

On the Synthesis of Higher Paraffins from Water Gas. The use of Promoters for Activating Iron-copper Catalyst.

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"In April, 1926, Fischer and Tropsch (*Brennstoff-Chemie*, 1926, 7, 97; *Ber.*, 1926, 59B, 830, 832) announced that higher homologues of methane up to solid paraffin together with inappreciable quantities of olefines were formed when water gas was passed at atmospheric pressure over catalysts of iron and cobalt around 270°. Elvins and Nash (*Fuel*, 1926, 5, 263) confirmed this and in July (*Nature*, 1926, 118, 154), reported the presence of oxygen-containing compounds in a product obtained on a cobalt catalyst. Closer examination of the oil by Elvins (*J. Soc. Chem. Ind.*, 1927, 46, 473T) further confirmed this. In September, 1927, Smith, Davis, and Reynolds gave preliminary results in which olefines as well as paraffins were obtained; complete results were published in 1928 (*Ind. Eng. Chem.*, 1928, 20, 462). In 1928, Fischer and Tropsch (*Brennstoff-Chemie*, 1928, 9, 21) gave results of exhaustive examination of hydrocarbons obtained by them and stated that O₂-containing compounds were present only in small quantities (traces of benzene and toluene were also obtained) besides olefines and paraffins.

Fischer supposed the mechanism to centre round carbide formation. Elvins and Nash suggest that the formation of O₂-containing compounds is an intermediate step in the formation of hydrocarbons. Elvins suggests that carbonyls are the intermediate products. The latest ideas of Fischer and Tropsch as to the possible mechanism of the process are: (i) CH₂ may be primarily formed from H₂ and carbide carbon followed by polymerisation, (ii) complex molecules of 3 or 4C atoms may form as a primary act and may undergo (a) polymerisation or (b) cracking on the catalyst, (iii) secondary hydrogenation always occurs (Smith and co-workers, *J. Amer. Chem. Soc.*, 1930, 52, 3221)."

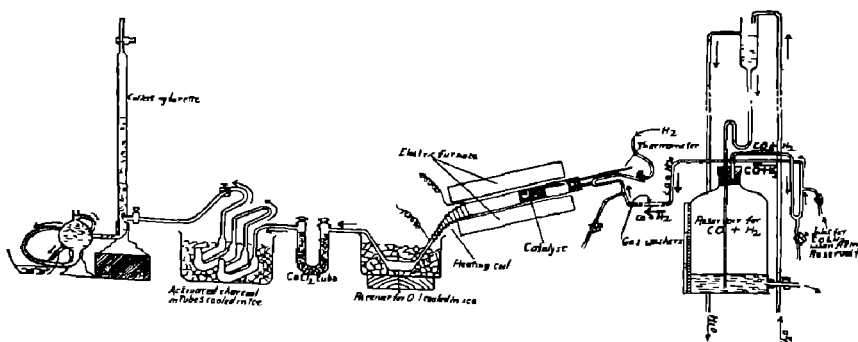
In support of mechanism (iii), Fischer and Pichler (*Brennstoff-Chemie*, 1929 10, 279) and Fischer, Peters and Coch (*ibid.*, 1929, 10, 383) showed that acetylene could of itself or in presence of H₂ or water gas, be converted into liquid hydrocarbons under suitable conditions of experiment; for example, with 10% acetylene in

water gas, Fe-Cu or Fe-Ni catalysts were found suitable. Smith and co-workers (*loc. cit.*) however found that with a Fe-Cu catalyst ethylene did not enter into any reaction with water gas, whereas Co-Cu-MnO₂ catalysts were satisfactory.

If CH₂ is the primary product which yields higher hydrocarbons by polymerisation, then any catalyst which helps the production of ethylene, the simplest polymer of -CH₂- from water gas would increase the yield of hydrocarbons. A pure iron-copper catalyst does not help this reaction. It was accordingly felt that promoters might be found which would accelerate this interaction of ethylene even on a Fe-Cu catalyst base, and this investigation was undertaken principally with that end in view. Berl (*Z. angew. Chem.*, 1930, 43, 435) has observed that the use of ZnO or MnO in a Fe-Cu catalyst, distinctly improves the yield of higher hydrocarbons. In this laboratory considerable work has been done on the promoter action of Ce and Th on nickel catalysts (Ghosh and Chakravarty, *J. Indian Chem. Soc.*, 1925, 2, 150, 157; Ghosh, Chakravarty, and Bakshi, *Z. Elektrochem.*, 1931, 37, 775; *Z. anorg. Chem.*, 1934, 217, 277). In the present paper results obtained with Ni alone or Ni, Ce, and Th in the ratio 8:03:0:13:0:95 as promoters on Fe-Cu catalyst have been described.

