III Products of Reaction

Paraffin and olefine hydrocarbons of different molecular weights, from methane and lower gaseous hydrocarbon to the high molecular weight solid paraffins are formed during the middle pressure synthesis with iron catalysts. Table 28 gives the yields in solid, liquid products and gasol hydrocarbons under a few varying reaction conditions, collected from current experiments.

Table 28

Solids, Liquid and Gases Hydrocarbons, under Different Reaction Conditions.

Catalysts	Percent K_2CO_3	Starting Temp. °C	Paraffin percent	Liquid Hydro-carbons	Gasol percent
Fe(Na_2CO_3 precipitant)	1/4	270	3	65	32
Fe - Cu	1/8	260	4	76	20
Fe-Kieselguhr	1	235	8	63	29
Fe(NH_3 precipitant)	0	235	12	67	21
Fe - Normal	1/4	235	26	56	18
Fe(Na_2CO_3 precipitant	1	235	42	47	11
Fe(Na_2CO_3 precipitant	5	235	46	44	10

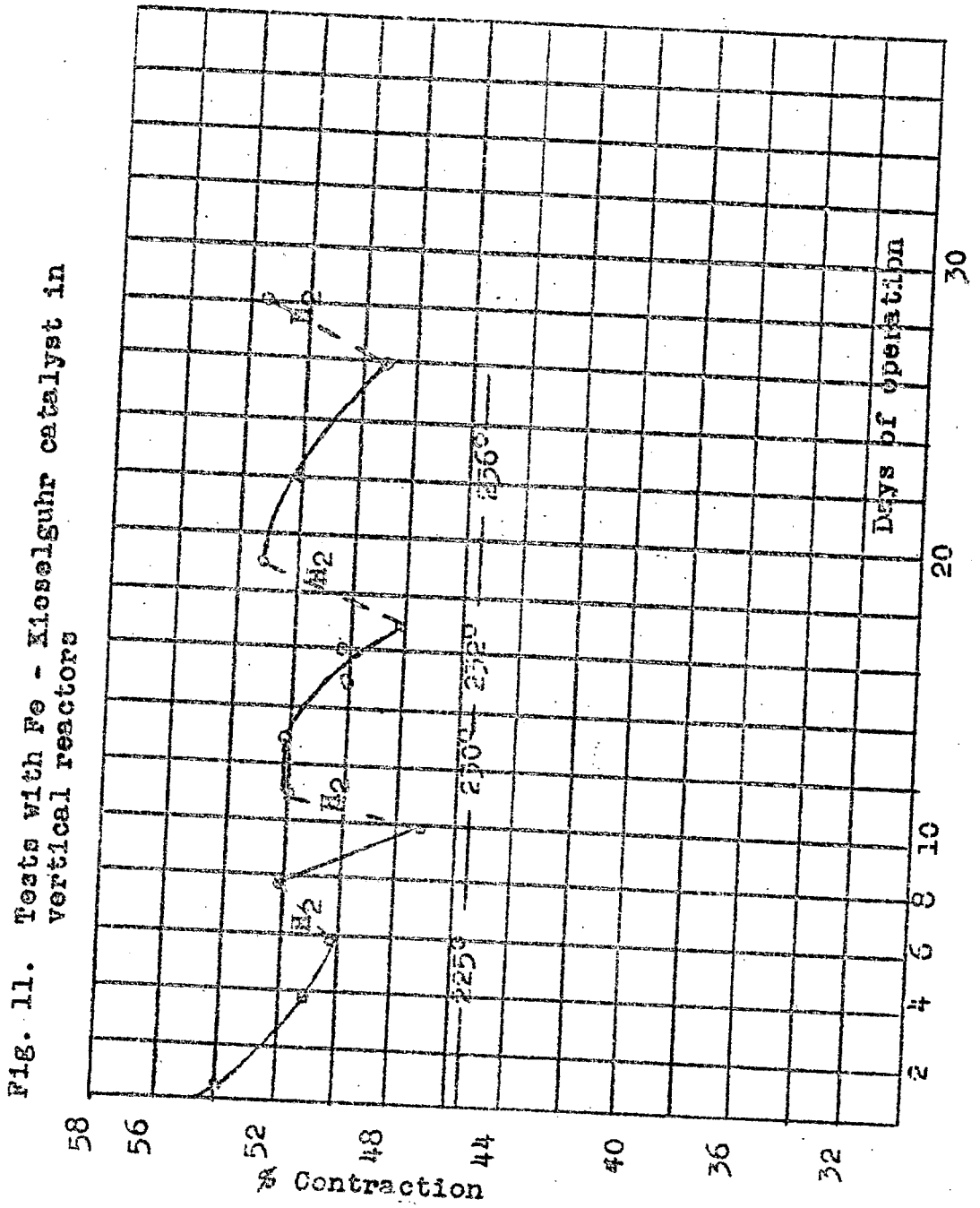


Fig. 11. Tests with Fe - Kieselguhr catalyst in vertical reactors

We can see from this table that the total paraffin contents in these test varied from 3 - 46 percent of the total reaction products. These amounts referred to solid and liquid products correspond to 5 - 51 percent. The proportion of liquid hydrocarbons varies between 44 to 76 percent of the reaction products, the proportion of gasol between 10 and 32 percent. Catalysts which produce good yields for particularily long times, especially those precipitated with sodium carbonate (at 235°C) and with ammonia (at 235°C) produce a proportion of solid, liquid and gasol hydrocarbons represented by the average of the values mentioned above; in general, a lowering of the reaction temperature and an increase in the alkali content changes the nature of the reaction products toward higher molecular weights. The iron-kieselguhr catalysts do not fall into this series.

The proportion of unsaturated hydrocarbons in the liquid products as well as in gasol was different under different reaction conditions, just like the boiling point variations. High melting paraffin is a by-product obtained during synthesis.

In addition oxygenated organic compounds are formed similar to the synthols described by Franz Fischer and Tropsch, 18/.

The iron catalysts may finally be used under certain conditions for the production of city gas conforming to specifications.

The middle pressure synthesis with iron catalysts permits one in particular to alter the production to form primarily one or another reaction products. No predications could be made in the normal and middle pressure synthesis with cobalt catalysts about the direction of the reaction, for regulating the formation of any individual type of hydrocarbons, nor the formation of any definite products, because of the great variability of these syntheses.

A. Liquid Hydrocarbon

The crude liquid products are not as a rule entirely colorless, but are slightly yellowish. Distillation produces water-clear gasoline, and smaller amounts of a yellowish oil is left in the residue. The gasoline is stable and remains colorless even after storage for many months.

