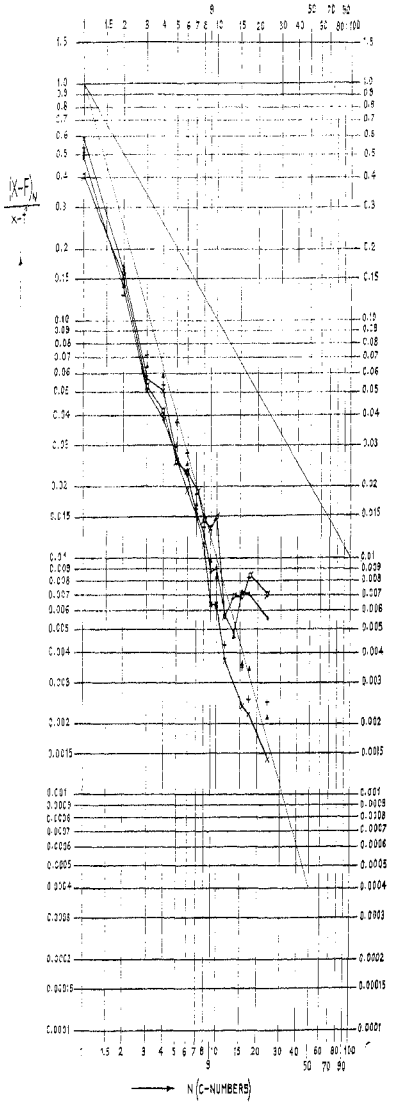
1. The catalysts may preferably form higher [illegible] thus saving hydrogenation hydrogen on the highly hydrogen consuming lower molecular side.

2. It may be that the surplus of the products on high boiling side (which can be observed with Brabag Catalyst) is due to alkylation reactions. It is more so in this case, as due to low hydrogenation activity, a higher [illegible] of olefines remains, so that alkylation reactions should occur more easily. This explanation would account for lower paraffin values on the low molecular side which might have been transferred to the higher side due to alkylation, where they can again appear as paraffins. Such side reactions can widely alter the original build-up.

3. Further, the slight differences on the light molecular side can be accounted by oxygenated compounds. If H_2O is partly substituted for [illegible] hydrogen, substantial amounts of oxygenated compounds appear in the products with catalysts having lower $(x - f)$-values. In our examples the sum of the volumes of all the oxygenated compounds accounts for the missing volume between the theoretical and experimental values. With the data available, however, it is not yet possible to decide which of these different assumptions given, is the most probable.

From our derivations, it can also be observed that the absolute value of $(x - f)$ for practically constant fundamental distribution (Q or R — 2) fixes the amounts of paraffins and olefines in the total products. This is strictly valid for the same relative methane formation, which means that for equal and constant ξ-values, the further influential factor on the subdivision into paraffins and olefines is then the ξ-value itself. This value decides the average chain-length of the paraffins. For every constant ξ-value, there must exist an optimum $(x - f)$-value, for which all the products must appear as paraffins. For m — 50, this optimum value of $(x - f)$ is found to be 7·77 and for m — 100, 6·83, and it changes between 6·5 and 8·0 according to polymerisation activity and the height of ξ-value. At a fixed $(x - f)$-value, with increasing ξ-value (the highest possible being 1·0), the relative methane formation increases and reaches its maximum, while simultaneously the possible olefine formation also reaches its maximum. This is due to the fact


$\frac{(X-F)_N}{X-F}$
N (C-NUMBERS)


$\frac{(X-F)_N}{X-F}$
N (C-NUMBERS)

that all the converted CO-volumes in excess to methane formation, must then appear as olefines. If $(x-f)$ and ξ increase simultaneously, the synthesis reaction finally ends into an exceptional total methane formation.

Below the optimum value of $(x-f)$ for complete hydrogenation, more and more olefines must appear in the products, as on one side hydrogenation hydrogen is no more sufficient for complete hydrogenation and on the other side polymerisation activity of most of the catalysts is limited and does not much extend beyond C-60 products. Therefore, an increasing amount of the polymerisation olefines remains unaltered. While in the first case, more medium and light olefines are formed, in the latter case more high molecular olefines are obtained. The increase in the quantities of olefines, and the chance for secondary reactions like alkylation, polymerisation, isomerisation and hydration is favoured due to the catalysts being able to activate such reactions. It is quite probable that these conclusions drawn for iron catalysts only may be valid for other catalysts also.

