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STUDY OF METHODS FOR CHEMICAL SYNTHESIS OF EDIBLE FATTY ACIDS AND LIPIDS

Final Technical Report

Prepared by
ESSO RESEARCH AND ENGINEERING COMPANY
Linden, N. J.
for Ames Research Center

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Edited by John W. Frankenfeld

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CONTENTS

FIGURES

TABLES

SUMMARY

A survey and critical evaluation of existing methods for the synthesis of fatty acids and lipids from metabolic wastes under conditions of space travel has been completed. An extensive literature search was conducted and the candidate processes were evaluated from the standpoints of chemical feasibility and nutritional value of the products. The only promising route involved synthesis of ethylene from carbon monoxide, polymerization to α-olefins *via* the Ziegler growth reaction, conversion to fatty acids by oxidative ozonolysis and combination with glycerol to form edible glycerides.

A first approximation engineering design was made and some rough estimates of power requirements were drawn up. The system was found to be extremely complex and unreliable. Hence it is not recommended as a method for food preparation on board a space craft.

Four methods for the synthesis of glycerol were discovered. The most promising are base catalyzed trimerization of formaldehyde followed by hydrogenation and hydrogenolysis of higher sugars which may be prepared by controlled polymerization of formaldehyde. The synthesis of glycerol is much less complicated than fatty acid production and hence is a recommended alternate.

A series of recommendations for further research and development were drawn up. These are mostly in the area of engineering and nutrition.

INTRODUCTION

The support of life in space presents many and varied problems. Two of the most pressing of these are food supply and waste gas disposal. The magnitude of these combined problems is apparent from Table 1.

	Per Man/Day	3 Yr. Total for 10 Man Crew
Food Req.	1.2 - 1.8 lbs.	12,000 - 19,500 lbs.
CO_2 Output	2.5 lbs.	27,300 lbs.
CO_2 Adsorbent	2.6 - 4.25 lbs.	28,500 - 46,500 lbs.
	Total	67,800 - 93,300 lbs.

Table 1 - Food Requirements and Waste Gas Control in Closed Environment(1-4, 9, 10).

For missions of long duration, control of CO_2 combined with O_2 regeneration becomes a virtual necessity. A variety of methods for CO_2 reduction have been devised(1, 5, 9, 10). Under such conditions the major weight contribution to life support becomes stored food. In missions exceeding two years this may amount to 85% of the entire life support system(5).

The intriguing possibility of controlling waste materials by converting them to foodstuffs is in the infant stage of development. Several schemes have been proposed including growth of plants (including algae and mushrooms)(3, 5-8,10), Hydrogenomonas bacteria(3, 5-7), secondary systems involving growth of fish on algae(10), and chemical synthesis of carbohydrates(5, 7), proteins(11, 12) and various nonfat energy sources such as glycerol(5, 7, 13), 1,3-butanediol(13-15) and 2,4-dimethylheptanoic acid(14, 15). The chemical processes have certain advantages over the biological systems. Potentially, at least, they are more efficient in the use of raw materials, energy and space and yield less inedible waste materials. A chemical process is inherently more reliable. More control may be exerted over reaction variables; chemicals are not susceptible to disease, mutation or virus attack. Finally, chemical systems make use of hydrogen, a by-product of oxygen recovery by water electrolysis. This permits maximum material and energy conservation. Only hydrogenomomas, of the proposed biological processes, makes use of hydrogen.

In addition to the schemes already mentioned, the possibility remains of synthesizing edible fats, patterned after natural materials, from CO_2 or its reduction product, CO. This report is concerned with such a possibility.

Human Energy Requirements - Advantages of Fats

The energy requirements for various activities during a flight mission are given in Table 2(16). Based upon such analyses allowances of 2500(10) and

Activity	Time hr.	Energy Expenditure Rate calories/min.	Total Performance calories
Sleep	7	1.2	504
Quiet Sitting or Standing	12	1.5	1080
Instrumentation	2	1.8	216
Complex Neuromuscular Tasks	2	2.6	312
Moderate Work	1	7.0	420
TOTAL -			2532

Table 2 - Energy Requirements for Various Activities during Space Flight(16).

2800(4) calories* per man-day have been suggested for space craft energy requirements. Fats, which provide 9.3 cal./g. vs. 4.1 cal./g. for carbohydrates and proteins,(17) are by far the most economical sources of energy. Even when allowance is made for the extra oxygen required for complete oxidation, fats possess a clear advantage from a weight standpoint.

Substance	Weight per 1000 Calories(16) Food (gm.)	Oxygen (gm.)	Total (gm.)
Carbohydrate (Sucrose)	253	284	537
Fat (Tri-olein)	106	307	413
	Savings in weight for fat (1000 calories)		124 gm.

In addition, fats are welcome addition to the diet both from the standpoint of taste and hunger satisfaction. Finally, the incorporation of at least small quantities of fatty acids in the diet may be essential(18, 19). There are, however, certain limitations to the amount of natural fats which may be consumed. An upper limit of 50% of total calories has been suggested(16). A more detailed discussion of fat requirements is given below.

Statement of the Problem

The purpose of this study was to survey and critically evaluate methods for the production of edible fats from metabolic wastes by chemical means under conditions of space travel. Five steps are involved in such a process.

1. Conversion of CO_2 to CO.
2. Reduction and polymerization of CO to hydrocarbons in the fatty acid range.
3. Conversion to fatty acids.
4. Synthesis of glycerol.
5. Esterification to form glycerides.

---

* Here and throughout this report "calories" are K-calories.

The project required (1) a literature search into current technology for conversion of gases (especially CO_2) to edible fats, (2) a judgment as to the best method with consideration of yield, technical feasibility, weight, volume and power requirements, and safety, (3) a nutritional evaluation of the products of the various approaches and recommendations concerning the maximum levels at which the synthetic fat might be incorporated in the diet and (4) recommendations for future research and development.

Approach - Assumptions

A comprehensive literature search was carried out to uncover methods of polymerizing CO selectively to high yields of hydrocarbons or hydrocarbon derivatives in the useful molecular weight range (C_{10}-C_{20}). Concurrent, but separate, searches were conducted in the areas of CO_2 reduction, conversion of hydrocarbons to acids, glycerol synthesis, conversion of glycerides, nutrition of synthetic fats and of the problems associated with a weightless environment.

In order to conduct an efficient search, some rough nutritional guidelines were set up concerning the potential usefulness of various fatty materials. These were arrived at by consultation with nutrition experts and by an examination of the literature on the German synthetic fat program carried out during World War II. The generalizations agreed upon are given below.

1. Hydroxy and keto acids are unsatisfactory mainly from the standpoints of odor, color and flavor.
2. Branched chain materials are not assimilated well, especially if the side chains are of C_2 or larger.
3. Fatty acids with odd numbers of carbon atoms are metabolized but perhaps not quite so well as natural fats.
4. Odor and flavor are functions of the amounts of branched chain and multi-functional compounds present. Carefully refined products appeared to be acceptable.
5. Fatty acids of carbon numbers C_{10} - C_{18} are optimum. Small amounts of higher and lower acids may be tolerated.
6. Dicarboxylic acids are undesirable.

A preliminary rating of all methods was made on the basis of the above nutritional guidelines and over all yield of useful products. The candidate systems which passed this screen were then to be further evaluated from engineering criteria and the most promising process selected. (However, the system selection was actually made on the basis of yield and nutritional value alone; only the Ziegler polymerization of ethylene was deemed feasible).

In order to facilitate the formulation of research and development recommendations, a rough, first approximation engineering study of the process was conducted. On the basis of this recommendations were drawn up concerning the feasibility of including a fat synthesis sub-system as part of a closed cycle recovery loop on a space craft. Areas requiring further research in chemistry, engineering and nutrition are indicated.

Crew and Mission Model

As a working model the following assumptions were made concerning the crew and mission type. The recommendations given below are not restricted to this model. In fact, the synthesis of fat would be much more applicable to missions of longer duration and greater crew size.

Crew:	10 Men
Mission:	Greater than one year
Gravity:	Zero or Limited
Power:	Nuclear
Cabin Environment:	Air

Raw Materials Available

The following materials were assumed as available from other sub-systems on board the space craft:

CO_2
O_2
H_2
H_2O
CH_4
HCHO

Requirement for the System

Based upon the above considerations, the sub-system discussed below was designed to produce up to 5 lb. of fat per day (0.5 lb/man for a 10 man crew).

TECHNICAL DISCUSSION

The key step in any synthesis scheme is the reductive polymerization of CO or CO_2 (whether in a single step or multiple steps) to straight chain materials of moderate molecular weight. Consequently, the major effort of the literature search was devoted to this aspect of the problem and no attempt was made to devise subsequent operations (such as oxidation to fatty acids) until the most promising polymerization methods had been established. After a brief historical review, therefore, the technical discussions begin with this key step. Only those processes which passed the first, preliminary screen will be discussed any detail. According to the format adhered to throughout this report, the least useful methods are discussed first and most briefly.

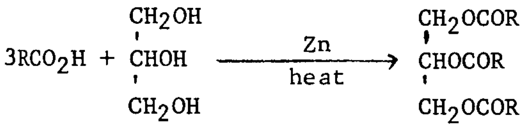
Historical - the German Process

A shortage of fats was experienced by Germany shortly before and during World War II(20-28). The German process consisted of converting CO to higher molecular weight hydrocarbons by means of the Fischer-Tropsch Process, followed by oxidation to acids and conversion to glycerides (Figure 1).

Yield of Purified Product

(1) $nCO + 2nH_2 \overset{cobalt}{\rightleftarrows} C_nH_{2n} + nH_2O$ 5-12%

(2) $C_nH_{2n} \xrightarrow[\text{heat, cat.}]{\text{air}} RCO_2H$ 40%

(3)  80-90%

$$3RCO_2H + \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow[\text{heat}]{\text{Zn}} \begin{matrix} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{matrix}$$

Overall: 1-4%

Figure 1. Summary of Germany Synthetic Fat Process (20)

The starting material for fat production was a paraffin wax fraction of the Fischer-Tropsch process called "gatsch". It consisted of a fairly narrow cut of the total hydrocarbon product boiling at 320-450°C (28). "Gatsch" was produced by hydrogenation of carbon monoxide over iron or cobalt catalysts(20, 21, 28). If iron was used, high pressures were required. However, iron gave better yields of the "gatsch" fraction(21, 28). At best, however, this was only 5-12% of the total Fischer-Tropsch product(20). It has been stated(21)(but not demonstrated) that higher percentages of "gatsch" could be realized. However, nothing in the voluminous Fischer-Tropsch literature could be found to substantiate this claim. Further details on the synthesis of hydrocarbons are given below in the section on Fischer-Tropsch.

The process for manufacture of fatty acids involved five discrete steps(20, 22): (1) oxidation, (2) saponification to form soaps, (3) purification of the soaps, (4) acidification, and (5) fractionation.

The oxidation(20-24, 26, 27) was carried out in aluminum vessels, the aluminum apparently acting as a catalyst, by passing air through a mixture of "gatsch", 0.2-0.5% of potassium permanganate and water at 105-120°C and atmospheric pressure. The addition of a little sodium or potassium carbonate was said to improve product quality(26).

$$RCH_2CH_3 \xrightarrow[105°]{\text{Air: } KMnO_4} RCH_2CO_2H$$

Invariably a complex mixture resulted which contained a large percentage of multifunctional compounds. To keep this to a minimum, the oxidation was terminated after 30-35% of the hydrocarbon was reacted, thus insuring an excess of unreacted paraffin at all times. The crude acids (79%) nevertheless contained considerable oxygenated by-products. This is apparent from the discrepancy between the saponification and neutralization numbers of the crude acids in Table 4. The crude acids were water-washed and saponified with caustic in the presence of steams to cleave esters. The resulting soap was allowed to settle and the upper layers, mostly unreacted hydrocarbons, were recycled. The soap was further purified by flash distillation. This process apparently dehydrates hydroxy acids to unsaturates and accounts for the iodine values given in Table 3(22). The soaps were acidified, washed with water until acid free and fractionally distilled by passage through a series of stills at various reduced pressures. A center fraction of C_{10}-C_{18} acids was taken (up to 55% of the crude (Table 3).

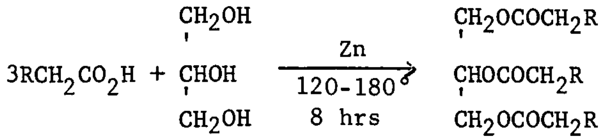
Acids	Boiling Range	Percent of Total
C_3-C_{10}	Up to 150°	7-15
C_{10}-C_{16}	150-240°	45-55
C_{10}-C_{25}	240-300°	2-5
Residue		5-20

Table 3 - Boiling Range of Fatty Acids from German Paraffin Oxidation(26)

	Crude Acids	Refined
Saponification value	224	257
Neutralization eq.	190	255
Iodine value	2.3	16.3
Unsaponifiable	5.6	2.6

Table 4 - Analytical Constants for German Synthetic Fatty Acids(22)

The purified fatty acids were converted to fats by heating with glycerol over 0.2% of zinc or tin for 8 hours under reduced pressure at 120-180°C(22) or 200-210°C(24) or at higher temperatures in the absence of catalyst(24).



$$3RCH_2CO_2H + \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{120-180}^\circ \;\text{8 hrs}]{Zn} \begin{array}{c} CH_2OCOCH_2R \\ | \\ CHOCOCH_2R \\ | \\ CH_2OCOCH_2R \end{array}$$

The free fatty acid content was usually less than 1% after this treatment(22). The glycerides were acid-washed, bleached and refined. They were converted to margarine by emulsification with 20% water. The mono- and diglycerides present served as emulsifiers. Salt (1-2%) and traces of diacetyl and carotene were added for flavor and color(20, 22). Typical flow sheets are given in Figs. 2 and 3.

The synthetic fat varied considerably in quality(20, 24). An analysis of one sample, brought to England after World War II is given in Table 5.

	Fat	
	English analysis	German analysis
Saponification value	227.0	228.5
% F.F.A.	Nil	0.28
Iodine value	15.5	13.8
M.p.	34.3°	34°
Unsaponifiable	4.0%	
Hydroxyl value	15.9	
Description	Dull brownish color, vaseline-like appearance and with an unpleasant taste.	White - vaseline - like with a taste reminiscent of machine oil, but no smell.

Table 5 - Analysis of German Synthetic Fat(22)

A breakdown of the fatty acid distribution, compared with natural butter and coconut oil is given in Table 6.

Type of Acid	%	Butter	C.N.O.
C_8 and below	---	5.9	6.2
C_{10}	4.2	3.0	8.4
C_{11}	12.0	---	---
C_{12}	10.2	4.1	45.4
C_{13}	10.5	---	---
C_{14}	8.8	13.7	18.0
C_{15}	10.5	---	---
C_{16}	9.5	29.3	11.8
C_{17}	8.0	---	---
C_{18}	9.1	42.4	9.8
C_{19} and C_{20}	17.2	1.6(C_{20})	0.4(C_{20})

Table 6 - Acid Analysis of German Fat, Butter and Coconut Oil(22)

The nutritional value of the German fats is somewhat open to question (20, 24). Reports from Germany range from complete support to grave doubts of the usefulness of such materials(20). Most of the reports were politically colored. However, it appears that the German product was non toxic and had some nutritive value. One ESSO employee, who resided in Witten during the war attests to the fact that he and others consumed the synthetic fat for a year or more with no ill effects(25). The consensus among American and English observers has been that the German work is interesting and deserves further study(20, 22). A more detailed discussion of the problems and advantages of synthetic fats in nutrition is given below.

As shown in Figure 1, the German process had too low an overall yield to be useful in a closed-loop regenerative system. However, the method had to be considered and it served as a jumping off point for the search for a satisfactory synthesis scheme.

A final note on this process is appropriate. The Russians have reported using captured German plants for the production of fatty acids recently(30). Scanty details are available but the Soviets are apparently using a linear, liquid feedstock rather than a waxy "gatsch" fraction.

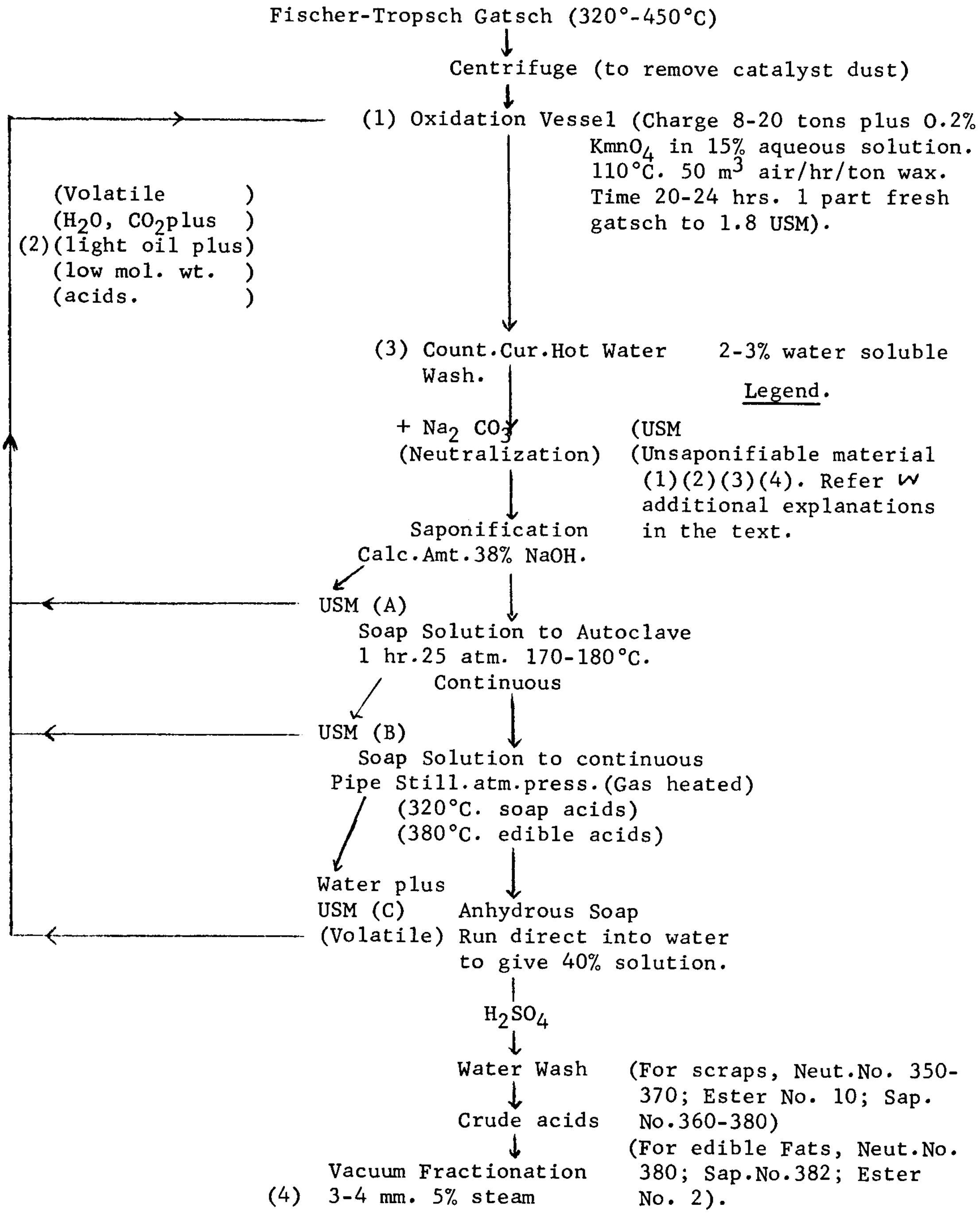


Figure 2 - Deutsche Fettsaure Werke Flow Sheet No.1 Fatty Acid Manufacture(29)

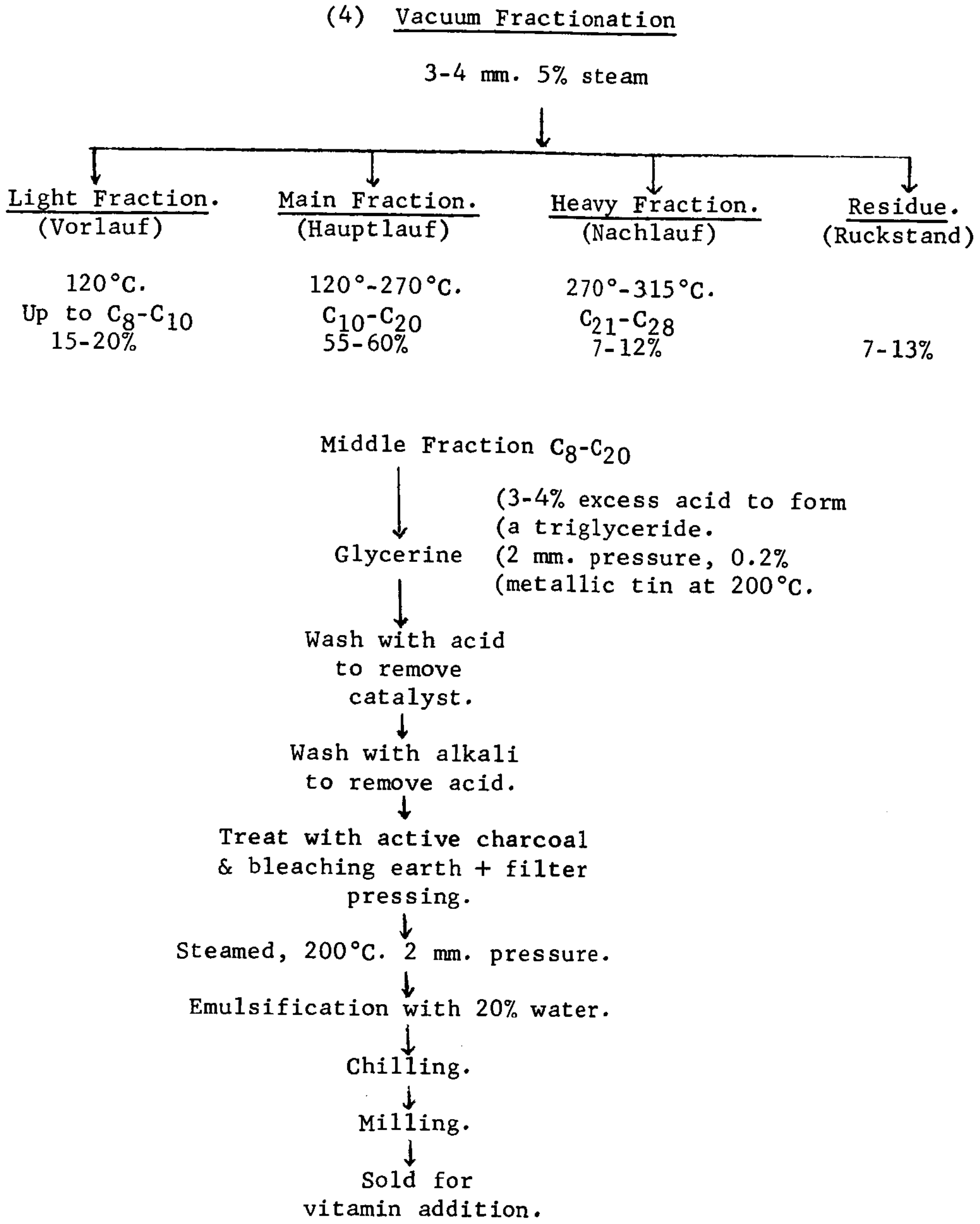


Figure 3 - Flow Sheet No. 2 Production of Edible Fats(29)

REDUCTIVE POLYMERIZATION OF CARBON MONOXIDE

The conversion of carbon monoxide to higher molecular weight, fatty materials involves a combination of reduction and polymerization.

$$xCO + (2x+2)H_2 \longrightarrow H\text{-}(CH_2)_x\text{-}H + xH_2O$$

This may be done in three basic ways: (1) production of hydrocarbons or oxygenated hydrocarbons having the correct molecular weight and structural skeleton directly in one step (the Fischer-Tropsch reaction); (2) a two stage process involving the synthesis of higher polymers followed by cracking to olefins in the desired molecular weight range (wax cracking and oxidative dehydrogenation); (3) reduction of carbon monoxide to a reactive small or medium sized compound (for example ethylene) which is subsequently subjected to controlled polymerization (Ziegler reaction). Each of these was examined in some detail. The results and evaluations are discussed in the following sections. Of the three basic routes and their many variants, only the Ziegler growth reaction of ethylene shows promise. The Ziegler process was, therefore, selected for the engineering study.

The Fischer-Tropsch Synthesis

The best known method of converting carbon monoxide to higher molecular weight material is the Fischer-Tropsch reaction (F-T). A major portion of the effort extended on this contract was devoted to the investigation of this synthesis. The basic F-T process involves the hydrogenation of CO to give a mixture of hydrocarbons. By varying the reaction conditions, the nature of the reaction product is changed - the formation of gaseous, liquid, or solid hydrocarbons, olefins, or oxygenated products can be promoted by the proper adjustment in catalyst type and operating conditions. Perhaps a better way of expressing this concept would be to say that the balance among these various products can be altered by changes in reaction conditions. It is possible to get highly selective formation of individual products at the ends of the spectrums: methane, low molecular weight alcohols, or high molecular weight hard waxes, but not in between. Selectivity is not a virtue of the F-T process (see Table 7 and Figure 4). One of the major objectives of the current survey was to find whether it would be possible to find a variant on the Fischer-Tropsch process which would produce, in good selectivity, either a fatty acid usable in edible fats or a convenient intermediate for the synthesis of such a fatty acid.

No Fischer-Tropsch process was found which would meet these criteria. No attempt was made to document the extensive researches in the F-T area in detail, since such documentation is amply available today. There are a number of excellent books, critical reviews, and bibliographies on the Fischer-Tropsch process. In particular, references 31-38. Of these, 31, 33, 34, and to a lesser extent, 35 and 37 present an immense amount of detail.

The approach taken was to learn the general conditions and products of Fischer-Tropsch processes from these reviews, and to search them--in particular, the Bureau of Mines' bibliographies--looking primarily for the unusual variant which might lead to materials useful for fatty acid synthesis. The recent reviews of Pichler and the Soviets were relied upon for the most up-to-date information. However, advantage was taken of the availability of a computer search of recent API abstracts, for the years 1964-April 1966, to supplement information obtained from the various critical reviews.

Catalyst	Temp. (°C)	Pressure (atm.)	Space-Time Yield[b] of C_3+, kg/cm³/hr (bbl./1000 ft³/day)	Liquid Product Distribution				Steel in Converter (ton/bbl/day)
				Gasoline	Diesel	Wax	Alcohol	
Ruhrchemie Process								
Co	175-200	1	8 (45)	56	33	11	[c]	2.7
Co	175-200	10	10 (57)	35	35	30	[c]	2.4
Lurgi Recycle Process								
Co	190-224	10	13 (74)	50	25	25	6	1.9
Fe	230	20	14 (79)	19	19	56	6	2.1
Fe	275	20	14 (79)	68	19	8	5	2.2
I.G. Liquid-Phase Process								
Fe	240-250	20	8 (45)	34	28	30	8	1.2
Fe	300-310	20	16 (91)	55	33	9	3	1.0
I.G. Oil Recycle Process								
Fe	240-290	25	30 (170)	51	10	29	10	0.7
Internally Cooled Converter Process								
Co	175-225	7	20 (113)	35	35	30	[c]	.8
I.G. Hot-Gas Recycle Process								
Fe	300-320	20	32 (181)	70	17	1	12	.7
Fluidized Iron Catalyst Process								
Fe	300-320	20	32 (181)	75	15	1	9	.6

[a] Reference 33.

[b] Weight of total product excluding methane, ethane, and ethylene, per volume of catalyst per unit time.

[c] Very small.

Table 7 - General Summary of Fischer-Tropsch Processes(a)

Brief History of the Fischer-Tropsch Process

Pichler has given a succinct summary of the history of the Fischer-Tropsch process(31). Its significant forerunners were the hydrogenation of carbon monoxide or carbon dioxide to methane, accomplished by Sabatier and Senderens in 1902, and the high pressure synthesis of a mixture of hydrocarbons and oxygenated compounds from carbon monoxide and hydrogen, covered in a Badische patent of 1913. In 1922 Fischer and Tropsch discovered their "synthol" process in which substantial amounts of oxygenated products were obtained from the hydrogenation of carbon monoxide over an alkalyzed iron catalyst at more than 100 atm. and about 400°C. About the same time, Badische developed a methanol synthesis process, using a $ZnO-Cr_2O_3$ catalyst at 200-300 atm. and 300-400°C. Then, in 1925, Fischer and Tropsch accomplished the normal pressure synthesis of a gasoline, using iron and cobalt catalysts, at 1 atm. and 200-250°C.

The announcement of the F-T process initiated a great deal of research in many places around the world, but the greatest effort, at least through most of the 1930's was in Germany. A number of significant advances were made, not only at Fischer's Kaiser Wilhelm Institute (now Ziegler's Max Planck Institute) for coal research, but also at several German companies, notably I.G. Farben and Ruhrchemie. Major research efforts also arose in the United States, Japan, and elsewhere, continuing in some areas right through the 1950's. Some Fischer-Tropsch work is still going on today. Among the major advances were the $Ni-ThO_2$-Kieselguhr precipitation catalyst for normal pressure synthesis (1931); the standard $Co-ThO_2$-kieselguhr precipitation catalyst (1932); the medium pressure cobalt synthesis at 5-20 atm. and 180-200°C (1936); the medium pressure iron synthesis at 5-30 atm. and 200-320°C (1937); and the high pressure synthesis of higher melting paraffins with Ru, at 50-1000 atm. and 100-200°C (1938). Also developed at about this time, and an outgrowth of the F-T process, was the Oxo synthesis. During the latter part of the 1930's, the first F-T commercial scale plants were built in Germany. Some typical product distributions from these plants are shown in Tables 8-14. These are included mainly to illustrate further the variety of compounds obtained in commercial Fischer-Tropsch operations.

The advent of World War II stimulated increased research on the F-T process primarily in an effort to synthesize gasoline. One advance of this period was the isosynthesis, which gave a high percentage of branched products more useful in gasoline than the largely straight chain products of the ordinary Fischer-Tropsch process. The isosynthesis, from 1941, used oxide catalysts, e.g., ThO_2, at 150-600 atm. and 400-500°C. In 1949, Kölbel was able to use carbon monoxide and water as synthesis gas. In 1950, a large F-T plant in Texas, the result of major efforts by a number of U.S. companies, was started up but eventually ran into difficulty and finally closed down. In the meantime, the German plants of World War II were all abandoned, with the possible exception of some that are behind the Iron Curtain and may still be operating today. The only modern F-T plant is one in South Africa, which dates to the late 1950's and is used for the preparation of a wide range of products. For the most part, research on Fischer-Tropsch processes has ceased, although some--for example, Pichler--are still in business. Within the last few years, one of Pichler's students developed a new, activated ruthenium catalyst for the preparation of high molecular weight polymethylene from carbon monoxide and hydrogen. According to Pichler, the list of commercial plants for the F-T process once included 9 in Germany, 1 in France, 4 in Japan, 1 in Manchuria, and the Texas plant in the U.S. as well as the plant in South Africa. By and large, the problems for the Fischer-Tropsch process have been that the value of the products has not been able to overcome the cost of the feedstock. Superimposed on this is the fact that a wide range of products are normally produced (Figure 4) including a gasoline fraction, which has very low octane. The one thing that seems to justify the South African plant is the fact that it has an extremely cheap source of coal on hand as a feed.

Possible Application to Fatty Acid Synthesis

The first thing that one might hope to get from the Fischer-Tropsch synthesis, and the most desirable one, would be a mixture of straight-chain fatty acids with carbon numbers primarily in the C_{12-18} range--in other words, something that would approximate the kind of fatty acid that is a constituent of edible natural fats. While the Fischer-Tropsch process has normally been aimed at the production of hydrocarbons, under certain conditions, it does produce oxygenated materials, and some acids have been reported among its products(32, 66).

Not quite so desirable would be a straight-chain fatty alcohol (or aldehyde) in the right carbon number range. This would provide a convenient reactive group for conversion to the fatty acid. One step less desirable would be an alpha olefin in the same carbon number range.

Other possibilities would include higher molecular weight mono-olefins, with the double bond internally located in the carbon chains (hopefully near the middle, so that two roughly equal molecular weight acids could be produced on oxidation), and, again somewhat less desirable, a normal paraffin of similar carbon number range. Another product which we might hope to get from an F-T process would be ethylene, which might be produced directly or from the cracking of higher Fischer-Tropsch products. The ethylene would then be converted to higher molecular weight products (see discussion of the Ziegler process below). Finally, one might hope to be able to run the Fischer-Tropsch synthesis with carbon dioxide as starting material, rather than having to convert it to carbon monoxide.

Characteristics of the F-T Reaction

The basic Fischer-Tropsch reaction is either:

$$CO + 2H_2 \longrightarrow -(CH_2)- + H_2O$$

or

$$2CO + H_2 \longrightarrow -(CH_2)- + CO_2$$

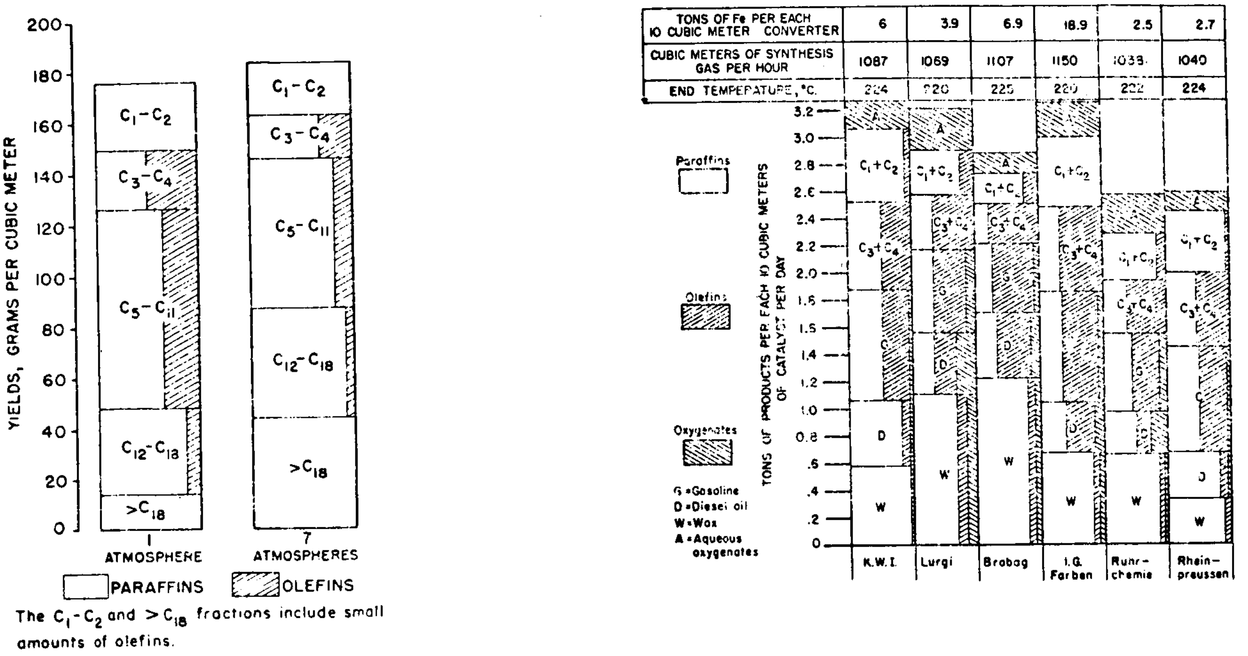
These two reactions differ by the water gas shift reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Of the two most important F-T catalysts, Co gives the first of these reactions primarily, the one which forms water; Fe can give either, depending on the reaction conditions. In essence, this depends on iron's ability to catalyze the water gas shift. Normally, this reaction is slow under Fischer-Tropsch conditions. However, with Fe catalysts it can be made to take place.

