Physico-Chemical Investigations on Catalytic Mechanism (X). On the Reaction Products in the Fischer-Tropsch Synthesis. Experimental Series II (6).

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Introduction. We have been publishing a series of papers[1] on the Fischer-Tropsch synthesis. As regards the nature of the reaction products, we have so far proceeded to determine the physico-chemical properties of the products collected in two fractions, one of which was condensed by air and water cooling and the other was condensed by the solid CO_2–C_2H_5OH mixture. Thus such properties as refractive index, specific gravity, apparent molecular weight, elementary analysis, have been obtained for these two fractions as well as the boiling point analysis by the Podbiliniak Distillation Apparatus and by a specially designed small-scale distillation apparatus, as the case may be, depending on the amount of the sample available. Some of these results have been reported in our earlier papers. Here, in this paper, we shall try to summarize some of our eariler results briefly so as to give us a more definite knowledge with regard to the nature of the reaction products as well as the relative amounts of various hydrocarbons possibly present.

Experimental Results. The results of the boiling point analysis are given for the products of the series of experiments F_{40}–F_{52}. First trap oil and second trap oil have been separately subjected to the boiling point analysis by using a specially designed small-scale distillation apparatus, and the relative amounts of possibly present hydrocarbons are graphically presented in the volume percent (Figs. 1–4). As seen in these graphs, the relative constituents in each of lighter and heavier fraction are definitely distinguishable. The lighter fraction seems to contain mainly C_6–C_9, while in the heavier fraction, predominantly C_9C_{13} are found. However, we must remember that these fractions, of course, cannot be sharply defined, but more or less they are overlapping. If the amount of a sample is sufficient, each fraction may be possibly separated and preferably subjected to more definite determinations of each physico-chemical property. At this stage we must be satisfied if we can estimate the relative magnitude of each constituent. As we have published already the data of the Podbiliniak distillation[2], correlating with these we can visualize at least what

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The most of the results given in this paper was obtained and completed in 1939–1940, but the publcation of them had been withheld.

(1) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, this Bulletin, **17** (1942), 166–171.
S. Hamai, S. Hayashi and K. Shimamura. this Bulletin, **17**(1942), 252–259.
S. Hamai, *J. Chem. Soc. Japan*, **63**(1942), 1606–1615.
S. Hamai, S. Hayashi and K. Shimamura, this Bulletin, **17**(1942), 463–477.

(2) S. Hamai, *J. Chem. Soc. Japan*, **63**(1942), 1606–1615.

fractions usually predominate in these synthesis reactions under such conditions. Table 1 shows refractive index, apparent molecular weight, specific gravity and elementary analysis for the first trap oil and second trap oil.

The most of these results need not be discussed, for they are self-explanatory in themselves as shown respectively in the diagrams and the table. However, it should be remembered that as seen in Figs. 3 and 4, the first trap oil contains C_{12}–C_{13} predominantly as compared with C_8–C_{11} fractions, while the second trap oil contains C_7–C_9 predominantly as compared with the other fractions.

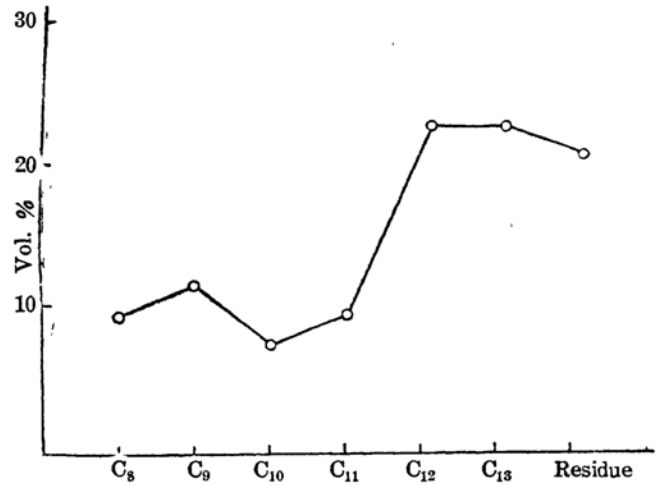

Fig. 1. Vol. % of Each Constituent.
(For 1st trap oil.)
($F_{46, 47, 49, 50, 52}$ Distillation.)