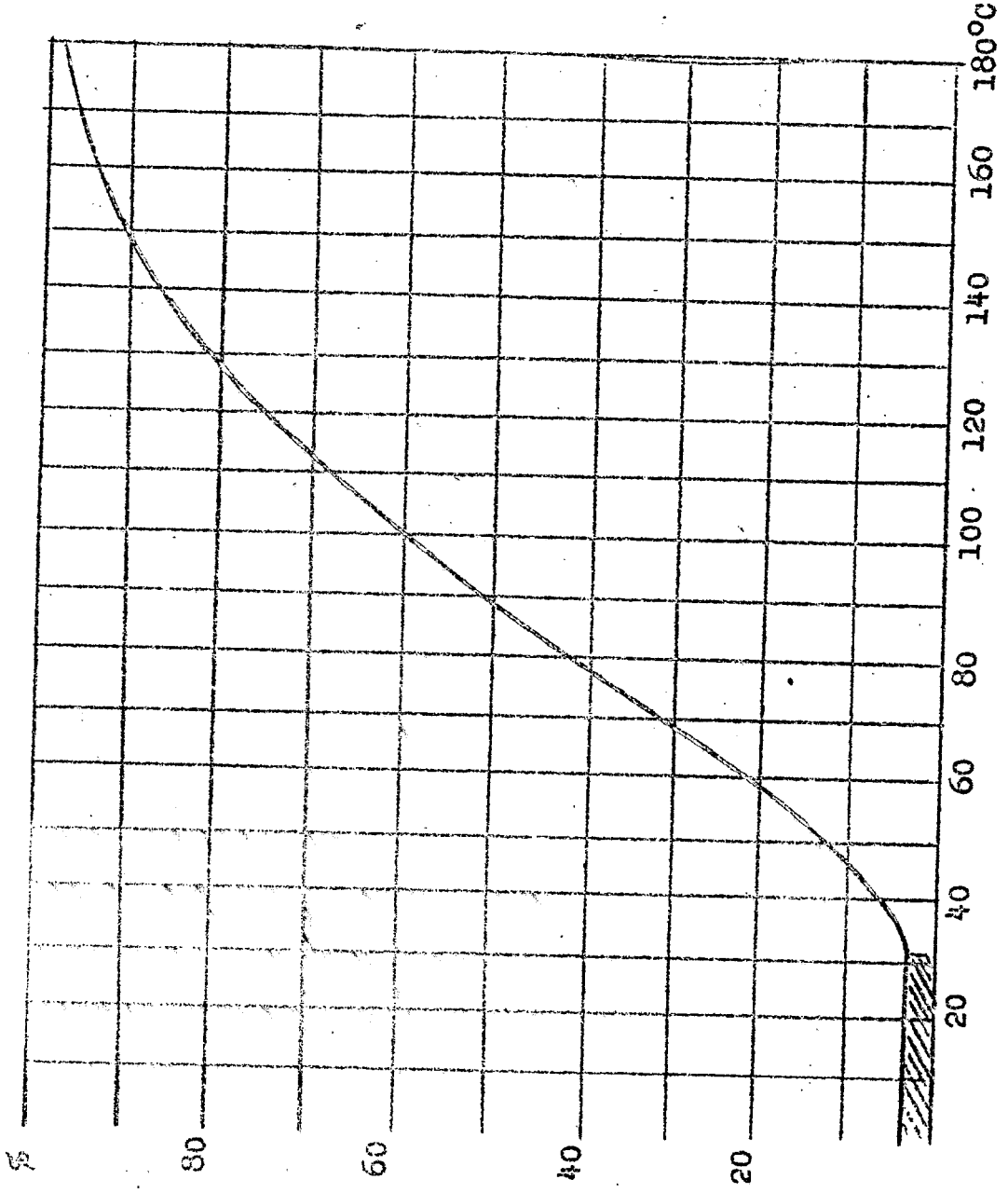


Fig. 13. Engler distillation of a gasoline

The proportion of liquid hydrocarbons boiling below 180°C to the total liquid hydrocarbons depends on experimental conditions. A catalyst precipitated with ammonia (with 1/4 percent K_2CO_3, at 250°C) gave 55 percent of a distillate -180°C, and with an iron-copper catalyst operated at 260°C, 80 percent of a distillate -180°C was obtained.

Figure 13 shows a Engler distillation of a gasoline produced with a normal iron catalyst at 250°C and boiling -180°C. 50 percent of this gasoline boiled -88°C, 60 percent -100°C. The boiling curve of the gasoline can be strongly affected by changing the operating conditions.

Table 29 shows the gravity, olefine content, boiling data and octane number of a few gasolines produced with some iron catalysts.

Table 29

Properties of Gasolines Obtained with Iron Catalysts

Numberd	washed with NaOH	d_{15}	Olef.	B.P. Analysis Start	10%	50%	90%	$n_{37.8°}$	O.N.
1	yes	0.696	64	30°	46°	88°	145°	0.54	61
2	"	0.678	65	30°	38°	73°	145°		62
3	no	0.698	38					0.48	63

Sample number 1, table 29 was obtained with a catalyst precipitated with ammonia, sample number 2 from an experiment with an iron-copper catalyst and sample 3 in a test with an iron-kieselguhr catalyst.

The gravity of the gasoline -180°C was 0.7. Phosphorus pentoxide-sulfuric acid extracted 64, 65 and 38 percent by volume respectively from the three gasolines. The octane number by the motor method of the three stabilized gasolines varied from 61 - 63.

