lower edge of the cone, it was turned outward. Also, to permit the filter cake to spread evenly, outlets were cut into the lower edge of the cone. These outlets were equilateral triangles about 1/s of the cone in height, spaced evenly around the base.

A piece of Klingerit about 1/s of the diameter of the Büchner funnel, was placed in the middle of the filter paper as a protective baffle. Asbestolite or asbestos sheeting could also be used but Klingerit can easily be cut out with a wad cutter and is durable as well.

The dimensions of the splash cone and the baffle depend on the size of the Büchner funnel used. The funnel should be 'chosen so that not more than 1/2 of its height is filled by the filter cake; otherwise it will be difficult to remove the cone.

FILTRATION PROCEDURE

The outlet tube, which reaches to the bottom of the autoclave, is provided with two valves. The main valve regulates, approximately, the pressure of the issuing solution. The second valve, located nearer the end of the tube fitting into the splash cone, regulates the amount of solu-

tion being run into the Büchner funnel. Before the funnel is used, the filter paper must be moistened—e.g., with water—

Figure 1. Diagram of Filtering Arrangement

> Australia, this work was carried out RECEIVED for review November 27, 1951.

under suction. Then the Klingerit baffle is placed in the middle of the filter paper and the whole covered with the splash cone. Suction must be applied before the actual filtration begins. All flames in the vicinity must, of course, be extinguished before the autoclave charge is run out should this contain alcohol. If, during the filtration, the alcohol should distill too quickly into the condenser trap and start to choke the condenser, suction can be interrupted for a moment at the upper end of the condenser.

Some 300 filtrations under the conditions described have been carried out successfully with the assembly described. The reflux trap facilitates recovery of most of the alcohol evaporating in the filter flask. About 250 ml. of a total of 2 liters of 90% alcohol are lost by evaporation in the funnel.

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Synthesis of Alcohols by Hydrogenation of Carbon Monoxide

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ROCESSES for the hydrogenation of carbon monoxide to alcohols may be divided into two groups. The first of these, in which the catalysts are difficultly reducible oxides (catalysts containing copper oxide are exceptions to this generalization), includes the methanol synthesis, the higher alcohol synthesis, and the iso synthesis. The second group includes variations of the Fischer-Tropsch synthesis over iron catalysts. Both types of syntheses were discovered in the period 1920-25 The methanol and higher alcohol syntheses were developed rapidly into practical commercial processes. The iso synthesis which may be considered a variation of the higher alcohol synthesis, was discovered in 1940. Although the Fischer-Tropsch synthesis using iron catalysts was discovered in 1923, catalyst and process development proceeded slowly and large scale processes employing iron catalysts for the production of hydrocarbons or of alcohols did not appear feasible until about 1940. By intensive research on the Fischer-Tropsch synthesis over iron catalysts, in Germany during World War II and in the United States since the war, several attractive synthesis methods have been developed. Neither the iso synthesis nor the Fischer-Tropsch process with iron catalysts has been exploited commer-

cially, except that the Hydrocol plant at Brownsville, Tex., employing a fluidized iron catalyst, is reported to be in operation. This represents the first commercial use of the Fischer-Tropsch synthesis with iron catalysts.

The hydrogenation of carbon monoxide to alcohols may be expressed by Equations 1 and 2 or combinations of them:

$$2n H_2 + n CO = C_n H_{2n+1}OH + (n - 1)H_2O$$
(1)

$$(n + 1)$$
 H₂ + $(2n - 1)$ CO = C_nH_{2n+1}OH + $(n - 1)$ CO₂ (2

The thermodynamics of these reactions have not been completely investigated, as indicated by a recent summary of available data (22). The equilibrium constants of Equations 1 and 2 decrease rapidly with increasing temperature, and the temperatures at which the equilibrium constants equal 1 may be taken as the upper limits at which sizable yields of alcohols may be obtained at low operating pressures. For reactions 1 and 2, respectively, these temperatures are 238° and 318° C. for ethyl alcohol, 316° and 358° C. for 1-propanol, and 330° and 378° C. for 1-butanol. For methanol, Equations 1 and 2 are identical and the equilibrium constant is unity at 146° C. Thus, at any given

temperature, reactions of the second type are thermodynamically favored over corresponding reactions of the first type and the synthesis of alcohols of higher molecular weight is more likely thermodynamical than alcohols of lower molecular weight in both cases. However, the production of paraffins and olefins is thermodynamically favored over that of alcohols under synthesis conditions (22). In addi-