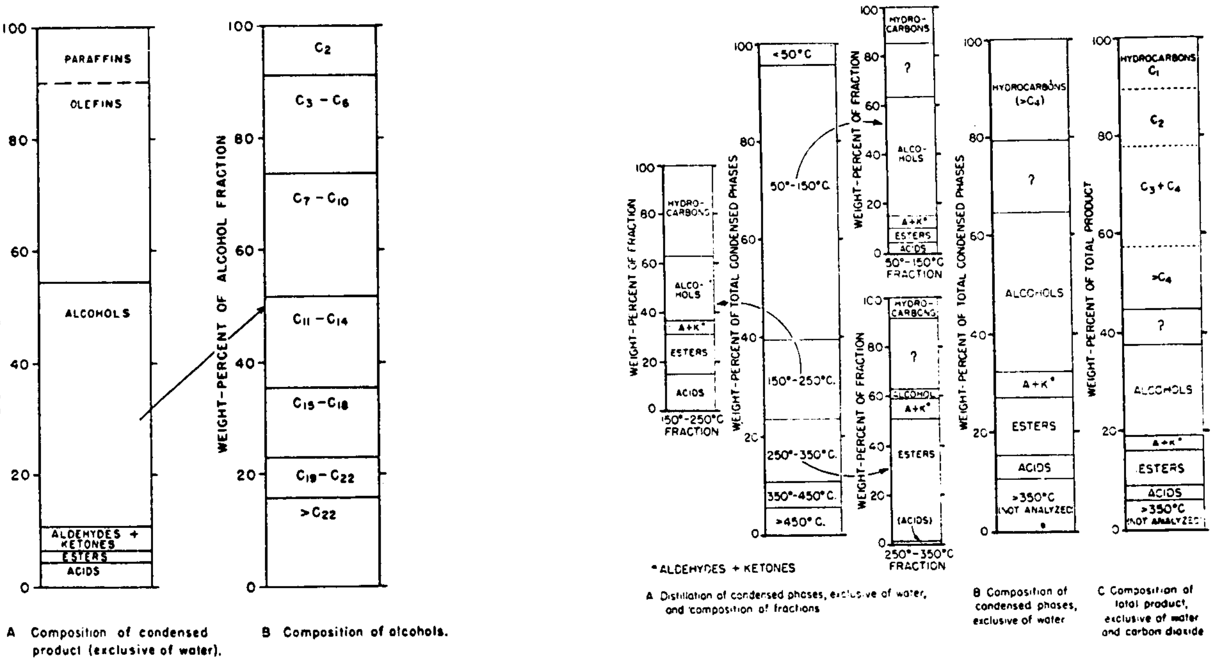
A third, related Fischer-Tropsch reaction is:

$$CO_2 + 3H_2 \longrightarrow -(CH_2)- + 2H_2O$$



a. $CO-ThO_2-MgO$-Kieselguhr Catalyst

b. Schwarzheide Tests, Fe Catalysts



c. Synol Process for High Oxygenates, $Fe_3O_4-Al_2O_3-K_2O$ Catalyst

d. Nitrided Fused $Fe_3O_4-Al_2O_3-K_2O$ Catalyst (a high oxygenate maker)

Figure 4 - F-T Processes Yield Complex Mixtures(33)

This reaction would have obvious appeal on a spacecraft, in which CO_2 is the source of carbon. Numerous workers have investigated this reaction, and some have indeed succeeded in preparing small amounts of liquid hydrocarbons or oxygenated materials, but none of this work gives much of a prospect of utility for making higher molecular weight material in good yield. Probably the best results were those of Russell and Miller, who reported getting (per m^3 of CO_2) as much as 95 ml of liquid hydrocarbon, along with 360 l of gaseous hydrocarbon, by hydrogenating CO_2 on an alkalyzed, Cu-activated, Ce-promoted Co catalyst(39). They point out the fact that their higher hydrocarbons can be accounted for by CO from the water-gas shift, but that CH_4 can apparently form directly from CO_2. It does seem that this reaction takes place in two discrete steps: the water-gas shift to CO, followed by the standard F-T reaction of the CO; methane-formation is probably a separate and competing reaction. If this is the case, it's obvious why the reaction is so poor. First of all, the concentration of CO at any point is going to be rather low; this is assured by the water-gas equilibrium. In addition, many workers have reported that CO acts as a poison for the F-T reaction of CO_2. It appears to be a competitive inhibition; CO reacts so much more rapidly than CO_2 that as long as any appreciable amount of CO is present, the CO_2 is essentially inert. In the light of this situation, any one-step synthesis of higher hydrocarbons from CO_2 seems out of the question. A separate CO_2- reduction step seems preferable by far.

One point might be made here: CO has a strong effect on the reaction of CO_2, but CO_2 has little or no effect on the F-T reaction of CO(40).

The Fischer-Tropsch reaction is strongly exothermic. For a C_{10} paraffin product, the average ΔH over a wide temperature range is about 38-39 kcal/mole/carbon atom, when H_2O is the product, and about 48 kcal/mole/C atom when CO_2 is produced. The difference of about 9.5 kcal reflects the water gas shift. Because of this strong exothermicity, one of the requirements in operating a Fischer-Tropsch plant is an efficient heat-exchange set-up; reaction conditions must be closely controlled, as will be shown shortly, and a considerable temperature rise would have a major effect on the products.

Many reaction mechanisms have been proposed for the F-T process, but the one most commonly accepted today strongly resembles that for the Oxo synthesis (Figure 5). An alkyl chain grows on a metal carbonyl by successive insertions of CO in the M-R bond, followed by reduction of the resulting acyl group. (Note that this reaction mechanism, if true, would probably explain the failure of CO_2 to undergo F-T reaction. Any insertion which did take place would give a salt, that would undoubtedly be stable to further reaction, and which may account for the small amounts of acid that sometimes is found in F-T products. However, it is unlikely that insertion occurs to any appreciable extent with CO_2.) A number of individual reaction steps can be pictured as possibilities once the initial metal-alkyl bond forms: hydrogenolysis of the M-R bond; elimination of olefin once R is C_2 or higher; further insertion of CO; partial or complete reduction of the acyl group; hydrogenation of any olefins or oxygenated materials which may be present in the reaction mixture; and isomerization come to mind. Also, if olefin is eliminated, leaving a hydride, olefin present in the reaction mixture could undoubtedly add (and probably form branching). In fact, Kölbel has apparently demonstrated that higher (C_{16-18}) olefins and paraffins can undergo further growth on iron Fischer-Tropsch catalysts(41). Just how the paraffins react is uncertain; perhaps some dehydrogenation can take place. The point being made here is that if many reactions can take place, and if several of these reactions have rates which are comparable, changes in reaction conditions will have a profound effect on what comes out of the reactor. This is clearly the case; yields and product distributions, both with respect to type of compound and molecular weight, are generally strongly affected by changes in temperature and pressure, space velocities, feed composition, and type of catalyst--including the metal used, the way in which it is prepared, any promoters used, particle size, and in some cases the type and amount of support.

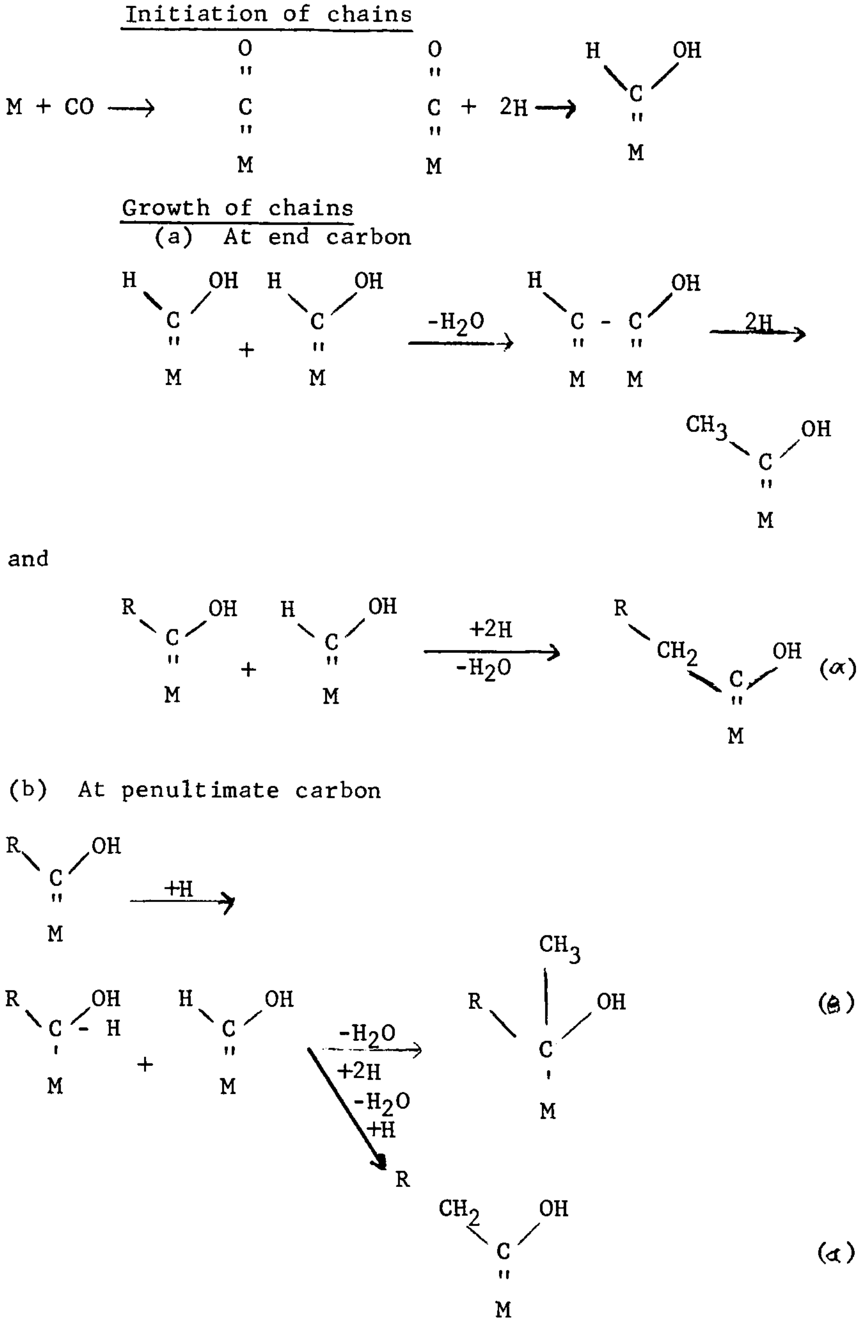
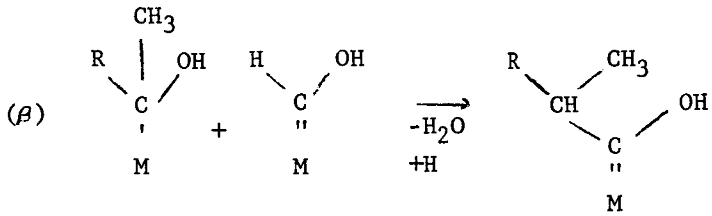


Figure 5 - Mechanism of the Fischer-Tropsch Synthesis(33)



Termination of chain

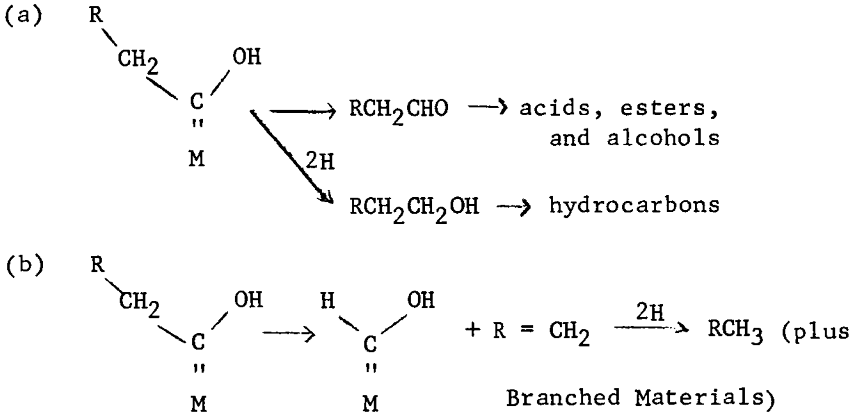


Figure 5 - (Continued)

Some partial generalizations on the effects of reaction variables are possible. These are illustrated in Tables 15-21 and Figures 6-10. Molecular weight generally increases with pressure up to a point--apparently CO insertion and hydrogenation are being favored--but usually passes through a peak and falls off with further increases in pressure, as volatile metal carbonyls form. With very high pressures, the product tends to be almost exclusively methane (Tables 15-19, Figure 6). Higher molecular weights are generally favored by the use of a temperature as low as possible, consistent with reasonable reaction rates; here termination steps are apparently slowed by temperature decrease more than are propagation steps (Table 18, Figures 7, 9). Formation of oxygenated products is favored by low temperatures and high pressures (Tables 10, 18, Figures 8, 10). Formation of olefin is favored by low pressure (Table 16); temperature changes have irregular effects on olefin content of the product (Figures 8, 10). Feeds rich in hydrogen tend to give a low-olefin product, as would be expected, as well as a relatively low molecular weight. One point of interest here is that Pichler has recently shown that 1-olefins are the primary product of the F-T synthesis(42). These can then undergo isomerization to internal olefins; re-addition to the catalyst to give additional growth, as suggested above (and, depending on the mode of addition to the double bond, either a straight-chain or methyl-branched product--and note that methyl branching is almost the only kind encountered) or hydrogenation to paraffin. Ni and Ru catalysts, the strongest hydrogenation catalysts in the group, tend to give saturated products; Co is somewhat weaker, but still gives largely paraffin along with some olefin, and with relatively little branching. Iron, the weakest hydrogenation catalyst of the four, allows other reactions to compete more favorably, producing more branching and more olefins than the other catalysts. Pichler's findings also explain why olefins are obtained in this synthesis. Thermodynamically, one would expect to get paraffins; the reaction to form paraffin is considerably more exothermic than that to olefins, although the difference shrinks as molecular weight increases and the proportion of double bond in the molecule drops. It would appear, though, that most of the paraffin is arising in a secondary reaction, hydrogenation of the olefin, and not by hydrogenolysis of the metal-alkyl bond (although this has probably not been proven conclusively, see Figure 5). At any rate, olefins are obtained when conditions are not ripe for their hydrogenation.

The Fischer-Tropsch Catalysts

As indicated above, the main catalysts for the Fischer-Tropsch reaction are four of the Group VIII transition metals: Ni, Co, Fe, and Ru. The other Group VIII metals have also been investigated to some extent, and have been found to be markedly inferior to these four. In addition to these, some hard-to-reduce metal oxides have activity for certain F-T variants, especially the synthesis of alcohols and branched products.

Nickel Catalysts

The nickel catalysts show little promise. In the earliest stages of investigating F-T chemistry, Ni, an extremely effective hydrogenation catalyst, gave exclusively methane. Apparently, hydrogenolysis of the Ni-C bond takes over as the most important reaction. In the early 1930's, Ni precipitation catalysts were developed (specifically 100 Ni-18 ThO_2-100 kieselguhr and 100 Ni-25 MnO-10 Al_2O_3-100 kieselguhr). These did make appreciable amounts of liquid products and were historically important in paving the way to the cobalt precipitation catalysts, but they always resulted in a relatively low molecular weight product. Certainly Ni is not adapted, so far as anyone has ever been able to ascertain, to the manufacture of a wax-range product. Finally, Ni is not a very adaptable catalyst, since it forms volatile carbonyls too readily. These deplete the catalyst; it must be run at just about one atmosphere and relatively low temperatures, below 200°C. The Ni products are almost entirely low molecular weight, n-aliphatics.

Cobalt Catalysts

It was with the cobalt catalyst that the Fischer-Tropsch process reached maturity. When the Ni catalysts proved unacceptable for several reasons, the knowledge gained in their development and improvement was applied to the Co catalyst. The German plants were all built to use Co catalysts, and while work continued--especially in the later days of the war--to develop a commercial process based on the cheaper and more readily available iron, ion catalysts did not pass the pilot plant stage until after the war.

There was a great deal of trial and error involved in developing the Co catalysts, working out the best promoters and carriers and the best proportions. Eventually, two "standard" catalysts were developed: 100 Co: 18 ThO_2: 200 kieselguhr and 100 Co: 5ThO_2: 8 MgO: 200 kieselguhr. The latter, less expensive than the earlier high-thoria catalyst, was also physically stronger and gave somewhat better yields.

Two commercial processes were developed with the Co catalyst. The first, run at one atmosphere and about 180-195°C, produced largely a gasoline-range product (roughly 50%), with 25-30% diesel oil and about 11% paraffin wax (7-10% soft wax, 2-3% hard wax--Reference 32, Abstract 444) (Tables 7-9, Figure 4a). This process is of little concern. A later development was the medium pressure Co synthesis. By running at 7 atm. and 175-195°C, it was possible to promote the formation of higher molecular weight materials. The medium-pressure process made roughly equal parts of gasoline, diesel oil, and wax (15-20% soft wax, 10-15% hard wax--Reference 32, Abstract 444).

In general, the Co products were relatively low in unsaturation and in oxygenated products (at least when compared with products from the Fe-catalyzed processes). Running at lower temperatures favored the formation of alcohol (as much as 40% could be obtained at 160-175°C and 10 atm. (Tables 10, 19) and of olefin. Also favored by lower temperatures was the formation of high molecular weight wax (Table 18). Pressure increase, as indicated above, increased the amount of high ends; as much as 50% of the condensed-phase products were waxes at about 15 atm. (Table 15, Figure 6). The Co process was normally run with a H_2:CO ratio of 2 or more; feeds lean in hydrogen produced more alcohol and olefin and also favored higher molecular weights (Table 19). Alkali had a promoting effect on the atmospheric pressure Co synthesis, but it had little or no effect on the medium pressure synthesis (Table 21). As indicated above, the promoters used were important; also, the amount and type of kieselguhr had a dramatic effect on the product.

The molecular weight distribution of the products was high at C_1, went through a minimum at C_2, then through a peak at about C_5, and fell off regularly after that; the ratio of the mole fraction of any carbon number to its lower homolog remained quite constant, with values between 0.75-0.85, over a wide range of molecular weights (Figure 14). The mole fraction of any molecular species up to about C_{14} was greater in the normal pressure synthesis as compared with the medium pressure synthesis; at this point the curves crossed over, and the mole fractions of products higher than C_{14} were greater in the medium pressure synthesis (Figure 14).

As the molecular weight of a product fraction increased, the percent of olefin decreased, and the ratio of internal olefin to 1-olefin increased. Perhaps most important, branching increased with molecular weight. For example, mass spectrometric analysis of a normal pressure Co product showed about 95% normal pentane in the C_5 fraction, only about 85% normal octane in the C_8 fraction (Table 25). Distillation data obtained for comparison with some subsequent Fe catalyst tests showed even higher branching (though distillation techniques are inferior to mass spectometry, and reference 33 does not indicate clearly whether the product was from normal or medium pressure operation) (Table 25). A further point is the report that, according to data obtained in hydrogenative demethylation work, "Gatsch" (soft paraffin wax, ave.:C_{23}) from atmospheric pressure Co synthesis was estimated to have about 30% branched material, and hard paraffin from medium pressure Co synthesis was estimated at about 38% branched material$^{(43)}$. The latter data are highly approximate, but the trend is quite clear even from the good data on low molecular weight materials. As the molecular weight increases, there is a considerably increase in branching. At first, this branching is just monomethyl branching. It is probable (if only by analogy with data from Fe catalyst products) that the degree of multiple methyl branching also increases with increasing molecular weight. This is certainly not a desirable trend if one considers the possiblity of using Fischer-Tropsch waxes as feeds to an oxidation process for acid manufacture; branching is undesirable, and the more, the worse.

We have indicated above that the medium pressure Co synthesis would make about one-third waxy materials. Ruhrchemie, in particular, developed Co catalysts which would make substantially larger amounts of wax, up to 80% and perhaps even more of the total product (Tables 27-33). The key to this process was using a catalyst with a high Co density; the kieselguhr content was cut down to 12.5 parts per 100 parts Co. Perhaps most important here is the fact that the greatest increase was in the hard wax--the fraction boiling above 450-460°C at 1 atmosphere. By and large, the Gatsch fraction, boiling roughly from 300-450°C or so and containing material roughly C_{18}-C_{30}, remained constant at about 20-25% of the total solid and liquid material(31). This is the fraction used by the Germans for synthetic fatty acid manufacture during World War II (the upper and lower limits may vary somewhat, but roughly they are as stated), and since that time others, most recently the Soviets, have confirmed that this is the best feed for making fatty acids in the edible or soap range(30, 44, 45).

Conceivably higher molecular weight waxes could be used in an oxidation process, but unless more vigorous conditions were used they would give increased amounts of higher acids, such as C_{20+}, which are undesirable. If more vigorous conditions were used, there would be more formation of by-products: diacids and hydroxy- and keto acids, as well as degradation of acids to very low ends. It would certainly appear, therefore, that one would not want to have much material boiling above 450°C in one's oxidation process. (Note, too, that this material would be likely to contain increasing amounts of branched material).

In summary on cobalt catalysts, then, cobalt tends to produce a relatively saturated hydrocarbon product and, at moderate pressures and with proper catalysts, will produce, perhaps, 25% of a soft wax that can be used fairly effectively for oxidation to edible-range fatty acids. All other material produced would then presumably have to be burned back to carbon oxides and recycled. Such a process hardly looks attractive. An alternative would be to use atmospheric pressure synthesis to produce largely liquid products, which could then be cracked to give ethylene for use in Ziegler growth. This would be a two-step process from CO to ethylene, and seems to be inferior to preparing ethylene process, directly from CO and H_2 (see below).

One final point, on catalyst life: it appears that the Co catalysts, if kept free of poisons (notably sulfur) and run with careful process control and occasional reactivation, can have useful lives of up to a year. After that, it would presumably be necessary to replace the catalyst with new material, since in addition to reversible deactivation there is a certain amount of irreversible destruction of the catalysts.

Iron Catalysts

The very first catalysts used in the Fischer-Tropsch process were made from alkalyzed iron. However, the early work was all done at atmospheric pressure, and iron does not give good results without elevated pressures. It was not until the medium pressure Co process was developed that pressure was applied to iron catalysts, with favorable results.

From that time on, a great deal of work was done with iron catalysts, although they were never used commercially until after the war. Iron has many advantages over cobalt. First of all, it is cheaper. Secondly, it is a highly adaptable catalyst. By proper control of the catalyst composition (and there are an enormous number of variables involved), it is possible to tailor the process to make a variety of products: gasoline, oxygenated materials, wax, etc. Also, the catalyst composition is not the only effective variable with iron catalysts;

Temperature, pressure, feed rates, medium (e.g., fixed bed, fluid bed, liquid phase) can all be used to favor one or another type of product.

There is no need to discuss here the effect of catalyst composition beyond a couple of points; the amount of detail in the available literature is too great, and can be consulted by the interested reader in the several chief references. One point worth notice, however, is the fact that small amounts of alkali are important in iron catalysts to promote the formation of higher molecular weight material, (Figures 12, 13) and is also important in various processes ("Synol", "Synthol", "Oxyl") devoted to manufacture of oxygenates (Tables 13, 22; Figure 4c). Nitrided iron catalysts are particularly effective in the formation of oxygenates(46) (Figure 4d). Supports such as kieselguhr are not generally used in iron processes; in many cases kieselguhr harms iron catalysts by neutralizing alkali.

Iron-catalyzed F-T processes are run at higher temperatures than Ni or Co processes. Temperatures may be as low as 220°C in fixed bed operations, and higher than 300°C with fluidized beds; however, 225-275°C comprises the usual range. Pressures are of the order of 20-30 atm.

The general considerations mentioned with Co usually apply here, only more so. Iron is even less selective. A weaker hydrogenation catalyst than Co, it makes far more olefins and alcohols (Tables 7, 11-14; Figures 4b, c, d). Pressure increase again favors high ends up to about 20-30 atm., above which it shifts the products towards lower molecular weights due to the formation of volatile carbonyls. Alcohol production is also favored by higher pressure.

Temperature increase favors formation of low molecular weight materials, decreases formation of alcohols, and has a small and varying effect on olefin (Figures 7-10). Small catalyst particle size favors wax formation (Table 20). Molecular weight distribution is again similar to that with Co: a minimum at C_2, a peak now around C_3, with a fall off after that. However, a semi-log plot of mole fraction vs. carbon number no longer produces a single straight line, but two straight lines with a break around C_{10} (Tables 22, 23; Figures 16-18).

Olefin content again drops with increasing molecular weight (Table 26; Figure 19). Branching--an important factor--again increases with molecular weight. However, if there is more branching in Fe products than with Co, the difference is not great(43) (Table 35).

Any fluid bed process can be ruled out. These processes, researched especially in the U.S., are aimed strictly at the manufacture of gasoline-range (C_5-C_{11}) material (Table 11). On the other hand, running in a liquid phase, in one of several processes that have been piloted but never commercialized (e.g., U.S. Bureau of Mines, I.G. Farben-Duftschmid process) favors the formation of wax and other relatively high molecular weight compounds.

It is possible to make high yields of wax with iron catalysts, supported on kieselguhr, though many of the Fe catalysts were actually used without any carrier (Tables 32-34; Figure 20). The quality of this wax (with respect to branching) was claimed to be comparable to that of Co wax(43). It was touted to have contained only about 20% branched material (Table 34), but this value may be low. Again, it must be noted that when the process is modified to change the amount of wax present, the total amount of soft wax remains relatively constant--it's just the hard wax that can be varied significantly (Figures 7, 9).

Thus, with iron catalysts, the situation is similar to that with Co in dealing with wax. It is quite possible to make wax to the extent of about 70% of the total product, but when high wax yields are obtained, most of it is hard, boiling above 450°C. The soft wax again runs only about 20-30% of the total.

One interesting piece of work is that of Kölbel, who found that on feeding a C_{16-18} Fischer-Tropsch paraffin to a Fe-catalyst F-T synthesis, he obtained a substantial amount of growth of the paraffin to higher molecular weight material(41). This was true whether he used olefin-containing (11%) or hydrogenated (2% olefin) material, and there did not seem to be any difference in reactivity between the two. Presumably the olefin grew by adding to the catalyst, much as olefins do in the related Oxo synthesis. How this was done is uncertain, but conceivably there is a dehydrogenation-hydrogenation equilibrium set up.

There is one major difference between Fe and Co, and that is the fact that one can get a good deal more oxygenated material from Fe than from Co. This is useful if you are prepared to construct a multi-purpose plant such as the modern commercial plant in Sasol, South Africa, which utilizes a myriad of fractions from the process: gasoline, diesel, wax, various oxygenated chemicals, etc.(35). However, the bulk of the oxygenated material is low molecular weight alcohol, especially ethanol. Iron, like Co, catalysts do not give any reasonable selectivity to medium range materials.

A final point about iron catalysts is that they are a good deal more sensitive than Co or Ni catalysts to such things as phase changes, carburization, sintering, etc. Also, in common with other F-T catalysts (though perhaps not to so great an extent) they are sensitive to sulfur poisoning. Carefully tended, they can probably have useful lives of 6 months or more, but they do degrade, and their lives are probably not as great as are those of the Co catalysts. The need to carry along fresh catalyst is another debit against the F-T process, and especially the Fe catalyzed reaction.

Ruthenium Catalysts

Ruthenium is a unique Fischer-Tropsch catalyst. At atmospheric pressure, it does not cause F-T synthesis at all; rather, it is an extremely active catalyst for the reduction of CO or CO_2 to methane(47, 48). In fact, CO_2 reduction begins at about 100°C. Bahr felt that hydrocarbons higher than methane could be obtained from CO_2(48). However, it was only when Pichler tried to make carbohydrates by hydrogenating CO at elevated pressure and relatively low temperature that Ru came into its own (though carbohydrates were not produced).

In the Fischer-Tropsch reaction at 300-1000 atm. and about 195°C, Ru catalysts give high yields of very high molecular weight, extremely straight chain paraffin--polymethylene(48-61). Reactivity begins somewhere around 10 atm., levels off near 300 atm., and stays relatively constant to 1000 atm., above which it degenerates to a methane-former again. Reaction temperature is about 195°C. The Ru catalyst is extremely sensitive to sulfur poisoning, but in the absence of poisons it retains its activity unchanged for long periods of time. Recently, Pichler has developed especially active Ru catalysts from RuO_4 or irradiated RuO_2; the earlier catalyst was generally RuO_2, which was optionally pre-reduced. Kölbel has carried out this reaction with water as his hydrogen source, rather than molecular H_2(55-57).

The first point to note is that ruthenium makes an extremely straight-chain product. The second key point is that the Ru synthesis gives mostly high molecular weight product. The earliest runs made fractions as high as 23,000 MW, and more recent work has isolated material above 100,000 MW. The soft wax, which could be oxidized to fatty acids is again only a small proportion of the total solids.

Fatty Alcohols With Ruthenium Catalysts

Du Pont patent art claims that fatty alcohols can be made with Ru catalysts. One patent indicates that a mixture of C_{3-50} primary alcohols can be obtained by running the Ru synthesis in an aqueous or alcoholic medium(62). This is particularly surprising in light of the fact that some of Pichler's earliest work was in aqueous suspension, and he reported getting a normal hydrocarbon product(50). Some of the examples of the du Pont case indicate a product with a reasonable amount of material in the C_{10+} range. However, the yields were extremely low(62). Perhaps there is some reaction of this sort taking place--certainly some product is reported in the one run carried out in water, rather than an alcohol--but the yields are very poor, and the pressures required are over 300 atm.

There are two more related du Pont patents. According to the first(63) if the hydroxylic-phase Ru reaction is run at a basic pH, the product is almost exclusively C_{2-10} alcohol. According to a related patent(64), if the pH is kept strongly acidic (less than 1), the product is a high molecular weight polymethylene.

As indicated above, there is a considerable amount of disagreement between Pichler's work and the du Pont patents. Du Pont has apparently dropped all interest in this area, and never published, so that it is hard to tell just how reliable the work is; certainly the failure to commercialize is no indication, since Ru catalysts are so costly that their use in any massive catalyst form would be ruled out completely for a commercial operation. Nevertheless, the elements of interest are there. Ru makes straight chain material, and it might make alcohols, and the type of product obtained might be controllable by controlling the reaction medium, pH, etc. Certainly a Fischer-Tropsch process which gave good yields of fatty alcohols from CO would be preferable to the ethylene/Ziegler growth/ozonolysis route; conversion of the alcohols to acids would be relatively simple. This might be an area for fruitful research.

A final note on Ru catalysis: earlier work on Ru had employed massive amounts of Ru (in the form of RuO_2, usually), and had required very high pressures. It was reported that Ru catalysts did not respond to supports or promoters. Recently, however, Bureau of Mines researchers have found that catalysts consisting of 0.5% Ru on alumina will catalyze the Fischer-Tropsch reaction, and at pressures much more moderate than those used in standard Ru synthesis(65). Good conversion can be obtained at about 21 atmospheres, as opposed to the several hundred needed in the conventional Ru synthesis. The product distribution by boiling point looks very much like the sort obtained with Co or Fe catalysts--a range of products from methane to hard wax, the relative proportions in this work being very dependent on the feed composition; hydrogen-poor feeds gave the most wax, while H_2-rich feeds gave largely methane.

Conceivably some combination of this process with the du Pont work could give a desirable product for fatty acid manufacture. However, it is extremely difficult to see how any process based on Fischer-Tropsch will be able to give any degree of selectivity, that would obviate the need to burn up the rest and start again.

Other Group VIII Metals as Catalysts

Since four of the Group VIII metals are active as Fischer-Tropsch catalysts, it was obvious to test the remaining five members of the group, and this Pichler did(49). Rhodium was the best, giving conversions nearly as large as those with Ru, but making more oxygenates than Ru, and less wax. Conceivably Rh might be under further research today, although the usual objection of the low selectivity of Fischer-Tropsch processes with respect to molecular weight (even if high chemical type selectivity were achieved) would presumably apply. Osmium was somewhat less active; it required higher temperatures, and made a lot of gaseous product. Platinum was still less active for the preparation of higher hydrocarbons, and palladium and iridium gave only traces of material.

Difficultly-Reducible Oxide Catalysts

At high temperatures, usually 450°C, and pressures from 100-1000 atm. (usually about 500 atm.), synthesis on difficultly-reducible oxides (especially thoria) gives primarily branched hydrocarbons. Under certain variants of this process, it is possible to get significant amounts of aromatics, naphthenes, and dimethyl ether. At these conditions, the only products from ordinary F-T catalysts would be methane and carbon.

Of substantial interest, at first glance, is the synthesis of higher alcohols. As indicated in the discussion of Ru catalysts, a straight chain fatty alcohol in the carbon number range of the edible fatty acids would be an attractive intermediate. It is well known that methanol can be made directly by the hydrogenation of CO, using oxide catalysts, and especially those based on ZnO, along with such other oxides as CuO, Cr_2O_3, and Al_2O_3. By alkalyzing methanol-synthesis catalysts, running at higher temperatures (400-500°C vs. 325-375°C), and running at lower space velocities than in methanol synthesis, it is possible to prepare significant yields of higher alcohols. The higher alcohol synthesis has been reviewed extensively by Natta, et al(34), and it produces largely branched materials in the range up to about C_5. There does not appear to be any likelihood of this synthesis being of value. The propensity for branching (which is apparently an intrinsic attribute of high-temperature Fischer-Tropsch-related reactions) is against it. Secondly, even with these severe conditions there is little product, if any, in a range that might be useful for fatty acid synthesis. Milder conditions make lower molecular weight product, and more vigorous conditions would merely lead to decomposition. It appears that the only alcohol synthesis which would prove of value would be that on Ru, if it is indeed a real reaction (or conceivably a reaction on Rh, based on the extremely limited information at hand). And again, there is little hope for molecular weight selectivity.

Direct Synthesis of Acids Via Fischer-Tropsch

Acids and esters are sometimes found among the products of Fischer-Tropsch reactions, especially with Fe catalysts. Their proportions, however, are normally miniscule. An Esso patent claims a method of improving the yields of fatty acids (mainly acetic acid, although no specific data on the product are given) by including 25-40% CO_2 in the feed to an iron-catalyzed fluid bed F-T operation(66). Total acid yields at best seem to be only about 15% of the condensed phase product.

One can theorize that the CO_2 may be inserting in a metal-carbon bond of the F-T growth product, much as it does in the Ziegler reaction or with Grignard reagents. One can readily see that, with high CO_2 concentrations, growth will be suppressed. Ideally, such a reaction would best be carried out by growing to a given molecular weight and then inserting CO_2. Since there is no good way to get selective formation of an intermediate size F-T product, this scheme has little promise. There does not appear to be any way to make reasonable amounts of acids directly by F-T--much less acid in a desirable molecular weight range--no hints were uncovered as to how such a problem might be approached.

One point that might be made with respect to the Fischer-Tropsch process in general is that it has been researched very nearly to death. That is, an enormous amount of research effort has gone into the development of the process. This effort has been devoted towards a variety of aims; much of it, especially in the U.S., has had gasoline synthesis as its goal, but there has also been an extensive amount of work directed towards producing other products, especially in Germany. The Germans recognize that the gasoline produced by the F-T process was inferior, and one of their answers to this was to develop the iso synthesis, which produced large proportions of branched olefins that could be converted to a reasonably high octane fuel. They also recognized, however, that F-T produced a good grade of diesel oil, and tried hard to increase the yield of this cut. Also, the soft wax that was produced in the F-T process was extremely important in Germany during the war for the preparation of soaps and fats, and consequently they worked a great deal on increasing this fraction. Finally, the Germans were also responsible for the development of processes to make a very high molecular weight wax, and this, too, got a significant amount of research and development effort, although it was far less than that accorded to the other products. An indication of the research effort in F-T work is the number of references in the two Bureau of Mines bibliographies from the early 1950's. The total here, in both patents and literature is nearly 8,000; while not all of these are directly on the Fischer-Tropsch process, a substantial proportion of them are, and a considerable amount of work has been done since those bibliographies were prepared. Research has been devoted to all aspects of the process, but an interesting indication of the type and amount of work put in on catalysts is found on pages 204-206 of the Bureau of Mines' literature bibliography(32). It is obviously dangerous to suggest that, since so much work has already been done, there is little room for new discoveries. Among other things, it might well be that a systematic and thorough study of the vast collected literature on Fischer-Tropsch processes to date would provide some hints on areas for new research. It may well be that others have done just this; one gathers that a great deal of this was done by the Bureau of Mines researchers in preparing both the Storch book(31) and the two bibliographies(32). Certainly, the Fischer-Tropsch area is not virgin territory; it has been researched most extensively, and as far as one can tell, offers little prospect of providing a good synthesis of fatty acid intermediates. In particular, the one intermediate which might most be expected to be prepared--the soft gatsch wax that the Germans did use to make synthetic fatty acids--can undoubtedly not be prepared in high selectivities. Chances for successfully recycling low ends seem to us to be quite low; recycling would undoubtedly lead to substantial amounts of branching, even if it did succeed in growing higher products. Perhaps one suggestion does offer itself, however; if a Fischer-Tropsch process could be carried out in a spatially limited environment, such as the cavity of a molecular sieve, in which further growth were prevented once a given molecular size was reached, it might conceivably be possible to prepare a tailor-make molecule. There is no indication that such a process has been attempted.