The possibilities of further raising the knock resistence of gasoline obtained from middle pressure synthesis are discussed in a special section on the subsequent working up of the primary products.

A comparison of the fractions removed with phosphorus-pentoxide-sulfuric acid from the gasolines with their octane numbers shows that the latter does not depend entirely on the olefine content.

The synthol like organic compounds found in the reaction products of iron-middle pressure synthesis are of importance. Their amount and nature varies greatly with the operating conditions. Table 30 gives the acid, ester, saponification and hydroxyl numbers of some synthesis products.

Table 30

Oxygen-containing Constituents of the Liquid Hydrocarbons

Catalysts	boiling range	acid no.	ester no.	Saponification no.	Hydroxyl no.
Fe 1/4% K_2CO_3	30 - 180				
Fe " "	over 180	0.2	0.2	0.5	2.3
Fe 1% K_2CO_3	over 180	1.8	8.1	9.9	7.0
Fe-kieselguhr 1% K_2CO_3	30 - 180	1.4	15.0	16.4	
Fe-kieselguhr 1% K_2CO_3	over 180	0.1	2.0	2.1	

The table shows that larger amounts of esters and alcohols, together with small amounts of free acids can be produced during synthesis and this applies not only to low molecular weight esters and alcohols occuring in gasoline, but also to those of higher molecular weight with boiling points above 180°C. The formation of these products, is strongly favored by the alkalizing of the iron catalysts. When the total products obtained with an iron-kieselguhr catalyst are washed with 30 percent calcium chloride solution, 2.5 percent were dissolved in the water solution, and 0.8 percent additional were dissolved in the subsequent washing with sodium hydroxide.