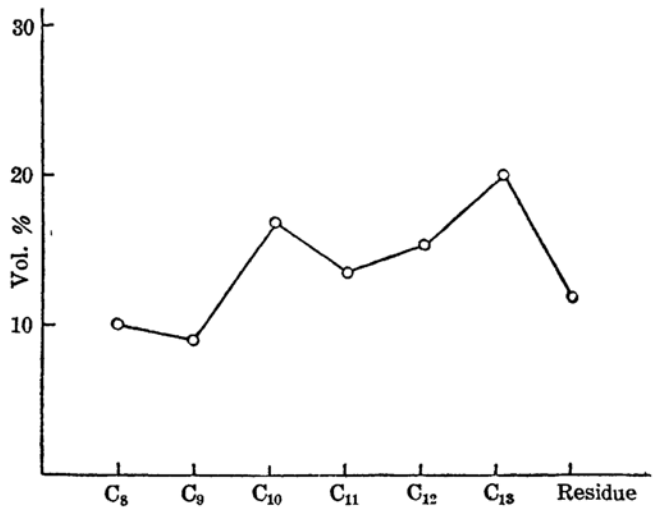

Fig. 2. Vol. % of Each Constituent.
(For 1st trap oil.)
($F_{40, 41, 42, 43, 45, 46}$ Distillation.)

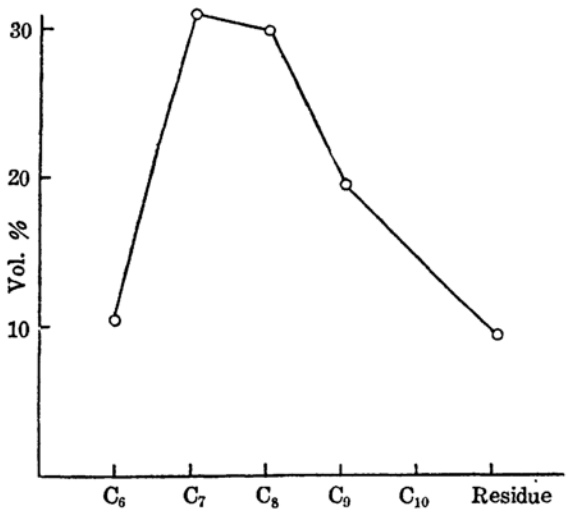

Fig. 3. Vol. % of Each Constituent.
(For 2nd trap oil.)
($F_{42, 43, 45, 46, 48, 50, 52}$ Distillation.)

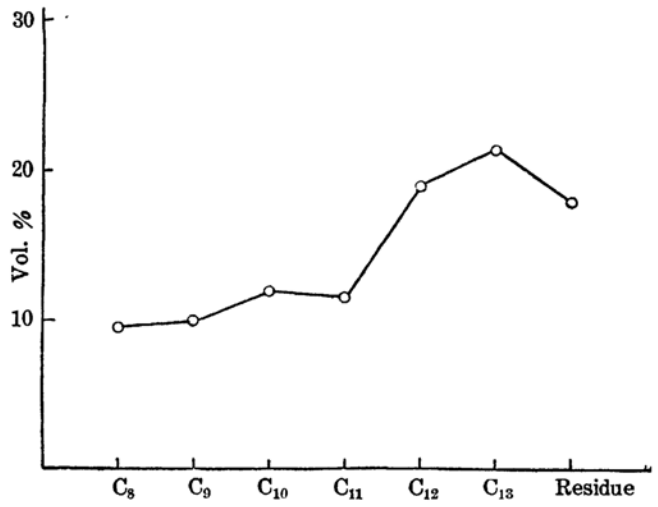

Fig. 4. Vol. % of Each Constituent.
(Fig. 1, Fig. 2, data combined.)
(For 1st trap oil.)
($F_{40, 41, 42, 43, 45, 46, 47, 49, 50, 52}$ Distillation.)