In Summation on Fischer-Tropsch

There seems little doubt that a standard Co- or Fe-based F-T plant could be used to make large proportions of liquids, which would then be cracked to ethylene--which can certainly be done in good yield. However, this may be done in a single step as discussed below.

A Co- or Fe-based wax process could be run, the "Gatsch" separated and oxidized. Possibly a variant of the Ru process could be used, too--perhaps the Bureau of Mines supported Ru catalyst. However, it does not appear that selectivities to soft wax exceeding about 30% at best can be anticipated. Higher molecular weight material would probably not be an efficient source of edible-range fatty acids, and would presumably have to be burned back to CO and CO_2. Lower ends, which would produce primarily lower acids, would also probably be burned. At that, all of the separation and purification problems of "Gatsch"-oxidation would be encountered.

While substantial amounts of oxygenates can be obtained, either along with hydrocarbons in such processes as Synol (alkalyzed Fe) or in the higher alcohol synthesis (ZnO-based), the preparation of straight-chain primary oxygenates with desirable molecular weight does not appear likely, unless the Ru/hydroxylic medium (or perhaps a related Rh-process) could be developed to give better yields than are disclosed in du Pont's patents. It is hard to see how molecular weight selectivity might be achieved by any variant of the F-T process. Consequently, it is not recommended as a source of starting material for fatty acids.

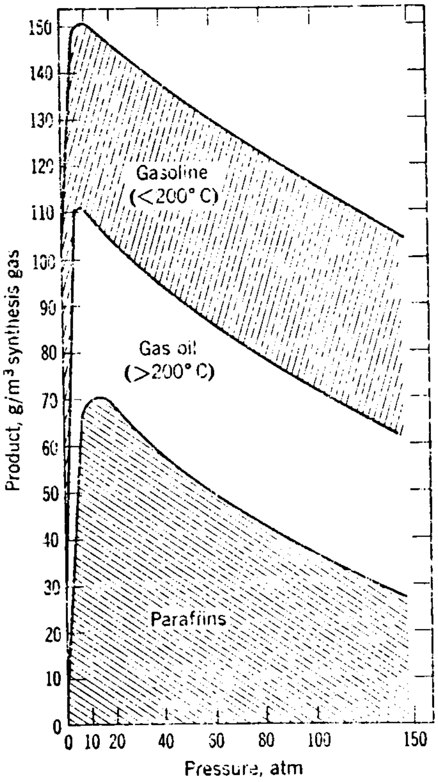


Figure 6 - Effect of Pressure on Product Distribution(35)

Constituent	Wt % of total products listed[a]	d_4^{15}	Olefins, vol %	Bp index[b]	Mol wt, av	Number carbon atoms	Cloud pt, °C	Pour pt, °C	Octane number, research method	Cetane number	
										Motor	Research
						Normal-pressure synthesis[c]					
gasol ($C_3 + C_4$)	12		50			$C_3 + C_4$					
gasoline, to 185°C	49	0.689	37	108	100	C_4-C_{10}			52		
gasoline, to 200°C	54	0.693	34	115	115	C_4-C_{11}			49		
diesel oil, 185–320°C	29	0.760	15	245	190	C_{11}-C_{18}	−13	−18		87	100
diesel oil, 200–320°C	24	0.766	13	260	205	C_{12}-C_{19}	−5	−9		92	105
soft paraffins, 320–450°C	7	0.900	iodine value, 2			$>C_{19}$		60–70			
hard paraffins, >450°C	3	0.930						90			
						Medium-pressure synthesis[d]					
gasol ($C_3 + C_4$)			30			66% C_4 33% C_3					
gasoline, to 185°C	35	0.685	20	110	100	C_4-C_{10}			28		
gasoline, to 200°C	40	0.689	18	120	115	C_4-C_{11}			25		
diesel oil, 185–320°C	35	0.760	10	240	190	C_{11}-C_{18}	−7	−11		87	100
diesel oil, 200–330°C	35	0.766	8	255	205	C_{12}-C_{19}	−2	−5		92	105
soft paraffins, 320°C	30	0.90	iodine value, 2			C_{18}		80 approx			
soft paraffins, 330°C	25	0.90				C_{19}		90 approx			

[a] Total yield per cubic meter of synthesis gas: normal-pressure synthesis, 148 g; medium-pressure synthesis, 145 g of liquid products and 10 g gasol.

[b] The bp index is the sum of the temperatures at which 5, 15, 25, . . . 95 vol % distill over, divided by 10.

[c] At 1 atm; 180–195°C; catalyst, 100Co:5ThO_2:7.5MgO:200 kieselguhr; 1CO:2H_2 (18–20% inert components); throughput, 1 m^3 synthesis gas/(hr)(kg Co); two stage; no recycle.

[d] At 7 atm, abs; 175–195°C; catalyst, 100Co:5ThO_2:7.5MgO:200 kieselguhr; 1CO:2H_2 (18–20% inert components); throughput, 1 m^3 synthesis gas/(hr)(kg Co); two stage: no recycle.

Table 8 - Breakdown of Hydrocarbon Fraction Obtained with Cobalt Catalyst(35)

Fraction	Grams per Cubic Meter $2H_2 + 1CO$ gas		Weight Per Cent of Liquids Plus Solids		Density, 150°C		Olefins, volume per cent		Pour Point, °C		Cooperative Fuel Research Committee Octane No.		Cetane No.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$C_1 + C_2$	26	21	. .	. .	. . . . .	. . . . .	. .	. .	. .	. .	. .	. .	. .	. . .
$C_3 + C_4$	24	17	. .	. .	. . . . .	. . . . .	50	30	. .	. .	. .	. .	. . .	. . .
C_4-C_{10}	70	51	56	35	0.689	0.685	37	20	. .	. .	52	28	. . .	. . .
C_4-C_{11}	77	58	62	40	0.693	0.689	31	18	. .	. .	49	25	. . .	. . .
C_{11}-C_{18}	41	51	33	35	0.760	0.760	15	10	−18	−7	. .	. .	100	100
C_{12}-C_{19}	34	51	27	35	0.766	0.766	13	8	−9	−2	. .	. .	100	105
Soft wax	10	36–43	8	25–30[a]	0.900	0.900	. .	. .	. .	. .	. .	. .	. . .	. . .
Hard wax	4		3		0.930		. .	. .	. .	. .	. .	. .	. . .	. . .

[a] Higher percentage of wax may be obtained from Co-Mn catalysts at 165°-168°C and 10 atm, but with no increase in Diesel oil yield

Table 9 - Product from 100Co:5ThO_2:5ThO_2:7.5MgO:200 Kieselguhr Catalyst at 175°-200°C and at (a) Atmospheric, (b) 7 atm Pressure of $2H_2$ + 1CO Gas, 18-20 per cent Inerts(31)

Type of Compound	Weight-Per cent of Liquid Products Exclusive of Water	Weight-Per cent of Oxygenated Molecules
Alcohols	40.0	92.4
Acids	0.5[b]	1.2[b]
Esters	0.8[c]	1.8[c]
Carbonyl compounds	2.0	4.6
Hydrocarbons	56.7	—

[a] From Ref. 66.
[b] Calculated as acetic acid.
[c] Calculated as ethyl acetate.

Table 10 - Products from Cobalt Catalysts at Low Temperatures(33)

Product	Fixed-bed process		Fluid-bed process	
	Selectivity over average catalyst life, %			
CH_4	7.8		13.1	
C_2H_4	0.6		4.4	
C_2H_6	2.6		5.8	
C_3H_6	3.9		12.8	
C_3H_8	2.2		3.4	
C_4H_8	2.5		10.0	
C_4H_{10}	2.4		3.2	
C_5 and above	75.7		39.0	
nonacid chemicals	2.3		7.3	
acids			1.0	
	Liquid product composition			
liquefied petroleum gas (C_3–C_4)	5.6		7.7	
petrol (C_5–C_{11})	33.4		72.3	
middle oils (diesel, furnace, etc)	16.6		3.4	
waxy oil or Gatsch	10.3		3.0	
medium wax, mp 135–140°F	11.8			
hard wax, mp 203–206°F	18.0			
alcohols and ketones	4.3		12.6	
organic acids	traces		1.0	
	C_5–C_{10}	C_{11}–C_{18}	C_5–C_{10}	C_{11}–C_{14}
paraffins, vol %	45	55	13	15
olefins	50	40	70	60
aromatics	0	0	5	15
alcohols	5	5	6	5
carbonyls	traces	traces	6	5

Table 11 - Fixed-Fed and Fluid-Bed Process: Selectivities and Distribution Pattern in Terms of Products Actually Made (Sasol 1963)(35)

Product	Percent	Product	Percent
aldehydes, C_2–C_4	4.0	*n*-propyl alcohol	14.0
acetone	10.5	isopropyl alcohol	3.0
methyl ethyl ketone	3.0	*n*-butyl alcohol	4.0
methyl propyl ketone	1.0	isobutyl alcohol	1.0
methanol	1.5	*sec*-butyl alcohol (2-butanol)	0.5
ethanol	55.5	C_5 and higher alcohols	2.0

Table 12 - Distribution of the Nonacid oxygenated Compounds from Fluid-Bed Synthesis Product Water Solution (Sasol)(35)

Fe_3O_4-Al_2O_3-K_2O catalyst reduced in hydrogen for 60 hr at 500°C. Synthesis with 20 atm. of water gas at space velocity of 350.

Conversion maintained at 50 per cent, yield C_3+ = 45 g/m³, and temperature 191°–193°C.

Distillation of C_3+

	Days					
	7–17			20–30		
	Weight (%)	Per cent in fraction		Weight Per cent	Per cent in Fraction	
		Alcohols	Olefins		Alcohols	Olefins
$C_3 + C_4$	13.1			15.3		
<200°C	50.0	29.5	45	42.6	34.6	42
200–230°	2.2	34.5	35	3.8	35.7	34
230–350°	16.5	53.5	28	11.5	59.8	25
350–400°	4.3	37.5	24	8.1	56.5	28
>400°	13.9			17.8		

Table 13 - Synol Operation of Catalyst WK17(33)

Product	Yield, wt %		
	$1.3H_2:1CO$	$1H_2:1CO$	$1H_2:1CO$ (steel-lathe turnings)
gasoline, C_{3+}, –400°F	54.2	52.4	70.2
diesel oil, 400–600°F	10.4	10.0	13.3
heavy distillate, 600–842°F	12.2	16.0	10.4
wax, >842°F	11.5	11.1	6.1
oxygenated compounds	11.7	10.5	

Table 14 - Distribution of Liquid Product (Pilot Plant, U.S. Bureau of Mines)(35)

Pressure (atm. gage)	Hydrocarbon Products (g/m³)					
	Total Hydrocarbons	C_1-C_4	Liquid plus Solids			
			Total	Gasoline <200°	Diesel Oil >200°	Wax
0	155	38	117	69	38	10
1.5	181	50	131	73	43	15
5	183	33	150	39	51	60
15	178	33	145	39	36	70
50	159	21	138	47	37	54
150	144	31	104	43	34	27

Table 15 - Products from Synthesis at Different Pressures (Average of 4-week tests with standard Co-ThO_2-kieselguhr catalysts)(35)

Pressure, atm., absolute	1	3	5	10	20
Conversion of CO, %	95	75	70	75	75
Yield of C_3+ , g/m³	90	98	86	118	120
Liquid plus solids, wt-%					
Gasoline	57	32	30	25	22
Diesel oil	24	30	25	20	22
Wax	19	38	45	55	56
Olefin content, vol %					
Gasoline	68	64	63	62	63
Diesel oil	41	48	49	47	46

Table 16 - Selectivity as a Function of Pressure (Precipitated iron catalyst with $1H_2$ + 1CO gas, temperatures not specified)(33)

Catalyst: Composition Type Number	Fe_2O_3-CuO-K_2CO_3 Precipitated[b] P-3003.24		Fe_3O_4-K_2CO_3 Sintered[c]		Fe_3O_4-MgO-K_2O Fused[c] D-3001			
			A-2101	A-2106.05				
Test number	X101	X204	X160	X228	X152	X200	X215	X225
Pretreatment:								
Gas	$1H_2 + 1CO$	$1H_2 + 1CO$	H_2	H_2	H_2	H_2	NH_3[d]	NH_3[d]
Space velocity[e]	135	135	1000	1000	600	2700	5000	1000
Hours	24	24	43	24	43	40	4	6
Temperature, °C	230	230	400	400	450	450	385	350
Testing data:								
Pressure, psig	100	300	100	300	100	300	100	300
Temperature, °C	232	241	221	226	263	257	226	238
Average activity, A_{Fe}[f]	148	337	89.7	254	18.4	62.1	67.8	120.4
Usage ratio, H_2/CO	0.59	0.68	0.61	0.74	0.73	0.72	0.74	0.79
Product composition: hydrocarbons[g], wt-% as:								
C_1	4.7	5.0	4.8	6.7	13.2	11.3	16.0	16.4
C_2	5.3	4.4	4.7	6.2	8.8	8.3	10.6	8.3
$C_3 + C_4$	8.5	9.1	11.6	13.9	20.6	12.2	22.5	17.9
C_1-C_4	18.5	18.5	21.1	26.8	42.6	31.8	49.1	42.6
Liquids + solids	81.5	81.5	78.9	73.1	57.4	68.1	50.9	57.4
Acid number[h]	--	2.1	6.2	10.4	0.8	7.7	0.3	3.0
Distillation of liquids + solids wt-%								
<185°C	2.6	14.0	11.8	32.1	36.5	36.8	61.9	67.3
185-352°C	19.6	27.0	25.9	33.8	36.5	29.8	34.5	25.0
352-464°C	17.5	14.0	10.5	11.1	15.3	13.2	2.9	5.2
>464°C	60.3	45.0	49.5	23.0	11.7	20.2	0.7	2.5
Infrared analysis, weight per cent of functional group								
<185°C								
CO + COOH	1.6	2.8	3.7	4.0	0.6	1.7	1.5	1.4
COO	0.5	0.5	1.3	1.3	.1	0.5	0.2	0.3
OH	3.1	7.9	4.5	7.5	.2	3.4	13.5	11.7
α-olefins (C=C)	2.8	4.1	5.7	6.2	4.9	7.0	1.5	1.7
Other olefins (C=C)	1.0	0.3	0	0	5.1	0.9	0	0
Bromine number	25	29	38	41	66	53	10	12
185-352°C								
CO + COOH	1.0	1.0	1.5	1.7	0.3	0.8	0.8	1.3
COO	0.0	1.2	2.0	2.8	.1	.9	.6	1.0
OH	.7	1.9	0.9	2.2	0	.7	2.0	2.7
α-olefins (C=C)	1.9	1.8	3.8	4.2	1.1	4.0	0.4	0.6
Other olefins (C=C)	1.4	0.6	0.4	0.5	3.9	1.3	.9	.5
Bromine number	22	16	28	28	33	35	9	8

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[a] From Reference 33.

[b] 6- to 14-mesh granules.

[c] 6- to 8-mesh granules.

[d] Reduced in hydrogen at space velocity of 2,500 at 550°C for 20 hours, and converted to ε-phase nitride by the ammonia treatment.

[e] Volumes of gas at standard temperature and pressure per volume of catalyst space per hour.

[f] Average activity of weeks 1 to 5.

[g] Total hydrocarbons and liquids + solids include oxygenated compounds dissolved in hydrocarbon phases.

[h] Acid number of liquids + solids.

Table 17 - Effect of Operating Pressure on Activity and Selectivity[a]

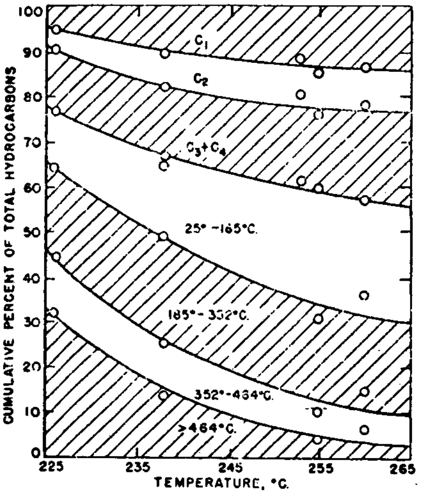


Figure 7 - Effect of Temperature on Hydrocarbon Distribution(33)

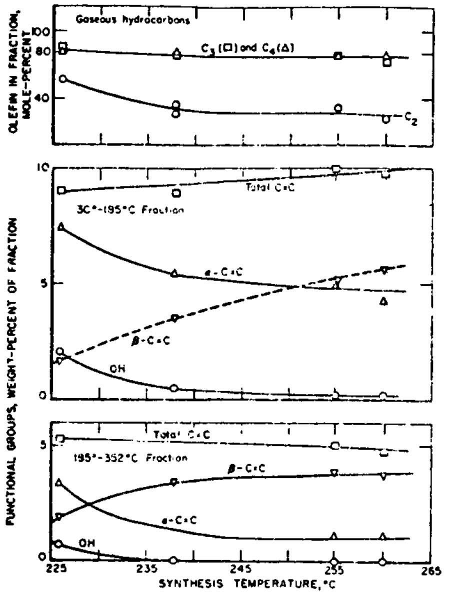


Figure 8 - Effect of Temperature on Functional Group Distribution(33)

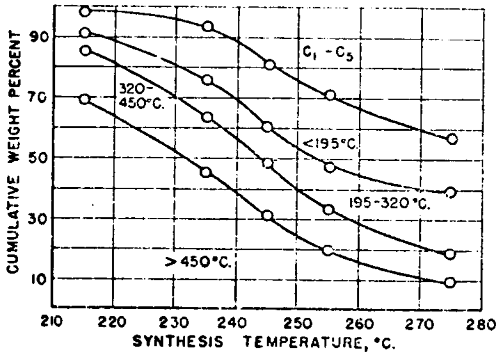


Figure 9 - Selectivity as a Function of Temperature with Precipitated Iron Catalyst, $1H_2 + 1CO$ Gas, Space Velocity 720 hr^{-1}, and 12 atm.(33)

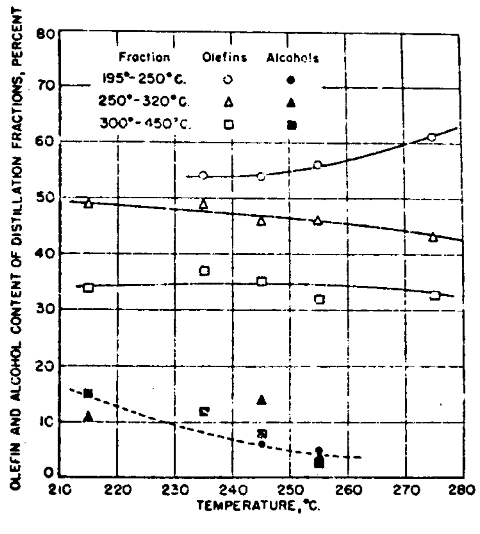


Figure 10 - Alcohol and Olefin Content of Distillation Fractions in Figure 9 (33)

($2.5H_2$ + 1CO gas at atmospheric pressure, space velocity = 125 hr^{-1})

Temp. of Operation (°C)	Condensed Hydrocarbons (%)		
	35 to 200°C	200 to 320°C	>320°C
185–191	46.4	35.6	18
170	29.5	33.2	37.3

Table 18 - Effect of Temperature on Selectivity of Co-MgO-Kieselguhr Catalysts(33)

Temp. (°C)	Contraction (%)	CO Conversion (%)	Yields (g/m³)	Per cent Paraffins (>320°C)	Composition of Boiling Ranges (%)					
					195–250°C		250–320°C		320–450°C	
					Olefins	Alcohols	Olefins	Alcohols	Olefins	Alcohols
					$2H_2$ + 1CO gas					
160	55	50	97	53	12	15	9	--	9	25
170	---	56	93	69	10	10	6	9	3	5
180	72	71	138	58	10	8	3	3	3	3
					$1H_2$ + 1CO gas					
170	47	38	71	49	29	27	19	21	17	17
175	50	49	96	58	33	29	19	23	14	17
195	62	62	115	54	38	19	23	8	16	8

EFFECT OF H_2:CO RATIO ON PRODUCTS FROM COBALT CATALYSTS[a]
(Atmospheric pressure, space velocity = 125 hr^{-1}, temperature = 190 – 192°C)

Synthesis Gas	Condensed hydrocarbons				
	35–200°C		200–320°C		>320°C Weight (%)
	Weight (%)	Bromine Number	Weight (%)	Bromine Number	
$1.2H_2$ + 1CO	30.4	72	22.6	33	47
$2.5H_2$ + 1CO	51.0	34	37.0	10	12

Table 19 - Products from Cobalt-Kieselguhr Catalysts in the Medium-Pressure Synthesis

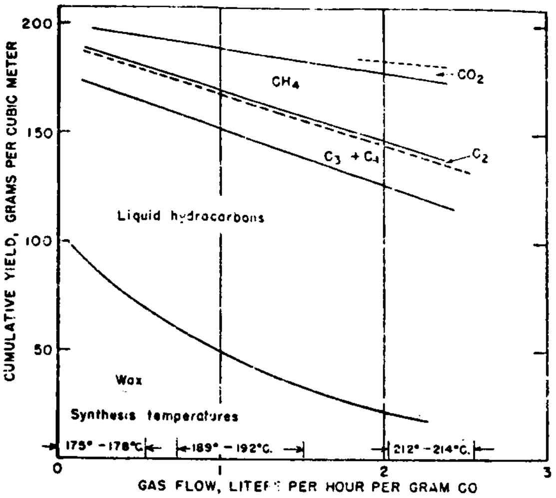


Figure 11 - High Flow Rate Reduces Wax Yield(33)

(All catalysts reduced in hydrogen at 450°C and tested at 7 atm of $1H_2 + 1CO$ gas.)

	Test, X . . .							
	212		152		118		201	
Mesh size	4-6		6-8		14-18		40-60	
Geometric area, sq cm per g [a]	4.0		5.2		11.9		44.7	
Space velocity	97.6		97.0		98.9		99.0	
Contraction, per cent	63.1		65.2		62.3		64.8	
Average synthesis temperature, °C	266		256		238		220	
Equivalent activity at 238°C [b]	14.1		19.9		37.5		73.2	
Products, weight per cent [c]								
C_1	17.8		17.8		10.7		7.1	
C_2	9.1		9.5		7.4		5.8	
$C_3 + C_4$	17.1		19.9		15.2		14.0	
Liquids plus solids	56.0		52.8		66.7		73.1	
Total acid number [d]	1.33		1.98		5.67		3.62	
Distillation analysis of C_5+, weight per cent								
<185°C	48.7		38.1		27.8		19.8	
185°-352°C	34.2		35.5		34.9		24.3	
352°-464°C	10.3		14.9		16.9		15.9	
>464°C	6.8		11.5		20.4		40.0	
Infrared analysis of fractions [e]	<185°	185-352°	<185°	185-352°	<185°	185-352°	<185°	185-352°
OH	0.15	0.04	0.17	0.04	0.48	0.10	2.10	0.70
α-Olefins	4.16	1.10	4.87	1.10	5.40	1.29	7.40	3.40
β-Olefins	5.60	3.66	5.05	3.88	3.46	3.43	1.60	1.90

[a] Computed as smooth spheres or cubes.

[b] Cubic centimeters $1H_2 + 1CO$ gas converted per gram of catalyst per hour. An activation energy of 20 kcal per mole was used in calculation at 238°C.

[c] Total of C_1–C_4 and liquids plus solids, per cubic meter of feed gas, varied from 100–110 g.

[d] Average acid number of aqueous plus hydrocarbon phases.

[e] Weight per cent of actual group, i.e., OH or C=C.

Table 20 - Activity and Product-Distribution Data of Various Particle Sizes of Fused Catalyst D3001(33)

(1 liter $2H_2$ + 1CO gas per gram Co per hour at 12 atmospheres)

Parts K_2O per 100 Co	Temp. (°C)	CO Consumed (%)	CH_4 in Off Gas (%)	Solid + Liquid Hydrocarbons (g/m³)	Wax Content, % of Condensed Hydrocarbons	
					>320°C	>450°C
0.8	190	71	6.5	139	61	37
0.2	189	71	8.0	135	67	40
0.4	182	67	5.6	130	60	34
0.1	188	73	8.8	137	61	37
0.1	180	75	9.5	133	58	29

Table 21 - Effect of Alkali Content on Selectivity of Co-Kieselguhr Catalysts(33)

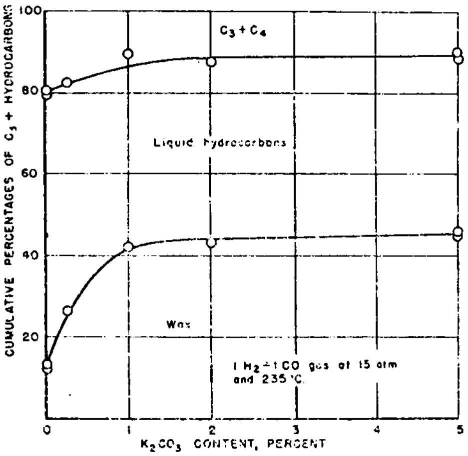


Figure 12 - The distribution of C_{3+} Hydrocarbons as a Function of K_2CO_2 Content of Precipitated Fe_2O_3-K_2CO_2 Catalyst(33)

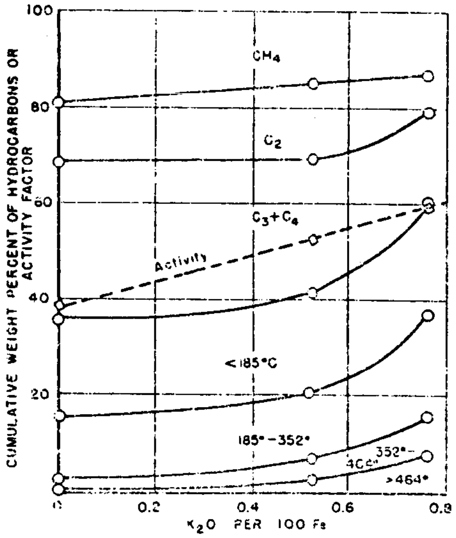


Figure 13 - Selectivity and Activity of a Precipitated Iron-Copper Catalyst as a Function of Alkali. ($1H_2$ + 1CO Gas at 7.8 Atmosphere)(33)

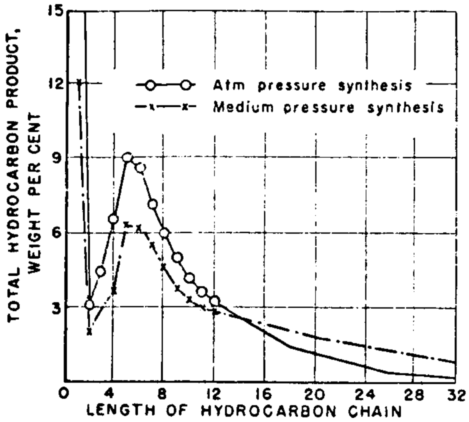


Figure 14 - Typical Molecular Weight Distribution with Cobalt Catalyst(33)

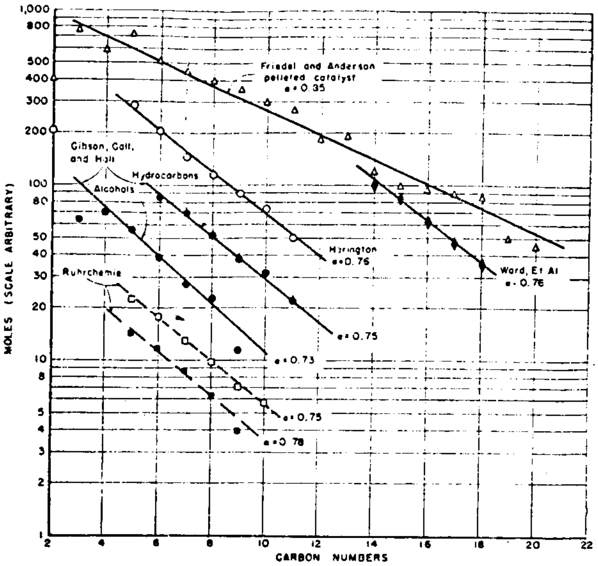


Figure 15 - Molecular Weight Distributions (Co Catalyst)(33)

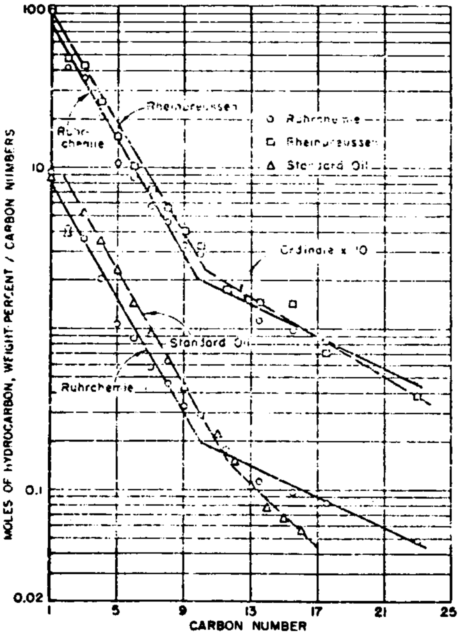


Figure 16 - Molecular Weight Distribution with Iron Catalyst(33)

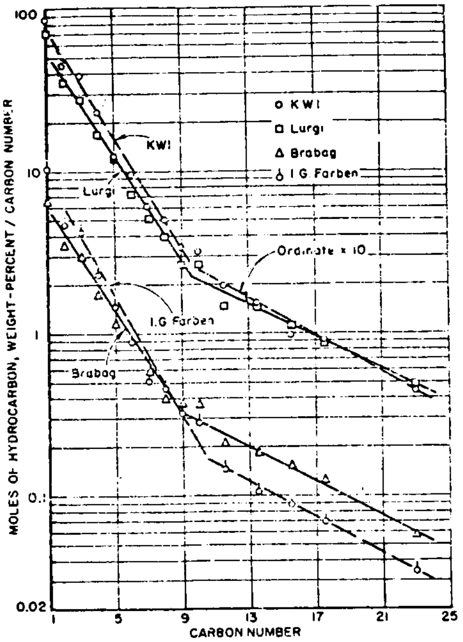


Figure 17 - Molecular Weight Data (Iron Catalyst)(33)

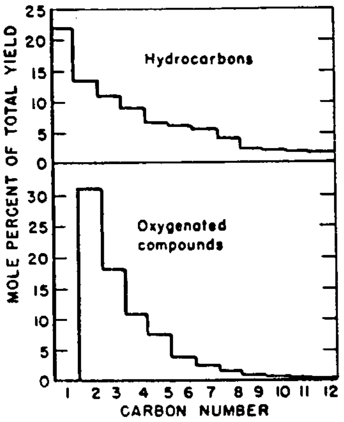


Figure 18 - Fluid Bed Process - Iron Catalyst(33)

Carbon Number	Mole Per cent[b]			
	Alcohols	Olefins	Paraffins	Total
1	2.35	—	37.3	39.65
2	4.36	5.98	1.37	11.71
3	4.55	9.68	2.33	16.56
4	1.47	7.41	1.79	10.67
5	0.765	2.09	0.67	3.52
6	.681	3.17	.78	4.63
7	.783	1.075	.87	2.73
8	.645	0.938	.39	1.97
9	.627	.424	.36	1.41
10	.651	.245	.19	1.09
11	.502	.125	.13	0.757
12	.460	.203	.045	.708
13	.269	.120	.032	.421
14	.209	.131	.020	.360
15	.275	.090	.019	.384
16	.203	.108	.009	.320
17	.096	.084	.008	.188
18	.141	.078	.011	.230
19	.140	.072	.007	.219
20	.123	.078	.007	.208
21	.116	.045	.006	.161
22	.191	.030	.006	.227
>22	.848	.930	.045	1.823

a From Reference 33.

[b] 7.2 weight per cent of esters + aldehydes + ketones + acids is not included in this distribution.

Table 22 - Distribution of "Synol" Products[a]

Carbon Number	Weight Per cent of Total Hydrocarbons						
	K.W.I.	Lurgi	Brabag	I.G. Farben.	Ruhr-chemie	Rhein-preussen	Fluid Reactor[a]
1	8.5	7.1	6.6	10.4	9.4	9.6	8.9
2	9.0	7.0	6.9	9.3	8.3	9.5	7.8
3	11.7	8.5	8.7	12.7	10.8	12.9	15.9
4	9.2	6.8	7.0	9.1	8.2	10.2	13.9
5	6.2	6.0	5.8	7.4	5.4	7.8	11.5
6	5.7	4.4	5.5	5.3	5.2	6.0	8.6
7	4.3	3.6	4.1	3.6	4.0	5.1	6.6
8	4.0	3.2	3.1	3.7	3.7	4.4	5.0
9	3.1	2.4	3.3	2.8	3.0	3.6	3.9
10	3.2	2.7	3.6	2.8	2.9	3.3	3.0
11 12	4.5	3.4	4.8	3.3	4.1	4.1	2.4 1.8
13 14	4.1	3.8	5.0	2.8	3.0	4.0	1.4 1.1
15 16	3.0	3.3	4.7	2.7	3.0	4.4	1.0 0.9
17 18	3.2	3.0	4.4	2.4	2.9	2.5	6.3[b]
19–27	7.7	8.3	10.0	5.9	8.3	6.6	
>27	12.6	26.5	16.5	15.8	17.8	6.0	
C_1–C_4	38.4	29.4	29.2	41.5	36.7	42.2	46.5
C_2–C_4	30.1	22.3	22.5	30.9	27.3	32.6	37.6
C_5+	61.6	70.6	70.8	58.6	63.4	57.8	53.5
C_5–C_{12}	31.0	25.7	30.2	28.9	28.3	34.3	42.8
C_{13}–C_{18}	10.3	10.1	14.1	7.9	8.9	10.9	
C_{19}+	20.3	34.8	26.5	21.7	26.1	12.6	
C_{13}+	30.6	44.9	40.6	29.6	35.0	23.5	10.7

a From Reference 33.

[b] Average carbon number of 30.

Table 23 - Carbon Number Distribution for Hydrocarbons from Synthesis with Iron Catalysts[a]

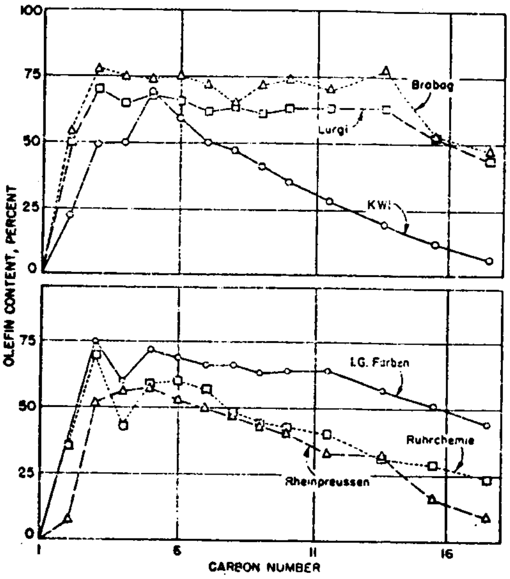


Figure 19 - Olefinic Products with Iron Catalysts(33)

(Cobalt catalyst at 1 atmosphere)

Fraction	Volume Per cent		
	α-olefins	Internal Double Bond Olefins	
		trans	*cis*
C_6[b]	36 ± 2	39 ± 3	25 ± 3
C_7	28 ± 2	42 ± 5	30 ± 5
C_8	18 ± 2	52 ± 5	30 ± 5

a From Reference 33.

