combine with olefins or alcohols to produce oxygenated compounds of higher molecular weight than the starting materials. Cobalt usually is the catalyst, probably in the form of cobalt hydrocarbonyl, $HCo(CO)_4$, which may be formed from dicobalt octacarbonyl under synthesis conditions according to the equation

$$[Co(CO)_4]_2 + H_2 \rightleftharpoons 2HCo(CO)_4.$$

Although cobalt hydrocarbonyl can be prepared directly, it is difficult to keep as it becomes unstable above -33 C. The storage problem was partly overcome by collecting the acid in toluene and storing it in an atmosphere of carbon monoxide. Under these conditions, only very little decomposition was observed at room temperature during 24 hours (fig. 34). Methods were developed for the analysis of mixtures of cobalt carbonyl and hydrocarbonyl. A considerable amount of cobalt hydrocarbonyl was found in the reaction product from cobalt carbonate, benzene, and synthesis gas.

The formation of complexes of dicobalt octacarbonyl with organic compounds has previously been explained as a displacement of 1 or more moles of carbon monoxide by the entering organic molecule. This view has been shown to be untenable. Instead, the organic molecule effects a disproportionation of the dicobalt octacarbonyl into cobalt ion and cobalt carbonyl anion according to the generalized equation

$$2xB + 3[Co(CO)_4]_2 \rightarrow 2[Co(B)_x]^{++}[Co(CO)_4]_2^{-} + 8CO.$$

The electrons necessary for the formation of the anion may be derived from some of the cobalt or from an external source. The tendency to form the stable cobalt carbonyl anion (rare-gas structure) is probably the driving force for the reactions. Addition of electrons from an external source is illustrated by the reaction of sodium with dicobalt octacarbonyl:

$$2Na + [Co(CO)_4]_2 \longrightarrow 2Na[Co(CO)_4].$$

A study is being made of the effects of contact time, temperature, catalyst concentration, and pressure on typical oxo reactions.

Characterization of Synthesis Products

Analyses

The total liquid product obtained from hydrocarbon synthesis over a nitrided-iron catalyst at 240° C. and 20 atmospheres pressure was separated into fractions by a scheme involving several distillations, extractions, and phthalation, and the fractions were analyzed by chemical and spectrographic methods (figs. 35-37). A new mass spectrometric method was developed to determine the higher alcohols in this product. The total aqueous phase represented 26.1 percent of the condensed product. Some of its components and their amounts are shown in table 15; alcohols were predominant, and ethyl alcohol was by far the largest constituent of this phase. The oil phase, 73.9 percent of the condensed product, contained more than 45 percent of oxygenates, chiefly alcohols but also significant amounts of esters. The hydrocarbons were predominantly saturated. More than 80 percent of the oil phase boiled between 50° and 350° C., and a detailed analysis of this part of the product is given in table 16.

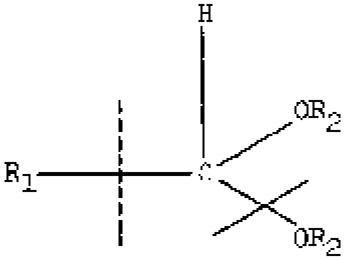
TABLE 15. - Some oxygenated substances in condensed product of Fischer-Tropsch synthesis over nitrided catalysts

Component	Composition concentration by weight, percent, of			Fraction of total component in aqueous phase
	Oil phase	Aqueous phase	Total	
Acids	-	5.28	1.38	-
Acetone	-	.12	.031	-
Methyl ethyl ketone	-	.09	.023	-
Methyl propyl ketone	-	.06	.016	-
Alcohols	20.46	14.32	18.84	0.198
Methanol	.05	.51	.38	.66
Ethanol	5.70	11.53	7.22	.417
n-Propanol	3.28	1.51	2.61	.140
i-Propanol	.08	-	.06	-
n-Butanol	2.85	0.48	2.23	.056
i-Butanol	.01	-	.008	-
n-Pentanol	2.29	.23	1.76	.034
n-Hexanol	1.89	.06	1.41	.017
n-Heptanol	1.54	0	1.14	0
n-Octanol	.95	0	.70	0
n-Nonanol	.63	0	.47	0
C_{10} and higher alcohols	1.18	0	.87	0
Total identified oxygenates	20.46	19.87	20.29	0.26