In an analogous way as used for $(X-F)_N$, the sum of all $(A+B)_P$ from equation (3) can be represented as a series:

$$\sum_{N=1}^{N=m}(A+B)_P=\sum_{N=1}^{N=m}N\cdot(X-F)_N=(x-f)\cdot\sum_{N=1}^{N=m}1=(a+b)_P \qquad (18)$$

and

$$\sum_{N=1}^{N=m}(A+B)_P=e+\frac{x-f}{2}+\frac{x-f}{3}+\frac{x-f}{4}+\ldots+\frac{x-f}{m}=(a+b)_P,$$

or in general,

$$\sum_{N=1}^{N=m}(A+B)_P=(x-f)\left[\xi+\tfrac{1}{2}+\tfrac{1}{3}+\tfrac{1}{4}+\ldots+\frac{1}{m}\right]=(a+b)_P, \qquad (19)$$

and further

$$\left[\xi+\tfrac{1}{2}+\tfrac{1}{3}+\tfrac{1}{4}+\ldots+\frac{1}{m}\right]=\frac{(a+b)_P}{(x-f)}=p. \qquad (20)$$

The series in equations (19) and (20) is a diverging one. The development of this series for different N-values is therefore better expressed by tabulation. From this table an average chain-length, p, of the paraffin hydrocarbons in each case can be found, and we find that each hydrocarbon contributes to this average chain-length by the factor $1/N$. $(a+b)_P$, the CO-amount converted into paraffins, can be calculated according to equation (20), with the help of $(x-f)$ and ξ-values (obtained from C-balance) for each chosen paraffin hydrocarbon of the highest chain-length. By doing so, simultaneously we obtain the part of CO, served for olefine formation.

The highest N-value equal to m can be calculated by equation (12) for each normal synthesis case and this value of m can be used for the proper calculation of $(a + b)_p$ and p by equation (20). It is not possible to calculate these values, where alkylation and other side reactions are taking place. As the olefine content on high molecular side is negligibly small, we can thus obtain simultaneously by these calculations the highest hydrocarbon, produced by the catalyst (assuming that no side reactions occur).

IV. The Distribution of the Olefines

According to the scheme of the product built-up, followed so far, the polymerisation of (CH_2)-radicals should occur to obtain the olefines. This polymerisation which results in the built-up of hydrocarbons of different chain-lengths obviously follows a statistical principle. For the consecutive hydrogenation of a part or all of the olefines, such statistical distribution is rather simple, as we have already explained. It now remains to prove whether similar laws are valid for the remaining or original olefines.

In order to find this out, it appears reasonable to apply the same principles for olefines, which were quite successful for the paraffins. The olefine distribution in absolute quantities is already given in Tables I and IV and is graphically shown in Figs. 1 and 2. In Table VII, the relative olefine distribution figures F_N/f for the iron catalysts are given, similarly to the paraffin distribution values, in Table V. The graphical representation of F_N/f is given in Fig. 4. From this we can say as a first approximation that the absolute olefine distribution except the first olefine and the higher-most molecules, present only in negligible quantities, follows a similar statistical distribution law with different constants. For the olefine distribution we can write:

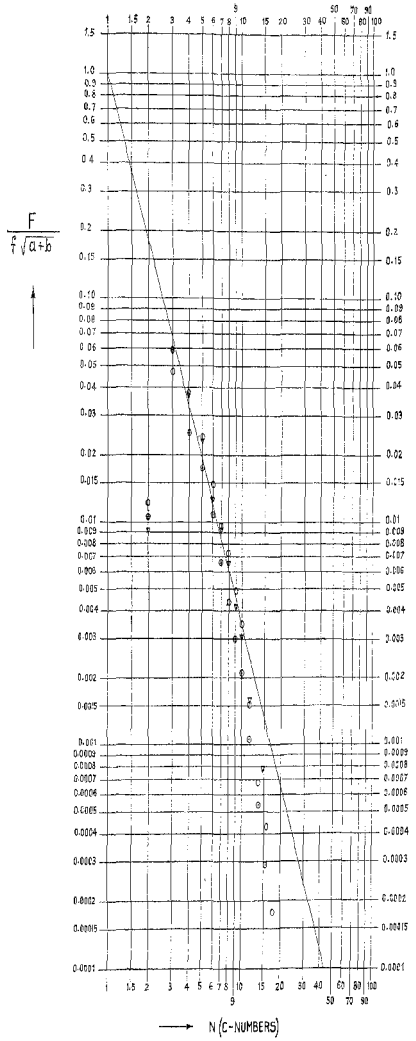
$$\log\left[\frac{F_N}{f}\right] \quad \log \sqrt{(a + b)} \quad S \log N \tag{21}$$