[b] The equilibrium concentration of straight chain hexenes in mole per cent at 227°C is hexene-1, 4.7; *trans* hexenes, 64; and *cis* hexenes, 31.

Table 24 - Olefin Content of Liquid Products ($Co-ThO_2$-Kieselguhr Catalysts at Atmospheric Pressure)(33)

Component	Composition (Vol. %)	Component	Composition (Vol. %)
n-Pentane	94.9	*n*-Octane	84.5
Isopentane	5.1	2-Methylpentane	3.9
		3-Methylpentane	7.2
n-Hexane	89.6	4-Methylpentane	4.4
2-Methylpentane	5.8	3-Ethylhexane	0.1
3-Methylpentane	4.6	2,3-Dimethylhexane	[b]
2,2-Dimethylbutane	[b]	2,4-Dimethylhexane	[b]
2,3-Dimethylbutane	0.04	2,5-Dimethylhexane	[b]
n-Heptane	87.7		
2-Methylhexane	4.6		
3-Methylhexane	7.7		
3-Ethylpentane	[b]		
2,3-Dimethylpentane	[b]		
2,4-Dimethylpentane	[b]		

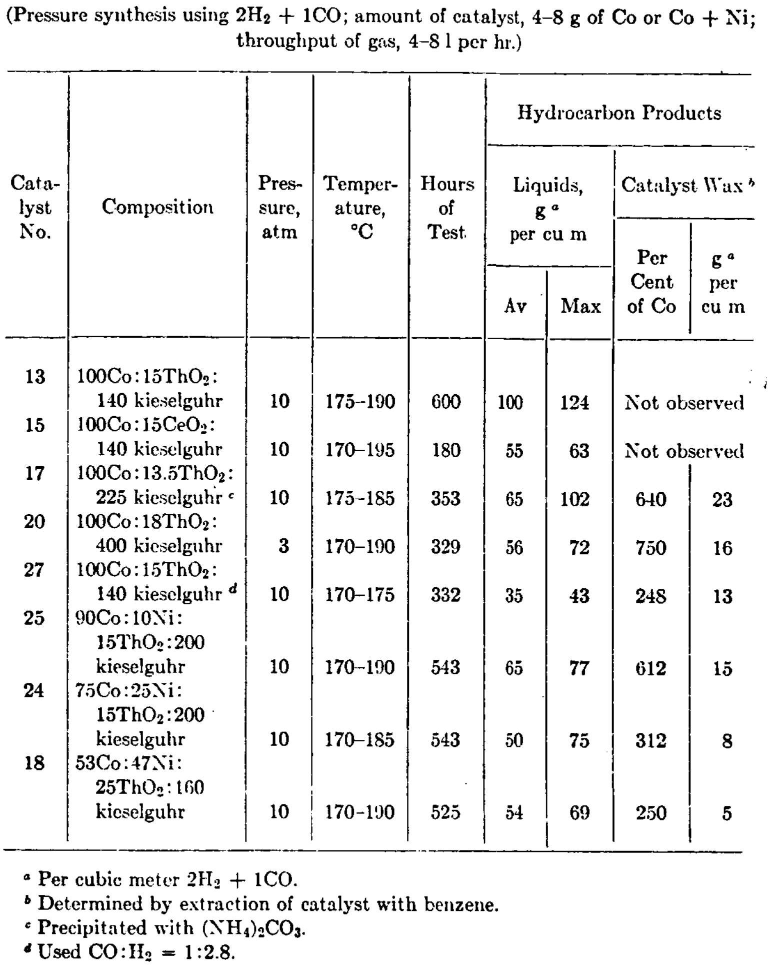
a From Reference 33.

[b] Values computed actually very slightly negative, and hence may be regarded as zero.

Table 25 - Mass Spectrometric Analyses of Paraffins from Cobalt Catalyst at Atmospheric Pressure[a]

Hydrocarbons				Oxygenated products	
Component	Weight %			Component	Weight %
C_3 fraction				*Water-dissolved chemicals*	
propane	20.2			alcohols	
propene	79.8			methanol	0.3
C_4 fraction				ethanol	36.9
isobutane	1.9			*n*-propyl alcohol	8.7
n-butane	13.6			isopropyl alcohol	0.8
methylpropene (isobutylene)	8.7			*n*-butyl alcohol	4.0
1-butene	64.3			C_5 and higher alcohols	1.2
2-butene	11.5			*total*	51.9
C_5 fraction				aldehydes	
isopentane	3.5			acetaldehyde	6.0
n-pentane	7.9			propionaldehyde	2.2
1-pentene	67.2			butyraldehyde	2.1
2-pentene	5.8			*total*	10.3
2-methyl-1-butene	3.5			ketones	
3-methyl-1-butene	11.1			acetone	7.5
2-methyl-2-butene	0.7			methyl ethyl ketone	2.2
cyclopentane	0.1			methyl propyl ketone	0.9
cyclopentene	0.2			methyl butyl ketone	0.2
	C_6	C_7	C_8	*total*	10.8
normal	75.9	60.2	55.4	acids	
monomethyl	20.0	29.3	36.4	acetic	18.1
dimethyl	0.4	1.7	2.4	propionic	4.7
cyclics	3.7	8.8	5.6	butyric	3.4
unsaturates, wt %, total	85.2	39.2	89.8	valeric and higher	0.8
				total	27.0
				Oil-dissolved chemicals	
				alcohols	32.9
				aldehydes and ketones	33.8
				acids	33.3

Table 26 - Fluid Bed-Iron Catalyst(35)



(Pressure synthesis using $2H_2 + 1CO$; amount of catalyst, 4–8 g of Co or Co + Ni; throughput of gas, 4–8 l per hr.)

Catalyst No.	Composition	Pressure, atm	Temperature, °C	Hours of Test	Hydrocarbon Products: Liquids, g[a] per cu m: Av	Liquids, g[a] per cu m: Max	Catalyst Wax[b]: Per Cent of Co	Catalyst Wax[b]: g[a] per cu m
13	100Co:15ThO$_2$: 140 kieselguhr	10	175–190	600	100	124	Not observed	
15	100Co:15CeO$_2$: 140 kieselguhr	10	170–195	180	55	63	Not observed	
17	100Co:13.5ThO$_2$: 225 kieselguhr[c]	10	175–185	353	65	102	640	23
20	100Co:18ThO$_2$: 400 kieselguhr	3	170–190	329	56	72	750	16
27	100Co:15ThO$_2$: 140 kieselguhr[d]	10	170–175	332	35	43	248	13
25	90Co:10Ni: 15ThO$_2$:200 kieselguhr	10	170–190	543	65	77	612	15
24	75Co:25Ni: 15ThO$_2$:200 kieselguhr	10	170–185	543	50	75	312	8
18	53Co:47Ni: 25ThO$_2$:160 kieselguhr	10	170–190	525	54	69	250	5

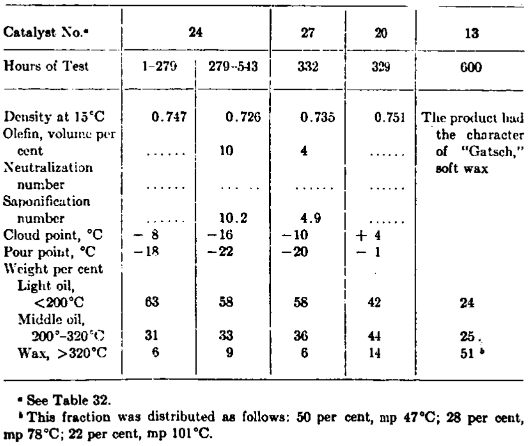
[a] Per cubic meter $2H_2 + 1CO$.

[b] Determined by extraction of catalyst with benzene.

[c] Precipitated with $(NH_4)_2CO_3$.

[d] Used $CO:H_2 = 1:2.8$.

Table 27 - Effect of Composition of Co and Co-Ni Catalysts Upon Distribution of Products(31)



Catalyst No.[a]	24		27	20	13
Hours of Test	1–279	279–543	332	329	600
Density at 15°C	0.747	0.726	0.735	0.751	The product had the character of "Gatsch," soft wax
Olefin, volume per cent	......	10	4	......	
Neutralization number	......	......	......	......	
Saponification number	......	10.2	4.9	......	
Cloud point, °C	−8	−16	−10	+4	
Pour point, °C	−18	−22	−20	−1	
Weight per cent					
Light oil, <200°C	63	58	58	42	24
Middle oil, 200°–320°C	31	33	36	44	25
Wax, >320°C	6	9	6	14	51[b]

[a] See Table 32.

[b] This fraction was distributed as follows: 50 per cent, mp 47°C; 28 per cent, mp 78°C; 22 per cent, mp 101°C.

Table 28 - Properties of Liquid Products of Co and Co-Ni Catalysts

Fraction, per cent	Boiling Range, °C	Time, hr			
		1-552	552-1,099	1,099-1,720	1,720-2,240
Gasoline	<200	21.0	13.9	6.1	5.0
Diesel oil	200-320	20.5	16.0	14.7	16.7
Soft wax	320-460	25.8	22.9	23.8	21.5
Hard wax	>460	32.7	47.2	55.4	56.8
Total wax	>320	58.5	70.1	79.2	78.3

Table 29 - Products Obtained from 100Co:15Mn:12.5 Kieselguhr Catalyst(31)

Properties	Soft Wax	Slab Wax	Catalyst Wax	Refined Plastic Wax	Refined Hard Wax
Setting point, °C (rotating thermometer)	42.5	50-52	87-91	75	90
Melting point, °C	44.0	53	...	About 85	110
Flow point, °C	40.2	48-49	...	77	98
Drop point, °C	41.8	49-50	...	79	99
Iodine number	.....	2.5	3.5	2.0	2.0
Acid number	0.14	0.03	...	0.05	0.1
Saponification number	0.35	0.6	1.0	0.9	0.8
Penetrometer number	.....	35.0	About 30	17.0	4.0
Mean molecular weight	.....	380	...	500	600
Mean carbon number	.....	27	...	36	43

Table 30 - Properties of Ruhrchemie Fischer-Tropsch Waxes(31)

(Space velocity of $2H_2 + 1CO$ gas = 100 hr^{-1}; pressure = 10 atm.)

	100 Co:15ThO$_2$: 12.5 Kieselguhr	100Co:15Mn: 12.5 Kieselguhr
Temperature, °C	175-178	165-168
CO conversion, per cent	85	65
CO conversion. to CH_4	10	11
C_3^+/C_1^+	0.90	0.89
Usage ratio, H_2:CO	2.02	2.05
Hydrocarbon yields, g/m³		
$C_3 + C_4$	15	15
C_5^+	130	130
Distillation of C_5^+, wt-%		
<200°C	22 (16)[b]	20 (18)[b]
200°-320°C	24 (12)	16 (12)
320°-460°C	21	22
>460°C	33	42

[a] From Reference 33.

[b] Numbers in parentheses represent volume per cent olefins.

Table 31 - Ruhrchemie Wax-Producing Catalysts[a]

1	2			3	4				
Fe-Cu-CaO-kieselguhr		100:5:30:100		100:5:10:150			100:5:8:30		
Process conditions									
Time, days		......		120	30	30	30	30	40
Pressure, atm		20		20			10		
Temperature, °C	246	267	280	251–257	200–218	218–220	220	220	220
Gas, H_2:CO	1.22 [a]	1.19 [a]	1.23 [a]	1.27 [a]			1		
Recycle ratio, residual:fresh	2.7	2.4	2.0	2.5			2.2		
Hourly space velocity	100	200	284	90			......		
Contraction, per cent	......	......	......	52	......	......	......	......	......
Conversion CO + H_2, per cent (*U*)	72	68	69	......	63	64	66	64	62
CH_4, per cent *U* (M_r)	......	......	......	......	7.0	6.6	6.8	8.8	8.9
CH_4, per cent of CO converted	6.10	8.10	15.6	......	3.6	3.5	3.7	4.6	4.7
C_1 + C_2, per cent of CO converted	......	......	......	11.0	......	......	......	......	......
CO_2, per cent of CO converted	......	......	......	26.8	......	......	......	......	......
Utilization ratio, H_2:CO (*X*)	1.14	1.11	1.13	1.23	1.04	1.14	1.17	1.11	1.12
Yields, g per cu m $1H_2$ + 1CO gas									
C_2+	114	96	76	......	105	107	111	104	102
C_6+	......	......	......	103	......	......	......	......	......
C_3 + C_4	......	......	......	13.5	......	......	......	......	......
Composition C_5+, per cent by weight (olefins+O-compounds, volume per cent of fraction) [b]									
Gasoline, <200°C	33	41	62	46 [c] (66)	16.5(44.8)	15.4(30.9)	13.3(28.0)	19.8(48.7)	25.1(66.3)
Oil, 200°–290°C	..	..	..	18 (52)	11.8(46.9)	5.9(42.6)	7.5(38.4)	8.5(52.8)	11.8(64.2)
Soft wax, 290°–320°C	..	..	..		4.1(44.7)	3.7(44.6)	4.6(39.0)	3.8(54.5)	6.0(66.8)
Soft wax, 320°–460°C	..	..	..	19	27.9	27.2	22.9	22.3	25.5
Hard wax, >460°C	..	..	..	17	39.7	47.8	51.7	43.6	31.6
Hard wax, >290°C	..	..	..	..	71.7	78.7	79.2	69.7	63.1

[a] Contains 13.7 per cent inerts.

[b] Soluble in sulfuric-phosphoric acid mixture.

[c] OH number = 24.

Table 32 - Tests of Some Ruhrchemie Iron Precipitated Catalysts(33)

(Single-stage operation at 12 atm of 1CO + $2H_2$ gas and space velocity of 240.)

	1	2	3	4	5	6	7	8	9	10
Catalysts,[a] MgO(Al_2O_3)-K-SiO_2	(100):10:0	MgO:K:SiO_2 [b]	36:6:50	48:6:48	42:11:49	47:12:95	34:10:88	32:7:91	89:8:49	95:8:48
Synthesis temperature, °C	210	235	210	210	222	210	225	215	218	230
CO converted, per cent	80	70	53	46	71	50	52	56	63	66
Yield										
C_5+, g per cu m 1CO + $2H_2$ gas	82	90	86	67	88	72	78	75	91	99
CH_4, g per cu m 1CO + $2H_2$ gas	..	..	14	12	21	14	..	..	14	12
Distribution, C_5+, weight per cent										
Gasoline, <195°C	23	40	30	43	48	21	22	46	46	30
Diesel oil, 195°–320°C	18	15								
Soft wax, 320°–450°C	24	20	70	57	52	76	78	54	54	70
Hard wax, >450°C	35	25								
Composition, >320°C fraction										
Straight chains, per cent [c]	91	81	95	85	94	92	88	84	93	86
Olefins, per cent	8	8	23	28	14	6	22	19	13	25
Alcohols, per cent	6	3	5	2	4	2	4	5	3	7

[a] Catalysts all contained 100Fe:25Cu in addition to constituents shown.

[b] Precise composition not given.

[c] Degree of branching determined by empirical method of Schaarschmidt, using antimonypentachloride.

Table 33 - Development of Precipitated 100Fe:25Cu:50MgO:(6-8)K:50 Kieselguhr Wax-Producing Catalyst for Medium-Pressure Synthesis (Oppau)(33)

Time, days	121	141	42
Test number	587/590	620/623	677/680
Catalyst number	1,382	1,383	1,462
Catalyst analysis, per cent			
Fe	23.6	24.2	23.4
Cu	5.6	6.2	6.2
MgO	2.1	7.4	8.3
SiO_2	33.7	23.3	22.2
K	2.4	2.5	3.0
CO_2	2.2	6.0	6.0
Synthesis gas, ratio $CO:H_2$		0.9–1:1[a]	
Utilization ratio, $CO:H_2$		1.1–1.2:1	
Hourly space velocity, l gas per l catalyst per hr		120	
Synthesis temperature, °C	240	230	225
Yield of primary product + gasol, g per cu m $1CO + 1H_2$	147	145	142
Space-time-yield, kg product per l per catalyst per day	0.42	0.42	0.41
Contraction, per cent	53	57	51
CO conversion, per cent	83	83	70
Per cent CO converted to			
CO_2	33	32	25
CH_4	3	4	2
Higher hydrocarbons	47	47	43
Total	83	83	70
Distribution, weight per cent			
Gasoline, <195°C	19	24	21
Middle oil, 195°–320°C	15	23	18
Paraffin, >320°C	66	53	61
	100	100	100
Composition of middle oil (195°–250°C), per cent			
Olefins	63	53	48
Alcohols	18	16	13
Straight chains	48	42	52
Composition of middle oil (250°–320°C), per cent			
Olefins	52	42	47
Alcohols	16	14	12
Straight chains	64	68	70
Composition of paraffin (320°–450°C), per cent			
Olefins	35	28	34
Alcohols	8	9	10
Straight chains	80	77	83

[a] Sulfur-free; contained 2 per cent N_2 and no CO_2.

Table 34 - Pilot-Plant Tests of Precipitated Iron, Magnesium-Promoted Catalysts (I.G. Farben. Ammonia Laboratory, (Oppau)(33)

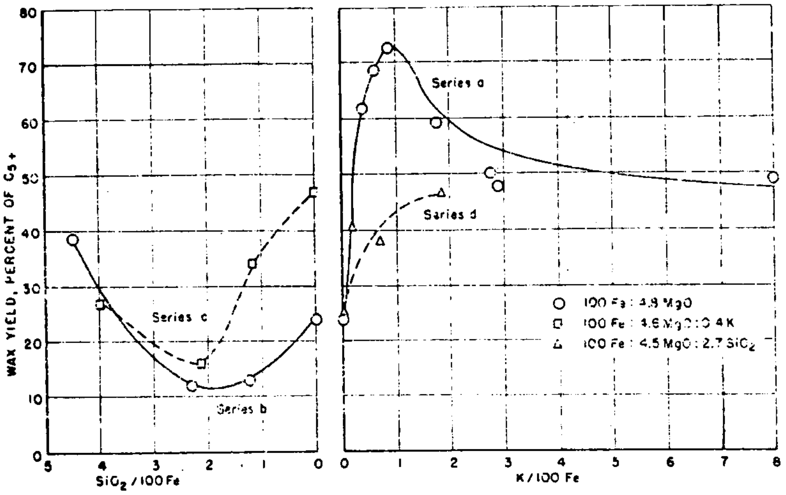


Figure 20 - Wax Yields from Fused Catalysts as Functions of Alkali and Silica Content(33)

	Per cent Branched Hydrocarbons in Following Fractions		
	C_4	C_6	C_7
Brabag	—	13	13
Ruhrchemie	9.6	11	11
Lurgi	—	13	13
Kaiser Wilhelm Institut	6.7 7.9	14.5	17
I. G. Farben.	—	16	18
Rheinpreussen	—	11	12
Normal cobalt catalyst	—	12.5	16.5

a. Fe Catalyst.

Table 35 - The Extent of Branching of Hydrocarbons from the Schwarzheide Tests(33)

Wax Cracking and Oxidative Dehydrogenation

A second way to obtain hydrocarbons in the desired molecular weight range consists of convering carbon monoxide to high polymers and cracking these back to olefins. Since it appeared that

$$RCH_2CH_2R \xrightarrow[\text{Heat}]{\text{Steam}} RCH{=}CH_2 + R'CH{=}CH_2$$

polymers which have a high degree of linearity could be produced by the Fischer-Tropsch synthesis, especially with ruthenium catalysts, the cracking route at first looked attractive. It would provide a convenient method for obtaining olefins and would be less complex than the Ziegler synthesis. However, it was discovered that all cracking processes are vapor phase reactions and therefore are limited to paraffins of carbon numbers 35 or less(67). It has already been pointed out that this is the molecular weight range most difficult to obtain by carbon monoxide hydrogenation. This severely limits the usefulness of paraffin cracking as a method for fatty acid synthesis. As a result, these processes will be described only briefly.

Wax Cracking

Paraffins in the range of C_{16}-C_{36} are cracked to olefins under high temperature conditions, with or without steam(67-69). In the steam process(67), the petroleum fraction to be cracked is first pre-heated to nearly 500°C. It is then contacted with steam and cracked by radiant heat at 500-700°C. The residence time in the cracking coils is short (0.65-1.9 seconds). The mixture is quenched quickly and fractionated into four cuts. These are olefins of 4-6 carbons, 6-12 carbons, 11-16 carbons and greater than 17 carbons(67). At low conversion per pass (5-10%), mono olefins make up about 95% of the product. These are generally 95-98% alpha. Paraffins of carbon numbers C_{20}-C_{35} were found to be the best feeds for the production of C_{11}-C_{20} olefins.

Other processes claim cracking without steam at about the same temperatures(68, 69). Certain cracking catalysts, compounds of lithium and nickel, have been employed(69).

Oxidative Dehydrogenation

This process involves converting hydrocarbons to polyolefins without chain cleavage(71-74). It has been utilized almost exclusively for the production of butadiene from butane.

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_2{=}CHCH{=}CH_2 + 2H_2$$

However, the procedure might be used to produce sites of unsaturation in a long chain molecule which could be oxidized or ozonized to lower acids.

$$R(CH_2)_nCH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} RCH{=}CH(CH_2)_xCH_3$$

$$\xrightarrow{(O)} RCO_2H + CH_3(CH_2)_xCO_2H$$

Catalysts, such as alumina, palladium, metal oxides and the like are used,(71-74) with temperatures up to around 475°C(75). This method leads to considerable by-products. Branched materials and aromatics are among them(73, 74).

The two routes just described offer simplicity of operation as their major advantage (see Figure 21).

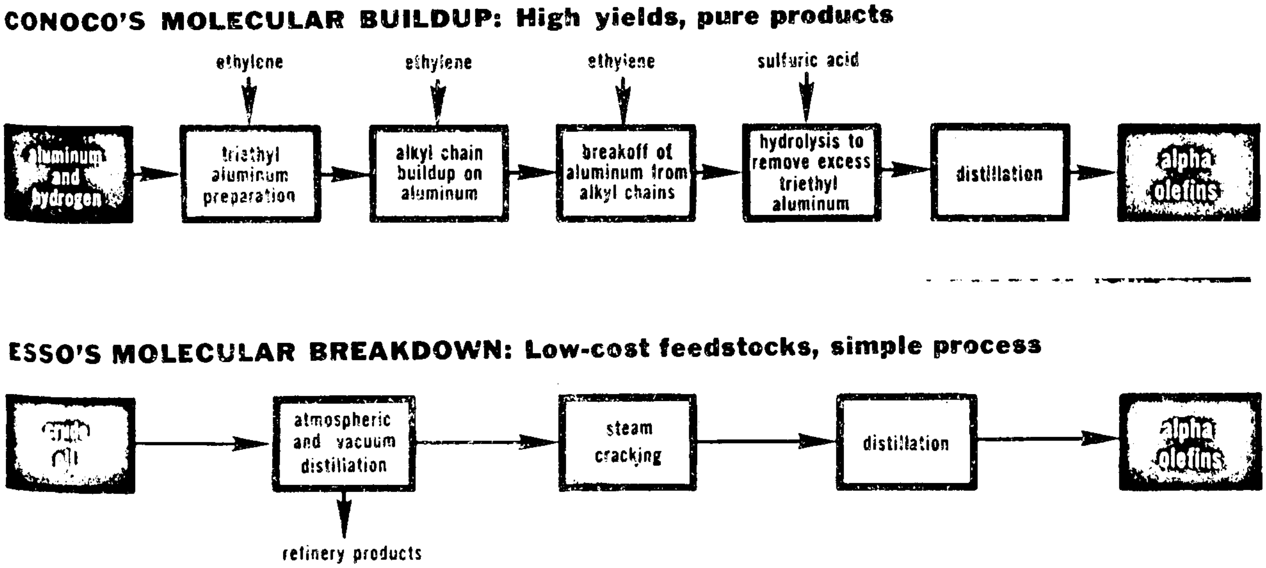


Figure 21 - Comparison of Molecular Buildup (Ziegler) and Breakdown (Wax Cracking) Routes to α-Olefins(67)

The drawbacks include lower yields, a wider distribution of products (Figures 22 and 23) and formation of branched and aromatic by-products. However, the most important limitation to this type of synthesis lies in the unavailability of paraffins in the necessary C_{20}-C_{35} range. Consequently, hydrocarbon cracking was not considered as a potential source of fatty acid precursors.

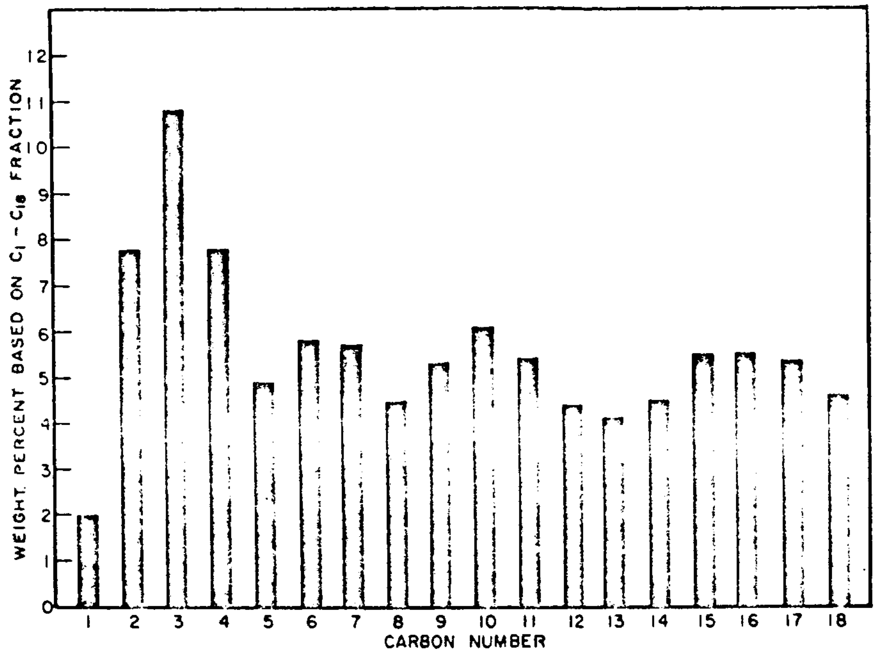


Figure 22 - Product Distribution from Typical Wax Cracking Run(80)

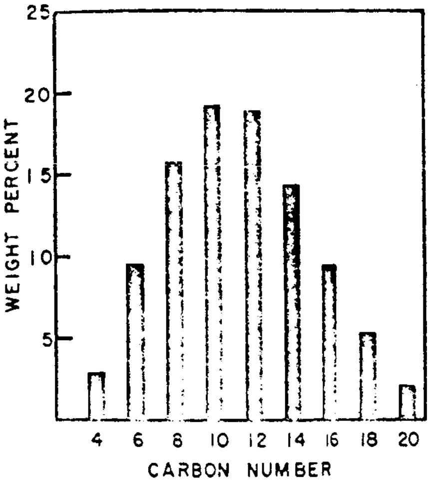


Figure 23 - Typical Distribution of α-Olefins from Ethylene Buildup (Ziegler)(80)

The Ziegler Reaction

A third method for reductively polymerizing carbon monoxide involves a two-stage process. This consists of reduction to ethylene followed by polymerization by means of the Ziegler growth reaction.

$$(1)\quad CO \xrightarrow[\text{Cat.}]{H_2} CH_2 = CH_2 + H_2O$$

$$(2)\quad CH_2 = CH_2 \xrightarrow{Al\ (C_2H_5)_3} RCH = CH_2$$

This route affords much greater selectivity to straight chain materials in the desired molecular weight range than any of the variants of the Fischer-Tropsch synthesis or wax cracking and appears to be the best method for accomplishing the crucial polymerization. This section of the report deals only with the Ziegler reaction. Ethylene production and conversion of the olefins to acids are discussed elsewhere.

In the late forties, Ziegler polymerized ethylene to a high molecular weight material by contacting the olefin with an alkyl lithium(76, 77).

$$C_2H_5Li \xrightarrow{C_2H_4} C_2H_5(CH_2CH_2)_nLi$$

The resultant lithium alkyls could be converted readily to linear alcohols or acids. The reaction was also shown to be catalyzed by sodium and potassium compounds(76). However, the alkali metal alkyls proved to be extremely reactive and led to too many by-products(76, 77). Ziegler quickly extended the reaction to beryllium, magnesium and, most important of all, aluminum alkyls(76, 77). With aluminum, the reaction proceeds at a reduced rate and can be controlled to give good selectivities to linear, α -olefins(76-79). This synthesis has great versatility since the intermediate metal alkyls may be converted to a variety of functional groups(76, 77).

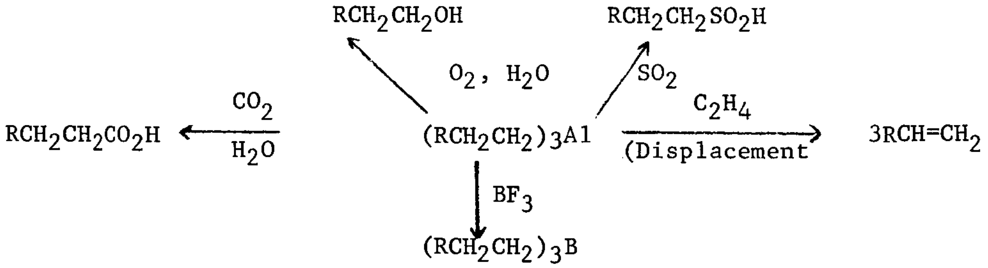


Figure 24 - Versatility of the Ziegler Reaction

For the present discussion, only the synthesis of α-olefins will be considered. Other methods for converting metal alkyls to functional groups leading to fatty acids are summarized and evaluated below.

The Ziegler growth reaction may be carried out in one or two stages(78, 79, 81-83). The single stage process consists of three steps occurring in rapid succession(78):

$$\text{(a)}\quad C_2H_5\text{-al} + (n-1)C_2H_4 \longrightarrow C_2H_5(C_2H_4)_{n-1}\text{-al}$$

$$\text{(b)}\quad C_2H_5(C_2H_4)_{n-1}\text{-al} \longrightarrow \text{alH} + C_2H_5(C_2H_4)_{n-2}CH{=}CH_2$$

$$\text{(c)}\quad \text{alH} + C_2H_4 \longrightarrow C_2H_5\text{-al}$$

$$\text{(d)}\quad nC_2H_4 \longrightarrow -(C_2H_4)_n^-$$

NOTE: "alH" = $>$AlH in R_2AlH; C_2H_5 - al $\hat{=}$ $(C_2H_5)_3Al$

The combination of steps (b) and (c) is called the "displacement" reaction. It may be formulated as:

$$\text{Alkylaluminum}^{I} + \text{Olefin}^{II} \rightleftarrows \text{Alkylaluminum}^{II} + \text{Olefin}^{I}$$

Reaction (b) is slower than (c) and is rate determining(78). The overall effect of displacement is to regenerate $Al(C_2H_5)_3$ which may be recycled. In general, the single stage process results in very low molecular weight olefins. A typical distribution(78):

	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_8	C_{20}
Wt. %	33.3	25.0	16.7	10.4	6.3	3.6	2.1	1.2	0.7

Higher α-olefins are obtained by means of a two-stage process in which reaction (a) above is allowed to proceed, under milder conditions, until the growth reaches the desired proportions. The displacement is then carried out as a separate one-step operation(78-83).

$$\text{(a)}\quad (C_2H_5)_3Al + 3nC_2H_4 \xrightarrow[\text{100 Atm.}]{100°} \left[C_2H_5(C_2H_4)_n\right]_3Al$$

$$\text{(b)}\quad \left[C_2H_5(C_2H_4)_n\right]_3Al + 3C_2H_4 \xrightarrow[\text{Ni. Cat.}]{60\text{-}70°} 3C_2H_5(C_2H_4)_{n-1}CH{=}CH_2 + (C_2H_5)_3Al$$

The distribution of olefins is now governed by the Poisson equation:

$$X_{(p)} = \frac{n^{P}\,e^{-n}}{p!}$$

Where n = the number of moles of ethylene consumed per equivalent of R-Al; p is the number of ethylene residues in the individual chains of carbon atoms formed; and $X_{(p)}$ is the mole fraction of chains with p added ethylene residues. Some typical plots are shown in Figure 25. By controlling the ratio of ethylene to R-Al, the distribution of molecular weights may be shifted to give nearly any desired average number. It is apparent, however, that the curves flatten out considerably at higher n-values.

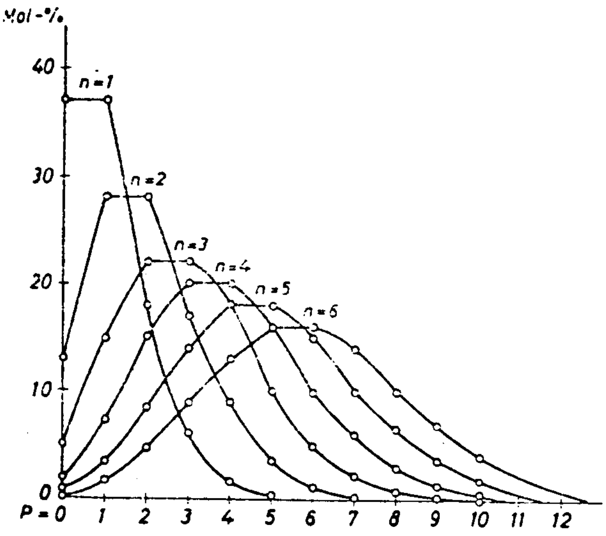


Figure 25 - Distribution of Alkyl Residues of the Form $R\text{-}(C_2H_4)_p\text{-}$ on Aluminum in Growth Products from One Mole of R-Al and n Moles of Ethylene(78, 82)

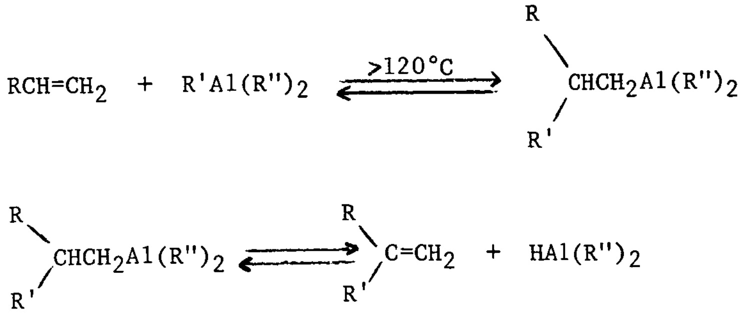
The Ziegler process as formulated above has two major drawbacks, (1) the growth reaction is very slow under the conditions shown (an hour is required to add one mole of ethylene to one equivalent of R-Al) and (2) the nickel catalyst employed in the displacement step greatly increases the recovery problems(76-83).

Raising the reaction temperature enhances the reaction rate somewhat but is accompanied by increased amounts of undesirable by-products(79, 81). In practice, an upper limit of 120°C was established above which a satisfactory product could not be obtained(79). The reaction is complicated by the energy released (22 Kcal/mole). This occurs in sudden bursts and causes severe heat transfer problems(81). The intermittent temperature increases, brought about by these energy bursts, causes some cleavage of the aluminum alkyl to olefins:

$$(RCH_2CH_2)_3Al \xrightleftharpoons{\text{Heat}} RCH{=}CH_2 + (RCH_2CH_2)_2AlH$$

$$(RCH_2CH_2)_2AlH + C_2H_4 \rightleftharpoons (RCH_2CH_2)_2AlC_2H_5$$

The α-olefins freed in this manner react, at temperatures of about 120°C, with the aluminum alkyls to afford undesirable branched olefins(81).