		TABLE I.	Alcohol	SYNTHESES			
	Catalysts						
Synthesis	Main constituents	Promoters	Pressure, Atm.	° C.	Products		
Methanol	ZnO, Cu, Cr2-		100-500	250-400	Largely methanol		
Higher alcohol	ZnO, Cu, Cr2- Oz, MnO	Alkali oxides or carbon-	100-500	300-400	Methanol, isobutyl alcohol, and other branched chain alcohols		
Iso	ThO_{2}	Al ₂ O ₃ , K ₂ CO ₃	100-500	350-400	Alcohols, as with higher alcohols, and small yields of branched hy- drocarbons		
Iso	ThO2	Al2O8, K2CO2	100-500	400-475	Branched hydrocarbons and small yields of alcohols		

tion, dehydration of alcohols to olefins and their subsequent hydrogenation to paraffins are thermodynamically possible under most synthesis conditions (22). Hence, the production of alcohols depends upon the selectivity of the catalyst as well as upon thermodynamics.

This review of the various processes considers the catalysts, conditions of operation, nature of the products, and reaction mechanisms. The production of alcohols by the Oxo reaction, the hydroformylation of olefins or alcohols in the presence of cobalt, will not be discussed. For recent studies of the production of alcohols by the Oxo reaction, see references (25-28).

ALCOHOL SYNTHESES

Table I summarizes the catalytic components of, conditions of operation for, and types of products from the alcohol syntheses. Usually relatively high temperatures and pressures compared with those of the Fischer-Tropsch process are employed, and moderately high space-time yields result. The fact that these processes can be operated at considerably higher temperatures and pressures than the Fischer-Tropsch synthesis is probably related to the stability of the oxide catalysts in the presence of carbon monoxide and hydrogen under these conditions

METHANOL AND HIGHER ALCOHOL SYNTHESES. Mixed catalysts containing two or more active components are usually employed in the methanol and higher alcohol syntheses. Methanol is the principal product in the former synthesis, although appreciable yields of dimethyl ether may also be formed. Presumably dimethyl ether is formed from methanol in a secondary reaction, as the ratio of dimethyl ether to methanol decreases with increasing space velocity (3). For a survey of the literature on the methanol synthesis up to 1945, see reference (10). The higher alcohol synthesis employs lower space velocities and higher temperatures than the methanol synthesis. The catalysts are



Figure 1. Conversion of Carbon Monoxide to Higher Alcohols as a Function of Reciprocal of Space Velocity

the same in both cases except that small amounts of alkali oxides, hydroxides, or carbonates are added as promoters in the former (14). The products of the higher alcohol synthesis are principally methanol and isobutyl alcohol, with smaller amounts of a wide range of primary and secondary alcohols, aldehydes, ketones, and hydrocarbons. Of particular interest is the apparent absence of higher straight-chain primary alcohols, such as 1-butanol, in products from the higher alcohol synthesis. The separation and identification of the alcohols are extremely difficult and a complete analysis of the products from the higher alcohol synthesis has not been reported. Graves's (9) analysis of products from a commercial higher-alcohol synthesis is given in Table II. Data of Frolich and Cryder (7) in Figure 1 show the yields of C_1 and C_4 alcohols as a function of space velocity, and indicate that methanol is probably the primary product from which the higher alcohols are formed by subsequent reactions.

TABLE II. QUALITATIVE ANALYSIS OF ALCOHOLS FROM HIGHER Alcohol Synthesis^a

(1-Butanol was not found and tests for tertiary alcohols were negative; some alcohols were not identified; traces of aldehydes, ketones, and saturated and unsaturated hydrocarbons were found)

	one obmo nore to ana,
Primary Alcohols (48.5%)	Secondary Alcohols (51.5%)
1-Propanol Isobutyl alcohol 2-Methyl-1-butanol 2-Methyl-1-pentanol 2,4-Dimethyl-1-pentanol 4-Methyl-1-hexanol 2,4-Dimethyl-1-hexanol 4- or 5-Methyl-1-heptanol	Isopropyl alcohol 3-Methyl-2-butanol 2,4-Dimethyl-3-pentanol 3-Pentanol ^b 2-Pentanol ^b 2-Methyl-3-pentanol ^b
From reference (9).	