Fischer's investigation of the high pressure conversion of water gas into synthol demonstrated that in the effluent gases the concentrations of the various gases did not remain constant but showed periodic variations with the progress of reaction. It was accordingly decided to determine quantitatively the composition of samples of gas mixture leaving the catalyst surface at intervals.

FIG. 1.



(Not to scale)

EXPERIMENTAL.

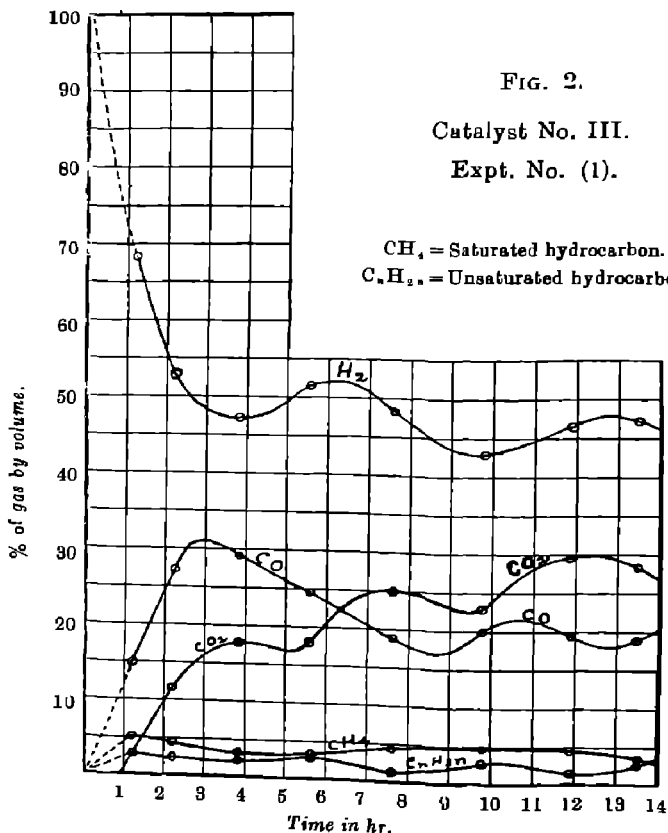
The experimental arrangement will be apparent from Fig. 1. A known volume of an approximately 1:1 mixture of CO (from formic acid) and H_2 was prepared in the aspirator bottle. The gas was passed through washers containing the usual purifying agents to the reaction tube in the electric furnace at the desired temperature. The catalyst was held in the reaction tube between asbestos plugs and the bulb of the thermometer was embedded in the catalyst. The furnace was set in an inclined position to facilitate the removal of the solid and liquid products formed. The exit end of the tube was tapered downwards to a modified U-shaped receiver, which was kept immersed in ice during the progress of the experiment for the condensation of the more easily condensible portion of the product—the "heavy liquid hydrocarbons." The water formed was then removed by a $CaCl_2$ U-tube and the "light liquid hydrocarbons" removed by adsorption by means of active charcoal. Two charcoal tubes were used in series to ensure complete removal of the higher hydrocarbons. The exit end of the reaction tube up to a few inches inside the furnace, was kept heated by means of a heating coil in order to bring down the high melting products formed. For estimation the whole system was flushed with H_2 after the experiment was over and the receiver was cut off just above the point where the solids collected, weighed, and connected with two U-tubes containing dehydrite, one at each end, to remove the water mixed with the hydrocarbons. The weights of the receiver after removal of water and after it had been cleaned and dried, gave the weights of the heavy hydrocarbons and the water condensed with them.

The estimation of the light liquid hydrocarbons was effected by weighing before and after experiment, in each case after flushing with pure dry H_2 to constant weight. When flushing with H_2 after experiment, the charcoal tubes were kept immersed in an ice-bath to prevent any loss of adsorbed hydrocarbons. The exit gases were analysed by the usual gas analytical methods (the unsaturated hydrocarbons being determined by absorption with bromine water and the saturated hydrocarbons by explosion with oxygen) and the amount of contraction taking place determined at frequent intervals.