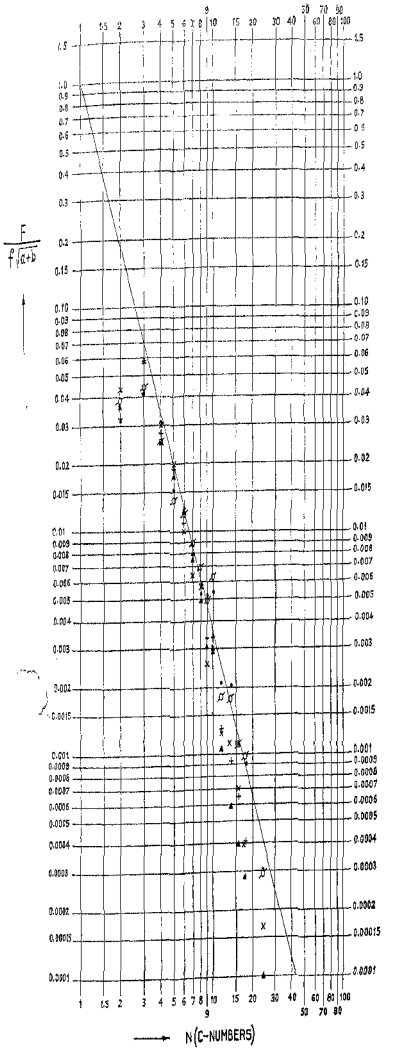
where $\sqrt{(a + b)}$ is a constant for each catalyst and S is the exponent, or slope of the curve, which is approximately equal to 2·5, but which changes from catalyst to catalyst, due to slight changes in $(a + b)$, and thus it must be calculated separately for each catalyst. The step from one C-number to the next higher one is much steeper. f is the sum of all olefine volumes, which can be expressed similar to the respective value of paraffins according to equation (12), as:

$$\sum_{N=1}^{N=m} F_N = f\sqrt{(a + b)}\left[\frac{\nu}{2^s} + \frac{1}{3^s} + \frac{1}{4^s} + \ldots + \frac{1}{m^s}\right] = f.1 \tag{22}$$

Here, the expression for the series in the bracket multiplied with the constant can again become only equal to 1·0 and also

$$\nu = \frac{h}{f}, \tag{23}$$





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○ RPR I × LURGI
▽ RPR II ● BRABAG I
+ I.G.F. ⌀ BRABAG II

FIG. 4. DISTRIBUTION OF OLEFINES IN RELATION TO $f\sqrt{a+b}=1$, ACCORDING TO C-NOS.

TABLE V

Distribution of the Paraffins of Iron Catalysts in relation to $(x - f) = 1$

C Nos. N	$1/N^2$ $(x-f)=1$ (theor.)	K.W.I. 5·394	R.P.R. I 5·456	R.P.R. II 5·229	I.G.F. 4·071	R. Ch. 4·024	Lurgi 3·112	Brabag I 2·237	Brabag II 1·983
1	0·3567	0·4236	0·4252	0·4043	0·5842	0·5179	0·5373	0·4850	0·4014
2	0·2500	0·2269	0·2236	0·2239	0·1639	0·1645	0·1272	0·1381	0·1503
3	0·1111	0·1032	0·1048	0·1002	0·0572	0·0649	0·0717	0·0506	0·0519
4	0·0625	0·0629	0·0614	0·0698	0·0506	0·0587	0·0530	0·0384	0·0409
5	0·0400	0·0247	0·0350	0·0381	0·0283	0·0293	0·0369	0·0264	0·0252
6	0·0278	0·0214	0·0261	0·0266	0·0192	0·0251	0·0276	0·0224	0·0227
7	0·0204	0·0173	0·0191	0·0218	0·0150	0·0171	0·0161	0·0152	0·0187
8	0·0156	0·0143	0·0159	0·0161	0·0113	0·0152	0·0135	0·0121	0·0141
9	0·0124	0·0108	0·0123	0·0117	0·0064	0·0097	0·0061	0·0085	0·0131
10	0·0100	0·0111	0·0106	0·0119	0·0064	0·0082	0·0062	0·0089	0·0146
11·5	0·0076	0·0078	0·0071	0·0067	0·0034	0·0067	0·0042	0·0058	0·0055
13·5	0·0055	0·0068	0·0062	..	0·0027	0·0047	0·0045	0·0049	0·0066
14·5	0·0048	..	..	0·0059	..	..	..	..	..
15·5	0·0042	0·0054	0·0057	..	0·0025	0·0035	0·0035	0·0072	0·0066
17·5	0·0033	0·0045	0·0035	0·0031	0·0022	0·0035	0·0026	0·0067	0·0081
24+>	0·0017	0·0023	0·0015	0·0017	0·0015	0·0020	0·0026	0·0054	0·0066
m	..	0·0009	0·0004	0·0008	0·0007	0·0010	0·0013	0·0022	..