^b There is some uncertainty as to these identifications, since derivatives of these compounds have not been described in the literature.

Iso SYNTHESIS. In addition to alcohols similar to those of the higher alcohol synthesis, the iso synthesis also produces branchedchain and cyclic hydrocarbons. Pichler and Ziesecke (15-18) have presented excellent quantitative characterizations of iso synthesis hydrocarbons and alcohols. In the range 375° to 425° C, the iso synthesis produces high yields of alcohols (18) as shown in Table III. At 450° C. (Table IV) the iso synthesis produces mostly hydrocarbons, with isobutane as the chief component (17). At 500° C appreciable yields of aromatic and naphthenic hydrocarbons have been obtained with some catalysts. The optimum synthesis pressure is about 300 atmospheres. At pressures higher than 300 atmospheres and in some cases at even 300 atmospheres but at lower temperatures, sizable yields of dimethyl ether were obtained (15).

Thoria is the principal constituent of most good iso synthesis catalysts. Alkali is not necessary as a promoter in this type of synthesis; nevertheless, the average molecular weight of iso synthesis products is increased by addition of alkali to the catalyst. The oxygenated product of the iso synthesis consists chiefly of branched primary alcohols. If Graves's results (Table II), indicating about equal yields of primary and secondary alcohols, are considered to be typical of the higher alcohol synthesis, there is a

TABLE III. PRODUCTS	of Iso	Synthesis	5 AT 400°	C.ª
		$\frac{\text{ThO}_2}{\text{and}}$	${ m ThO}_2$ and 3%	$_{ m and}^{ m ThO_2}$
Catalyst Composition	ThO_2	K_2CO_3	K_2CO_3	Al_2O_3
Pressure, atm.	300	300	1000	300
water), g./cubic m. Composition of liquid (exclusive	104	94	119	81
of water), wt. %	18 2	18.1	34.4	26.4
Ethyl alcohol	0.4	0.4	3.5	0.1
Isopropyl alcohol	·+	0.2	0.3	~ ~
n-Propyl alcohol	0.5	0.7	1.7	0.0
2-Methyl-1-propanol	22.5	24.7	24.0	8.2
2-Methyl-2-butanol	-		<u>_+</u>	
3-Pentanol	-	<u>,</u>	0.8	_
2-Pentanoi 2-Methyl-1-butenol	10	2.0	3.5	0.5
2-Methyl-2-pentanol	-	0.3	+	_
3-Hexanol			<u>, +</u>	-
2,2-Dimethyl-1-butanol	1 7	2 1	0.4	0 5
2-Metnyl-1-pentanol 2 4-Dimethyl-1-pentanol	2 6	5.2	1.1	0.5
Alcohols with b. pt. <160° C.	$47.\tilde{2}$	54.9	73.3	36.8
Aldehydes and ketones	2.9	3.0	1.9	0.3
Ethers	>0.7	1 1	3 0	0.5
Acids	0.2	0.2	0.3	0.1
Hydrocarbons and alcohols	48.3	40.8	21.5	60.4
with b, pt. $> 160^{\circ}$ C.				
^a From reference (18).				
TABLE IV. PRODUCTS	of Iso	Synthesis	s at 450°	C.ª

Catalyst Composition		ThO_{2}	2	10% Al ₂ O ₈	
Pressure, atm. Products, g./cubic m. Hydrocarbons	300	1000		300	
C_1 C_2	$\substack{11.1\\4.2}$	}	67.0	$13.2 \\ 2.7 \\ 5.5$	
$n-C_4$ Iso-C4	$ \begin{array}{r} 10.9 \\ 3.2 \\ 22.7 \end{array} $	}	12.0	$5.4 \\ 37.6 $	
Cs ⁺ Alcohols Total liquida	$42.2 \\ 19.3 \\ 98.3$		39.0	$32.8 \\ 15.9 \\ 97.2$	
Dimethyl ether	•••		49.0	••	

considerable difference between the relative abundance of primary and secondary alcohols in the products of the iso synthesis and of the higher alcohol synthesis.