TABLE 16. - Chemical composition of oil fraction boiling from 50° to 350° C. from nitrided catalyst

	Fraction number			
	2	3	4	(2-4)
Boiling range, °C	50-150	150-250	250-350	50-350
Components, weight, percent:				
Total oil	51.95	17.06	13.60	82.61
Hydrocarbons	17.6	38.4	6.0	20.2
Double bonds				
Total α	4.1	5.0	.8	3.6
Total β	2.4	.6	1.4	1.8
Hydrocarbon α	2.28	2.28	0	1.9
Hydrocarbon β-	.09	.22	0	.1
Hydrocarbon branched-α	.13	.06	0	.1
Carboxyl (acid)	.6	1.6	0.2	.8
Carboxyl (ester)	3.4	5.0	10.4	5.0
Carbonyl	2.0	1.1	1.1	1.7
Hydroxyl	10.6	3.5	.3	7.4
Acid in fraction	1.2	15.2	1.0	1.9
Acid in total oil	0.6	.9	.1	1.6
Ester in fraction	6.8	16.4	50.4	14.8
Ester in total oil	3.5	1.8	6.9	12.2
Aldehyde and ketone in fraction	5.1	5.0	7.9	5.6
Aldehyde and ketone in total oil	2.6	.9	1.1	4.6
Alcohol in fraction	46	27	3.5	35.2
Alcohol in total oil	24	4.6	.5	29.1
Oxygenated compounds in fraction	59.1	53.6	63.1	57.5
Oxygenated compounds in total oil	30.7	9.1	8.6	48.4

By means of new methods developed with the mass spectrometer, other constituents in the liquid Fischer-Tropsch product can be identified. These are the acetal-type compounds,



in which R_1 is H for formal, CH_3 for acetal, C_2H_5 for propional, etc. In analogy to the mass fragmentation of simple ethers, one may expect the C-O bond to rupture most easily (as indicated by the solid line), and the C-R_1 bond not quite as readily (shown by the dashed line). The resulting mass fragments are distinguishable because of the mass difference between C and O. The spectra of several formals, acetals, and propionals exhibited odd mass peaks that could be correlated by a simple empirical equation which may be used to predict the positions of corresponding mass peaks for the acetals of higher aldehydes. This correlation is applicable also to certain compounds related to acetals, such as dioxolanes. It shows, furthermore, that no acetal-type compound can have a mass peak of 61, which occurs commonly in mixtures of oxygenated compounds. This odd peak may be attributable to hemiacetals.

Product and Isomer Distribution in the Hydrocarbon Synthesis

Schemes for predicting the isomer distribution of each paraffin hydrocarbon were developed some time ago at the Bruceton laboratories. These schemes are based on a few simple rules for chain growth and are in satisfactory agreement with actual isomer distributions as determined in the products from iron and cobalt catalysts. A similar scheme, accounting for the carbon-number distribution of the hydrocarbon product, was available but not easily applicable because fractionation of the hydrocarbons into close cuts was required. Further development of this method has made it applicable to relatively crude fractionation data, and agreement of theory and practice permits some valuable conclusions concerning the mechanism of the synthesis. The method is based on the assumption that chain growth in the synthesis proceeds by stepwise addition of single carbon atoms and that the probability of growth, α , of a given hydrocarbon chain is independent of the carbon number above C_5, although it may vary with experimental conditions. Agreement of data and theory is illustrated in figure 38, where product distribution is plotted as a function of the probability of growth. This graph is of practical interest, as it shows that not more than about 30 percent of the total liquid and solid product can be expected to be in the range of Diesel oil. Furthermore, this amount of Diesel oil should be readily obtainable, because the maximum yield of the fraction remains nearly unchanged over a rather wide range of probabilities of growth, that is, conditions of operation of the synthesis. As a matter of fact, attempts made in other laboratories to increase the yield of Diesel oil obtained in the gas synthesis process have been unsuccessful.