As regards the physico-chemical properties of these fractions of oil, the results are shown in Table 1 along with the conditions under which they are synthesized and the catalyst used. The correlations of the catalytic activity with the gas contraction and the amount of the oil yield as well as the nature of the effluent gas have already been discussed in our earlier paper[3] (VI). Also as to the effects of the promoters as boron oxide

(3) S. Hamai, this Bulletin, 17(1942), 339–344.

Table 1. Properties of the Products.

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.						Pretreatment* (hrs.)	Pretreatment* (°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_4^{25°}$	App. M.W.	Elementary Analysis C (%)	Elementary Analysis H (%)
F_{40}(A-G) 1st trap oil	200	XII_{11}-1	100	15	15	–	–	100	5 5	400 375	$1.4319^{20°}$	$0.766^{20°}$	153	85.69	14.42
F_{40}(A-G) 2nd trap oil	200	XII_{11}-1	100	15	15	–	–	100	5 5	400 375	$1.4071^{20°}$	$0.702^{20°}$	90	85.08	15.23
F_{41}(A-E) 1st trap oil	190	XII_{12}-1	100	15	15	5	–	100	5 5	400 375	$1.4282^{20°}$	$0.756^{20°}$	150	84.54	15.04
F_{41}(A-E) 2nd trap oil	190	XII_{12}-1	100	15	15	5	–	100	5 5	400 375	$1.4050^{20°}$	$0.693^{20°}$	91	84.67	15.49
F_{42}( ) 1st trap oil	200	XII_{13}-1	100	18	18	5	–	100	5 5	400 375	—	—	—	—	—
F_{42}( ) 2nd trap oil	200	XII_{13}-1	100	18	18	5	–	100	5 5	400 375	—	—	—	—	—
F_{43}(A-I) 1st trap oil	200	XII_{14}-1	100	15	15	5	5	100	5 5	400 375	$1.4238^{20°}$	$0.753^{20°}$	141	84.62	15.23
F_{43}(A-I) 2nd trap oil	200	XII_{14}-1	100	15	15	5	5	100	5 5	400 375	$1.3863^{20°}$	$0.669^{20°}$	84	83.95	16.02
F_{43}(A-I) 1st trap oil	200	XII_{14}-1	100	15	15	5	5	100	5 5	400 375	1.4222	0.7507	166	84.62	15.23
F_{43}(A-I) 2nd trap oil I	200	XII_{14}-1	100	15	15	5	5	100	5 5	400 375	1.3924	0.6991	119	83.95	16.02
F_{43}(A-I) 2nd trap oil II	200	XII_{14}-1	100	15	15	5	5	100	5 5	400 375	1.3932	0.6991	119	—	—
F_{44}(A-D) 1st trap oil	200	XII_{15}-1	100	18	18	5	5	100	5 5	400 375	—	—	—	—	—

* The first line indicates the heat treatment prior to H_2 reduction and the second line shows the reduction condition by H_2.

Table 1.—(*Continued*)