ALCOHOLS FROM THE FISCHER-TROPSCH SYNTHESIS

Table V is a summary of the catalytic components, conditions of operation of, and products from, various Fischer-Tropsch syntheses. These syntheses are usually operated at lower temperatures and pressures than the alcohol syntheses of group 1, otherwise two side reactions would make the Fischer-Tropsch

synthesis inoperable: First, metals of the iron group deposit elemental carbon in increasing amounts with increasing temperature, resulting in catalyst disintegration. For cobalt and nickel catalysts the rate of carbon deposition is prohibitively high at temperatures above 250° C.; for iron the rate is prohibitively high above 300° C. (The fluidized iron catalyst processes, which usually operate at temperatures above 300° C., use hydrogenrich synthesis gas to minimize carbon deposition. Nevertheless, catalyst disintegration is a serious problem in these processes.) Presumably the rate of deposition of elemental carbon also increases with operating pressure. Second, for iron-group metals, volatile carbonyl formation may seriously impair catalyst activity and life at higher operating pressures.

Nickel and ruthenium catalysts produce only negligible amounts of oxygenated products and hence need not be considered further. Similarly, cobalt catalysts usually produce only small yields of oxygenated products, mainly alcohols, but under some special conditions—for example, when the catalyst is promoted with alkali—as much as 10% alcohol may be formed (20). Recently, Gall, Gibson, and Hall (8) reported that a standard





Left. Composition of condensed product, exclusive of water *Right.* Composition of alcohols

	TABLE V.	VARIATIONS OF	THE FISCI	HER-TROPSCI	H SYNTHESIS
$egin{array}{c} { m Active} \\ { m Constituent} \end{array}$		Promoters	Pressure, Atm.	Temp., °C.	Products
Nickel	ThO2,	MgO	1	170-200	Gaseous and liquid paraffinic hy-
Cobalt	ThO ₂ , ThO ₂ ,	MgO MgO, MnO, K ₂ O	$\begin{smallmatrix}&1\\1-15\end{smallmatrix}$	250-450 170-210	Chiefly methane Chiefly paraffinic hydrocarbons plus small yields of alcohols and other oxygenated mole- cules
Ruthenium			10-100	170-200	Chiefly solid paraffinic hydrocar- bons of very high molecular weight
Iron Conventional	Cu, M ZrC	IgO, Al ₂ O ₂ , CaO, 2, TiO ₂ , K ₂ O, K ₂ -	10-30	200-270	Predominantly olefinic hydrocar- bons; about 10% oxygenated
Fluidized catal	yst ^o	3	15-50	290-400	Predominantly olefinic hydrocar- bons; 10-25% oxygenated products chiefly alcohols.
$Symol^b$		••••	20	190-220	Olefinic hydrocarbons and more than 50% oxygenated prod- ucts chiefly alcohols
Nitrided b		· · · · · · · · · ·	7-30°	190-200	Paraffinic and olefinic hydrocar- bons and more than 60% oxy- genated products, chiefly alco- hols.

^a Upper limit of pressure has not been fully investigated. ^b Same promoters used as for the conventional iron. cobalt-thoria-magnesia-kieselguhr catalyst produced high yields of alcohols when operated at temperatures from 20° to 30° C. lower than those usually used. Thus, at a temperature of 160° to 175° C. and a pressure of 11 atmospheres, a yield of oxygenated molecules, chiefly primary straight-chain alcohols, of 40 weight % of the total condensed hydrocarbon plus oxygenated fraction was obtained.

Alcohols		Aldehydes		Ketones		Acids	
Methanol Ethyl alcohol n-Propyl alcohol Isopropyl alcohol	$0.3 \\ 36.9 \\ 8.7 \\ 0.8$	Acetaldehyde Propionaldehyde	6.0 2.2	Acetone	7.5	Acetic acid Propionic acid	18.1 4.7
Butanols	4.0	Butyraldehyde	2.1	Methyl ethyl ketone	2.2	Butyric acid	3.4
Higher alcohols	1.2	•••••	••	Higher methyl ketones	1.1	Higher acids	0.8

TABLE VI. OXYGENATED PRODUCTS FROM HYDROCOL PROCESS^a

FISCHER-TROPSCH SYNTHESIS ON IRON. For iron catalysts, small amounts of alkali (usually potassium carbonate or potassium hydroxide) are essential to high activity and suitable selectivity. Usually the activity, the average molecular weight of the products, and the fraction of oxygenated molecules increase with increasing alkali content up to a maximum at 0.5 to 2 parts of alkali per 100 parts of iron. Although alcohols are the principal oxygenated products obtained with iron catalysts, sizable amounts of organic acids, aldehydes, ketones, and esters are also produced. For example, the oxygenated fraction of the product obtained by the fluidized process (Table VI) contained 51.9% alcohols, 10.3% aldehydes, 10.8% ketones, and 27% organic acids; esters were presumably hydrolyzed during the separation (5). The alcohols from iron catalysts are principally primary straight-chain alcohols. Ethyl alcohol is the major constituent of Fischer-Tropsch alcohols; the yield of methanol is usually very small.