Preparation of catalysts.—The catalysts were prepared by the slow ignition of the nitrates on asbestos at the lowest temperature possible, soaked with $\frac{1}{2}\%$ solution of K_2CO_3 , and dried. The catalyst base for

the promoter was always of the composition $\text{Fe} : \text{Cu} = 4 : 1$ on 2.5 g. of asbestos impregnated with K_2CO_3 . The catalysts were reduced in a slow current of H_2 . For catalyst No. I the reduction was carried out at 390° for 12 hours. In the case of the other catalysts, the first stage of reduction was carried out at the lowest temperature at which water began to be produced rapidly, the second stage at the higher temperature at which water again appeared, and finally the temperature was raised to the desired point and reduction carried to completion.

General characteristics of the catalysts.—Graphical representation of the composition of the effluent gases always showed a periodic variation in the case of hydrogen and carbon dioxide gas, their maxima and minima practically occurring at the same time (cf. Fig. 2).



Rapid diminution in the concentration of CO in the effluent gases is also always associated with a regular increase in the concentration of CO₂. These results, therefore, indicate that the velocities of the following reactions on the catalyst suffer periodic variation:—



when the velocity of (i) is greater relative to (ii), concentrations of CO₂ and H₂ in the effluent gases increase, and when after sufficient accumulation of active carbon on the catalyst surface, the velocity of (ii) relative to (i) increases, the concentrations of both CO₂ and H₂ diminish. Again, the concentration of H₂ in the first 2 hours is much larger than its average concentration during the next 12 hours, while the concentration of CO suffers an opposite change. As will be explained later, CO displaces the H₂ adsorbed on the surface of the catalyst during the process of formation of the hydrocarbons at the initial stages.

Products.—The heavy liquids melted within a range of 8° to 31°. The highest melting point of the solids was 81°.

Calculations.—The saturated hydrocarbons have been estimated as CH₄. Following approximate values of heat of combustion have been used in making the calculations (Landolt's Tables, 1923, p. 1589).

Unsaturated hydrocarbons—	11800 cal. per g.
Saturated „ —	13340
Light liquid „ —	11360
Heavy liquid „ —	11300
Solid „ —	11200

Catalyst I.

Composition of the catalyst: Fe, 4 g. ; Cu, 1 g. ; Ni, 0.055 g.

Reduced at 330° for 12 hours.

Expt. (1).—The activity of the catalyst did not remain steady. The amount of CO in the effluent gases continued to increase and that of CO₂ to diminish. The yield of hydrocarbons was 8.1% by weight of the reacting gases at space velocity 63, 38.8% of the hydrocarbons formed being gaseous.

Expt. (2).—The catalyst was regenerated by heating in a current of H_2 for 3 hours at 930° . The regeneration was not effective. The percentage of CO was quite large from the beginning and continued to increase with the progress of the reaction; the amount of CO_2 continued to diminish simultaneously. The yield was 8.2% of the reacting gases by weight at space velocity 65, 41.7% of the hydrocarbons obtained being gaseous.

Expt. (3).—An attempt was made to regenerate the catalyst by prolonged heating in H_2 . The hydrocarbons formed at one passage was 8.8% of the weight of the reacting gases but 76.4% of the total yield was gaseous. The space velocity was 65.

In Table I, experimental data for catalyst I in experiment (2) are recorded. Experiments (1) and (3) were carried out in a similar fashion, but the data being similar are not recorded here.

TABLE I.

Reaction temp. = 265° . Expt. period = 14 hr. 19 min. Rate of flow per min. = 10.8 c.c. Space velocity = 65.

	Composition of inflowing gas			Residue.			Converted.		
	CO.	H_2 .	Total.	CO.	H_2 .	Total.	CO.	H_2 .	Total.
Vol. (c.c.) ...	4700	4800	9500	2200	8280	5480	2500	1320	3820
Wt. (g.) ...	5.88	0.41	6.29	2.75	0.29	3.04	3.13	0.12	3.25
Heat of combustion (cal.)	14290	13910	28200	6680	9840	16520	7610	4070	11680

Products of reaction.