TABLE VI

Distribution of the CO-volumes, $(A - B)_p$, required for the Paraffins in relation to $(x - f) = 1$

C Nos. N	$1/N^3$ $(x-f)=1$ (theor.)	K.W.I. 5·394	R.P.R. I 5·456	R.P.R II 5·229	I.G.F. 4·071	R. Ch. 4·024	Lurgi 3·112	Brabag I 2·237	Brabag II 1·983
1	0·3567	0·4236	0·4252	0·4043	0·5842	0·5179	0·5373	0·4850	0·4014
2	0·5000	0·4538	0·4472	0·4490	0·3278	0·3290	0·2544	0·2762	0·3006
3	0·3333	0·3096	0·3144	0·3012	0·1716	0·1947	0·2151	0·1518	0·1557
4	0·2500	0·2516	0·2456	0·2800	0·2024	0·2348	0·2120	0·1436	0·1636
5	0·2000	0·1235	0·1750	0·1905	0·1415	0·1465	0·1845	0·1320	0·1260
6	0·1668	0·1284	0·1566	0·1596	0·1152	0·1506	0·1656	0·1344	0·1362
7	0·1428	0·1211	0·1337	0·1533	0·1050	0·1197	0·1121	0·1064	0·1309
8	0·1248	0·1144	0·1272	0·1288	0·0904	0·1216	0·1080	0·0968	0·1128
9	0·1116	0·0972	0·1107	0·1053	0·0576	0·0873	0·0549	0·0765	0·1179
10	0·1000	0·1110	0·1060	0·1190	0·0640	0·0820	0·0610	0·0890	0·1460
11·5	0·0874	0·0897	0·0816	0·0770	0·0391	0·0771	0·0483	0·0667	0·0633
13·5	0·0742	0·0918	0·0837	..	0·0365	0·0635	0·0608	0·0661	0·0891
14·5	0·0696	..	..	0·0856	..	..	..	..	..
15·5	0·0651	0·0837	0·0884	..	0·0388	0·0542	0·0542	0·1116	0·1023
17·5	0·0577	0·0787	0·0613	0·0543	0·0385	0·0612	0·0455	0·1173	0·1417
24	0·0408	0·0552	0·0360	0·0408	0·0360	0·0480	0·0624	0·1296	0·1584

TABLE VII

Distribution of the Olefines in relation to $f = 1$

C Nos. N	F_N/f	K.W.I.	R.P.R. I	R.P.R. II	I.G.F.	R. Ch.	Lurgi	Brabag I	Brabag II
f	5·7750	1·8320	2·0980	2·1540	2·5320	1·9360	1·9930	1·9330	2·0180
$f \times \sqrt{a+b}$	1·0000	0·0797	0·0691	0·0534	0·1805	0·2056	0·2398	0·1784	0·2101
ν/N^a	0·1800	0·0143	0·0123	0·0093	0·0325	0·0371	0·0440	0·0320	0·0380
1	5·7750	..	..	..	..	..	..	..	..
2	1·0000	0·0797	0·0691	0·0534	0·1805	0·2056	0·2398	0·1784	0·2101
3	0·3670	0·3597	0·3360	0·3380	0·3227	0·3295	0·2378	0·2302	0·2414
4	0·1800	0·1921	0·2107	0·2191	0·1548	0·1426	0·1671	0·1828	0·1392
5	0·1030	0·1332	0·1349	0·1342	0·1074	0·0986	0·1109	0·0854	0·0758
6	0·0653	0·0824	0·0815	0·0743	0·0612	0·0702	0·0557	0·0709	0·0669
7	0·0447	0·0502	0·0529	0·0539	0·0442	0·0408	0·0351	0·0486	0·0484
8	0·0315	0·0333	0·0405	0·0367	0·0324	0·0269	0·0321	0·0295	0·0387
9	0·0243	0·0224	0·0276	0·0241	0·0186	0·0170	0·0140	0·0290	0·0322
10	0·0184	0·0158	0·0195	0·0190	0·0193	0·0160	0·0166	0·0300	0·0352
11·5	0·0134	0·0152	0·0172	0·0176	0·0174	0·0176	0·0230	0·0238	0·0248
13·5	0·0090	0·0076	0·0076	..	0·0126	0·0092	0·0200	0·0310	0·0288
14·5	0·0076	0·	..	0·0084	..	..	..	..	..
15·5	0·0064	0·0044	0·0048	..	0·0086	0·0062	0·0130	0·0166	0·0198
17·5	0·0048	0·0010	0·0018	0·0018	0·0056	0·0040	0·0070	0·0134	0·0128
$(a+b)$	33·333	31·535	31·515	31·582	31·976	31·992	32·295	32·588	32·670
$\sqrt{a+b}$	5·77	5·625	5·62	5·62	5·65	5·66	5·68	5·71	5·72
S	..	2·449	2·388	2·431	2·529	2·559	2·600	2·521	2·528