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.						Pretreatment* (hrs.)	(°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_{4°}^{25°}$	App. M.W.	Elementary Analysis C (%)	H (%)
F_{44}(A–D) 2nd trap oil	200	XII_{15}–1	100	18	18	5	5	100	5 5	400 375	—	—	—	—	—
F_{45}(A–H) 1st trap oil I	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	—	0.7553	200	—	—
F_{45}(A–H) 1st trap oil II	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	1.4259	0.7546	200	84.36	15.52
F_{45}(A–H) 1st trap oil	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	—	0.7536	194	84.33	15.28
F_{45}(A–H) 2nd trap oil	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	1.3966	0.6979	114	84.49	15.50
F_{46}(A–G) 1st trap oil I	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	1.4240	0.7499	198	—	—
F_{46}(A–G) 1st trap oil II	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	—	0.7492	204	83.73	15.40
F_{46}(A–G) 2nd trap oil	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	—	—	—	84.42	15.52
F_{47}(A–E) 1st trap oil	200	XII_{18}–1	100	18	18	10	–	–	5 5	400 375	1.4302	0.7679	212	84.59	15.41
F_{47}(A–E) 2nd trap oil	200	$X I_{18}$–1	100	18	18	10	–	–	5 5	400 375	1.4107	—	131	84.77	15.61
F_{48}(A–F) 1st trap oil	200	XII_{19}–1	100	15	15	10	5	100	5 5	400 375	1.4340	0.7730	233	84.48	15.43

Table 1.—(*Concluded*)

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.						Pretreatment* (hrs.)	(°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_{4°}^{25°}$	App. M.W.	Elementary Analysis C (%)	H (%)
F_{48}(A–F) 2nd trap oil	200	XII_{19}-1	100	15	15	10	5	100	5 5	400 375	—	—	—	84.07	15.41
F_{49}(A–C) 1st trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 375	1.4311	—	158	—	—
F_{49}(A–C) 2nd trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 375	1.4130	—	—	—	—
F_{49}(D–G) 1st trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 375	1.4358	0.7707	207	84.52	15.44
F_{49}(D–G) 2nd trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 375	1.4242	0.7316	146	85.08	15.06
F_{50}(A–J) 1st trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 300	1.4258	0.7526	200	84.41	15.60
F_{50}(A–J) 2nd trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 300	1.3954	0.6783	109	84.84	15.35
F_{51}(A–F) 1st trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 400	1.4279	—	192	—	—
F_{51}(A–F) 2nd trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 400	—	—	125	—	—
F_{52}(A–H) 1st trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 350	1.4245	0.7508	183	84.56	15.36
F_{52}(A–H) 2nd trap oil	200	XII_{16}-1	100	15	15	10	–	100	5 5	400 350	1.3995	0.7014	118	84.99	15.50

(B_2O_3), copper as well as thorium oxide (ThO_2) and cerium oxide (CeO_2) —the effect of the pretreatment on the catalytic activity and the products etc.—, they have been collaborated in the mentioned paper. With regard to the effects of the catalyst composition on the nature and the composition of the products, we may possibly state that in main there is practically no definite conclusion[4], however, a slight variation in the properties may be found as far as these data are concerned. These facts amply justify that the distillation analysis of the products obtained by using the same series of the catalyst but differing in some of the promoters, as indicated in this paper, may be employed.

Summary.

(1) The results of the distillation analysis of the products have been graphically presented in the volume percent against each constituent and correlated.

(2) The physico-chemical properties such as refractive index, specific gravity, apparent molecular weight and the elementary analysis of the products along with experimental conditions and the catalyst used have been tabulated.

(3) As regards the effects of the catalyst composition on the nature and the composition of the products, we may posibly state that there is practically no definite conclusion, however, a slight variation may be found, as far as these series of data and the catalyst are concerned.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director, and to Dr. S. Sato, Director of the Institute, for their interests and constant encouragement in carrying out this series of investigations and for the permission for this publication. Also the author takes this occasion to extend his thanks to Messrs. Hayashi, Shimamura, Fujiwara, Igarashi and Kuwabara, who have been willing to assist him in the experimental part of this investigation and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped him in the part of the analytic work.

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(4) It is rather difficult to estimate, from these physico-chemical properties, whether these fractions contain normal or isomeric forms, but as we have already mentioned that Boron Oxide (B_2O_3) or Cerium Oxide (CeO_2) play a very important role as an "Electron Carrier" or "Oxygen Carrier" enabling us to explain a possible existence of isomeric forms detected by the Podbiliniak analysis. See also reference (2) and Egloff, "Physical Constants of Hydrocarbons," Vol. I.