From the rather diverse but incomplete studies of the variables of the Fischer-Tropsch synthesis, the following tentative summary of factors favoring the production of alcohols may be made. High yields of alcohols and other oxygenated products are favored by high pressure, low temperature, high space velocity, high recycle ratio, and carbon monoxide-rich synthesis gas. Conventional fixed-bed or oil-phase processes operating at 220° to 300° C., space velocities of 100 to 600 per hour, and with low



Figure 3. Product from Fischer-Tropsch Synthesis with Nitrided Fused Iron Catalyst

recycle ratios produce the smallest yield of oxygenates, approximately 5 to 15% of the condensed products (exclusive of water). Although high temperatures and hydrogen-rich gas are employed in the fluidized process, somewhat higher yields of oxygenated products are obtained, (as shown in Table VI), presumably because of the high space velocity and high recycle ratio. The conditions of the synol process (19) are probably the optimum ones for alcohol production using nonnitrided iron catalysts; the high attainable yields are shown in Figure 2. The oxygenated synol products consist almost completely of straight-chain alcohols. The synol alcohols consist of about equal weight percentages of the C₃ to C₁₈ alcohols, a low percentage of methanol, and a rather high percentage of ethyl alcohol. About 16% of the alcohols contain more than 22 carbon atoms.

The synthesis over nitrided iron catalysts has produced unique and unexpected results. Although the usage ratio of hydrogen and carbon monoxide is the same as for other iron catalysts, the activity, stability, and life of nitrided catalysts are considerably greater than those of corresponding reduced or inducted catalysts. In addition, the products of the nitrided catalysts contain very large amounts of alcohols and other oxygenated molecules. Comparison of products from reduced and nitrided iron catalysts and corresponding reduced or inducted iron catalysts have been made in recent publications (2).

Table VII and Figure 3 present the distribution of products obtained with nitrided fused iron catalyst D3008 (Fe₃O₄-Al₂O₄-K₂O) at 21.4 atmospheres and 243 ° C. The conditions of operation of this test (X337) are given in (21). The details of the analytical procedure are summarized as follows:

The product from nitrided catalysts consists of an aqueous phase containing water and oxygenated organic molecules; an oil phase containing hydrocarbons, oxygenated organic molecules, and traces of water; and light hydrocarbons in the gas phase. The aqueous layer was saponified with caustic and distilled in a 10-plate column to 90° C. The distillation residue was extracted with ether, the ether removed, and the residue combined with the previous distillate. This combined material was redistilled from aqueous sulfuric acid to 90° C. and the distillate examined spectroscopically for alcohols and ketones. The portion boiling above 90° C. was extracted with ether, the solvent evaporated, and the alcohols were isolated by the quantitative formation of half-acid phthalates with phthalic anhydride in a refluxing pyridine-benzene solution (11). The half-phthalic esphthalic annyurus benzene solution (11). The half-phthalic op-ters were separated by extraction with so-the resulting solu-tion other extraction was freed of neutral oils by ether extraction and acidified to separate the phthalic esters. These were extracted with ether and washed with water, and the ether was evapo-rated. The alcoholic esters were saponified with sodium hydroxide in a suitable solvent, and the alcohols were extracted with ether.

This extract was washed with water and the ether was evaporated. The resulting alcohol mixture was fractionated and the cuts were examined spectroscopically. The analysis for ketones in-cludes only those distilling below 90° C.

The alkali raffinate from the saponification of the aqueous phase was acidified and extracted with ether. The acid number of the residue from evaporation of the ether corresponded to a C4 acid. In the analysis of the aqueous phase esters were hydrolyzed and the alcohols and acids included those present as esters.