The ultimate analysis of the total reaction products obtained with three different iron catalysts are shown in table 31.

Table 31

The Ultimate Analysis of Synthesis Products

	In the total product			Gasoline		
	C	H	O	C	H	O
Fe-normal Fe-Cu Fe-Kieselguhr	84.60	15.16	0.24	83.94	14.97	1.09

Unwashed products were analyzed. The oxygen content of the low boiling gasoline is higher than in the total product.

B. Paraffin

From 5 to 50 percent of the solid and liquid reaction products consist of paraffins (determined by the butanone method). With hydrogen-rich synthesis gas and low-alkali catalysts the paraffin is white to pale yellow, with carbon monoxide-rich gases and catalysts containing one or more percent of potassium carbonate it is yellow to yellow-brown. The coloring matter may be derived from iron or iron salts, but it only constitutes a small amount of high boiling oils and may be removed by extraction or be decolorized by hydrogenation.

The melting point of the paraffin extend over the whole range of the known paraffins. The total product contains particularly high melting constituents, and melts only at a relatively high temperature. A meniscus formed at 80°C in the melting point tubes with a paraffin freed from liquid hydrocarbon by means of butanone, when produced with a catalyst containing 1/4 percent K_2CO_3, and at 104°C when the catalysts contained 1 percent K_2CO_3.

The paraffin obtained with an iron - 1 percent K_2CO_3 catalyst was 50 percent soluble in boiling ether. The product precipitated with methyl alcohol melted completely in melting point tubes between 66 and 70°C. 41 percent were insoluble in ether (24 hours extraction in Soxhlet, using boiling hexane). Their end melting point was between 90 and 104°C. The remaining 9 percent

of the hexane-insoluble paraffin had an end melting point of 122°C.

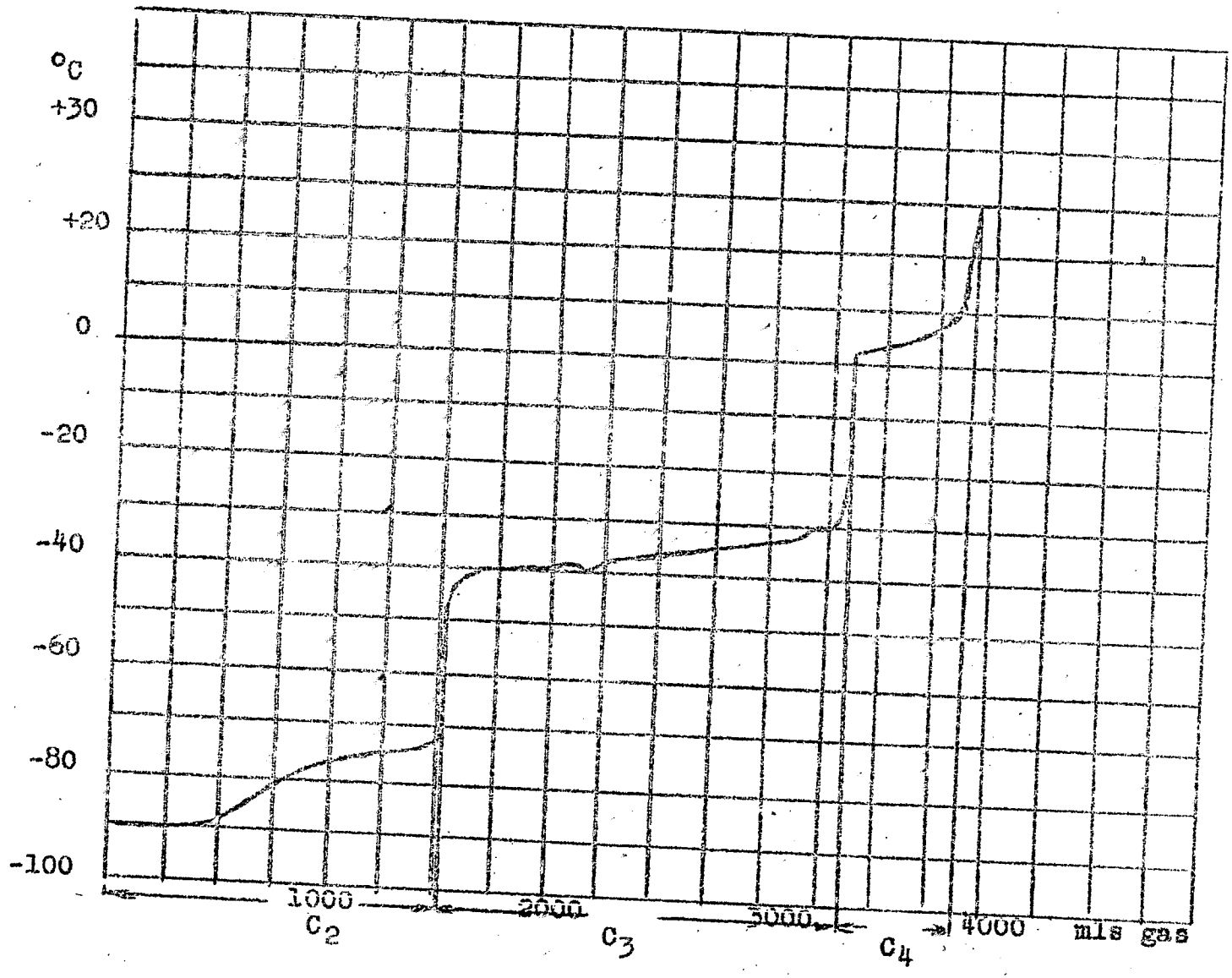
The so-called catalyst paraffin obtained when an iron catalyst was fractionally extracted in boiling benzol, leaving some insoluble residue which was soluble in boiling toluol and melted at about 126°C.