However, Zosel has shown that if the reaction is carried out continuously in thin copper tubes, where good heat exchange is achieved and the chain growth products are continuously removed, this problem can largely be avoided(79, 81). He was able to operate at temperatures of 160°C and 100-200 atmosphere pressure. This increased the reaction rate ten-fold and yielded less than 4% of branched materials(81). In this process, the degree of chain growth is regulated by controlling the residence time. Alternately, one may recycle the aluminum trialkyl through the reactor with low residence times until the desired average molecular weight is attained(81).

The second major problem in olefin production by the Ziegler growth reaction is caused by the nickel catalyst employed in the displacement step(76-83, 85). Either solid or colloidal nickel preparations have been used(79-81). The solid catalysts are preferable from the standpoint of product quality but have a short life time cannot be regenerated easily(81). Colloidal nickel may be reused but it is extremely difficult to separate from the reaction stream. The products cannot be distilled since, on heating, the nickel causes a reversal of the displacement reaction leading to branched chain and internal olefins(78, 81). In addition, the reformed triethylaluminum invariably contains traces of nickel. Nickel-containing triethylaluminum is ineffective as a growth catalyst, yielding only butylene by a dimerization reaction(78, 81).

Zosel, however, found that the displacement could be effected by heating the aluminum alkyls with ethylene to 300-350°C for very short reaction times (0.2-2 seconds). No catalyst is required(79, 81, 85). The very brief contact times are necessary to prevent migration of the double bond and decomposition of the triethylaluminum. Zosel developed, and has described, special equipment for this rapid displacement(81).

Other olefins have been used in the displacement reaction(78-81, 84, 85). However, only with ethylene is the equilibrium favorable(79). With higher α-olefins, the equilibrium constant is = 1. Thus, if the displacing olefin is present in n-fold excess, the degree of displacement is:

$$D = \frac{n}{n + 1}$$

For ten moles of olefin per equivalent of alkylaluminum, the degree of displacement is 90%. By contrast, a 10-fold excess of ethylene effects a virtually complete displacement(85).

Nevertheless, the use of higher olefins has been suggested to overcome a difficulty experienced in displacement using ethylene(79, 81). The C_{12} and C_{14} α-olefins co-distil with the reformed triethylaluminum and cannot be recovered directly. If a higher olefin (hexene or octene) is used as the displacing agent, the resultant trihexyl- (or trioctyl-)aluminum boils high enough to be readily separable from all olefins up to C_{16} or C_{18}. The alumintrihexyl or trioctyl- may then, in turn, be displaced with ethylene. This liberates hexene or octene and forms triethylaluminum which is recycled(79, 81).

$$\text{(a)}\quad (RCH_2CH_2)_3Al \xrightarrow{CH_3(CH_2)_3CH=CH_2} 3RCH=CH_2 + Al\left[(CH_2)_5CH_3\right]_3$$

$$\text{(b)}\quad Al\left[(CH_2)_5CH_3\right]_3 \xrightarrow{C_2H_4} Al(C_2H_5)_3 + 3CH_3(CH_2)_3CH=CH_2$$

This sequence, however, entails a double displacement step. Such a process is rather complicated for commercial (or space) applications. Simpler methods have been devised(79-81) in which the mixture of reformed triethylaluminum, and C_{12} and C_{14} olefins were returned to the original reactor and contacted once more with ethylene. After growth is complete, the C_{12}-C_{14} olefins are separated easily from the high boiling trialkylaluminum which is passed on to the displacement chamber where the operation is repeated(80). This is represented schematically by Figure 26. Theoretically this could result in a high percentage of branched materials by reactions of the C_{12} and C_{14} olefin with triethylaluminum. However, in practice this is not a problem(80, 81). Ethylene has an appreciably greater affinity for triethylaluminum than do higher olefins and is present in large excess anyway so that branching is held to around 5%(80, 81).

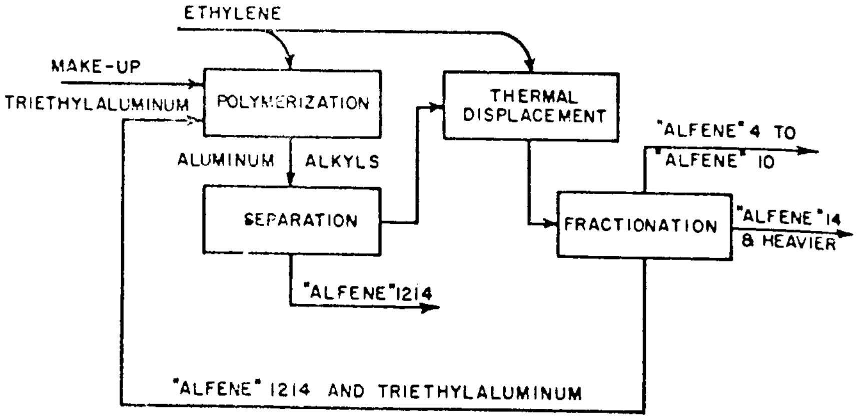


Figure 26 - Continuous Process for Production of α-Olefins via Ziegler Growth Reaction(80) ("Alfene" is α-Olefin)

Further details on the process are given in a later section of this report.

Although it is not directly applicable to space craft use, another variant to the Ziegler 2-stage reaction must be mentioned. This is the so-called "antistatistical" synthesis in which the Poisson distribution is upset and a narrower range of carbon numbers is obtained(76, 78, 79, 81). This variant employs octene-1 as the displacing olefin rather than ethylene. After displacement, all olefins up to C_{16} are separated by distillation leaving behind aluminumtrioctyl and olefins C_{18} or greater. The latter, being on the tailing portion of the Poisson curve, are present only in very small amounts. This residue is now contacted with the appropriate amount of ethylene to affect chain growth to an average carbon number of C_{10}-C_{12}. This product is once again displaced with octene and the sequence repeated several times. Finally, the process is terminated by displacement with ethylene which liberates the higher olefins and reforms triethylaluminum (79) (see Figure 27). This technique afforded Zosel an 88% yield of olefins in the C_{10}-C_{18} range (vs. 71% for the usual case). The amount of higher olefins (C_{20} and greater) was also increased. Since higher acids are thought to be less desirable nutritionally than those of C_8 or lower(89), and because the process is more complex, there appears to be no especial advantage in the "antistatistical" method so far as space applications are concerned. For an excellent discussion of the Ziegler reaction from both theoretical and experimental standpoints beyond the scope of this report, a series of articles in Annalen is recommended (reference 83).

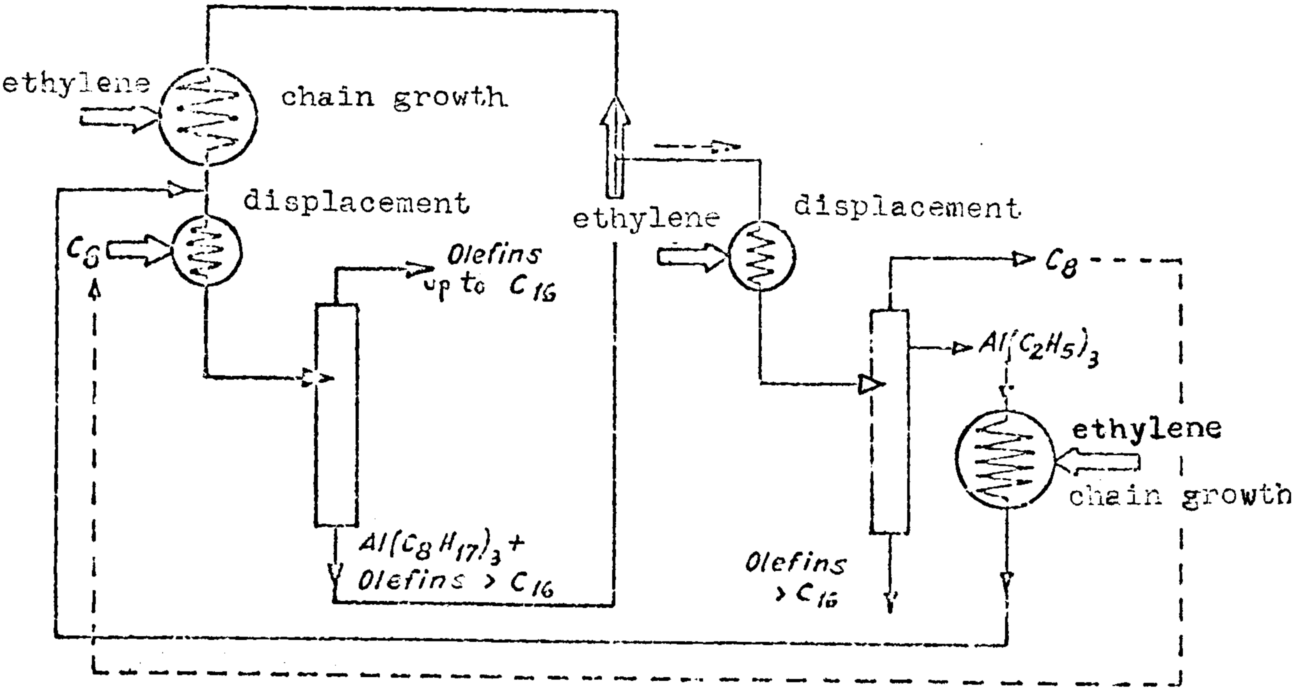


Figure 27 - The "Antistatistical" Process(79)

The Ziegler method has three distinct advantages over less selective processes: (1) The molecular weights of the olefins can be controlled to within narrow limits. In fact, it appears likely that the entire product may be used without fractionation(89), thus affording nearly quantitative conversion of CO; (2) a 95% linear material is obtained; (3) The "polymer" contains a reactive terminus (double bond) which can be converted to an acid grouping in good yield with few side products.

However, certain disadvantages obtain as well. (1) The olefins are all of even numbered carbon chains giving use to exclusively odd carbon acids by most methods of conversion. Such acids are of unproven value nutritionally. (2) The process is fairly complicated, requires some experience and practice in operation and may be very difficult to automate(86). The last two difficulties would be magnified in a zero gravity environment. Thus, although it is clearly the method of choice for the synthesis of fatty acids from CO_2, it does not permit an optimistic prognosis for the more general problem of production of synthetic foods.

Telomerization of Ethylene and Acetylene

Two other methods for controlled polymerization of two-carbon fragments were considered. These are telomerization of ethylene and polymerization of acetylene. Ethylene may be polymerized in the presence of methanol to give polymers of the general structure:

$$xCH_2{=}CH_2 \ + \ CH_3OH \ \xrightarrow[\text{initiation}]{\text{free radical}} \ H\text{-}(CH_2CH_2)_xCH_2OH$$

However, such reactions, as is true of nearly all free radical processes, are highly non-selective and produce considerable branched compounds(87). In addition, a non-regenerable free-radical initiator is required.

Acetylene has been converted to polyolefins of the type $(-CH{=}CH-)_n$ by a variety of catalysts of the Ziegler-type(88). However, the reaction is very poor and leads to highly colored and unstable products(88). Because of these considerations, both these methods were discarded in the preliminary screen.

SYNTHESIS OF ETHYLENE AND CONVERSION OF CO_2 TO CO

The sequence of reactions chosen for the synthesis of edible fats includes the Ziegler growth reaction for the preparation of higher alpha olefins. This in turn necessitates a scheme for the conversion of carbon dioxide to ethylene. Two general reaction routes are apparent. The first involves the reduction of carbon dioxide to methane, conversion of methane to acetylene, and reduction of acetylene to ethylene. The second route involves the reduction of carbon dioxide to carbon monoxide and the conversion of carbon monoxide directly to ethylene. The first of these routes has as its obvious attraction the fact that each of the three steps is a very well known and well documented reaction. On the other hand, it does involve three separate reaction steps, whereas the second of the routes needs only two reaction steps. A possible drawback to the second route, however, is the fact that data in the literature on the conversion of carbon monoxide to ethylene are not abundant and may not be entirely reliable.

Ethylene Via Methane and Acetylene

The acetylene route to ethylene is a three step process involving the hydrogenation of carbon dioxide to methane, conversion of methane to acetylene, and reduction of acetylene to ethylene. The immediate advantage of this route is that each step is well known and documented. Disadvantages are the fact that three chemical reactions are involved as opposed to the two in the carbon dioxide-carbon monoxide-ethylene route, and the fact that a great deal of energy is required to convert methane to acetylene.

$$(1) \quad CO_2 \xrightarrow{H_2} CH_4 + H_2O$$

$$(2) \quad 2CH_4 \xrightarrow{Heat} CH{\equiv}CH + 3H_2$$

$$(3) \quad CH{\equiv}CH \xrightarrow{H_2} H_2C{=}CH_2$$

The conversion of carbon dioxide to methane was not investigated. This is a time tested reaction, that goes all the way back to the work of Sabatier in 1902. As pointed out above, methane was assumed as an available starting material.

Processes for the cracking of methane and other hydrocarbons to yield acetylene have achieved considerable commercial importance over the past 15 years or so. Fortunately, this importance has led to the extensive documentation of the different processes that are currently available. Hence, only a general outline will be given, referring the reader to several excellent source publications for further information. The most valuable of these sources are a comprehensive book by Miller(90), an outstanding review by Goldstein and Scarffe(91), and the article in the Kirk-Othmer encyclopedia(92). Also valuable are the most recent editions of Hydrocarbon Processing's Petrochemical Handbook(93), a survey book by Hardie(94), and a recent review by Stobaugh(95). A special virtue of the Hydrocarbon Processing Petrochemical Handbook is the fact that it generally refers the reader back to extended articles prepared by industrial organizations describing their processes.

Most of the processes for preparing acetylene from hydrocarbons fall into one of a small number of categories: regenerative cracking, one-stage and two-stage flame cracking, and arc processes, including plasma arcs. The conversion of methane to acetylene is an extremely endothermic process which does not begin until very high temperatures are reached; the free energy change for the conversion of methane to acetylene is positive below about 1480-1490°K. The endothermicity of this reaction can be expressed by the following equation at 1500°K:

$$2CH_4 + 97 \text{ kcal/mol} \longrightarrow C_2H_2 + 3H_2$$

Complicating the whole situation are two further facts: methane does not begin decomposing to form acetylene until about 1500°F, so that the feed stock must be heated to the necessary cracking temperature very rapidly to avoid carbon formation; further, while acetylene is more stable than methane at the reaction temperature of 1500°K or more, it is less stable than the elements, and so must be rapidly quenched to temperatures about 550°K before equilibration begins. The time interval for the reaction should be of the order of milliseconds.

Goldstein and Scarffe have neatly summarized the advantages and disadvantages of the various commercial processes for acetylene preparation(91). One of these can be dismissed immediately--the regenerative cracking process, exemplified by the commercial Wulff process. The Wulff process is a cyclic process in which a fuel is burned in a furnace, heating a refractory lining, and then a hydrocarbon feed stock is fed into the furnace and is cracked by reaction heat provided by the refractory. The Wulff process is normally run at temperatures below that needed to crack methane to acetylene; it is limited by the ability of the refractory to withstand constant temperature changes, and is not considered useful for methane feedstock, although it is usable for just about anything from ethane on up.

A number of organizations have developed one-stage flame cracking processes, also known as partial combustion or partial oxidation processes. Among examples in commercial operation are those of Badische, Union Carbide, Montecatini, SBA and Dow. In the one-stage flame process, the gaseous hydrocarbon feedstock is used as both fuel and reactor feed. It is fed with oxygen to the reaction vessel where a part of the hydrocarbon is burned, providing a reaction temperature of the order of 2700-2900°F. This cracks the feed to acetylene and also some carbon black. Acetylene yields are of the order of 30-36% by weight on the methane feedstock. Advantages of the one-stage flame process are its low electrical power requirement as compared with arc processes and the fact that the off-gas (CO) can be used as synthesis gas. One stage flame processes are considered to be very good for natural gas feedstocks. Disadvantages include the fact that nearly 5 tons of oxygen and approximately 3 tons of methane are required to produce one ton of acetylene; the combustion products go together with the reaction products into the recovery system, increasing its size, complexity, and cost--the acetylene content of the cracked gas is only about 8 volume %; carbon is formed which gets into the quench water or oil, and must be either separated or burned to provide process heat; the calorific content of the off-gas, which is high in carbon monoxide, is rather low; and there are sometimes problems with stability of the partial combustion flame. With respect to spacecraft application, the high carbon monoxide off-gas might well be used as a source of formaldehyde, if this were to be used in the synthesis of glycerol. The very high reaction temperature and the need to remove a great deal of reaction heat should be quite a problem.

The high oxygen requirement, normally stated as 4.75 parts by weight per part by weight of acetylene product, is an obvious disadvantage aboard a spacecraft where oxygen is a valuable commodity. Also, the relatively low yield, of the order of 30%, does not look anywhere nearly so attractive as the high selectivity carbon monoxide to ethylene process, described below.

Two-stage flame cracking processes have been developed by Farbwerke Hoechst, S.B.A., and Kureha among others. In these a fuel, which is usually a liquid, is burned, and then the hydrocarbon feedstock is fed into the hot combustion gases. These processes were developed so that liquid fuels could be used, and they have a certain amount of flexibility in that they can be used to make ethylene (but not from methane). There are several minor differences in the advantages and disadvantages of these, as compared with the one-stage flame process, but basically, this type of process would be no more adapted to use aboard the spacecraft than the one-stage flame process. If a flame process were to be used, it would undoubtedly be the one-stage process.

Electric arc processes have been developed primarily by Chemische Werke Hüls and duPont. Advantages of arc processes are that the necessary high temperature is readily achieved; by-products, particularly carbon oxides, are minimal; and the yield on feedstock is relatively high since the feedstock is not used to provide energy. Disadvantages include high power consumption; difficulty in controlling the arc when it is sufficiently long to give reasonable residence time of the feed in the arc; narrow chamber confines required for adequate contact time lead to low volumes per unit (which would probably not be a difficulty aboard a spacecraft); carbon deposition on walls and electrode erosion necessitates frequent cleaning and replacement; and the very high reaction temperatures cause a large heat loss on quenching. Obvious advantages of arc processes for spacecraft use include the fact that oxygen is not required, and that the acetylene content of the product stream is substantially higher than that found in flame processes. The latter run about 8 to 11% acetylene, while the duPont arc process reports about 22% acetylene in the product gas, and the Hüls arc process runs about 16%(91). One immediate disadvantage is the fact that the reaction temperature is even higher than that in flame processes, of the order of 1750 to 1850°K. This requires the quenching of a great deal of reaction heat. Also, power consumption is quite high; that for the Hüls process is about 12,800 kWh/ton, and that for the duPont process is estimated at about 15,000 kWh/ton.

Many other processes for converting hydrocarbons to acetylene have been investigated. Among these are various plasma processes, including the Kanpsack-Greisheim plasma arc process which has received a good deal of research effort and is described in considerable detail in the literature. This process requires very high temperatures in order to produce an arc containing atomic hydrogen; temperatures run to about 3700 to 4200°K. Perhaps the most interesting of the new acetylene processes is the Happel-Othmer-Kramer(95-102). By a fundamental study of the kinetics of hydrocarbon pyrolysis reactions, these investigators found the optimum conditions for methane cracking. At temperatures between 3000 and 3200°F, they are able to get overall yields of about 95 to 97% acetylene from methane, with little or no carbon formation. Reaction heat can come from any convenient source, such as an electrical heating device. The high yield and clean reaction are obviously an attractive feature. However, the reaction temperature which is considerably higher than that for the flame processes, requires the dissipation of a great deal of reaction heat. In addition, this process has never been commercialized leading some observers to wonder about its utility(114).

Acetylene has been observed in products of the action of silent discharge on various hydrocarbons. It is not considered a good process and is not commercial. In addition, methane is reported to be a poor feedstock. Better results are obtained with other light hydrocarbons(90).

Before leaving the topic of converting methane to acetylene, there seems to be little or no prospect of developing a process for the direct conversion of methane to ethylene. First of all, this transformation does not become thermodynamically possible until about 1580°K, 100°C higher than the temperature required for the conversion of methane to acetylene. Further, at these temperatures, ethylene is less stable than acetylene. At best only small amounts of ethylene are ever obtained in the cracking of acetylene. There is one reference that indicates it is possible to convert methane to ethylene. About 35 years ago, Brewer and Kueck reported on the reaction of methane in glow discharge at liquid air temperature(103). By fractional condensation of their products, and spectroscopic analysis of the residual gas (which proved to be H_2), and by measuring pressure changes, they reached the conclusion that methane had been converted quantitatively to ethylene and hydrogen. They report that 3.1 molecules of ethylene were produced per electron. The only chemical test of their product was to show that it absorbed bromine, and there seems to be considerable question as to the actual composition of the product.

Some data on the composition of product streams from various commercial acetylene processes are given in Table 36. These are derived from the review by Goldstein and Scarffe.

Component	Hüls arc	Du Pont arc	Knapsack plasma arc	BASF One-stage flame on methane	BASF One-stage flame on naphtha	HOECHST Two-stage flame	WULFF Regenerative
N_2, O_2, Ar	0.8	NA	0.7	1.0	0.9	0.9	4.7
H_2	50.1	NA	60.3	56.8	43.5	30.0	49.2
CO	0.7	0.5	0.1	25.9	37.3	14.0	13.0
CO_2	--	NA	--	3.4	3.9	12.3	2.9
CH_4	17.0	NA	9.0	4.2	4.2	12.9	11.9
C_2H_2	15.9	22.5	13.8	8.0	9.3	10.6	14.0
C_2H_4	7.1	NA	10.5	0.2	0.2	14.9	3.0
C_2H_6+	8.4	NA	5.6	0.5	0.7	4.4	1.3

Table 36 - Composition of Reaction Products of Acetylene from Hydrocarbon Processes. (NA = no annotation). (mol. %)(91)

Selective Hydrogenation of Acetylene to Ethylene

Here again, the literature provides excellent documentation. Reviews have appeared at regular intervals: by Nieuwland and Vogt in 1945(104), Bond in 1955(105), and more recently by Bond and Wells within the past two years(106, 107). Bond and Wells, in particular, have done a great deal of work to elucidate the nature of selective acetylene hydrogenation processes.

It has long been known that different hydrogenation catalysts provide varying degrees of selectivity in the conversion of acetylene to ethylene. Palladium is clearly superior. It can provide selectivity to ethylene that exceeds 95%, while operating at room temperature. Among other hydrogenation catalysts, platinum and rhodium are useful, but only at higher temperatures, and even then they cannot approach the selectivity obtained with palladium. During World War II, the Germans actually used a selective acetylene hydrogenation process, with a palladium catalyst, to produce much of their ethylene. The German process, which has been described in some detail, used a palladium-on-silica gel catalyst, although one report indicates that diatomaceous earth was used as the carrier(108-110). The reaction was carried out at 1 atm., at temperatures variously reported as 150° to 210°C, and which were raised as the reaction proceeded and the catalyst lost its activity. More recent research results show that palladium catalysts have good activity even at room temperature, and a process aboard the spacecraft which did not require the use of heat would have its obvious attractions. However, it is well known that selectivity of acetylene hydrogenation with other catalysts increases with increasing temperature, and in a long term continuing operation the temperatures used by the Germans may well have been necessary on a practical basis. Further, they would undoubtedly give increased reaction rates, which would obviously be important for a commercial process.

There seems little virtue at this point in going into all the details of the various processes reported in the literature. The most recent of Bond and Wells' papers provide access to most of these references, and basically Bond and Wells have done the most important work themselves(107). There is some indication that the nature of the catalyst support may play a part in determining the selectivity of the catalyst. It would appear that silica gel is superior to alumina or pumice, although the data reported are at different temperatures, which may confuse the issue. A couple of points may be worth noting, however; one is that under certain circumstances, there is some polymerization to C_4 and C_6 products. Another is that palladium catalysts which include silver seem to have particularly good activity and selectivity. Especially recommended is a catalyst containing 70% palladium and 30% silver(111). A palladium-silver catalyst has also been the subject of a patent on a process for removing small amounts of acetylene in ethylene streams(112). Finally, palladium catalysts sometimes tend to lose their selectivity, especially when the ratio of hydrogen to acetylene in the feed exceeds 2:1(107). At hydrogen to acetylene ratios below 2:1, it would appear that long periods of effectiveness can be expected from palladium catalysts. One more point to note is that Shcheglov and Sokol'skii have reported that deactivated palladium catalysts for acetylene hydrogenation can be readily reactivated by air blowing(113). And, finally, the German commercial process of World War II is reported to have produced about 85% yields of ethylene, somewhat below that which might be expected from recent research results.

Reduction of Carbon Dioxide to Carbon Monoxide

A number of methods are conceivable for the preparation of carbon monoxide from carbon dioxide, including:

(1) dissociation

$$CO_2 \rightleftarrows CO + 1/2\ O_2$$

(e.g., thermal, irradiation, electric discharge)

(2) reverse water gas shift

$$H_2 + CO_2 \rightleftarrows CO + H_2O$$

(3) metal reduction

$$CO_2 + \text{metal} \rightleftarrows CO + \text{metal oxide}$$

(4) Boudouard reaction

$$CO_2 + C \rightleftarrows 2CO$$

A number of government contracts have been devoted explicitly to the conversion of carbon dioxide, generally for the purpose of regeneration of oxygen(115-119). In particular, the work of Chandler(116) who has actually developed a working device for the electrolytic conversion of carbon dioxide to carbon monoxide plus oxygen is recommended. Also of particular interest is the analysis by Foster and McNulty of a number of schemes for carbon dioxide reduction (although, to be sure, this analysis does not appear to be especially thorough)(117). They are able, however, to eliminate thermal, irradiative, and photochemical dissociation of CO_2 as impractical. Still another reference of special interest is a review by Hollander and Spialter of a variety of methods for reducing carbon dioxide(119).

It may serve a useful purpose, however, to discuss several references on carbon dioxide reduction, particularly those on the reverse water gas shift reaction and metal reduction. The Boudouard reaction can be ruled out since it would necessitate carrying along an expendable supply of carbon, or else the regeneration of carbon aboard the spacecraft.

Metal Reduction

Metal reduction does not appear to have been given any consideration. If metal reduction were to be employed, it would then become necessary to reconvert the metal oxide to the starting metal, so as not to require the transportation of non-regenerable metal. Possible methods for recycling the metal oxides have not been investigated, although silver oxides may be decomposed easily to free silver. At least three metals are known to react with carbon dioxide to give carbon monoxide and a metal oxide. Tin and carbon dioxide, for instance, react by the following equation:

$$Sn + 2CO_2 \rightleftarrows SnO_2 + 2CO$$

Literature on this reaction was surveyed by Quinn and Jones as long ago as 1936(120). As can be seen from the equation, this is an equilibrium reaction; the equilibrium constant is approximately 0.3 at temperatures around 650°C, and drops off at higher temperatures.

Weinhouse studies the reduction of carbon dioxide by zinc metal(121). This is a reaction that was reported in the literature as early as the 1880's. In practice, Weinhouse used calcium carbonate as his source of carbon dioxide. On heating dried powdered calcium carbonate with zinc dust at 700-750°C, he obtained quantitative yields of carbon monoxide. It is obvious that the actual reagent here is carbon dioxide and not the calcium carbonate. When barium carbonate, which is more stable to dissociation that calcium carbonate, was used, there was no carbon monoxide formation. It would also appear that temperatures as high as 700° are not needed for the zinc reduction of carbon dioxide, and that the only reason Weinhouse had to go this high was in order to obtain dissociation of his calcium carbonate. Senegavnik has studied isotope effects in the zinc reduction of carbon dioxide at 400°C(122). Unfortunately, we have only a limited amount of information on this study, which is contained in a French Atomic Energy Commission report.

Campbell and Brown have studied the reduction of carbon dioxide by manganese metal(123). Manganese is capable of quantitatively reducing carbon dioxide to carbon monoxide. At about 300°C the reaction is slow and conversion is not complete; at higher temperatures the reaction rate increases, and becomes quite rapid between 500-600°C. In this temperature range, some carbon formation also occurs.

Reverse Water Gas Shift

The obvious attraction of using the reverse water gas shift to prepare carbon monoxide is that hydrogen will presumably be available aboard the spacecraft as a result of the electrolysis of water. If a smooth reaction were possible over a stable catalyst, the use of this reaction would probably be highly desirable. There are a number of literature references which suggest that this may indeed be possible.

The water gas shift reaction is, of course, an equilibrium reaction, and has been studied extensively. Values for the equilibrium constant show that the formation of hydrogen and carbon dioxide is favored at temperatures below 800°C; however, the formation of carbon monoxide can be promoted at lower temperatures by using an excess of hydrogen(124).

H. Bahr studied the hydrogenation of carbon dioxide to carbon monoxide over a variety of catalysts, including activated copper, copper-CrO_3, iron, and iron-copper(125). His best results were obtained with an iron-copper catalyst, with which a 1:1 H_2-CO_2 feed was converted at 435°C to a gas which contained 16% CO. However, the activity of this catalyst seems to be short-lived, since after an hour and a half the CO content of the product gas dropped to 12%.

Th. Bahr studied the hydrogenation of CO_2 over $3MoO_3/7Al_2O_3$ and ThO_2-MnO catalyst(126). The latter gave about 36% conversion of a 3:2 H_2-CO_2 feed to CO at 30 atm. and 450°C.

A German patent to I.G. Farben indicates that uranium-activated iron and ThO_2-activated cerium oxide have been used as hydrogenation catalysts for CO_2(127). It claims that these lose their activity rapidly, particularly in the case of the iron catalyst, by sintering as a result of local overheating. This patent claims that alkaline earth metal oxides, including magnesium oxide, are active catalysts for the reverse water gas shift reaction, and maintain their activity for extended periods. For example, it claims that a calcium oxide catalyst retains its full activity for at least one month. In an example, a 5:2 H_2/CO_2 feed is reacted over CaO at 1000°C. Conversion of CO_2 to CO is about 76%; only minor amounts of methane are formed.

An unusual, indirect reduction method is described in the U.S. patent issued to Standard Oil Development Co.(128). Here, a fluidized bed of a Group VI metal oxide is reduced by hydrogen. This reduced metal oxide is in turn used to reduce carbon dioxide to carbon monoxide. An advantage of this procedure is that it does not depend on the water gas equilibrium and thus can give conversion to carbon monoxide at lower temperatures than are normally required. In an example, molybdenum tri-oxide is reduced by hydrogen at 1000°F and 1 atm. In two runs, the product gas contained 30 and 24.4% carbon monoxide, respectively. Such a process would of course operate as a cyclic process in which the Group VI oxide is alternately reduced by hydrogen and reoxidized by carbon dioxide.

Barkley and co-workers at the Bureau of Mines studied the catalytic reverse shift reaction, using a catalyst that comprised 67.6% Fe_2O_3, 19.4% CuO, and 13.0% water of hydration(129). The reaction was studied at 1000°F and rate and product composition were obtained for feeds containing 20, 50 and 80% carbon dioxide, the remainder being hydrogen. Conversion depended on the amount of catalyst employed, and leveled off in each case after sufficient catalyst was added to attain equilibrium. With 20% CO_2 feeds, conversion reached approximately 60%; with 50-50 feeds maximum conversion was between 30 and 35%; and with feeds containing 80% carbon dioxide, conversion reached a maximum of about only 15%. Kinetic analysis derived a value for the equilibrium constant of 0.267 at 1000°F, which agrees quite well with those previously reported in the literature(124). It will thus be seen that, if there is sufficient hydrogen in the feed, good conversion of carbon dioxide to carbon monoxide can be achieved at 1000°F without the need to resort to an indirect process(128).

A British patent to Esso Research describes a process for the catalytic reaction of 2 gases which are flowing at different rates(130). The process is not limited to use in the reduction of carbon dioxide, but one of the examples cited is of this reaction. According to the patent, the rapidly moving gas is injected into the more slowly moving gas in pulses which are sufficiently separated in time so that the products of one pulse do not mix with the products of a second pulse. In the example, carbon dioxide is injected into a stream of hydrogen and reacted at 1100°F over a 100 iron:1 CeO_2:100 kieselguhr catalyst. The overall ratio of hydrogen to carbon dioxide is 3:1, and 80% conversion to carbon monoxide is achieved. By comparison, using a 5 hydrogen/1 carbon dioxide feed but without pulsing the carbon dioxide, only 45% conversion is obtained with the same reaction conditions.

A rather bizarre British patent describes the conversion of a 90% CO_2 + 10% H_2 feed by a reaction mixture containing distilled water, while phosphorus, pulverized quicklime, copper chips and carbonated magnesia in which the entire reaction mixture has been activated by blowing with ozone. A hydrogen-carbon monoxide mixture is reportedly formed(131).

In 1930, Peters and Küster reported on a study of the water-gas equilibrium in which the equilibrium was set up by an electrical discharge at reduced pressure(132). In some of their runs conversions between 60-80% were obtained. Equilibrium is set up quite rapidly so that conversion remains constant over a wide range of feed rates, and thus electrical efficiency increases with feed rate over this range. However, the best electrical efficiencies they reported were slightly below 10%.

Finally, Akerlof has studied this reaction under a NASA contract using glow and silent discharge(133). With the glow discharge method, conversions of 80% per pass at a power cost of 4 KWH per pound of monoxide are claimed.

Dissociation of CO_2

There are many reports in the literature on studies of carbon dioxide dissociation, caused by various types of electrical discharge and radiation. It is worth noting that in such processes a flow system is quite necessary, since recombination of radicals under static or slow flow conditions gives very low conversions and efficiencies.

Conversion of Carbon Monoxide to Ethylene

$$CO + H_2 \xrightarrow[\text{Heat, Pressure}]{\text{Cat.}} CH_2{=}CH_2$$

Ethylene is frequently found among the products of Fischer-Tropsch synthesis; however, the selectivity to ethylene is usually extremely low. Ethanol, a potential ethylene source, can be obtained with somewhat better selectivity, but even at best this is nowhere near acceptable.

Under certain conditions, it is possible to achieve reasonable selectivity to ethylene. It was reported in 1908 that 6.6 and 8.3% ethylene in effluent from the reaction of 1:1 H_2/CO at 95-100°C over a Ni-Pd/coke catalyst could be obtained(134). The reaction conditions seem unusually mild, and the ethylene did not behave chemically as expected. This work was re-examined and appears to be open to question(135).

Two Badische Anilin patents, filed in Germany in 1949, have appeared. The first of these(136) deals with the synthesis of unsaturated hydrocarbons over finely divided iron melt catalyst at temperatures in excess of 450°C. Disclosures of the patent may be summarized as follows:

Temperature: 450-(470-600°C), Pressure: 1-25 atm
Catalyst: finely divided iron melt catalyst
Promoters (optional): compounds of Cu, Ti, Mn, Cr, Mo, Al, Th, Ce, Zr, F, etc.
Desirable catalyst component: cracking catalyst, 0-(20-50)-70% of total catalyst; generally a silicate, which may be activated, e.g., by acid
Feed ratio: CO/H_2 = 1:1-1:2, but especially 5:4
Feed rate: 200-(500-5000)-8000 vol/reaction vol/hr
Feed additive (advantageous): halogen acid source, e.g., NH_4F, NH_4Cl

The patent teaches further that it is necessary to burn off carbon deposits, followed by reduction with H_2 at 400-800° to give metallic iron. A fluidized operation is preferred, and recycle of the effluent after removal of CO_2 and hydrocarbons other than methane is discussed.

One example is presented, and it must be noted that it is written in the present tense. In a U.S. patent this could suggest that it might be a paper example; however, German usage may be different. It will be noted that neither of the BASF patents has ever issued in the U.S. The example reads as follows:

A 1:1 by weight mixture of an iron melt catalyst and a synthetic aluminum silicate is milled until it passes a 1000 mesh sieve, with 80% being retained on a 10,000 mesh sieve. The catalyst is reduced by H_2 at 5 atm and 450°C in a 50 l. vertical reactor. The reactor is thus largely filled with catalyst, which is fluidized by the H_2 stream; entrained catalyst is collected in a cyclone and returned to the reactor.