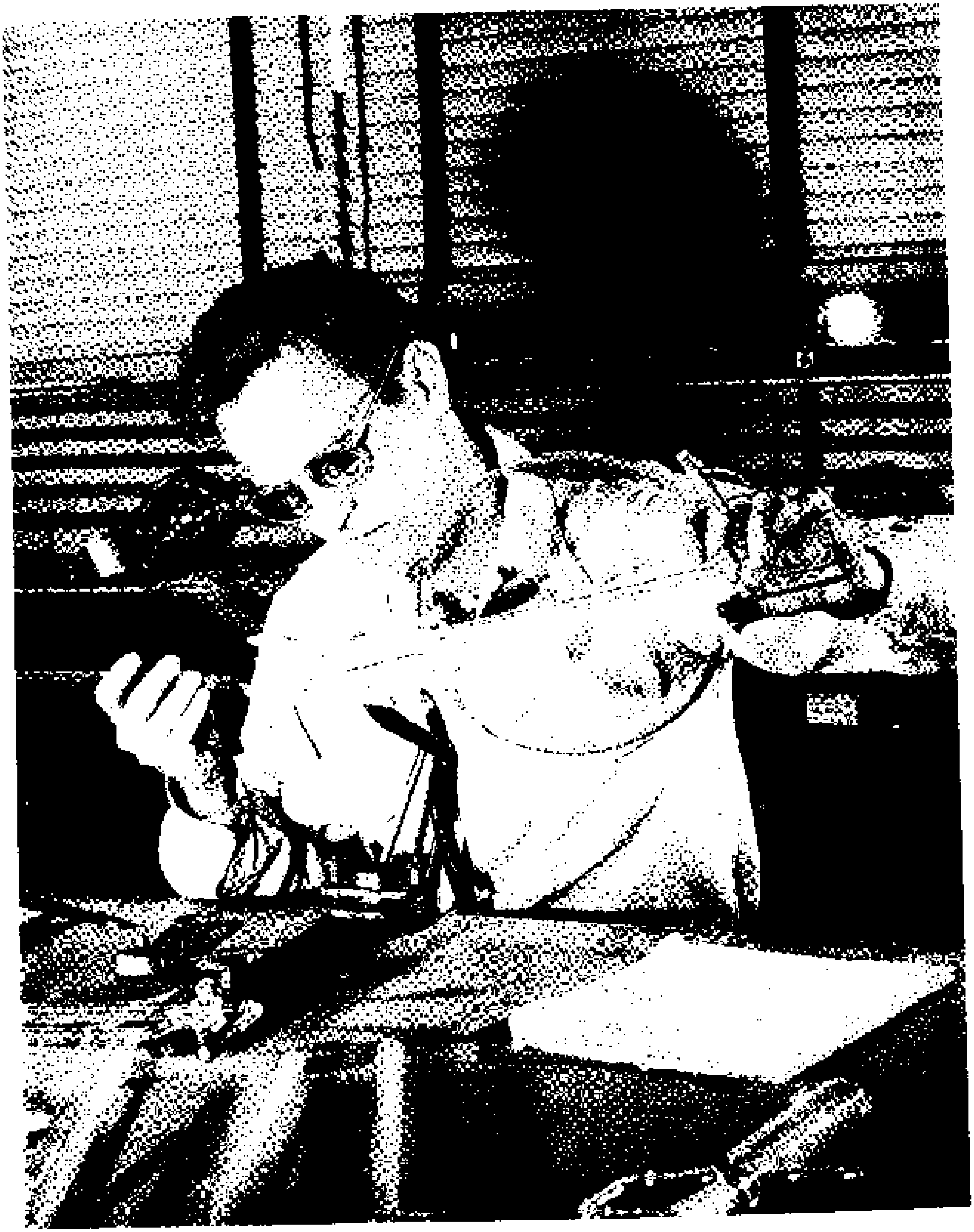


Figure 36. - Glass-blowing shop.