The oil layer was fractionated into 100° C. cuts from 50° to 450° C., and the fractions boiling from 50° to 350° C. were analyzed individually by the following method. Hydrocarbons were isolated from oxygenated material by adsorption on silica were isolated from oxygenated material by adsorption on silica gel. Oxygenated functional groups—carboxyl (13), ester (13), carbonyl (4), and hydroxyl (6)—were determined by chemical and spectrographic methods; the results of the two methods agreed satisfactorily. From the results of the chemical method, the distribution by weight of alcohols, aldehydes, and ketones, esters, and acids was estimated, assuming average carbon num-bers of 4, 8, and 13 for the 50° to 150° C., 150° to 250° C., and 250° to 350° C. distillation fractions, respectively. These data combined with the analyses of the aqueous and gaseous phases are presented in Figure 3.

are presented in Figure 3. In addition to being identified by the analysis based on func-tional groups, the alcohols in the 50° to 350° C. distillate frac-tions obtained from the oil phase were isolated by quantitative conversion to half-acid phthalates as described. The phthalic esters were saponified and the alcohols were fractionated. Distillation cuts up to C_6 were analyzed spectroscopically, and higher alcohols were estimated from the distillation curve. These data for alcohols in the oil phase, together with free and combined alcohols in the aqueous phase, are presented in Table VII.

TABLE VII.	ALCOHOLS	SEPARATED	FROM	PRODUCT	OF NITRID	ED
		IRON CATAL	TAL			

(Fused FeiO4-Al2Oi-K2O, operated at 21.4 atmospheres and 243° C.) Composition Wt fl in

pnase	$H_2O)$	Aqueous Phase
5.28	1.740	
0.12	0.040	• •
0.09	0.03	
0.06	0.02^{b}	
c 14,32d	23.79	19.8
0.51	0.23	66.0
11.53	9.12	41.7
1.51	3.54	14.0
a' 'ra	0.07	
0.48	2.82	5.6
a' 'aa	0.10	÷.,
0.23	2.22	3.4
0.00	1.78	1.1
0 0	1.44	U O
Ň	0.00	ŏ
ŏ	1 10	0
0	1.10	0
	0.48 0.23 0.06 0 0 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^a These organic molecules were not separated
 ^b Only from aqueous phase.
 ^c Does not include alcohols combined in esters
 ^d Includes alcohols combined in esters.

The products from nitrided iron catalyst D3008 contained, in addition to hydrocarbons, sizable amounts of alcohols, aldehydes, ketones, esters, and organic acids, as shown in Figure 3. These data include the approximate composition of the oil phase (based on functional group analyses) and of the organic molecules isolated from the aqueous phase. In part A, the organic molecules from the aqueous phase are added to those from the 50° to 150° C. distillate fraction of the oil layer. The data in parts A and B are reported as weight percentage of condensed material, exclusive of water, and in part C as weight percentage of total product, exclusive of water and carbon dioxide. Part A contains the distillation fractions of the condensed phases and the analyses of the individual fractions, whereas parts B and Ccontain the fractions of various types of organic molecules in the condensed phase and in the total product, respectively. Not all of the material is accounted for by these approximate analyses; the remainder is indicated by question marks in the block diagrams. The condensed phase consists of 29% alcohols, 20%hydrocarbons, 12% esters, about 4% aldehydes plus ketones, and about 4% acids. If the esters in the oil phase had been saponified, the percentage of alcohols would probably have been increased significantly.

Table VII indicates that about 24% of the condensed product has been actually isolated as alcohols. These alcohols are predominantly primary straight-chain alcohols. The distribution of alcohols shows a small amount of methanol, a maximum yield of ethyl alcohol, and a subsequent decrease in weight per cent with increasing carbon number. Although the alcohol fraction obtained from nitrided catalysts (Figure 3 and Table VII) does not exceed that obtained from the synol process, nitrided catalysts produce high yields of alcohols and other oxygenated molecules under the conditions of normal fixed-bed processes which usually yield a minimum of oxygenated molecules. The change in selectivity is produced by changing the chemical nature of the catalyst and not by changing the process variables such as gas flow and recycle ratio. Possibly the yield of alcohols from intrided catalysts could be greatly increased by operation at high space velocities and with a high recycle ratio.