After reduction is complete a 5 CO/4 H_2 feed is introduced at 480°C, at a rate of 2000 normal l/l/hr. The specification then says that the off gas is recycled at the rate of 2000 N 1/1/hr, after removal of liquid and gaseous hydrocarbons (except methane) and CO_2. [This is a confusing statement; perhaps it means there is a total feed rate of 4000 1/1/hr, half fresh feed and half recycle.]

Yield is given at about 120g unsaturated gaseous hydrocarbons/m^3 of fresh feed. After a day of operation the reaction is sparged with nitrogen, the coke burned off with an air-nitrogen mixture, and the catalyst re-reduced with H_2.

There is no indication of selectivity, and the rate of coking is apparently high. The process does not look attractive.

The second BASF patent(137) employs a promoted, stable metal oxide catalyst at temperatures above 520°C, and a high recycle ratio. Again coke must be burned off the catalyst periodically. Also, the one example is again given in the present tense, with the possible implications discussed above, although here more detailed data are presented. Products are described as good yields of $C_2^=$, $C_3^=$, or $C_4^=$, along with CH_4 and liquid, largely unsaturated hydrocarbons. Conditions disclosed are:

Temperature:	$>520°C$, preferably $>550°$, e.g., 600-700°C
Pressure:	atmospheric
Catalyst:	Difficult reducible Group II-VII metal oxides, rare earth oxides; especially of Al, Cr, Mo, W, Mn, Si, Zn. Also usable are compounds which give stable oxides at the reaction conditions, and various mixtures; activated Al_2O_3 appears most desirable
Activators:	various acids
Carriers:	optional (e.g., Al_2O_3, SiO_2, etc. with other metal oxides)
Feed:	1 CO/1-2 H_2; 5-6 CO/4 H_2 preferred
Feed rate:	50-(100-2000)-5000 v/v/hr
Recycle:	2-10 x fresh feed, after removing C_{2+} hydrocarbons and CO_2

In the example, 20 1 of 1:1 CO/H_2 and 180 1 of recycle gas are passed at atmospheric pressure at 600°C over 100 cc of alumina activated with 10% molybdic acid. Yield per normal m^3 of fresh feed includes 80g $C_2^=$, 10g $C_3^= + C_4^=$, 40g ethane and higher hydrocarbons. It is not clear whether the 40g refers to C_2 or to (C_2+ higher hydrocarbons).

The data are sketchy, and selectivities are only fair especially by comparison with some of the other patent art on this reaction. Again, the suggestion of high coking is discouraging, and high ethane production necessitates complicated separation techniques (see Reference 139).

Another Patent(138) issued in France and Austria, claims the preparation of ethylene from CO and H_2 over a partially reduced metallic catalyst. The one example in the French case is written in the past tense, but data are sketchy. A product is claimed containing 95-100% ethylene (apart from inert gases). The disclosure include:

Catalyst:	partially reduced metallic catalyst; chemical nature not critical, but Fe probably preferred over Co; specific gravity < 2.0; reduction ratio 0.4-(0.55-0.6); lower reduction ratio would give better selectivities, but conversion with Fe catalyst drops sharply in going to a reduction ratio of $\sim$0.35-0.4

Catalyst Support: must be light, to keep density down, preferably
50-90% of total catalyst.
Temperature: 180°; depends on catalyst
Pressure: 0.05-1.5 atm, preferably below 1 atm
Feed: can be 1 CO/2 H_2 with very low density, water forming catalyst,
but preferably CO/H_2 = 1-(2)-3:1

(Variables such as pressure and feed ratio can be kept at less preferred values with very good catalysts, but requirements tighten with poorer--e.g., denser--catalysts.)

In the example, 200 l/hr of 2 CO/1 H_2 are passed over 1 liter of catalyst, at 265°C and 450° mm Hg. The finely divided, agitated catalyst contains 15 pts. Fe - 1 pt. Ca - 30 pts. kieselguhr. The Ca is all present as CaO, while the reduction ratio of the iron is 0.55; catalyst was prepared by simultaneous precipitation of the salts on the kieselguhr, followed by reduction at 350-400°C. Product gas contains 85% ethylene and 6% other hydrocarbons; the remainder is CH_4, CO_2, and H_2. This would make selectivity 93.5% but conversions are very low.

It was suggested that, by experimenting with reaction variables, and especially by going to lower conversions, selectivity to ethylene can be increased. However the evidence for this is poor.

Tsutsumi has filed three different patent applications on ethylene synthesis from CO. Unfortunately two of these cases appear to have issued in Japan only, so limited information is available.

The first patent is one of the Japanese-only group, 4172/58(140). A 1:100 Co/Al_2O_3 catalyst is used to convert a CO/H_2 mixture to ethylene. The abstract gives data relating reaction variables to products is shown in Table 37.

Molar ratio CO/H_2	1:1	2:1	2:1	3:1
Pressure, mm Hg	140	140	200	140
Temperature, °C	350	350	375	350
Mole % product gases				
CO_2	0.0	0.5	0.0	0.4
ethylene	3.3	5.1	2.5	6.2
CO	48.3	66.5	64.9	67.8
H_2	48.0	30.4	32.2	25.2
CH_4	0.6	0.5	1.4	0.4
Selectivity, %*	(84.9) 91.7	(90.1) 95.3	(92.7) 78.2	(94.0) 97.9

Table 37 - Conversion of CO to Ethylene (Tsutsumi)(140)

* The selectivity to ethylene is termed % yield by CA, and in the case of columns 1, 2, and 4, is clearly the mole, or volume ratio of ethylene to (ethylene + methane). This seems a strange quantity to be using; more meaningful would be a selectivity calculated by: (moles CO converted to $C_2^=$)/(moles CO converted to $C_2^=$ + CH_4)). And at that the moles converted to CO_2 should probably be taken into account. Recalculated values are presented directly below the CA figures, which are given in parentheses. The selectivity value in column 3 is clearly way off line. Note, too, that the product in column 2 adds up to 103%; in column 3 to 101%.

Given the various errors noted above, it is rather difficult to draw too much in the way of conclusions from this patent. Selectivities are quite good, but conversions are low, as would be expected for a sub-atmospheric process. Apparently selectivity to ethylene is increased by dropping the pressure and by increasing the CO/H_2 ratio; temperature increase seems to increase methane formation, a standard phenomenon, although the data unfortunately tie in a temperature change with a pressure change, rather than isolating them. CO_2, rather than water, seems to be the by-product, but there has been no attempt to do a material balance, and one is skeptical of the fact that there is not even any mention of water or higher hydrocarbons.

In the second of his patents(141) Tsutsumi uses a silica gel or alumina gel catalyst, which may be activated by compounds of Cr, Cu, Ni, Co, etc. Temperature is usually around 250°C, pressure desirably between 20 and 40 atm. High CO/H_2 ratios, preferably at least 2:1, favor ethylene formation, despite the fact that the stoichiometry for conversion of CO and H_2 to ethylene and water has a 1:2 ratio. Increase in pressure allows a lower reaction temperature, and favors ethylene formation. Thus, from the specification the following data are given for runs with alumina gel alone as catalyst:

CO/H_2	T, °C	P, atm.	Feed Rate, l/hr	Max. $C_2^=$ in Product
3:1	350-450	1	100-150	5.5%
1:1	"	"	"	4.2
1:2	"	"	"	3.0
3:1	250	2-4	200	5.6
1:2	"	"	"	3.0
1:2	250	20-40	200	4.0

A tubular reactor not made of iron is used (e.g., quartz, copper, aluminum, porcelain, etc.). The following examples illustrate the process.

Example 1(141)

Reactor: copper-lined pressure tubing, 1 m long, 2 cm i.d.;
catalyst (10g) packed into an 80 cm portion
Temperature: 250°C (from electric furnace)
Pressure: 20-40 atm
Feed rate: 200 l/hr

CO/H_2 ratio:1/2 catalyst data are given below:

Catalyst	Maximum Ethylene % in Product Gas
alumina gel + 3% Cu oxide	7.6
alumina gel + 7% Cu oxide	7.6
alumina gel + 3% Ni	7.2-7.6
silica gel + 3% Cu oxide	6.4
alumina gel + Co	5.6
silica gel	5.4
silica gel + 5% alumina	5.4
alumina gel + 2% Cr oxide	5.2
alumina gel + 2% $K_2Cr_2O_7$	4.8
alumina gel	4.6
alumina gel + 2% ThO_2	4.2
alumina gel + 2% Mo oxide	2.4

Alumina gel is apparently inferior to silica gel if used alone, but is is far more sensitive to the effects of promoters. Cu oxide, up to 3%, seems to be the best of the promoters. Detailed results from the alumina gel-3% Cu oxide runs were given:

	Feed Gas, %	Product Gas, %
CO_2	0.4	0.2
ethylene	0.6	7.6
O_2	0.0	--
CO	34.4	27.8
H_2	64.4	59.6
CH_4	--	1.0
N_2	--	3.8

Selectivity to ethylene was 94% but conversion was low ($<$ 20%). The origin of N_2 in the product is an interesting question; presumably it was just not analyzed for in the feed. These data were obtained with the undesirable CO/H_2 of 1:2. With alumina gel alone the maximum ethylene is 4.6% with a 1:2 feed, and 6.4% with a 1:1 feed. The patent does not state what happens with high CO feeds and the promoted catalysts.

Example 2(141)

Here metal salts were used to activate alumina gel. Results were:

Activator	Maximum $C_2^=$ in Product
3% Cu sulfate	6.6%
3% Ni chloride	6.5%
3% Ni sulfate	5.0%

The conditions here were the same as in the first example. Again, copper was the best promotor. Selectivity is said to be 95%.

The most recent Tsutsumi patent is assigned to Kurashiki Rayon, rather than Chiyoda(142). Only an abstract is available. A 74.2/24.8 CO/H_2 mixture (note: this adds up to 99) is passed through a Cu tube, with a 310 mm length of 19 mm inner diameter heated to 550°C, at the rate of 100 l/hr. The results:

	Vol. %	
	Feed	Product
CO	74.2	71.6
H_2	24.8	19.8
ethylene		5.6
CH_4		0.8

This adds up to only 97.8%; the rest of the product stream is not given. The selectivity appears to be 93.3%, again at low conversion.

(143) Tsutsumi also has a paper that appeared in 1956 in a Japanese journal, describing the conversion using CO/H_2 = 1:2, at 300-350°C and 10-120 mm Hg. The catalyst is Co or Ni on alumina gel, and the product, which is about 10-20% of the treated gas, contains about 90% ethylene. This appears to be quite similar to, if not identical with, the process of the first Tsutsumi patent, Jap. 4172/58.

Peters has obtained a patent that has issued in at least the U.S., Britain, France, and Austria(139). The French and Austrian patents are assigned to the Österreichische Stickstoffwerke. These show the greatest promise and were used in the engineering study. The reaction is carried out at 350-450° over a four component catalyst which contains:

1) Chromium oxide + (ZnO, Cu, or Ag); a metal or metal oxide activator is optional, and several alternates to the chromium oxide are disclosed, but the preferred component is Cr oxide + ZnO, optionally activated

2) A group 8 metal, preferably Co. This constitutes up to 10% preferably 0.1-1% of the total catalyst; it may be activated e.g., by Mn oxide, Cu, or Ag

3) An Al, Si, Ti, Zr, Hf, Th, Sc, Y, or rare earth oxide or hydroxide, especially Al_2O_3 or Kieselguhr

4) An alkali metal carbonate, oxide or hydroxide in small amounts. A salt which is convertible to the oxide or hydroxide may be used. Traces of alkaline precipitating agents left by incomplete washing constitute a suitable amount.

An inert carrier may be used, or component (1) or (3) may be used as carrier. Various catalyst preparation methods are disclosed, including the use of mixtures. Reaction temperature is (350-450)-520°C, and contact time is no more than 5 seconds, to minimize secondary reactions.

The data show excellent selectivities, generally above 90% (although no data is given on methane formation, and it is reasonable to assume there is some). These results are obtained with conversions of 5-10%, at temperatures around 400°C and atmospheric pressure. However, in one run at 20 atm, the reported data indicate a selectivity of nearly 88% even at a CO conversion level of 36.2%. Peters indicates a low degree of carbon deposition, and claims a long catalyst life. If all claims are true, this process is a very attractive one. A summary of Peters' data is given in Table 38.

In the absence of any further information, it is probably best to dismiss the BASF work(136, 137) which should give lots of coke, and seems to give poor selectivity. Asboth's patent(134) has the disadvantage of being a low pressure, hence low conversion, process. The Tsutsumi work(140, 143) is very confused, full of errors, and poorly reported. Also, the conversions are low.

Peters' work, however,(139) seems to be based on considerable data, and gives excellent selectivities. The one run in which 88% selectivity is obtained at 36% conversion seems, if true, to be far and away the best reported in the literature, and it might well be possible to back off a bit on conversion and bring the selectivity back up over 90% again. Consequently, this method was selected as the basis for the engineering study.

TABLE 38

DATA FROM PETERS PATENT(139)

Example #	Reactor Feed % CO	Reactor Feed % H_2	Reactor Feed % inerts	T, °C	P, atm	Catalyst #	Vol Feed/Contact Vol/hr	Products, Liters/m^3 Feed $C_2^=$	Products, Liters/m^3 Feed Other	CO Conversion	Selectivity to $C_2^=$	$C_2^=$ Yield(a)
1	46.4	42.5	11.1	430	1	I	350	25	2 C_2	11.6%	92.6%	10.8%
2	54.7	40.6	4.7	390	20	II	500	87	7 C_2 $3(C_3^= + C_4^=)$(b)	36.2	87.8	31.8
3	68	28	4	410	1	III	300	26.6	small amts C_2, C_{3+}	--	--	7.83
4	62	24	14	450	1	IV	365	20.4	0.97 C_2 C_{3+} insignificant	6.88	95.6	6.58
5	77.8(c)	22.2	--	400	1	V	315	23	1 $(C_3^= + C_4^=)$(b)	6.33	93.3	5.91
6	77.8(c)	22.2	--	430	20	V	315	31	0.5 C_2 0.5 $C_3^=$	8.30	96.2	7.97

N.B. Conversion, selectivity, and yield data have been calculated by us from Peters' product reports; he gives only one selectivity figure--95.6 for Example 1--which appears to be a misprint.

(a) Yield based on CO in feed, not on limiting reagent

(b) Assumed to be 2/3 $C_3^=$ by volume for calculation purposes

(c) Feed reported as having CO/H_2 ratio of 3.5:1, with no mention of inerts. If inerts were actually present, conversion and yield would be greater

Catalyst Compositions

I	II	III	IV	V
ZnO 51 pts.(31.0%)	ZnO 40 pts.(25.4%)	ZnO 51 pts.(30.7%)	Cu 29.1%	ZnO 30.7%
Cr oxide 13 pts.(7.9%)	Cr oxide 12 pts.(7.6%)	Cr oxide 13 pts.(7.8%)	Cr oxide 23.9%	Cr oxide 7.8%
Co 0.64 pts.(0.39%)	Cu 3 pts.(1.9%)	Co 1 pt. (0.6%)	Co 1.0	Co 0.6
K_2O 0.04 pts.(0.02%)	Mn oxide 2 pts.(1.3%)	Ag 1 pt. (0.6%)	K_2O 0.05	Ag 0.6
Al_2O_3 carrier 100 pts. (60.7%)	Co 0.15 pts.(0.10%)	K_2O 0.05 pts.(0.03%	Al_2O_3 carrier 46.0	K_2O 1.0
	K_2O 0.02 pts.(0.01%)	Kieselguhr carrier 100 pts.(60.2%)		Al_2O_3 carrier 59.7
	Al_2O_3 carrier 100 pts.(63.6%)			

CONVERSION OF HYDROCARBONS TO ACIDS

The products of the reductive polymerization of carbon monoxide may be converted to fatty acids by various means. In the case of n-paraffins only direct oxidation is pertinent; with olefins a greater variety of methods are available. These include oxidation, ozonization, epoxidation and rearrangement and carbonylation. In addition the metal alkyls, intermediates in the Ziegler process may be oxidized or carboxylated directly to acids without prior olefin formation.

Oxidation of Paraffins

Most of the work in this area was carried out in Germany and is summarized above. However, a few additional comments are appropriate. Stossel(27) and Gall(44) stress the importance of having a linear feed stock of below C_{30} (BP 300-400°C). If the feed contains a large percentage of iso-paraffins not only leads to branched acids but also to larger amounts of low molecular weight and hydroxy and keto acids(27). Alicyclic hydrocarbons are especially undesirable if present in the feed stocks(27). This illustrates the problems in the Fischer-Tropsch route to fatty acids; linear hydrocarbons of the desired molecular weight are the most difficult to prepare.

Temperature, air flow and catalyst composition all have a significant effect on the rate and course of the oxidation(21, 22, 27, 44, 144).

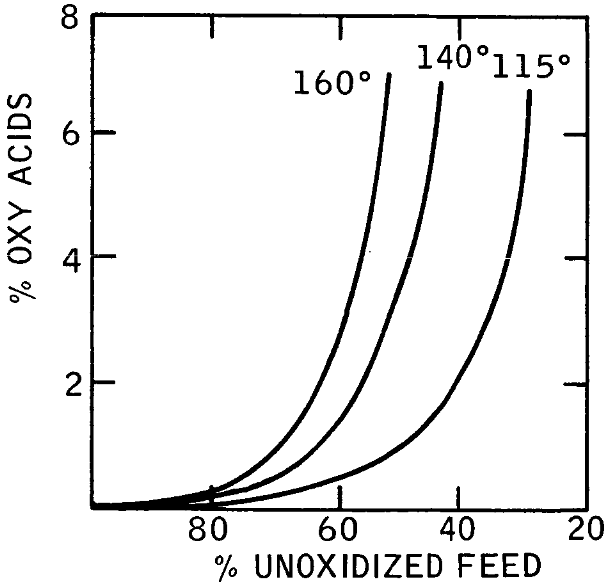


Figure 28 - Effect of Temperature and Degree of Oxidation on Formation of Hydroxy and Keto Acids (27)

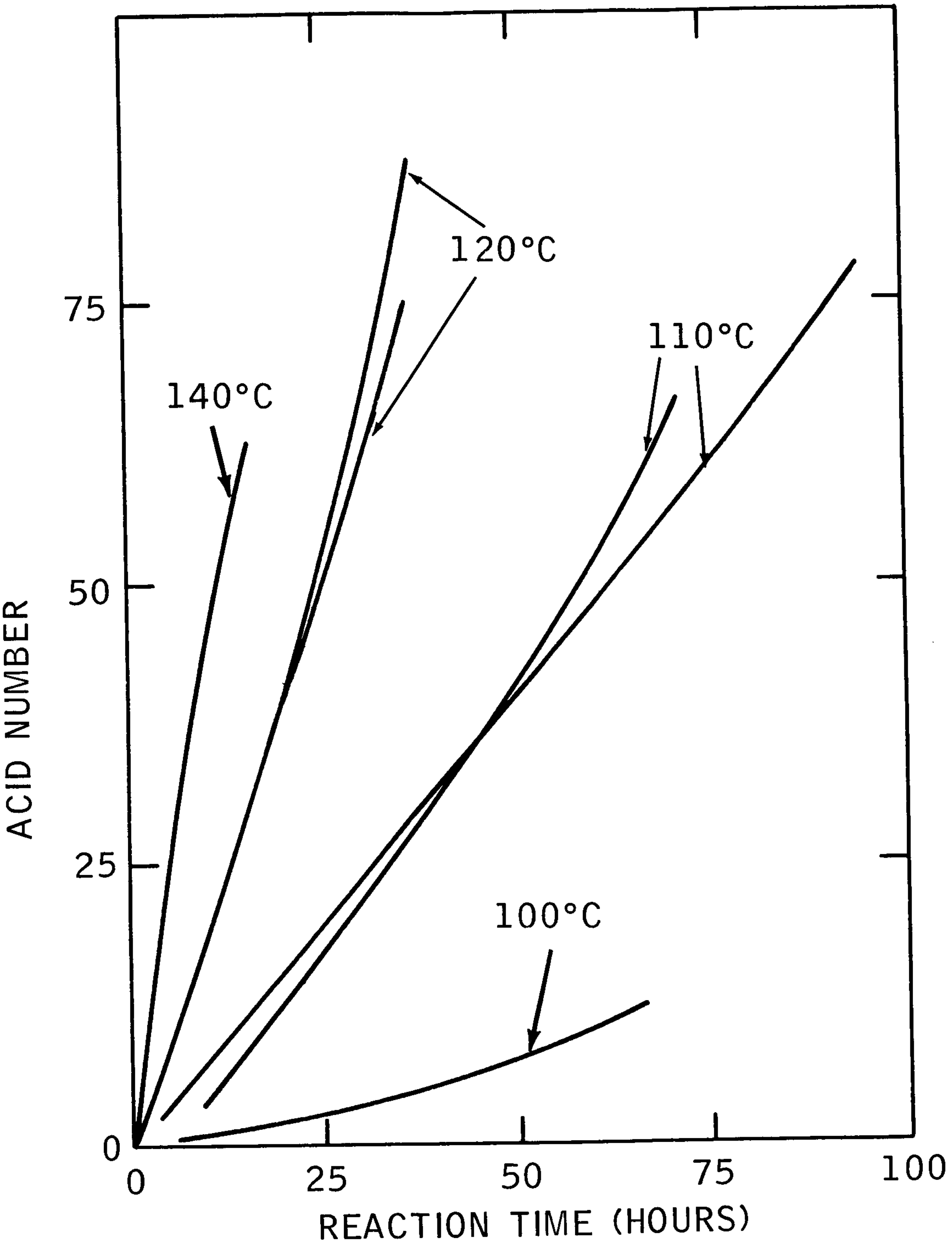


Figure 29 - Variation of Reaction Rate with Temperature(44)

Increasing the temperature reduces the reaction time considerably but has an averse effect on quality of the product(21, 27, 44) (Figures 28 and 29). The trouble arises because partially oxidized materials react faster than the hydrocarbons themselves leading to undesirable oxy-acids. Two methods for reducing overoxidation have been employed(27): (1) the oxidation is interrupted while a large excess of paraffin is still present and (2) oxidation temperatures as low as possible are employed (see Figure 29).

An increase in the air flow rate accelerates the oxidation up to a point after which the rate levels off(27). Pardun developed are empirical equation for the optimum air flow rates at various temperatures:(21, 27)

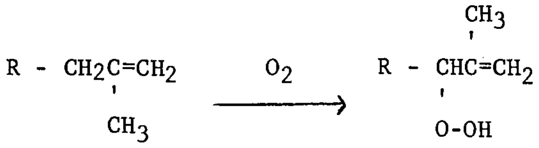
$$\log D = at-b$$

where D = l air/gm. substrate/hr.
a = const. = 0.03
b = const. = 4.3 for optimum rate and 4.6 for maximum acid yields
t = temp., °C.

Gall has studied various oxidation catalysts(44). He recommends manganese salts with cobalt as second choice. The efficiency of the catalyst preparation was found to be dependent on its solubility in the reaction medium. Gall also found that higher (> C_{20}) acids could not be successfully recycled. Taking all these observations into account, Gall recommends a reaction temperature of 110°C. air flow rate of 16.5 l/hr/100g paraffin and manganese resinate as a catalyst(44). The reaction should be continued to a final saponification number of 150. By recycle of non-oxidized paraffins a yield of C_{10}-C_{20} acids of 50-70% is claimed(44). These were suitable for industrial soaps but required further purification for use as edible fats or toilet soaps.

Oxidation of Olefins

Unsaturated hydrocarbons may be cleaved to acids by the action of air or oxygen (autoxidation) or with various oxidizing agents. Unfortunately the air oxidation of olefins is even less selective than that of the corresponding saturated hydrocarbons(44, 147-148). Olefins react more rapidly and the oxidation is more deep seated and complex. It has been used commercially only in the case ethylene and propylene(147). Surprisingly the site of initial attack is allylic to the double bond:(145, 146, 148)



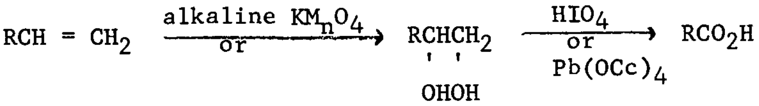
$$R - \underset{CH_3}{CH_2C}{=}CH_2 \xrightarrow{O_2} R - \overset{CH_3}{\underset{O-OH}{CHC}}{=}CH_2$$

Gall investigated the air oxidation of olefins under conditions similar to those employed in paraffin oxidation and found significantly lower yields of the desired C_{10}-C_{20} acids(44).

Somewhat better selectivity is achieved with other oxidizing agents. The most commonly used are chromic(149-151) and nitric(152) acids. However, allylic attack is still a problem and mixtures occur(149, 150). For example, Hickinbottom obtained hexanoic acid, heptanoic acid and oct-1-en-3-one (the product of allylic attack) along with traces of other products from the chromic acid oxidation of octene-1(150). In fact, about the only cases where the oxidation occurs cleanly are those in which the olefin is disubstituted with groups containing no methylene groups. An example is the last step of the classical Barbier-Wieland degradation: (149).

$$RCH = C(C_6H_5)_2 \xrightarrow{(O)} RCO_2H$$

Splitting of olefins may be accomplished by a two step oxidation involving hydroxylation followed by clearage with periodate(149).



$$RCH = CH_2 \xrightarrow[\text{or}]{\text{alkaline } KMnO_4} \underset{OH\,OH}{RCHCH_2} \xrightarrow[\text{or } Pb(OCc)_4]{HIO_4} RCO_2H$$

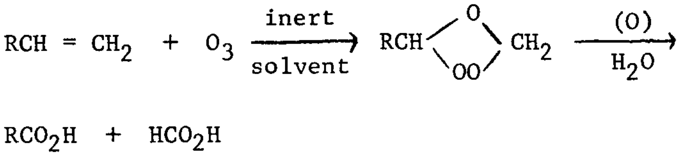
This procedure has been simplified by utilizing a mixture of permanganate and periodate at nearly neutral pH(149).

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H \xrightarrow[\substack{K_2CO_3 \\ H_2O}]{\substack{NaIO_4 \\ KMNO_4}} \xrightarrow{H_3O}$$

$$CH_3(CH_2)_7CO_2H + HO_2C(CH_2)_7CO_2H$$

Ozonolysis

The most reliable method for degradation of an olefin to a carboxylic acid is ozonolysis followed by oxidative decomposition of the ozonide(145, 153, 162). Ozone attacks the

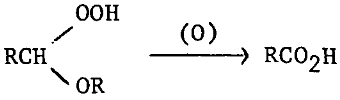


double bond selectively and no rearrangements occur. As a result this method is commonly used as an analytical tool for determining the position of double bonds (145, 153-157).

In an active solvent, such as an alcohol or acid, an oxyperoxide rather than ozonide is formed(153, 155). This may also be

$$\overset{H}{RC} = CH_2 + O_3 \xrightarrow{R'OH} RCH{\begin{smallmatrix} OOH \\ OR' \end{smallmatrix}}$$

oxidized to acids.



$$RCH{\begin{smallmatrix} OOH \\ OR \end{smallmatrix}} \xrightarrow{(O)} RCO_2H$$

The procedure has advantages in that formation of the potentially hazardous ozonide is avoided. However, the oxidation of these "active intermediates" is somewhat less selective and appreciable quantities of oxyacids are obtained(157). The use of inert diluents and low reaction temperatures effectively reduces the danger of explosion in ozonolysis reactions.

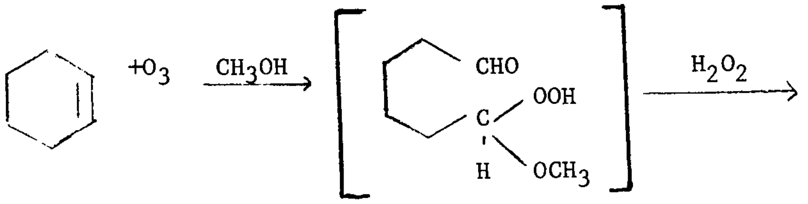
The yields of acids achieved by ozonolysis are very high (Table 39). Excellent laboratory procedures are available illustrating the use of inert(153, 156) and "active"(155, 158, 159) solvents. Asinger produced various acids in 95-98% yield by ozonolysis of α-olefins.

Product	Yield	Compound Ozonized	Solvent	Method of Decomposition
	per cent			
Adipic acid	73	Cyclohexene	Methanol	O_2-O_3-formic acid
Heptanoic acid	83	1-Octene	Methylene chloride + acetic acid	O_2-O_3-acetic acid
Hendecanoic acid	77	1-Dodecene	Acetic acid	O_2-O_3-acetic acid
ω-Aminononanoic acid	25	Oleylamine	Chloroform	Air-manganese catalyst-HCl
Pinonic acid	40–60	Pinene	Acetic acid + chloroform	O_2–O_3
Adipic acid	85	Cyclohexene	Methanol	H_2O_2-formic acid
Phthalic acid	88	Naphthalene	Methanol	H_2O_2-formic acid
Quinolinic acid	92	8-Hydroxyquinoline	Acetic acid	H_2O_2-acetic acid
Diphenic acid	65	Phenanthrene	Methanol	H_2O_2-NaOH
Adipic acid	86	Cyclohexene	Acetic acid	Peracetic acid
Lauric acid	94	1-Tridecene	Chloroform	Ag_2O-NaOH
Hendecanoic acid	93	1-Dodecene	Pentane	Ag_2O-NaOH

Table 39 - Synthesis of Acids by Oxidative Ozonolysis of Olefins(153)

He carried out the ozonolysis in chloroform solution(156). If chloroform is the solvent it is best to avoid an excess of ozone. Greenwood found that chloroform reacts with ozone to liberate phosgene(160). Greenwood recommended water, acetic acid, ethyl chloride and carbon tetrachloride(160). The freons would seem to be reasonable alternates. For the engineering study described below Freon 11 (fluorotrichloromethane) is suggested.

Bailey obtained high yields of adipic acid from ozonolysis of cyclohexene in methanol solution(158, 159). The reaction



$HO_2C\ (CH_2)_4CO_2H$

was carried out at -70°C. At higher temperatures methanol is reactive toward ozone(158, 160).

Various oxidizing agents have been used to convert the intermediates ozonide to acids. Especially good are basic silver oxide(155, 156), per acids (155, 158, 159) and oxygen(155, 161, 162). A trace of ozone(155, 161) or iron salts(162) promotes the oxidation with molecular oxygen or air.

The ozonolysis reaction is used in several commercial processes. In addition to adipic acid mentioned above(158, 159, 162), azelaic and pelargonic acids are produced this way from oleic acid(155, 161).

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H \xrightarrow{O_3} \xrightarrow[H_2O]{O_2}$$

$$HO_2C(CH_2)_7CO_2H \ + \ CH_3(CH_2)_7CO_2H$$

In this process excess acid is used as the "reactive" solvent for the ozonolysis step. Oxidation is carried out by passing oxygen containing a trace of ozone through the ozonized acid. Care is exercised to make sure that no large quantities of free ozonide is present at any time. Yields of up to 86% are claimed(155, 161). However, the product appears to contain some oxyacids and other dibasic acids(155, 157).

Ozonolysis appears to be the best of the simple methods for the conversion of Ziegler olefins to pure fatty acids. The disadvantage of handling explosive intermediates is more than offset by the high yields and quality of the products. However, such products would contain strictly odd-carbon acids, the nutritional value of which is not known with certainty. This aspect of the problem is discussed in more detail below.

The requisite ozone may be prepared conveniently by passing an electrical discharge through oxygen or air(153, 155). Simple ozonators have been described (153) and others are commercially available(155). Ozone has also been produced by electrolysis of sulfuric or perchloric acids(153). For the purposes of the present engineering study a laboratory ozonator as described by Maggiolo(155) was assumed. Further details are given below.

A source of ozone of special interest to space technology is afforded by irradiation of oxygen by ultraviolet

$$3/2\ O_2 \xrightarrow{hv} O_3$$

light of wavelength shorter than 2100Å(153, 182-184). The mechanism of the photolysis is not fully understood. One proposal suggests that decomposition into oxygen atoms is followed by recombination with molecular oxygen(182). This scheme accounts for the

$$O_2 \longrightarrow 2O$$

$$O + O_2 \longrightarrow O_3$$

observed quantum yield of two but predicts an effective wavelength of 2427Å, a range in which no O_3 formation is observed(182). Another possibility involves the formation of activated O_2.

$$O_2 + Hv \longrightarrow O_2^*$$

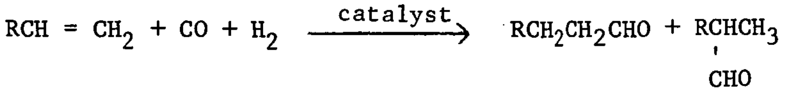
$$O_2 + O_2 \longrightarrow O_3 + O$$

$$O + O_2 \longrightarrow O_3$$

The efficiency of the photochemical method is low if the ultra-violet radiation must be obtained by conversion of electrical energy (5 gm. O_3/kwh vs. up to 300 gm. O_3/kwh by silent discharge)(182). However, if a tailor-make source of ultraviolet were available, as in space, the method could become practical.

The Oxo Reaction

The oxo reaction involves the catalytic addition of CO and H_2 to olefins (31).



$$RCH = CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + \underset{\displaystyle CHO}{RCHCH_3}$$

Olefin	RCH_2CHO	$RCH(CHO)CH_3$	T °C	Ref.
Propylene	50	50	210	31
Butene-1	75	25	70-90	163
Butene-1	45	55	180	163
Heptene-1	80	20	70	163
Heptene-1	43	57	180	163

Table 40 - Distribution of Products from the Oxo Reaction

The products are aldehydes which are easily oxidized to acids. The oxo reaction is usually carried out in the liquid phase at temperatures of 110-190°C. with pressures of 1,500-6,000 (commonly 3,000) p.s.i.; the H_2:CO ratio is 1:1(163). A variety of catalyst have been claimed including compounds of iron, calcium, magnesium and zinc. However, the best catalyst appears to be cobalt. Either metallic cobalt or its salts may be used, the active catalyst being the octacarbonyl, formed by the action of carbon monoxide on the cobalt.

$$2\ Co + 8CO \longrightarrow \left[Co\ (CO)_4\right]_2$$

In addition to primary and secondary aldehydes (Table 40) a variety of other compounds may be formed. These include ketones, acids, acetols and polyaldol products(163). The carbon skeletin may undergo rearrangement. This is catalyzed by cobalt hydrocarbonyl, a strong acid formed by hydrogenation of the octacarbonyl.

$$Co(CO)_4\ {}_2 + H_2 \longrightarrow 2\ HCo(CO)_4$$

The percentage of straight chain aldehydes has been increased by carrying out the reaction with a stoichiometric amount of cobalt hydrocarbonyl in the presence of certain nucleophiles(165).

$$RCH{=}CH_2 + 2HCo(CO)_4 + CO \xrightarrow{R'CN} RCH_2CHO + \left[Co(CO)_4\right]_2$$

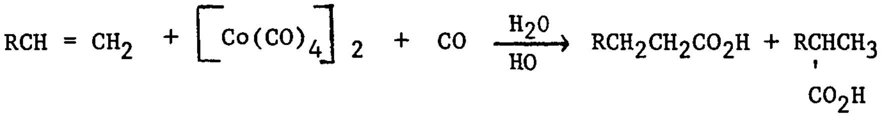
The nucleophile is claimed to both accelerate the reaction and increase selectivity to the primary aldehyde (Table 41). However, considerable amounts of branched aldehyde are still formed and large quantities of the nucleophile are required.

Nucleophile[a]	Aldehydes, %	B/S[b]	Time Min. C
Benzonitrile	91	0.7	2-3
Acetonitrile	82	0.7	2-3
Thioanisole	58	1.2	2-3
Propionitrile	55	1.0	2-3
Thiophenol	52	1.7	2-3
Anisole	47	0.5	6
Phenylacetonitrile	42	0.7	6
None	44	2.0	10
Triphenylphosphine	0	---	Instant
Pyridine	0	---	---

[a] 1 atm of CO; 25°; molar ratio of nucleophile/Hco(CO) =2.
[b] Ratio of branched to straight-chain aldehyde.
[c] For disappearance of $HCo(CO)_4$.