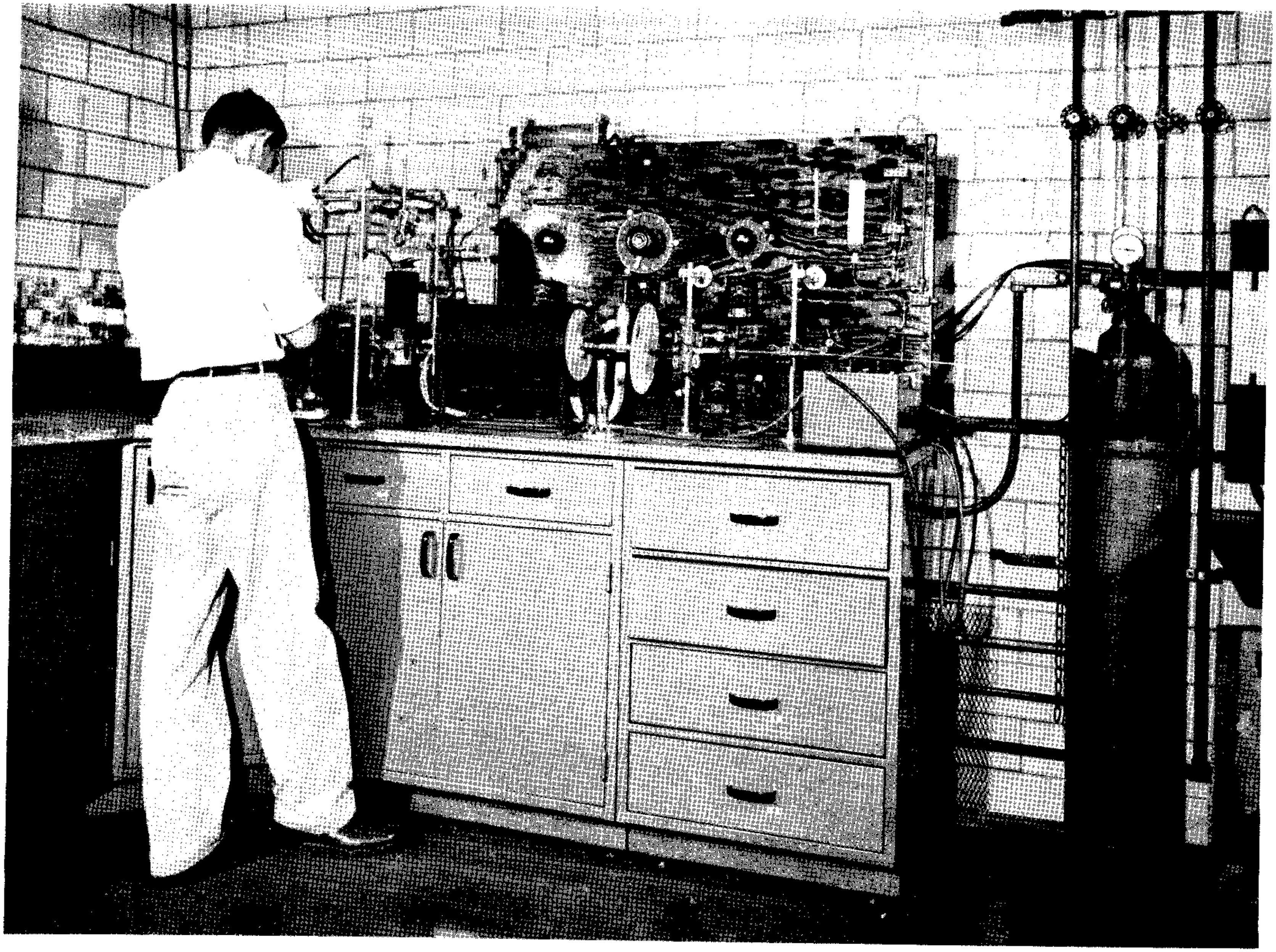


Figure 37. - Modified Unterzaucher apparatus for direct determination of oxygen.