REACTION MECHANISMS

At first sight there appears to be a continuous gradation from alcohol to hydrocarbon production in the order: methanol synthesis, higher alcohol synthesis, iso synthesis, synthesis over nitrided iron, synol process, fluidized iron process, conventional iron catalyst process, cobalt and nickel catalyst syntheses, and methane synthesis on nickel. However, the mechanisms of the processes here classed as alcohol syntheses appear to be drastically different from those classified as Fischer-Tropsch syntheses. The differences in the extent of branching of the carbon chains of hydrocarbons and alcohols obtained by the two types of syn-



Figure 4. Carbon Chains in C₅ and C₆ Hydrocar-bonsfrom the Iso and the Fischer-Tropsch Syntheses Compared with the Equilibrium Distribution of Pentanes and Hexanes

theses adequately illustrate the contention that the hydrocarbons from the iso synthesis have principally branched chains with a greater degree of branching than corresponds to thermodynamic equilibrium among hydrocarbon isomers, whereas the hydrocarbons from the Fischer-Tropsch synthesis have predominantly straight chains with considerably less branching than corresponds to thermodynamic equilibrium, as shown in Figure 4.

Many workers have postulated that formaldehyde is an intermediate in the alcohol syntheses; the amount of formaldehyde found in synthesis products is negligible because of its very low concentration at equilibrium and its great tendency toward hydrogenation to methanol. Methanol, in turn, has been regarded as a primary product and as an intermediate in the higher alcohol synthesis, since the ratio of methanol to higher alcohols increases with increasing space velocity (7). Frolich and Cryder (7) postulated the production of higher alcohols by dehydration of two alcohol molecules to form a higher alcohol, and on this basis, with simple rules for addition, Graves (θ) was able to predict qualitatively the presence or absence of certain alcohols. For example

$$CH_{3}OH + \mathring{C}H_{3}OH \longrightarrow CH_{3}CH_{2}OH + H_{2}O$$
 (3)

$$CH_{3}OH + \dot{C}H_{3}CH_{2}OH \longrightarrow CH_{3}CH_{2}OH + H_{2}O \qquad (4)$$

 $CH_{3}OH + CH_{3}\dot{C}H_{2}OH \longrightarrow CH_{3}CH(OH)CH_{3} + H_{2}O$ (5)

$$CH_{3}CH_{2}CH_{2}OH + CH_{3}OH \longrightarrow CH_{3}CH(CH_{3})CH_{2}OH + H_{2}O$$
(6)

where * indicates the carbon from which a hydrogen atom is removed by reaction with the hydroxyl group of the other alcohol molecule. In Equations 3 and 5 a hydrogen atom is removed from the alpha carbon atoms and in Equations 4 and 6 from the beta carbons. Graves postulated that reactions involving removal of hydrogen atoms from alpha carbons are slow compared with those involving beta carbons and that addition does not occur on CH groups. In addition, any alcohol formed may react with any other alcohol according to reactions consistent with the above rules. Thus, the principal reactions forming higher alcohols may be summarized as given in Figure 5, using the quantitative analyses of products for the iso synthesis as a basis for the relative abundance of alcohol molecules.

The distribution of the alcohols of the iso synthesis may be explained by the same postulates of chain growth, and that of the hydrocarbons may be explained by assuming that the alcohols are dehydrated to the corresponding olefins, which are subsequently partly hydrogenated. These postulates are reasonable because the principal component of iso synthesis catalysts, thoria, is one of the best dehydrating catalysts. However, Pichler (15) suggests that this mechanism may not be correct, as thoria catalysts usually isomerize hydrocarbons during the dehydration of known alcohols. Pichler suggests that dimethyl ether may be an intermediate since it reacts under conditions of the iso synthesis to yield products typical of this synthesis. Nevertheless, the dehydration picture is attractive because of its simplicity, and it is not impossible that the ability of thoria catalysts to isomerize hydrocarbons may be suppressed by some component of the synthesis such as carbon monoxide. In any case, the carbon chain appears to grow by combination of the alpha or beta carbon atom, predominantly the beta atom, of one chain with the alpha carbon atom of another chain.