Table 41 - Effect of Nucleophile on Hydroformylation of 1-Pentene(165)

In another modification of the Oxo reaction olefins may be converted directly to acids(164).



$$RCH = CH_2 + \left[Co(CO)_4\right]_2 + CO \xrightarrow[HO]{H_2O} RCH_2CH_2CO_2H + \underset{CO_2H}{RCHCH_3}$$

The reaction occurs at temperatures of 160°C with carbon monoxide pressures of 50 atmospheres if an equivalent amount of cobalt octacarbonyl is employed. Under "catalytic" conditions temperatures of about 250°C. and pressures of 200 atmospheres are required(164). The best catalysts are nickel and cobalt carbonyls. This reaction suffers from the same limitations of the ordinary Oxo synthesis in that appreciable amounts of iso-acids are formed (Table 42).

Olefin	Product	Yield, %
Ethylene	Propionic acid	90
Propylene	Butyric and isobutyric acids(1:1)	60
But-1-ene	n-and iso-valeric acids	--
Isobutene	Isovaleric acid and trimethylacetic acid(6:1)	--
Hex-1-ene	2-Methylhexanoic and heptanoic acids	70
Oct-1-ene	2-Methyloctanoic and nonanoic acids	84
2-Ethylhex-1-ene	2-Ethylheptanoic acid	60
Dodec-1-ene	2-Methyldodecanoic and tridecanoic acids	28
Octadec-1-ene	2-Methyloctadecanoic acid	67
Cyclohexene	Cyclohexanecarboxylic acid	78
Cylooctene	Cyclooctanecarboxylic acid	31
Cyclooctatetraene	Cyclooctanecarboxylic acid	51
Bicyclo(2.2.1)heptene	Bicyclo(2.2.1)heptane-2-carboxylic acid	80
Bicyclo(2.2.1)heptadiene	Bicyclo(2.2.1)hep-5-ene-2-carboxylic acid	80
Carvomenthene	Little reaction	--
Pinene	Little reaction	--
Hexa-1,5-diene	2-Methylhex-5-enoic acid	20
Buta-1,3-diene	2-(Carboxycyclohexyl)-propionic acid	--
Undecylenic acid	Dodecane-1,12-carboxylic acid	44
But-3-en-2-one	Levulinic and 2-methylacetoacetic acid	
Dihydrofuran	Tetrahydrofurancarboxylic acid	

Table 42 - Carboxylation of Olefins(164)

Aldehydes such as those obtained in the oxo synthesis, are readily oxidized to acids(149, 171, 173). Potassium permanganate

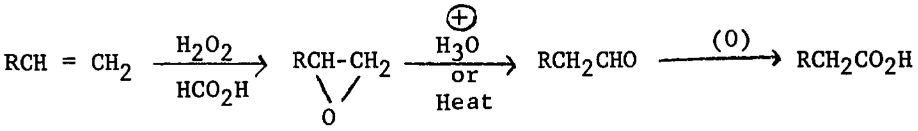
$$RCHO \xrightarrow[H_2SO_4]{KMNO_4} RCO_2H$$

in alkaline or acidic solution is frequently employed(149) although almost any common oxidizing agent may be used(149, 171). Laboratory favorites are silver oxide(149, 171) and peracetic acid(172). However, for purposes of synthesis on board a spacecraft molecular oxygen or air(172, 173) would be the reagents of choice. Salts of iron(172) and manganese(173) accelerate the oxidation.

$$RCHO \xrightarrow[Mn(+2) \text{ or } (Fe+3)]{Air,\ 70°}$$

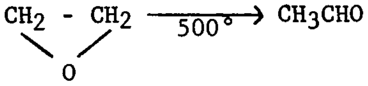
Rearrangement of Epoxides

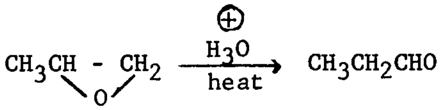
One of the question marks in the ozonolysis method is the nutritional value of the odd-carbon acids produced. One method for preserving the even carbon chain would be to epoxidize the olefin and rearrange to an aldehyde(166-170). This would be followed by oxidation to acids as described above.



Such acids would correspond exactly to the Ziegler olefins and, hence would contain only even numbers of carbon atoms.

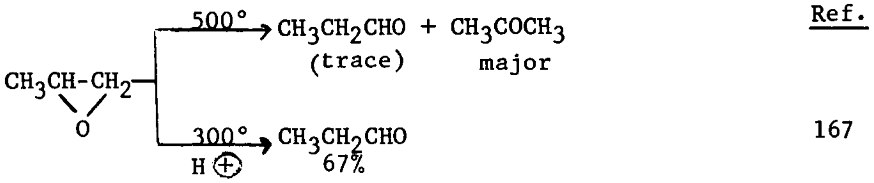
Epoxide rearrangements have been studied extensively in order to determine the migratory aptitude of various groups in simulated pinacol rearrangements. (168). The rearrangement may be brought about by heat or by the action of mineral or Lewis acids. Ethylene and propylene have been converted smoothly at high temperatures to the corresponding aldehydes(168, 169).

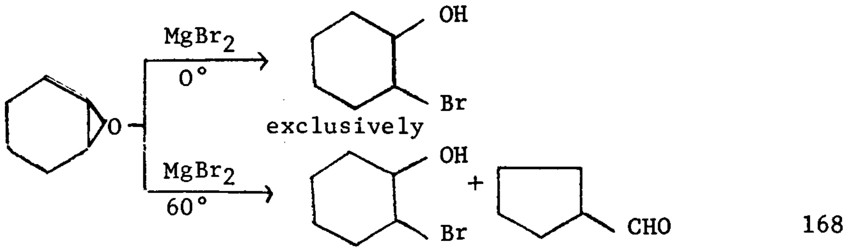




With higher oxides, however, the picture is less clear-cut and mixtures of olefins and ketones result(167, 168).

The course of the reaction is highly dependent on structure of the epoxide and reaction conditions, especially temperature, but is not greatly affected by the type of acid catalyst. The following example are illustrative:





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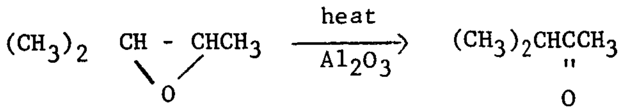

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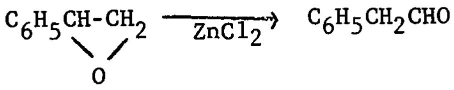

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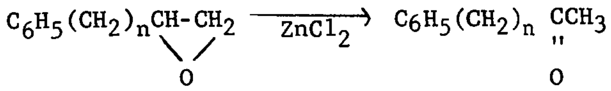
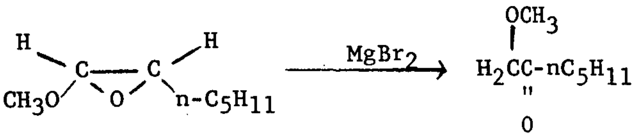


167, 170



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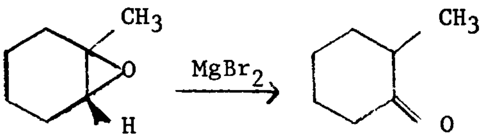

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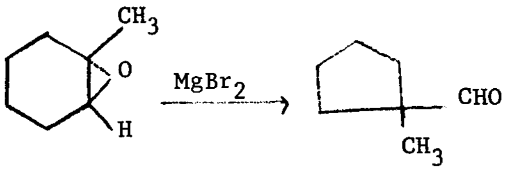

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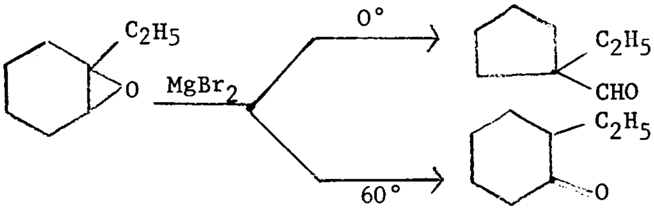
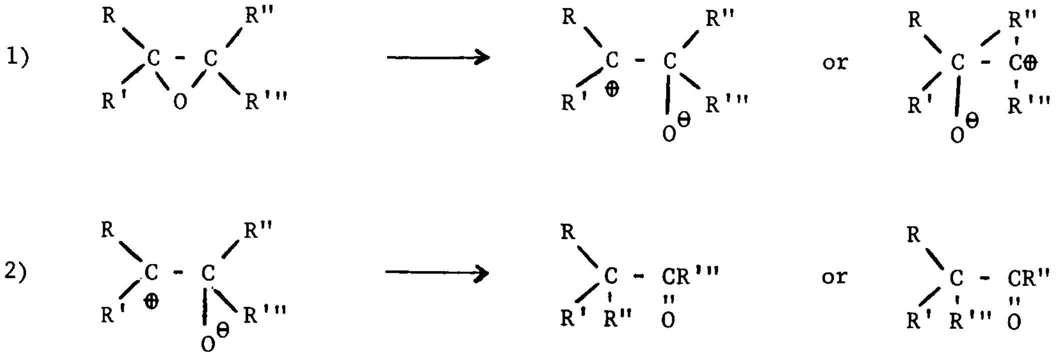


166

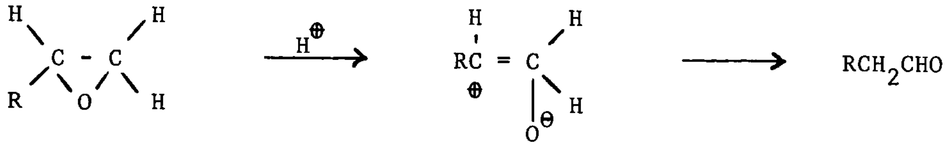
Parker has pointed out that, like pinacol rearrangements, the course of the reaction is determined by two factors: (1) the direction of ring opening and (2) the migratory aptitude of the substituents(166).



The ring opening proceeds to give the most stable carbonium ion. The relative migratory aptitudes are:(166)

$$\text{aryl} > \text{acyl} > H > C_2H_5 > CH_3$$

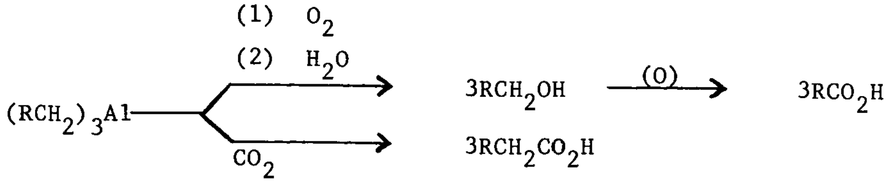
From these observations, oxides of α-olefins would be expected to afford the most substituted carbonium ion and, with only hydrogen to migrate, aldehydes should result. Where the R group



is small this appears to be the case(167). However, the higher molecular weight ($>C_3$) compounds have not been studied. Where R contains a long methylene chain the stabilizing effect on the secondary carbonium ion would be considerably diminished and larger amounts of undesired ketones might be produced.

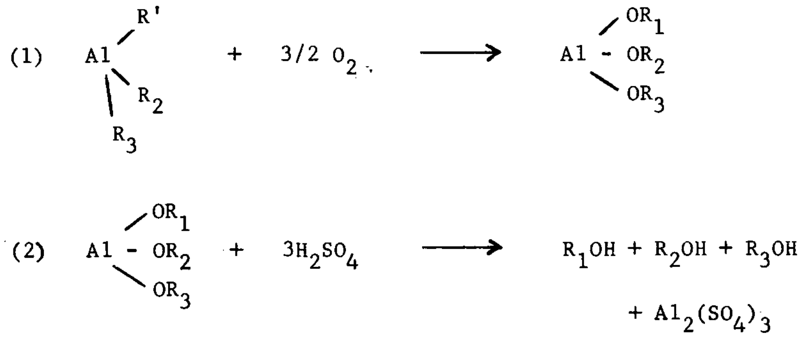
Conversion of Ziegler Intermediates to Acids

The intermediate aluminum alkyls from the Ziegler reaction may be converted to acids via the corresponding alcohol(72, 174) or by carboxylation(175, 179) with CO_2.



Oxidation to an Alcohol

The oxidation and hydrolysis of the aluminum alkyls to the corresponding alcohols provides a second method for preserving the carbon skeleton of the Ziegler growth product and, hence, for preparing acids of an even number of carbon atoms. The reaction has been commercialized(174). It proceeds in two discrete reactions:



$$(1)\quad Al(R')(R_2)(R_3) + 3/2\ O_2 \longrightarrow Al(OR_1)(OR_2)(OR_3)$$

$$(2)\quad Al(OR_1)(OR_2)(OR_3) + 3H_2SO_4 \longrightarrow R_1OH + R_2OH + R_3OH + Al_2(SO_4)_3$$

Considerable processing is required (Figure 30). This sequence would have to be simplified for space craft applications and some method (such as regenerable exchange resins) developed to prevent the loss of sulfuric acid and sodium hydroxide. The major problem, however, is that the Ziegler catalyst, aluminum triethyl, is converted to aluminum sulfate or oxide. Since a considerable amount of catalyst is required (see discussion of engineering study below) this represents a considerable loss. Regeneration of the Ziegler catalyst involves the following series of operations:

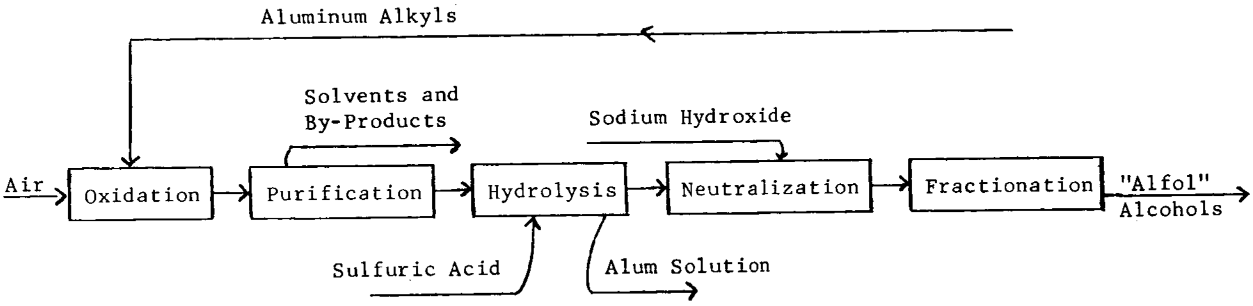


Figure 30 - Simplified process-schematic flow diagram of the "ALFOL" process(174)

$$1)\quad 2\ Al_2O_3 \xrightarrow[cryolite]{} 4\ Al + 3\ O_2$$

$$2)\quad Al + 3/2\ H_2 + 2Al(C_2H_5)_3 \longrightarrow 3\ AlH(C_2H_5)_2$$

$$3)\quad 3\ AlH(C_2H_5)_2 + 3CH_2{=}CH_2 \longrightarrow 3\ Al(C_2H_5)_3$$

This sequence was examined and found to be too costly in terms of power, weight and complexity to be considered.

Direct Synthesis of Acids by Reaction of Alumina Alkyls with CO_2

The direct conversion of Ziegler growth alkyls to acids by reaction with CO_2 is superficially most attractive. Such a reaction would avoid the necessity for recovering alpha olefins from the growth product and would also avoid necessity for ozonolysis or otherwise oxidizing intermediates. The immediate drawback is the fact that the aluminum alkyl would be converted in the hydrolysis step to alumina, or perhaps under some conditions, to an aluminum salt such as the chloride or sulfate. A most unattractive series of process steps would then be required to recycle the aluminum compound to aluminum triethyl as described above.

There does not seem to be a great deal of art relating to this process. The first pertinent reference seems to be an Esso Research patent, which describes the carrying out of the reaction by passing carbon dioxide through a heptane solution of aluminum alkyl(175). The exothermic reaction was carried out at 1 atm., and cooling was used to keep the temperature below 100°C. The yields of acids were only 17 and 16% from aluminum trihexyl and aluminum triethyl, respectively.

Soviet workers obtained considerably better results by using more vigorous conditions(176, 177). By carrying out the reaction in an autoclave at 220-240°C and pressures reaching 300 atm., in a mixed solvent consisting largely of heptane but with small and important amounts of diethyl ether, they reported yields of 60.3, 41.3, and 58.6% of the corresponding acids from tripropyl-, triethyl-, and triisobutylaluminum. The Soviets also carried out the reaction on mixed alkyls obtained by the growth reaction.

Work by Ziegler and his students clarifies and, to some extent substantiates the work of the earlier works(178). First of all, and most important, Ziegler found that only one aluminum-carbon bond of the aluminum alkyl reacts readily with carbon dioxide. Forcing conditions are required for the second mole of CO_2, and apparently a third mole cannot be reacted. Interestingly, Ziegler found that at 30-40°C very little acids was formed in the reaction of triethylaluminum with CO_2. Instead, the chief product, obtained in 90% yield based on the reaction of one aluminum-carbon bond per molecule, was triethylcarbinol. Ziegler postulates that this product is formed by the reaction of two more moles of Et_3Al with the intermediate Et_2AlO_2CEt. Perhaps the difference in products between Ziegler's work and the Esso patent results from the fact that in the Esso work temperatures were allowed to rise to near 100°C. Ziegler found that he could produce acids, at the rate of one mole of acid per mole of aluminum alkyl, (theoretical would be 3:1) by using one of two special techniques. In the first of these, the aluminum alkyl is added slowly to a vigorously agitated, saturated solution of CO_2 in a hydrocarbon solvent. This gave yields of 91%. In the second of these techniques, the aluminum alkyl is complexed with ether, which decreases its reactivity. Carbon dioxide is passing into the solution and begins reacting at about 100°C. The reaction was continued for five hours at 100-120°C, and 89% acid was obtained. Ziegler also treated the alkyl with one mole of carbon dioxide, and then oxidized before hydrolysis, thus producing 2 moles of alcohol and one mole of acid. In one example, using the technique of adding aluminum alkyl to the saturated CO_2 solution, 73% yield of alcohol and a 97% yield of acid were obtained, based on the theoretical values of 2 moles of alcohol and one mole of acid.

Finally, Ziegler found that by using a high temperature-high pressure technique very similar to that of the Soviet workers, he was able to force reaction of a second aluminum-carbon bond. He had two methods for accomplishing this. In one, the initial reaction product of aluminum alkyl with one mole of carbon dioxide was formed by his standard technique. This was then added to the autoclave and further reacted with CO_2 at high temperature and pressure. Alternatively, the etherate could be formed in the autoclave, pressured with CO_2, heated and reacted. Reacting at 220°C and atmospheric pressure was not effective; a mixture of products was obtained. Parenthetically, Ziegler felt called upon to comment on the Soviet and Esso reports and indicated that these workers really didn't understand what they were doing. As a matter of fact, since the Soviet workers claim yields of about 60% in their best cases, and Ziegler gets a 90% yield, using his forcing conditions, it will seem that these two processes are quite comparable, since Ziegler's 90% is figured on a theoretical yield of two moles of acid per mole of aluminum alkyl. This calculates out to a 60% yield using the basis which the Russians were using.

Another Ziegler publication discusses the possibility of using this process for the manufacture of edible fatty acids and dismisses it as impractical(179). In the course of his discussion in this paper, he suggests a complex laboratory method for synthesizing fatty acids. Boron triethyl is prepared by exchange of triethyl aluminum with a borate. In the presence of catalytic amounts of aluminum alkyl, the boron triethyl undergoes the growth reaction with ethylene to give a normal, Poisson-distributed product. This is then exchanged with a magnesium alkyl, such as ethyl-magnesium Grignard reagent or $MgEt_2$, to give a high molecular magnesium alkyl. The boron triethyl which forms is easily distilled and returned to the process, and the magnesium alkyl undergoes the standard Grignard reaction with CO_2, to give acids in nearly quantitative yields. Unfortunately, this process cannot be run with aluminum alkyls instead of boron alkyl, since first of all the boiling points of aluminum alkyls are about 100°C higher than those of the corresponding boron alkyl, and further, complex formation between the aluminum and magnesium compounds further depresses the boiling point of the aluminum alkyls. In any event, this process is not practical.

$$1)\quad Al(Et)_3 + B(OR)_3 \longrightarrow B(Et)_3$$

$$2)\quad B(Et)_3 + 3XC_2H_4 \xrightarrow{Al(R)_3} \left[CH_3CH_2(CH_2)_X\right]_3B$$

$$3)\quad 2\left[CH_3CH_2(CH_2)_x\right]_3 B + 3\ MgEt_2 \longrightarrow 3\left[CH_3CH_2(CH_2)_x\right]_2 Mg + B(Et)_3$$

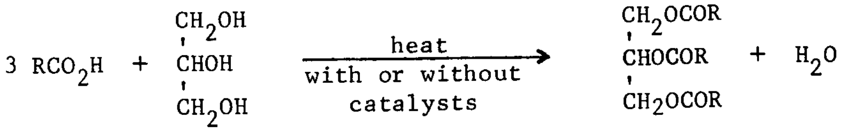
$$4)\quad \left[CH_3CH_2(CH_2)_x\right]_2 Mg + 2CO_2 \xrightarrow{H_2O} 2\ CH_3CH_2(CH_2)_xCO_2H + MgO$$

One last reference might be mentioned, a patent to Continental Oil Company on the preparation of ketones by the reaction of aluminum alkyls with CO_2(180). Thus, trihexylaluminum is converted to dihexylketone, in a yield of 65% along with 19% of heptanoic acid. Ketone synthesis is accomplished by running at a temperature between 200 and 300°C (250-250°C in the example), at high pressure (4800 psig), and, apparently quite important, for an extended time (72 hours in the example). This reaction is apparently related to that described by Ziegler, in which he obtained a trialkylcarbinol; the ketone is clearly one step removed from the acid, and one step short of the trialkylcarbinol in the reaction scheme outlined by Ziegler. Examples in the Conoco patent indicate that the combination of reaction conditions--high temperature, high pressure, and long time--is essential for the ketone synthesis.

This pretty well summarizes the existing art. There is no question that acid synthesis can be carried out by this route and apparently with fairly reasonable yields (60%), but the necessity to regenerate triethylaluminum from the salt and the consumption of acid and base combine to render this process unattractive.

CONVERSION OF FATTY ACIDS TO GLYCERIDES

The esterification of fatty acids with glycerol presents no special problems It was known as early as 1854 that fatty acids could be converted to their glycerol

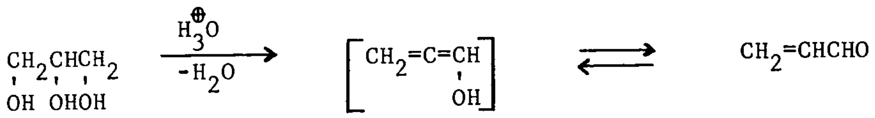


$$3\ RCO_2H + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} \xrightarrow[\text{with or without catalysts}]{\text{heat}} \begin{array}{l} CH_2OCOR \\ CHOCOR \\ CH_2OCOR \end{array} + H_2O$$

esters by heating the two compounds above 180°C in sealed tubes(185). Since that time, the esterification has been studied extensively especially for the synthesis of mixed glycerides of known structure(186). For this report only methods for production of simple, mixed glycerides will be considered.

Catalyzed Esterification

The reaction may be carried out either catalytically(20, 22, 27, 29, 186-19 or in the absence of catalysts(186, 187, 192, 195). Acid catalysts are frequently used(186, 188-191) and various sulfonic acids appear to be the best, especially if water is removed azeotropically during the reaction. Benzene- and toluenesulfonic acids are often used. The latter is claimed to be better(190). Camphor-β-sulfonic acid has been recommended as superior to the more common naphthalene-β-sulfonic acid (188). Acid catalysts frequently cause darkening of the products(188, 190, 191) and may catalyze dehydration of the alcohol(191). For instance, glycerol yields acrolein



$$\begin{array}{l} CH_2CHCH_2 \\ OH\ OHOH \end{array} \xrightarrow[-H_2O]{H_3O^{\oplus}} \left[\begin{array}{l} CH_2{=}C{=}CH \\ \qquad\qquad OH \end{array} \right] \rightleftarrows CH_2{=}CHCHO$$

Finely divided zinc or tin metal was used by the Germans(20, 22, 27, 29). About 0.2 weight percent was employed at temperatures of about 200°C. Apparently some color was produced since a bleaching step was included in the process(22, 29). Further details on the German process were given above.

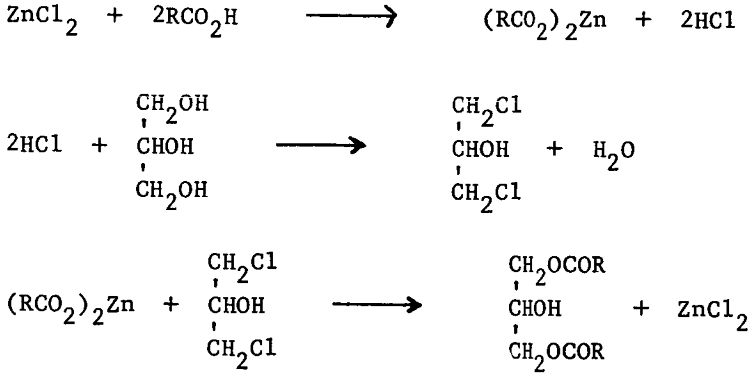
Feuge _et_. _al_. studied both the catalyzed and uncatalyzed esterification(187 They recommended the use of about 0.002 mole percent of tin or zinc chlorides as catalysts. Such catalysts permitted the use of 175°C temperatures (as compared to 250°C or higher in absence of catalyst) and seemed to yield a higher quality glyceride(187). However, separation of the metal salts from the product was difficul Feuge _et_. _al_. studied a variety of other catalysts as well. These are summarized in Table 43.

Catalyst	g. compound used per 100 g. FA's	g. metal per 100 g. FA's	FFA content of mixture, percent at end of specified reaction time		
			2 hrs.	4 hrs.	6 hrs.
Control	none	none	41.8	21.6	16.1
$AlCl_3 \cdot 6H_2O$	0.193	0.022	39.2	22.2	[illegible]
Al_2O_3[a]	0.032	0.043	39.6	20.9	[illegible]
SnO_2[a]	0.121	0.095	42.1	21.1	15.2
$SbCl_3$	0.183	0.097	33.1	20.2	[illegible]
$HgCl_2$	0.217	0.160	38.3	20.0	15.0
FeO[a]	0.058	0.045	38.0	18.1	13.9
$NiCl_2 \cdot 6H_2O$	0.190	0.047	56.8	18.6	[illegible]
NaOH	0.032	0.018	39.1	19.5	13.3
$MgCl_2 \cdot 6H_2O$	0.165	0.019	40.5	19.2	13.7
MgO	0.032	0.019	37.6	18.5	13.6
$MnCl_2 \cdot 4H_2O$	0.158	0.044	38.4	18.4	13.2
$PbCl_2$[a]	0.222	0.166	37.7	17.5	12.0
ZnO	0.065	0.052	30.9	15.0	11.8
$FeCl_3 \cdot 6H_2O$	0.215	0.045	32.5	14.9	11.4
$CdCl_2 \cdot 2\frac{1}{2}H_2O$	0.183	0.090	32.5	14.8	11.0
PbO	0.278	0.166	55.7	16.5	[illegible]
MnO_2	0.070	0.044	34.8	15.8	10.5
$ZnCl_2$	0.108	0.052	26.5	7.8	3.5
$SnCl_2 \cdot 2H_2O$	0.180	0.095	3.2	3.5	2.8
$SnCl_4 \cdot 5H_2O$	0.280	0.095	11.5	8.2	2.4[a]
HCl	0.058[b]	....	37.4	18.9	15.8

[a] Did not dissolve completely in reaction mixture.
[b] 0.0016 mole per 100 g. fatty acids.

Table 43 - Catalytic effect of various compounds in the esterification of glycerol and peanut oil fatty acids. All reactions carried out at 200°C and 2 mm pressure with 0.0008 mole of the compound per 100 g. fatty acids(187)

They formulated the mechanism of the catalyzed esterification as involving the intermediate formation of metallic soaps and chlorohydrins:



$$ZnCl_2 + 2RCO_2H \longrightarrow (RCO_2)_2Zn + 2HCl$$

$$2HCl + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} + H_2O$$

$$(RCO_2)_2Zn + \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \longrightarrow \begin{array}{l} CH_2OCOR \\ | \\ CHOH \\ | \\ CH_2OCOR \end{array} + ZnCl_2$$

Uncatalyzed Esterifications

The catalyzed esterifications have a common disadvantage. They are batch processes and involve loss of the catalyst. In most instances, separation from the catalyst is a major problem(28, 187). It has been amply demonstrated(186, 193-195) that the reaction proceeds readily at high temperatures in the absence of catalyst provided the water is removed as formed. Bellucci obtained single or mixed triglycerides in 95-98% yields by heating equivalent quantities of fatty acids and glycerol at a reduced pressure of 2 cm(193-195). The temperature was raised slowly from 180°C to 240°C over a 5-6 hour period. The function of the vacuum was to remove water to drive the reactions. Bellucci also found that esterification proceeded readily at atmospheric pressure if water was removed continuously in a stream of inert gas such as CO_2(194). Quantitative yields were obtained. With either procedure product quality was claimed to be good(193-195). Bellucci employed a maximum temperature of about 240°C(193). Glycerides are reported to be unstable above this point(189). Feuge *et. al.*(187) used higher temperatures in their studies of the uncatalyzed esterification and this may account for the coloring they observed.

The mechanism of the uncatalyzed esterification has been studied by several workers including Hartman(192) and Feuge(187, 189). The reaction proceeds in two stages and follows second order kinetics (Figure 31). The reaction rates for various fatty acids are reported to be the same provided *equivalent* amounts of acid and glycerol are present(192). With *equimolar* quantities rate differences occur and seem to parallel the relative solubilities of the acids in glycerol(192, 193).

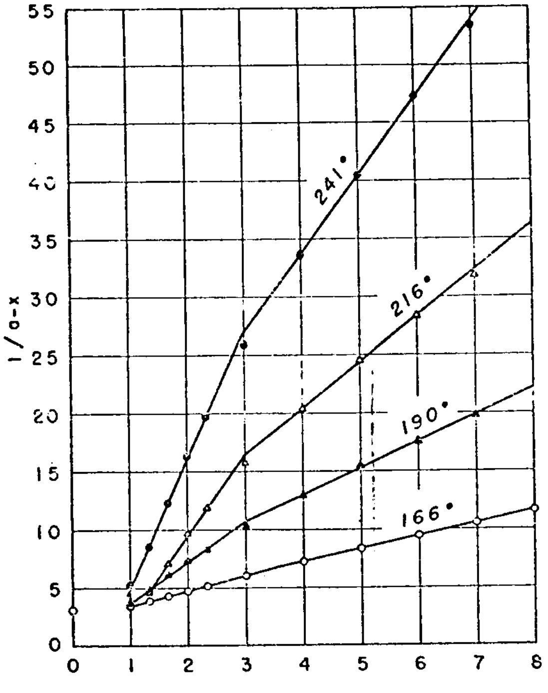


Figure 31 - Curves showing bimolecular nature of the uncatalyzed reaction at various temperatures (°C). Reciprocal of free fatty acid concentration (moles per 100 g.) vs. reaction time (hours)(187)

For spacecraft applications, the uncatalyzed esterification with vacuum water removal is clearly the superior method. It can be incorporated readily in a continuous process and does not require regeneration of spent catalyst. Since esterification represents the final step in the production sequence, provisions for purification must be made. The Germans washed their product with sodium hydroxide, bleached it and removed impurities by steam distillation(29, 196). Bellucci found that water washing and drying over a basic drying agent (calcium carbonate) was sufficient(195). For the purposes of the engineering design described below, high vacuum steam treatment was selected as the most convenient purification procedure. This would, of course, have to be verified in actual practice.

SYNTHESIS OF GLYCEROL

For the production of synthetic fats, patterned after natural models, a source of glycerol is necessary. In addition to its use in fat synthesis, glycerol has been suggested(5, 13) as a possible source of dietary energy in its own right. In a closed loop ecological system the glycerol must be synthesized from readily available materials on board the space craft.

Most glycerol is produced currently by hydrolysis of natural fats as a by-product of the soap industry(17, 197). Some is produced by fermentation(17, 197) and small amounts from propylene(5, 197, 198). None of these methods are applicable to glycerol synthesis under conditions of space travel. For this purpose four candidate processes were discovered. These are (1) preparation directly from CO and H_2 (2) synthesis from acetylene <u>via</u> acrolein and allyl alcohol,(3) trimerization of formaldehyde, and (4) hydrogenolysis of carbohydrates. The last of these was selected for the engineering model for reasons outlined below.

Glycerol Synthesis from CO and H_2

This method has the lowest recommendation of the four schemes. It has simplicity in its favor and employs readily available starting materials. However, yields are low, separations difficult and the available information is scanty and of doubtful value. In general the reaction is more promising for production of ethylene glycol then glycerol.

The only published information concerning this reaction is contained in a series of patents by Gresham(199, 204). He employed cobalt catalysts (but also claimed nickel, ruthenium, copper, chromium and manganese salts) at high temperatures and pressures to obtain ethylene glycol and its formate esters(199, 200). He formulated the reactions as follows:

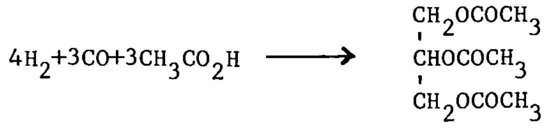
$$2CO + 3H_2 \longrightarrow HOCH_2CH_2OH$$

$$3CO + 3H_2 \longrightarrow HCO_2CH_2CH_2OH$$

$$4CO + 3H_2 \longrightarrow HCO_2CH_2CH_2O_2CH$$

Pressures above 1000 atmospheres were required at temperatures between 180-300°C.

No glycerol was produced under these conditions. However, when acetic acid was employed as the solvent glyceryl triacetate (triacetin) was obtained along with



$$4H_2+3CO+3CH_3CO_2H \longrightarrow \begin{array}{l} CH_2OCOCH_3 \\ \vert \\ CHOCOCH_3 \\ \vert \\ CH_2OCOCH_3 \end{array}$$

ethylene glycol diacetate in unstated yield(199, 200). The optimum CO:H_2 ratios were claimed to be 3:1 to 1:3. In later patents cobaltous fluoride(201) and mixed catalysts of manganese, zinc and chromium(202) were recommended. The CoF_2 catalyst was claimed to be reclaimable with virtually no loss due to cobalt carbonyl formation. In these patents it was claimed that high pressures reduced the amount of catalyst required. As might be expected, short reaction times are desirable to suppress side reactions(202). Diluents such as organic acids, (especially acetic if glycerol is desired), water or an organic solvent were used to facilitate heat removal.

In a modification of this process, Gresham and Brooks claimed the incorporation of formaldehyde in the reaction mixture offered certain advantages(203, 204).

$$2H_2 + CO + HCHO \longrightarrow HOCH_2CH_2OH$$

$$2H_2 + CO + 2HCHO \longrightarrow HOCH_2CH_2CH_2OH$$

In these reactions somewhat lower pressures (500-700 atmospheres) and temperatures (150°C) were employed. The catalysts were cobalt salts. It was also claimed that further hydrogenation (over a copper chromite catalyst at 155-164°C and 460-750 atmospheres) of the crude product gave higher yields. Apparently part of the formaldehyde had polymerized in the initial reaction and was subsequently hydrogenolyzed (see below). Again the major product was ethylene glycol (3-4 times the amount of glycerol).

None of the above patents give yields based on CO. In addition, ethylene glycol is the major product in all cases with the possible exception of examples where acetic acid is the solvent. Consequently, this method of glycerol synthesis is not recommended relative to those given below.

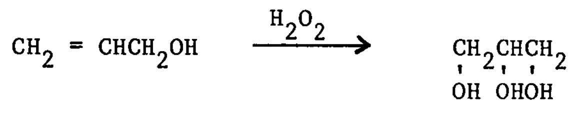
Synthesis from Acetylene or Ethylene

Glycerol may be produced from acetylene by this series of reactions:

(1) $$HC{\equiv}CH + HCHO \xrightarrow{Cu(C{\equiv}CH)_2} HC{\equiv}CCH_2OH$$

(2) $$HC{\equiv}CCH_2OH \xrightarrow{H_2} H_2C = CHCH_2OH$$

(3)



$$CH_2 = CHCH_2OH \xrightarrow{H_2O_2} \underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2}$$

This sequence is well known and a good deal of data on each step is available. It has the advantage of being reliable and of giving fair yields of pure products by established methods. However, the complexity involved, the need for handling hazardous materials and need for catalyst make-up combine to make this route less attractive than the schemes involving formaldehyde polymerization outlined below.