C. Gasol

Table 28 shows that 10 to 30 percent of the reaction products of synthesis consist of gasol hydrocarbon ($C_3 + C_4$). Ethylene is a product of the iron-middle pressure synthesis. Figures 14 and 15 show the results of low temperature distillation made at the Institute by F. Weinrotter. The gaseous reaction products of a synthesis (iron catalyst with 1 percent K_2CO_3) were led through a trap cooled with liquid air. Gasoline and all hydrocarbons except some of the methane are condensed in the trap. The C_2 - C_4 fraction of a sample distilled up to room temperature is shown in figure 14 (distillation I). The gasoline remaining in the trap still contained considerable amounts of C_4 hydrocarbons. They were removed by distillation. The C_4 fraction obtained is shown in figure 15 (distillation II). No isobutylene has been found in the two distillations.

Table 32 summarizes the results of the low temperature distillation. The distillation I was recalculated to the amount of gasol corresponding to that of the distillation II. The proportion of unsaturated hydrocarbon in the different fractions was determined with mecuric nitrate.

Fig. 14, Distillation of gaseous hydrocarbons



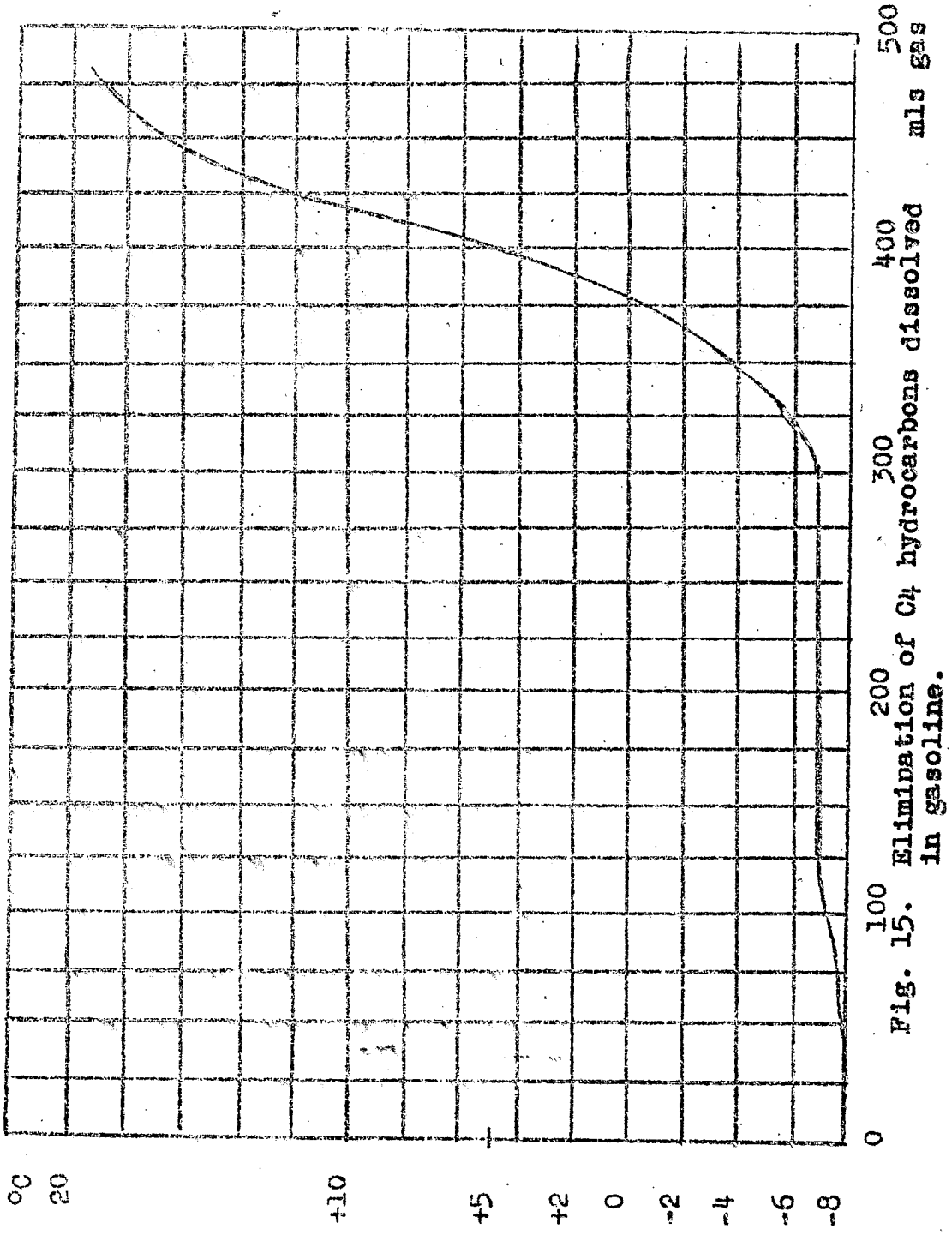


Fig. 15. Elimination of C4 hydrocarbons dissolved in gasoline.

Table 32

The C_2 - C_4 Hydrocarbons Produced During Synthesis

	Distill. I mls.	Distill. II mls.	Wt. Percent of C_2 + Gasol fraction
Ethylene	2360		15.8
Ethane	1830		13.1
Propylene	3480		34.9
Propane	1130		11.9
Butylene	1010	333	17.9
Butane	370	87	6.4

55 percent by weight of the C_2 fraction consisted of ethylene, and 74 percent of the gasol fraction consisted of unsaturated hydrocarbon. In these experiments 5.2 g ethylene, 11.1 g propylene and 6.0 g butylene were obtained from ncbm.