The mechanism of the Fischer-Tropsch synthesis has been the subject of many papers; however, the majority of these have demonstrated chiefly the inadequacies of the carbide-intermediate hypothesis. [For a review of this hypothesis see (23).] The production of appreciable to large amounts of oxygenated molecules, principally alcohols, with carbon chains similar to those of the hydrocarbon products, especially from iron catalysts, sug-



gests that oxygenated groups may be intermediates. The plausibility of this hypothesis has been strengthened by recent experiments involving the incorporation of ethyl alcohol into synthesis products (12). The observed distributions of isomers and carbon number fractions have been fairly quantitatively predicted by simple postulates regarding one-carbon-atom additions to the first or second carbon atoms from one end of the growing carbon chain (1, 24). Specifically over iron catalysts, growth at end carbon atoms occurs at roughly nine times the rate of growth at adjacent-to-end carbon atoms, and addition does not occur at adjacent-to-end carbons already attached to three other carbon atoms. Thus, for growth occurring at the right end of the growing chain, the following chain species may result:



Although Fischer-Tropsch alcohols have not been completely characterized, the alcohols appear to have carbon chains similar to those of the hydrocarbons. The very small yields of methanol may be related to the small yield that is thermodynamically possible under conditions of the Fischer-Tropsch synthesis. The alcohols from the alcohol syntheses and from the Fischer-Tropsch synthesis may be regarded as commercially complementary rather than competitive, since the two types of processes yield strikingly different amounts of the same alcohols as shown for C_1 to C_4 alcohols:



^a P = principal components, S = minor components, T = traces, and - = not present.

In addition, the oxygenated product from the Fischer-Tropsch synthesis contains sizable yields of acids, esters, ketones, and aldehydes.

Finally, the catalysts for the two types of syntheses have different sensitivities to poisoning by sulfur compounds in the synthesis gas: Fischer-Tropsch catalysts are extremely sensitive **to**

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sulfur poisoning, and to attain a reasonable catalyst life the sulfur content must be less than 1 grain per 1000 cubic feet. The sulfur sensitivity of catalysts for the alcohol syntheses appears to vary considerably with catalyst composition. However, these catalysts are in most cases less sensitive to sulfur poisoning than Fischer-Tropsch catalysts. Some alcohol catalysts, for example, those for the iso synthesis, are unaffected by high concentration of sulfur (15).

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Synthetic Fatty Acid Triglycerides and Natural Drying Oils

FILM STUDIES

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NHE subject of drying and deterioration of paint films has occupied for many years an important place in academic and industrial research. Most of the experimental work has been related to film studies of natural oils and recently to synthetically prepared fatty acid triglycerides containing a single fatty acid component, such as trilinolenin or trilinolein.

The purpose of this paper is to report experimental data accumulated over more than one year on the oxygen absorption and weight change of synthetic fatty acid triglycerides and natural drying oils. Many investigators have studied these subjects, but in most instances oxygen absorption and weight gain and loss have not been correlated on the same film and in the majority of cases the experiments were not conducted over a sufficient length of time. A further objective of this study is to gain information on film yellowing and to compare films cast with different oils under various conditions for their changes in physical appearance.

EXPERIMENTAL PROCEDURE

The glycerol esters of linolenic, linoleic, and oleic acid (trilinolenin, trilinolein, and triolein) were obtained from the Hormel Institute of the University of Minnesota. In addition, commercially available alkali-refined linseed oil and soybean oil were included in this study.

Table I gives the physical and chemical properties of these triglycerides and their approximate purity.

FILM APPLICATION AND DRYING OF OILS. To form a con-tinuous smooth oil film it was essential that the glass slides be thirdots smooth on min it was essential that the glass sides be scrupulously clean. For oils containing no drier it was necessary to use frosted-glass plates to prevent creeping. The microscope slides of uniform thickness $(0.10 \pm 0.002 \text{ cm.})$ were etched with a water-carborundum slurry prior to final cleaning. The films were applied with a Bird applicator resulting in approximate film thicknesses of 3 mils, weighing 0.05 ± 0.005 gram. For each in-diridual oil films were end on a baset 20 clides for of mils were find dividual oil, films were cast on at least 20 slides, five of which were used to obtain checks on the weight measurements: oxygen determinations were made by scraping the oil film at different times from the remaining plates. The percentage of oxygen was determined by using a combustion apparatus for the semimicro determinations of carbon and hydrogen. Excellent reproducibility on weight change and oxygen percentage was obtained by adhering

strictly to the given procedure. The drier consisted of a mixture of lead and cobalt naphthenate; 0.5% of lead and 0.05% cobalt metal based on the weight of oil were added to the samples. Drying occurred in a room conditioned at all times to $73^{\circ} \pm 2^{\circ}$ F. and $60 \pm 4\%$ relative humidity.