TABLE VIII

Distribution of the Olefines in relation to $f \times \sqrt{a - b - 1}$

C Nos.	$\frac{1}{N^2\sqrt{33 \cdot 33}}$	K.W. I	R.P.R. I	R.P.R. II	I.G.F.	R. Ch.	Lurgi	Brabag I	Brabag II
f	5·7750	1·8320	2·0980	2·1540	2·5320	1·9360	1·9930	1·9330	2·0180
1	1·0000	..	..	..	..	..	..	..	..
2	0·1731	0·0142	0·0123	0·0095	0·0319	0·0363	0·0422	0·0312	0·0367
3	0·0635	0·0640	0·0598	0·0601	0·0571	0·0582	0·0419	0·0403	0·0422
4	0·0312	0·0342	0·0375	0·0390	0·0274	0·0252	0·0294	0·0320	0·0243
5	0·0178	0·0257	0·0240	0·0239	0·0190	0·0174	0·0195	0·0149	0·0133
6	0·0113	0·0146	0·0145	0·0132	0·0108	0·0124	0·0098	0·0124	0·0117
7	0·0077	0·0089	0·0094	0·0096	0·0078	0·0072	0·0062	0·0085	0·0085
8	0·0055	0·0059	0·0072	0·0065	0·0057	0·0048	0·0057	0·0052	0·0068
9	0·0042	0·0040	0·0049	0·0043	0·0033	0·0030	0·0025	0·0051	0·0056
10	0·0032	0·0028	0·0035	0·0034	0·0034	0·0028	0·0029	0·0053	0·0062
11·5	0·0022	0·0028	0·0030	0·0032	0·0032	0·0032	0·0040	0·0042	0·0044
13·5	0·0016	0·0014	0·0014	..	0·0022	0·0016	0·0036	0·0054	0·0050
14 5	0·0014	..	..	0·0014	..	..	..	..	..
15·5	0·0012	0·0008	0·0008	..	0·0014	0·0012	0·0024	0·0030	0·0032
17·5	0·0008	0·0002	0·0004	0·0004	0·0010	0·0008	0·0012	0·0024	0·0022

where h is the ethylene volume. Again for $\nu = 1$, olefines, higher than ethylene cannot be formed, while for $\nu = 0$ the polymerisation will go more to higher olefines. One can see from the distribution curves that at lower values of ν, the formation of lower olefines is more favoured than for higher values of ν; compare the left and right sides of Fig. 4. For catalysts plotted on the right side of Fig. 4 due to lower $(x - f)$-values, also absolutely more olefines are formed than the catalysts plotted on the left. The slope of the distribution curve is however, practically the same for both the groups.

The higher steepness of the decrease in the olefine distribution, indicated by the exponent S (equal to approximately 2·5), shows that the polymerisation distribution decrease is quicker than the hydrogenation, which is more active on high molecular side, while the olefines get generally enriched on the low molecular side. This enrichment of the olefines on the lighter side is due to the higher slope of the olefine distribution curve and due to the fixed but less steep paraffin distribution. It is rather remarkable, that for all these iron catalysts, prepared by different firms, the olefine distribution is principally very uniform, and it is also remarkable that the results are different only with regard to their absolute values, which depend on different f-values only. Similar to methane formation in the paraffin distribution, ethylene-formation does not follow the hyperbolic function.