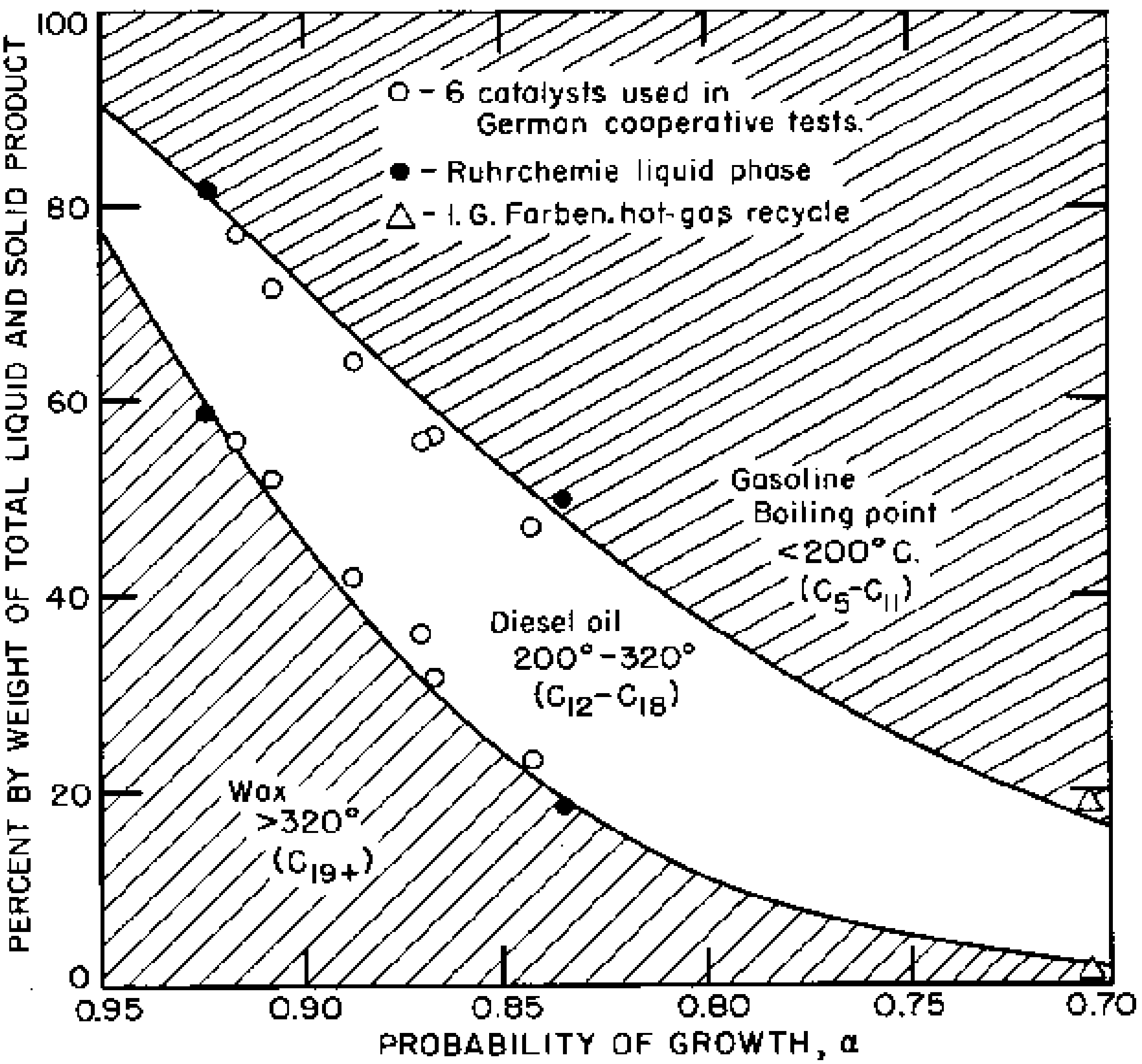


Figure 38. - Correlation of theoretical and observed product distributions of liquid and solid Fischer-Tropsch hydrocarbons obtained with iron catalysts.