The amount and the composition of the gaseous hydrocarbons depend on the nature of the catalysts and on the reaction temperature. Table 33 shows the yield of gasol hydrocarbons and their content of unsaturated constituents obtained under different conditions of synthesis. All tests were run with the synthesis gas 3 CO : 2 H_2 and at 15 atm pressure.

Table 33

Yield of Gasol Hydrocarbons with Different Catalysts*

Catalysts	Temp. °C	g Gasol /ncbm ideal gas	Percent of unsaturated hydrocarbons in gasol
Fe, NH_3 precipitated with 0 % K_2CO_3	235	30	70
Fe, Na_2CO_3 precipitated with "	235	28	80
Fe, " " 1/4% "	235	26	76
Fe, " " 1% "	235	17	80
Fe, " " 1/4% "	270	46	47
Fe, Kieselguhr 1% "	235	36	35

* The amount of gasol hydrocarbons obtained in the synthesis may be increased. Present work is devoted to that topic.

At a synthesis temperature of 235°C and with an iron catalyst precipitated with ammonia or with soda the amount of gasol hydrocarbons/ncbm ideal gas amounted to 20 - 30 g, with 70 - 80 percent of unsaturated hydrocarbons. The amount of gasol hydrocarbons was still higher at higher reaction temperatures, but their hydrogenation as well as their formation were both favored, so that the amount of unsaturated hydrocarbons/ncbm of the ideal gas obtained at the reaction temperature of 270°C amounted to around 20 g.

The gasol hydrocarbons obtained with the iron-kieselguhr catalyst differ quantitatively from those obtained with a catalyst free from kieselguhr. Just as in the case with gasoline, the gasol obtained with the kieselguhr catalysts containing a small proportion of unsaturated hydrocarbons.