Hydrocarbons.

	CO_2 .	Gaseous.				Liquid.	Solid.	Water.	Total.	Total hydrocarbon.
		Unsatd.	Satd.	Heavy.	Light.					
Vol. (c.c.) ...	1101	80	130	1330	...	
Wt. (g.) ...	2.18	0.17	0.12	0.13	0.07	0.07	0.24	2.98	0.56	
Heat of combustion (cal.)	...	2010	1600	1470	800	780	...	6680	...	

TABLE I (contd.).

To be accounted for.			Obtained.		
C.	O ₂ .	H ₂ .	C.	O ₂	H ₂
1.84 g.	1.76 g.	0.12 g.	From CO ₂ , 0.60 g. From hydro- carbons, 0.47 g.	From H ₂ O, 0.21 g. From CO ₂ , 1.58 g.	From H ₂ O, 0.08 g. From hydro- carbons, 0.09 g.
			Total 1.07 g	Total 1.79 g.	Total 0.12 g.
Unaccounted for			Remarks.		
C	0.27 g		Probably deposited on the surface of the catalyst		
O ₂					
H ₂					

Catalyst II.

Composition of the catalyst: Fe, 4 g.; Cu, 1 g.; Ni, 0.11 g.

Expt (1).—Reduction of the catalyst by H₂ at 330° gave a sample whose catalytic activity did not remain steady as in the case of catalyst I. When the temperature of reduction was not allowed to exceed 300°, a considerable improvement in steadiness was noted. CO did not show a progressive increase but showed a marked periodic variation as also did H₂. The yield of hydrocarbons was 9.7% by weight at space velocity 64, the gaseous hydrocarbons being 36.2%.

Expt (2).—The catalyst was regenerated by heating for 3 hours in H₂. The yield in this case was much better, *viz.*, 13% at space velocity 64, the gaseous hydrocarbons being 46.2%.

Expt (3).—The catalyst was heated for 3 hours at 800° before experiment. The yield of hydrocarbons was 12.1% by weight of the reacting gases at space velocity 56, the gaseous hydrocarbons being 33%.

In Table II, experimental data for experiment (2) with catalyst II are recorded.

TABLE II.

Reaction temp = 265°. *Expt* period = 13 hr. 23 min. Rate of flow = 10.6 c.c./min. Space velocity = 64.

	Composition of inflowing gas.			Residue.			Converted.		
	CO	H ₂	Total	CO.	H ₂ .	Total.	CO	H ₂ .	Total.
Vol. (c.c.)	4250	4250	8500	1300	3070	4370	2950	1160	4130
Wt. (g.)	5.31	0.36	5.69	1.63	0.27	1.90	3.69	0.11	3.80
Heat of combustion (cal.)	12900	12890	25790	3960	9160	13120	6970	9780	12700

TABLE II (contd.).

		Products of reaction							
		Hydrocarbons					Water.	Total.	Total hydrocarbon.
CO ₂ .		Gaseous		Liquid.		Solid.			
		Unsatd.	Satd.	Heavy.	Light.				
Vol. (c.c.) ...	1040	90	260	1890	...
Wt. (g.) ...	2.04	0.17	0.19	0.10	0.26	0.02	0.17	2.95	0.74
Heat of combustion (cal.)	...	2010	2540	1130	2950	220	...	8850	...
To be accounted for						Obtained.			
O.	O ₂ .	H ₂ .	C.			O ₂ .		H ₂ .	
1.58 g.	2.11 g.	0.11 g.	From CO ₂ , 0.56 g. From hydrocarbons, 0.61 g.			From H ₂ O, 0.15 g. From CO ₂ , 1.48 g.		From H ₂ O, 0.02 g. From hydrocarbon 0.13-g	
			Total 1.17 g.			Total 1.63 g.		Total 0.15 g	
Unaccounted for						Remarks.			
C, 0.41 g.		670 c.c. CO.			Hydrogen was used for flushing after expt. (1) and also for regenerating the catalyst. Excess of H ₂ must be due to liberation of adsorbed H ₂ and deficit in CO must be likewise due to adsorption on solid catalyst surface.				
O ₂ , 0.48 g.									
H ₂ , 0.04 g. in excess.		450 c.c. H ₂ in excess used up during reaction.							

Catalyst III.