The constant $\sqrt{a + b}$ should be of some significance in the formation of olefines. According to our equation, this constant represents the first term of the series, for N = 1, and therefore would be identical with the volume value of (CH_2)-radicals or any other intermediate products, if the latter would be more stable. However, this value is purely hypothetical, as the radicals or the respective intermediates polymerise almost immediately after their formation and disappear. Their concentration is therefore practically nil. From this representation, it can be concluded that the polymerisation which leads to the distribution of the olefines and further of the paraffins, must be predominantly radical polymerisation. As also the ethylene values are found lower than the theoretical values, it can be assumed that an ethylene-polymerisation also takes place to a smaller extent. Such an ethylene-polymerisation must prevail more in case of catalysts with higher $(x - f)$-values, than those with lower $(x - f)$-values, because in the latter cases ethylene values are found to be higher.

The higher order of the olefine distribution and therefore their more rapid decrease towards higher olefines is possibly a consequence of lower degree of hydrogenation, which tends to more complete hydrogenation in the high molecular region and less in the low molecular range.

After elimination of the constants $\sqrt{a + b}$, olefine distribution can be directly compared with paraffin distribution (*vide* Fig. 5). The series of equation (22) is of the converging type and for $m = \infty$, appr. $1 \cdot 341$ is the total value.[4] As the sum of the series cannot be higher than $1/\sqrt{a + b}$, this means that the first term of the series, the radical concentration, already omitted in our equation,

must become zero, and it also requires that the second term, representing ethylene formation, must remain much smaller, if at all higher olefines should form. These conditions are in fact found to be true for all the catalysts under investigation.

By using equations (22) and (23), and with the knowledge of ethylene formation (h), the value for (f) can be found directly, for which no method was known so far. With the knowledge of (f), it is further possible to calculate directly the CO-volume, which has been converted into olefines and which was already obtained from equations (18) and (19) as a differential value. The equations, necessary for such calculations, are as follows:—

$$\sum_{N=1}^{N=\infty}(A+B)_0 \quad \sqrt{a+b}\times f\times\left[\frac{\nu\times 2}{2^a}+\frac{3}{3^a}+\frac{4}{4^a}+\ldots+\frac{m}{m^a}\right]$$

$$\sqrt{a+b}\times f_{\max}\cdot[\nu\cdot 2^{(1-a)}+3^{(1-a)}+4^{(1-a)}+\ldots+m^{(1-a)}]$$

$$=(a+b)_0. \qquad (24)$$

The estimation of (h) from gas analysis, by using C-balance is quite simple. It is necessary only to carry out a fractional absorption of ethylene in the olefine fraction. By calculating (f) and $(a+b)_0$ we can also obtain 'q', the average chain-length of the olefines. The values of $(a+b)_0$, according to equation (19) as a differential value, and according to equation (24) as a direct value, can be compared with each other. The former value always includes the CO-volume which has served for the production of oxygenated compounds, and thus is usually found somewhat higher than the latter value. The difference between the two values may then give the CO-part $(a+b)_{A1}$, which has been converted into oxygenated compounds. With this, the calculations of the product distribution according to C-number fractions is complete. The calculation for the distribution of oxygenated compounds cannot yet be made, as the data at our disposal are considered to be not quite sufficient.

The meaning of $\sqrt{a+b}$-value for radical—or its equivalent—formation will become more clear by the following discussion. If the series in equation (24) becomes equal to 1, which is always the case when all the terms other than the first term become equal to zero, then we can write:

$$\sqrt{a+b}\times f_{\max.}=(a+b). \qquad (25)$$

For this condition only radicals would be formed and could be assumed to remain stable also. In this case (f) will have maximum value, indicated by $f_{\max.}$ In such circumstances, no hydrogenation hydrogen will be activated, and then $(a+b)$ would become 33·333.. and $f_{\max.}$ will become equal to $\sqrt{33\cdot33}$, *i.e.*, = 5·774. This means, that the intermediate compounds in question can be assumed as consisting of agglomerates on the catalyst surface, made up out of 5 or 6 carbon atoms.

Though this statement can only be made as an assumption and needs further investigations, it is interesting to note that other authors have recently confirmed the existence of iron-carbonyls on the surface of the iron catalysts and even in the exit gas which consist of $Fe(CO)_5$ and of $FeH_2(CO)_4$.

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