The Ni content was 0.25 g. and in addition it contained 0.0041 g. of Ce and 0.0296 g. of Th. Reduction temperature, 260°.

Expt. (1).—The temperature of reaction was 238°. The experiment was continued for 14 hours. Conversion into hydrocarbons at one passage was 12.7% by weight of reacting gases, gaseous hydrocarbons being 49.4%, at space velocity, 64.

Expt. (2).—After the first experiment the whole system was flushed with H₂ at the reaction temperature of 230° for 2 hours. The result obtained was better than in the first experiment, 15.4% by weight of the reacting gas having been converted into hydrocarbons ; gaseous

hydrocarbons however formed 68.5 % of the total amount of hydrocarbons obtained; water formed was negligible, space velocity being 60.

Expt. (3).—For this experiment the catalyst was further reduced at 271°. The yield of hydrocarbons was 19.2% of the reacting gases by weight at space velocity 59, gaseous hydrocarbons being only 34.3 %.

In Table III experimental data with catalyst III for *expt. (3)* are recorded.

TABLE III.

Reaction temp.=256°. Expt. period=14 hrs. 6 min. Rate of flow=9.8 c.c./min. Space velocity=59.

	Composition of inflowing gas.			Residue.			Converted.		
	CO.	H ₂ .	Total.	CO.	H ₂ .	Total.	CO.	H ₂ .	Total.
Vol. (c.c.)	... 4070	4260	8330	660	2550	3210	3410	1710	5100
Wt. (g.)	... 5.09	0.38	5.47	0.83	0.23	1.06	4.26	0.15	4.41
Heat of combustion (cal.)	... 12370	12890	25260	2020	7800	9820	10350	5090	15440

Products of reaction.

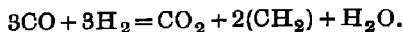
	Hydrocarbons.								Total hydrocarbon.
	CO ₂ .	Gaseous		Liquid.		Solid.	Water.	Total.	
		Unsatd.	Satd.	Heavy.	Light.				
Vol. (c.c.)	...1440	100	220	1760	
Wt. (g.)	...2.82	0.19	0.16	0.16	0.42	0.11	0.14	4.00	1.04
Heat of combustion (cal.)	...	2240	2140	1810	4770	1230	...	12190	

To be accounted for.			Obtained.		
C.	O ₂ .	H ₂ .	C.	O ₂ .	H ₂ .
1.83 g.	2.43 g.	0.15 g.	From CO ₂ , 0.77g.	From H ₂ O, 0.12g.	From H ₂ O, 0.02g.
			From hydrocarbons, 0.87 g.	From CO ₂ , 2.05g.	From hydrocarbons, 0.17g.
			<hr/> Total 1.64g.	<hr/> Total 2.17g.	<hr/> Total 0.19g.

TABLE III (contd.).

Unaccounted for.		Remarks.
C, 0.19 g.		
O ₂ , 0.26 g.	340 c.c. CO	Excess of H ₂ and deficit in CO should be accounted for in the same way as in Table II.
H ₂ , 0.04 g. in excess	450 c.c. H ₂	

While this investigation was in progress, Fischer and Koch (*Brennstoff-Chemie*, 1932 **13**, 61) published results obtained with the following catalysts:—Co + 18% Th or Co + 15% Mn, precipitated with alkaline carbonate. By continuous circulation of gases, the yield of liquid hydrocarbons approached 71% of the theoretical. In our experimental data recorded in Table III it will be seen that a single passage of water-gas above our catalyst at a space velocity of 59 gave 48.3% of the theoretical yield calculated on the basis of the equation,



This catalyst therefore appears to be very efficient one.

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Addition of Compounds Containing Reactive Methylene Group with Phenylvinylketone.

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In a work to be published later on, large quantities of phenylvinylketone were obtained as a bye-product. Since it combines very readily with substances containing reactive methylene group, it can be used for making saturated ketonic compounds which are unsaturated in the β -position and which it is difficult to prepare in any other manner. Allen and Bridgess (*J. Amer. Chem. Soc.*, 1929, **51**, 2151) and Kohler (*Amer. Chem. J.*, 1909, **42**, 375) have also done some work in this line. The additive properties of this $\alpha\beta$ -unsaturated ketone with substances containing reactive methylene group, e.g.