The addition of formaldehyde to acetylene has been studied extensively by Reppe(205). He found that under "normal" ethinylation conditions formaldehyde and acetylene gave mostly butyndiol-1,4,

$$HC{\equiv}CH + HCHO \longrightarrow HC{\equiv}CCH_2OH$$

$$HC{\equiv}CHCH_2OH + HCHO \longrightarrow HOCH_2C{\equiv}CCH_2OH$$

while higher aldehydes tended to give good yields of the mono adduct:

	% Monoalcohol	% Diol
Formaldehyde	6	92
Acetaldehyde	64	34
n-Butyraldehyde	80	17

However, the yield of propargyl alcohol can be increased greatly (up to above 60%) by employing tetrahydrofuran as the solvent and going to higher acetylene pressures to increase the acetylene concentration and lower the pH(205, 206). When water alone was the solvent, and the pH was somewhat higher, butynediol-1,4 was obtained in 90% yield(206). The ethinylation catalysts are copper acetylides. These are extremely hazardous materials when dry. However, they may be formed in situ by the reaction of copper salts and acetylene(206). Acetylene and formaldehyde may be continuously led into the reactor and the products drawn off without isolating the catalyst(207). To prolong the life of the catalyst, the addition of an oxide or iodide of potassium or bismuth is recommended(207). Other workers have described improvements in the process. Suzuki(203) confirmed the importance of a good solvent for acetylene (tetrahydrofuran and methanol) and suggested lower temperatures (below 120°C) and a pH of 2.1. He obtained a 56% yield at 30 atmospheres pressure and 105°C in a batch process but observed only a 29% yield in a continuous run (15 atmospheres and 110°C, however). Hecht(209) has described a catalyst he claims has a longer lifetime than those employed by Reppe(205, 207).

A kinetic study of the reaction has been reported(210, 211). The important findings, as far as synthesis of propargyl alcohol is concerned were that increased acetylene pressure and low pH favored mono alcohol formation while variations in formaldehyde concentration had no consistent effect on product ratios(210).

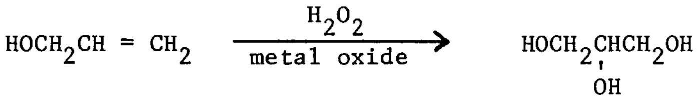
The partial hydrogenation of acetylenic to olefinic alcohols

$$HOCH_2C{\equiv}CR \xrightarrow[\text{Pd-BaCO}_3]{H_2} HOCH_2CH{=}CHR$$

is accomplished readily over palladium or Raney nickel catalysts(212, 217). The selectivity is apparently not a function of rate since the corresponding olefin is often reduced as rapidly, or even more so, than the acetylene(213, 215). More likely it represents selective absorption of the acetylene on the catalyst(213). Because of this it is best to control the hydrogen uptake to stop at one mole. Platinum catalysts do not give good yields of olefin unless poisoned(214).

Allyl alcohol was obtained in 90% selectivity (but only 24% yield) by hydrogenation over Raney nickel(216). The conditions employed were: hydrogen pressure: 20 atm; temp.: 120-130°C; time: 2 hrs. 1,4-Butene-diol and other olefinic diols are commonly prepared from the corresponding acetylenes in excellent yield by hydrogenation over palladium-calcium carbonate(212, 213, 218), Raney nickel(213, 219), Rhenium oxide(220) and various "poisoned" catalysts(209, 210, 217). Typical yields are 80%. The reduction of acetylene may also be effected electrolytically(213). For good experimental procedures for the partial reduction of acetylenes see references 212, 213 and 222.

Good procedures for hydroxylation of allylalcohol to glycerol are available (223). The best reagent for this purpose appears to be hydrogen peroxide:

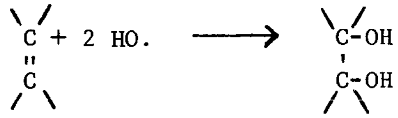


$$HOCH_2CH = CH_2 \xrightarrow[\text{metal oxide}]{H_2O_2} HOCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$$

Metal oxides in trace amounts are necessary to catalyze the reaction. Among those commonly employed are tungsten(223), osmium(224) and vanadium(224). Efforts have been made to avoid the use of such catalysts by use of peroxide in acidic media (224-226). The active agents in these instances are peracetic(225) or performic acids (226). Yields of 95% are claimed(226).

Allyl alcohol has also been hydroxylated to glycerol in fair yields by hydrogen peroxide in the presence of ultraviolet light(227). The reaction was formulated as follows:

(1) $H_2O_2 \xrightarrow{hv} 2\ HO.$

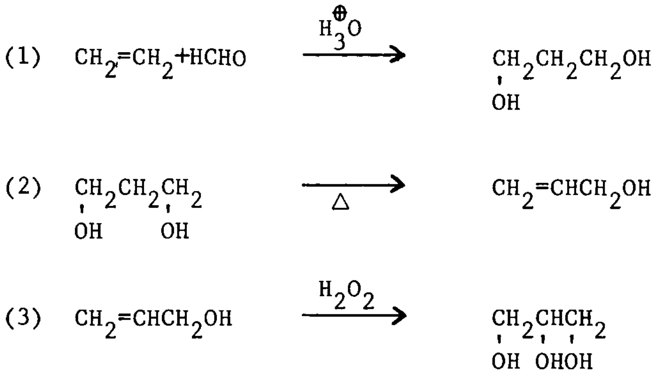
(2) 

$$>C=C< + 2\ HO. \longrightarrow >C(OH)-C(OH)<$$

Other modifications of the process have been described in a series of German patents(228).

Because of its complexity (in addition to the three steps discussed above, both acetylene and H_2O_2 would have to be synthesized) and the need to handle hazardous materials, the acetylene process is not recommended relative to the methods based on formaldehyde. However, if acetylene should become available (for instance as an intermediate in ethylene production) its use in glycerol production would become more attractive.

Since ethylene may be available for the Ziegler synthesis, it must be considered as a precursor to glycerol. One route involves condensation with formaldehyde in a Prins reaction,(229) followed by dehydration to allyl alcohol and hydroxylation as described above.

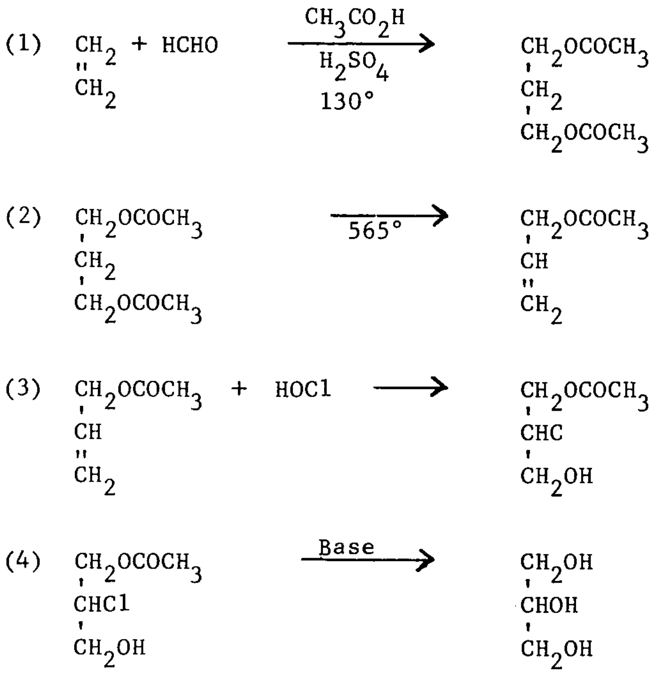


$$(1)\quad CH_2{=}CH_2 + HCHO \xrightarrow{H_3\overset{\oplus}{O}} \underset{OH}{CH_2}CH_2CH_2OH$$

$$(2)\quad \underset{OH}{CH_2}CH_2\underset{OH}{CH_2} \xrightarrow[\Delta]{} CH_2{=}CHCH_2OH$$

$$(3)\quad CH_2{=}CHCH_2OH \xrightarrow{H_2O_2} \underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2}$$

Ethylene, however, reacts very sluggishly under normal Prins conditions,(229, 230) requiring elevated temperatures, strong acid catalysts and affording poor yields of diol. Olsen went to higher temperatures (130°C) and employed sulfuric and acetic acids to produce the diester of trimethylene glycol in low yield which he claimed as a precursor for glycerol:(231, 233)



$$(1)\quad \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + HCHO \xrightarrow[H_2SO_4\ 130°]{CH_3CO_2H} \begin{matrix}CH_2OCOCH_3\\ |\\ CH_2\\ |\\ CH_2OCOCH_3\end{matrix}$$

$$(2)\quad \begin{matrix}CH_2OCOCH_3\\ |\\ CH_2\\ |\\ CH_2OCOCH_3\end{matrix} \xrightarrow[565°]{} \begin{matrix}CH_2OCOCH_3\\ |\\ CH\\ \|\\ CH_2\end{matrix}$$

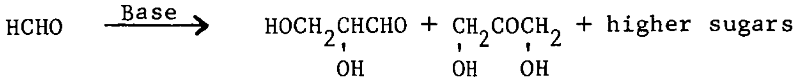
$$(3)\quad \begin{matrix}CH_2OCOCH_3\\ |\\ CH\\ \|\\ CH_2\end{matrix} + HOCl \longrightarrow \begin{matrix}CH_2OCOCH_3\\ |\\ CHC\\ |\\ CH_2OH\end{matrix}$$

$$(4)\quad \begin{matrix}CH_2OCOCH_3\\ |\\ CHCl\\ |\\ CH_2OH\end{matrix} \xrightarrow{Base} \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}$$

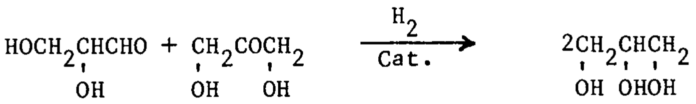
No overall yield is given but it was clearly only a few per cent. This, added to the fact that a number of materials are consumed in the process, render this scheme unacceptable as it now stands.

Trimerization of Formaldehyde

Formaldehyde may be self-condensed to three carbon sugars and hydroxy ketones under the influence of alkali. The products may be hydrogenated to glycerol.

(1) 

$$\mathrm{HCHO} \xrightarrow{\text{Base}} \mathrm{HOCH_2\underset{OH}{C}HCHO} + \mathrm{\underset{OH}{CH_2}CO\underset{OH}{CH_2}} + \text{higher sugars}$$

(2) 

$$\mathrm{HOCH_2\underset{OH}{C}HCHO} + \mathrm{\underset{OH}{CH_2}CO\underset{OH}{CH_2}} \xrightarrow[\text{Cat.}]{H_2} 2\mathrm{\underset{OH}{CH_2}\underset{OH}{C}H\underset{OH}{CH_2}}$$

The base catalyzed polymerization of formaldehyde to higher sugars was discovered over 100 years ago(234). Since that time a considerable amount of research has appeared. The reaction usually results in a complex mixture of products. However, recent work has been aimed at production of the lower, C-2 and C-3, sugars with some success. Only these later reports are germane to glycerol synthesis. Reviews of early work on the formaldehyde condensation, especially leading to glycerol and ethylene glycol, may be found in references 235, 236 and 251. For leading references to synthesis of higher sugars see references 241, 248 and 251. The mechanism of the reaction has received considerable attention(239, 241) and it has some bearing on the utilization of this process for synthesis. The reaction is autocatalytic and has a long induction period. To explain these observations Breslow(239) has proposed the following mechanism:

(1) $\mathrm{CH_2O + HOCH_2\text{-}CHO} \xrightarrow{\text{base}} \mathrm{HOCH_2\text{-}CHOH\text{-}CHO}$

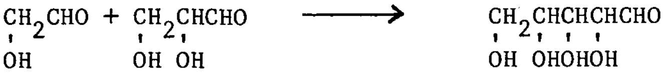
(2) $\mathrm{HOCH_2\text{-}CHOH\text{-}CHO} \rightleftharpoons \mathrm{HOCH_2\text{-}CO\text{-}CH_2OH}$

(3) $\mathrm{CH_2O + HOCH_2\text{-}CO\text{-}CH_2OH} \longrightarrow \mathrm{HOCH_2\text{-}CHOH\text{-}CO\text{-}CH_2OH}$

(4) $\mathrm{HOCH_2\text{-}CHOH\text{-}CO\text{-}CH_2OH} \rightleftharpoons \mathrm{HOCH_2\text{-}CHOH\text{-}CHOH\text{-}CHO}$

(5) $\mathrm{HOCH_2\text{-}CHOH\text{-}CHOH\text{-}CHO} \longrightarrow \mathrm{HOCH_2\text{-}CHO + HOCH_2\text{-}CHO}$

The crucial step and major point of departure of this mechanism from other suggestions is reaction (4), the tautomerization of the keto tetrose to the aldo tetrose. This material, by reverse aldol reaction, generates two molecules of glycolaldehyde each of which can serve to initiate a new sequence. This explains why no induction period is observed if glycolaldehyde is added to the reaction mixture. This scheme has been criticized(241) not only because of its over simplicity but because the reaction of the triose with glycolaldehyde to form a pentose:

(6) 

$$\mathrm{\underset{OH}{CH_2}CHO} + \mathrm{\underset{OH}{CH_2}\underset{OH}{C}HCHO} \longrightarrow \mathrm{\underset{OH}{CH_2}\underset{OH}{C}H\underset{OH}{C}H\underset{OH}{C}HCHO}$$

is supposedly more rapid than the formation of the triose itself [Breslow's reaction (1)]. Hence, not enough tetrose would be present to produce appreciable quantities of glycolaldehyde [reaction (5)]. In addition, Pfeil and Ruckert(241) have observed the "normal" splitting of tetrose is into formaldehyde and triose rather than into glycolaldehyde as required in Breslow's formulation. Pfeil and Ruckert's scheme is shown in Figure 32.

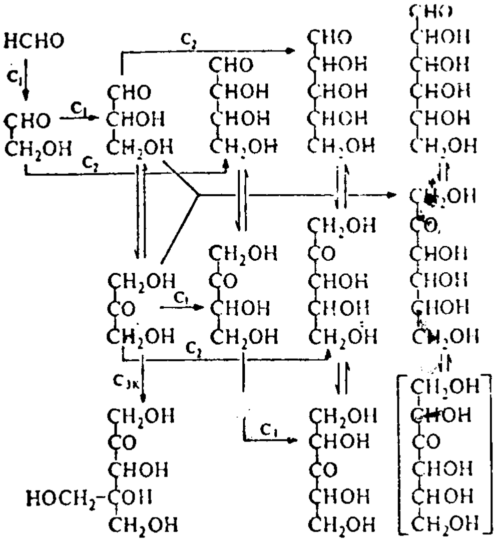
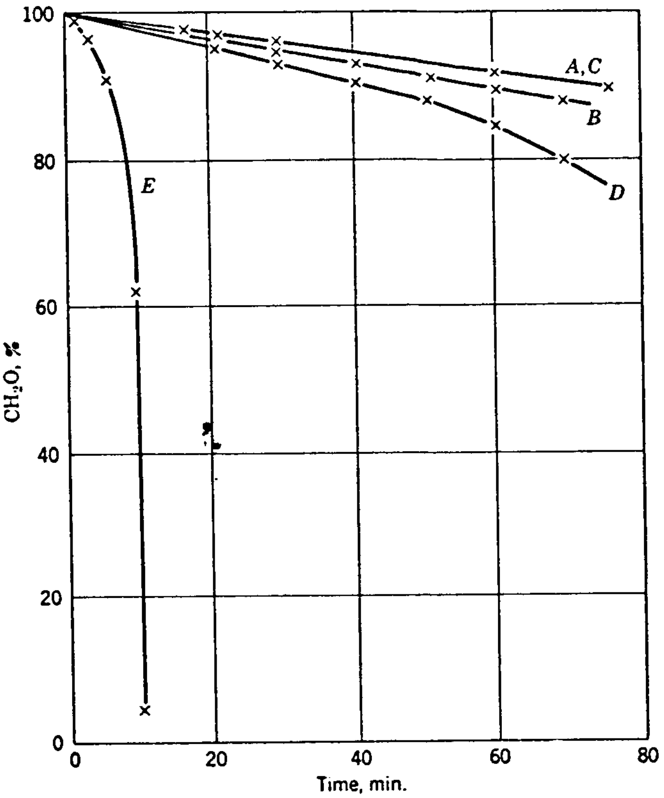


Figure 32 - Condensation of Formaldehyde under the Influence of Alkali (Pfeil and Ruckert)(241)

The condensation is further complicated by the concurrent formation of products from the Cannizzaro reaction:

$$2HCHO \xrightarrow{NaOH} HCO_2Na + CH_3OH$$

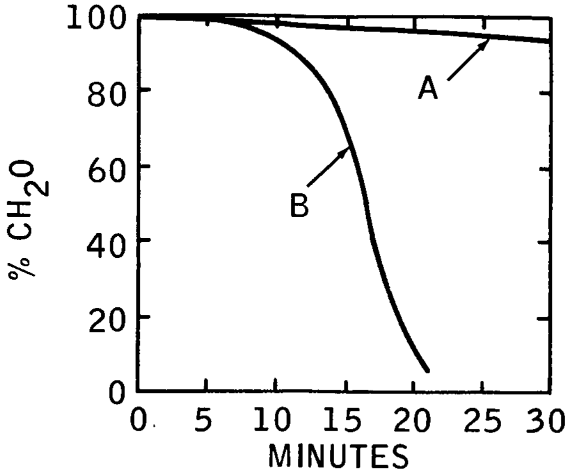
The amount of Cannizzaro product is dependent on the type of catalyst used. This was demonstrated by Pfeil and Schroth(240) (see Figure 33), who found tellurium hydroxide to be very beneficial in suppressing this undesired side-reaction.



Curve	Catalyst		CH_2O conc.	CH_2O/ alkali ratio	Cannizzaro reaction
A	NaOH	0.070*N*	0.583*M*	8.3	100%
B	$Ba(OH)_2$	0.082	0.514	6.4	100
C	LiOH	0.076	0.491	6.5	100
D	$Ca(OH)_2$	0.046	0.351	7.6	62
E	TlOH	0.082	0.553	6.7	9

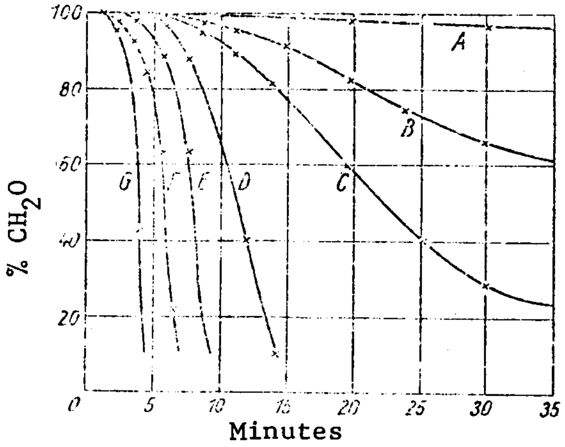
Figure 33 - Course of reaction of aqueous formaldehyde with alkaline catalysts at 60°C(240)

The same effect has been obtained by addition of a salt containing the $Tl^{(+)}$ Cation (Figure 34). The Cannizzaro reaction was greatly reduced at low formaldehyde concentration (Figure 35) and, more significantly, it is completely repressed by the addition of dihydroxy acetone to the reaction mixture. Dihydroxy acetone also had a catalytic effect on the rate of reaction(240). Other workers have found that, in addition to dihydroxyacetone, glyceraldehyde, glycolaldehyde and several other compounds possessing the "enediol" structure are effective in suppressing the Cannizzaro reaction. Thus the need for the expensive TlOH could be obviated. Currently the alkaline catalysts employed are $Ca(OH)_2$ or $Pb(OH)_2$, although a variety of others have been used, especially if higher sugars are desired(251).



Curve	Catalyst	CH_2O/ Alkali Ratio	% Cannizzaro Reaction
A	NaOH alone	8.3	100
B	NaOH + 0.008M Tl_2SO_4	7.3	12

Figure 34 - Effect of Added $Tl^{(+)}$ Cation to NaOH Catalyzed Condensation of Formaldehyde(240)

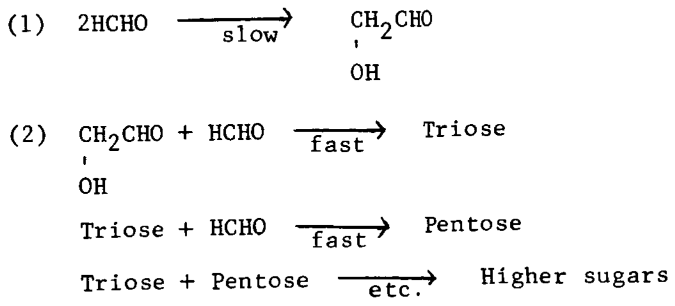


	A	B	C	D	E	F	G
Alkali Conc. (n)	0.068	0.076	0.078	0.086	0.082	0.072	0.085
CH_2O Conc. (M)	3.03	0.892	0.822	0.683	0.553	0.273	0.108
CH_2O/Alkali Ratio	44.5	11.7	10.5	7.9	6.7	3.8	1.3
% Cann. Reaction	100%	25%	15%	13%	9%	8%	0%

Figure 35 - Effect of Formaldehyde Concentration(240)

Catalysts to Favor Lower Sugars

The major problem in this synthesis lies in stopping the condensation at the 3- carbon stage. Pfeil and Ruckert(241) interrupted the condensation shortly after it began and demonstrated that glyceraldehyde and dihydroxyacetone were the primary products. However, at this stage, only a small amount of formaldehyde had reacted. Langenbeck(235) describes the condensation as proceeding in two discrete stages:



$$(1)\quad 2HCHO \xrightarrow[slow]{} \underset{OH}{CH_2}CHO$$

$$(2)\quad \underset{OH}{CH_2}CHO + HCHO \xrightarrow[fast]{} \text{Triose}$$

$$\text{Triose} + HCHO \xrightarrow[fast]{} \text{Pentose}$$

$$\text{Triose} + \text{Pentose} \xrightarrow[etc.]{} \text{Higher sugars}$$

The first step is of the acyloin type and is auto-catalyzed while the second sequence of reactions are base catalyzed aldol condensations. Thus a catalyst was sought which would accelerate step one, would be more effective as a catalyst than glycolaldehyde itself and would be active at low pH to inhibit the aldol condensation. The best system was benzoylcarbinol and its derivatives in conjunction with lead hydroxide (235-237, 243). Lead hydroxide was less effective as a catalyst than alkaline earth hydroxides requiring higher reaction temperatures. However, it favored the production of lower sugars (Figure 36).

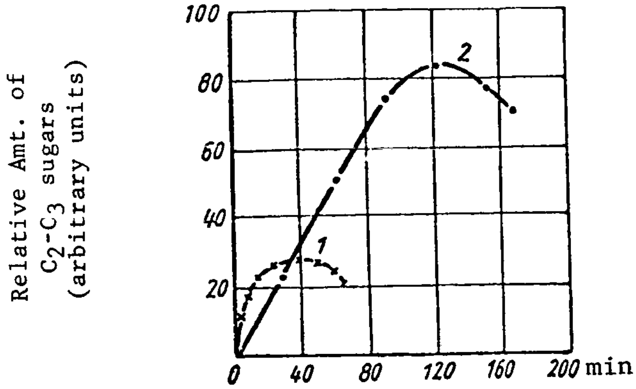


Figure 36 - Pb(OH)$_2$ vs. Ca(OH)$_2$ Catalysis; Both curves 4% HCHO Soln.;
Curve 1: 1/400 M Benzoylcarbinol, 1/100 M Ca(OH)$_2$;
Curve 2: 1/400 M Benzoylcarbinol, 1/100 M Pb(OH)$_2$(235)

Varying the amounts of lead hydroxide or benzoylcarbinol had little effect on yield of lower sugars (Figures 37 and 38), although the rate of formaldehyde disappearance was somewhat influenced(235). Raising the temperature served to speed up the reaction but did not effect the yield.

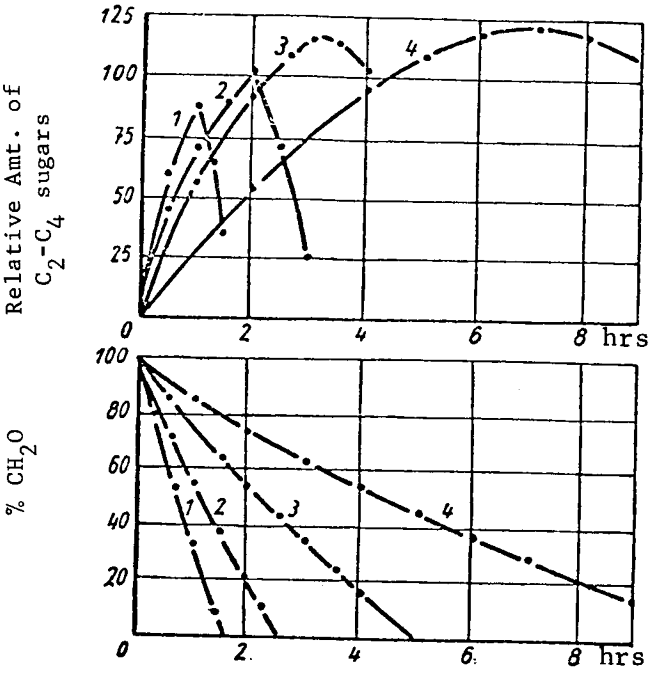


Figure 37 - Effect of $Pb(OH)_2$ Concentration Yield of Lower Sugars and Rate of CH_2O Disappearance; 100 ml 20% CH_2O Soln. and 1/100 M Benzoylcarbinol; Curve 1: 4% $Pb(OH)_2$; Curve 2: 2% $Pb(OH)_2$; Curve 3: 1% $Pb(OH)_2$; Curve 4: 0.5% $Pb(OH)_2$; T = 25°C(235)

From these observations Langenbeck(235) recommended the use of 20% formaldehyde in 30% methanol with 1% $Pb(OH)_2$ (measured as PbO) and 0.1 M Benzoyl-carbinol. The methanol was apparently added to suppress the Cannizzaro reaction. The condensation was carried out at 75-90°C and for best yields of C_2-C_4 sugars, was interrupted after 75% reaction. A typical product distribution is given below.

	% Yield
C-2 Fraction	40-42
C-3 Fraction	10-12
C-4 Fraction	18-21
Residue	20-25

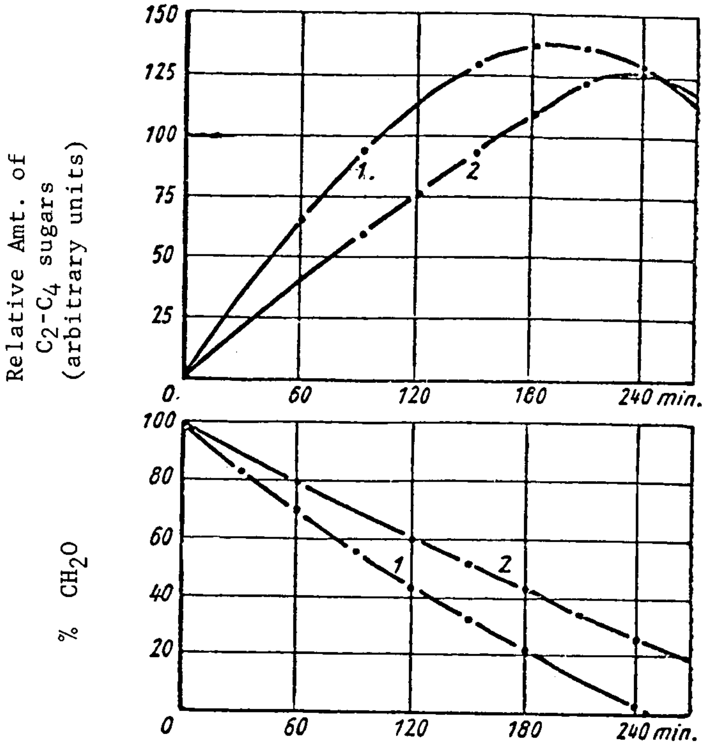
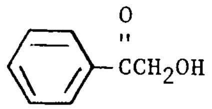
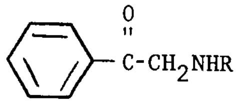


Figure 38 - Effect of Increased Benzoylcarbinol Concentration of Yield of Lower Sugars and Rate of CH_2O Disappearance; 100 mls 10% CH_2O soln.; 0.5% $Pb(OH)_2$; Curve 1: 1/100 M Benzoylcarbinol. Curve 2: 1/200 M Benzoylcarbinol(235)

Langenbeck also found that replacing the -OH group of benzoylcarbinol with -NHR afforded an effective catalyst(235) These are phenacylamines (Figure 39).


Benzoylcarbinaol


a Phenacylamine

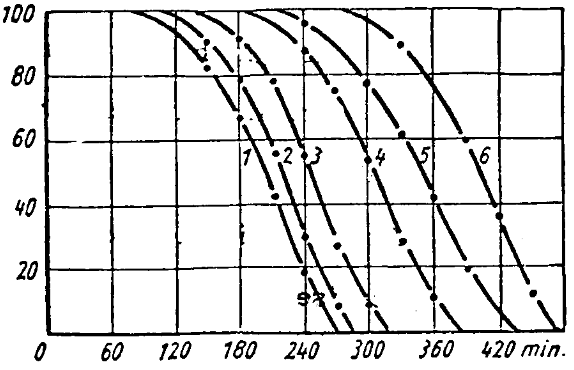


Figure 39 - Phenacylamines as Catalysts for Formaldehyde Condensation Curves: 1: phenacyl-p-phenetidine; 2: phenacylaniline; 3: phenacylmorpholine; 4: phenacyl-acetamide; 5: phenacyl-benzamide; 6: no catalyst(235)

Phenacyl derivatives of ion exchange resins are also good catalysts. Langenbeck recommended phenacylpolyaminostyrene(235). Such materials although somewhat less active than benzoylcarbinols, act as heterogeneous catalysts and are more easily separated from the reaction mixture(235, 237). In addition they are easily regenerable. These are compared with the carbinols in Figure 40. The product distribution with the heterogeneous catalysts is quite similar to that obtained with benzoylcarbinol:

C_2 Fraction	44-46%
C_3 Fraction	8-10%
C_4 Fraction	21-25%
Residue	18-20%

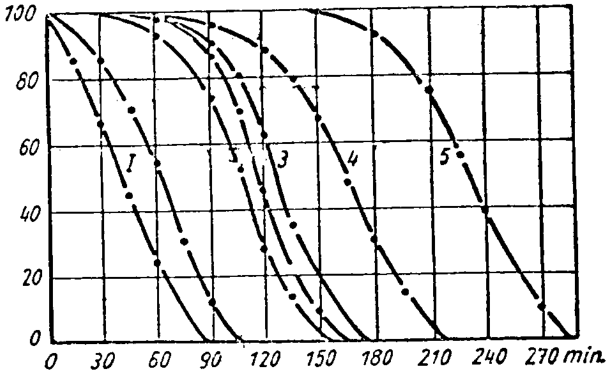
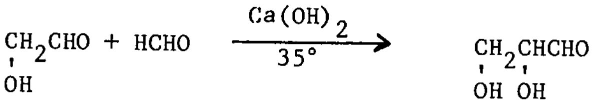


Figure 40 - Phenacyl-ionexchange Resins as Catalysts for the Formaldehyde Condensation. 4% CH_2O, 2% $Pb(OH)_2$, 2,5 m-valence catalyst, 75°C. I: benzoylcarbinol; II: p-acetamido-benzoylcarbinol; 1: acylamino compound of Amberlite XE64 and p-aminobenzoylcarbinol acetate; 2: phenacyl-polyaminostyrene; 3: phenacyl-Wofatite MD; 4: phenacyl-Wofatite N; 5: no catalyst(235)

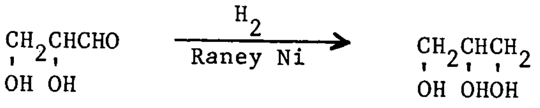
A Two Step Procedure

The easiest compound to prepare by formaldehyde condensation appears to be the simplest: glycolaldehyde(235, 236). Yields of 50% have been obtained using benzoylcarbinol and lead hydroxide (237). Kuzin(244) has demonstrated the conversion of glycolaldehyde into glyceraldehyde in 75% yield. The key to the successful isolation of glyceraldehyde is apparently rapid neutralization of the basic solution with oxalic acid before higher sugars can be formed. In view of the experience of other workers, Kuzin's result is somewhat surprising and requires verification. However, this claim is fairly well documented. Kuzin also prepared glycoaldehyde but in only 4% yield. The possibility exists, therefore, of synthesizing glycolaldehyde according to Langenbeck(235, 237, 243) and converting it to glyceraldehyde as described by Kuzin(244). However, the somewhat complicated recovery procedures would have to be refined.



$$\underset{OH}{CH_2}CHO + HCHO \xrightarrow[35^\circ]{Ca(OH)_2} \underset{OH}{CH_2}\underset{OH}{CH}CHO$$

Hydrogenation to Glycerol



$$\underset{OH}{CH_2}\underset{OH}{CH}CHO \xrightarrow[\text{Raney Ni}]{H_2} \underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2}$$

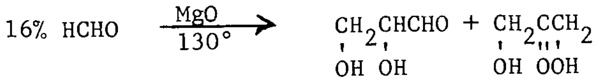
To convert glyceraldehyde to glycerol, Langenbeck used Raney nickel and a nickel-zinc "mixed oxalate" preparation as catalysts with pressures of 100-130 atmospheres and temperatures of 130°C(235). The solvent was aqueous methanol. Other catalysts which have been employed include platinum(235, 246), copper-chromium oxide(236) and other copper catalysts on various supports(245, 246). Yields are nearly quantitative. Glyceraldehyde has also been reduced electrolytically in good yield(247).

Other, poorly documented, reports of the synthesis of glyceraldehyde and/or dihydroxyacetone from formaldehyde have appeared. Hanford and Schreiber(242) claim the production of lower polyols by base catalyzed condensation of formaldehyde followed by catalytic hydrogenation. In addition to lead hydroxide, an "enediol" (nearly all common ones are claimed) is added to suppress the Cannizzaro reaction and speed up the condensation. Careful control of pH is required and the process is interrupted before all the formaldehyde has reacted to favor formation of lower sugars. The yields were only fair. A typical breakdown contained only 25-28% glycerol:

Polyhydric Alcohol	Grams	Percent Yield
Ethylene glycol	12	14.6
Glycerol	22.5	27.4
Erythritol	13	16
Higher polyhydride alcohols	34.5	42

Distinctly lower yields were obtained when the pH fell below 7 or if all the formaldehyde were allowed to react. This process does not appear attractive because of low yields of glycerol and large amounts of by-product ethylene glycol.

Binko and Kolar claimed the production of glyceraldehyde and dihydroxyacetone by the action of magnesium oxide or lead hydroxide on aqueous formaldehyde(249). The



$$16\%\ \text{HCHO} \xrightarrow[130^\circ]{\text{MgO}} \underset{\text{OH OH}}{\text{CH}_2\text{CHCHO}} + \underset{\text{OH OOH}}{\text{CH}_2\text{CCH}_2}$$

patent claims that higher temperatures and pressures increase the rate of reaction and represent a signficant advance over previous work. However, in light of other reports(241, 248, 251) that mostly higher sugars are obtained under similar conditions it is doubtful that high selectivities to glyceraldehyde or dihydroxyacetone could be realized. The patent mentions no yields and gives only sketchy experimental details. It is very likely only a "paper" patent.

An early report(250), largely ignored by later investigators, describes the isolation of osazones of lower sugars from sodium sulfite catalyzed condensation of "trioxymethylene" (probably paraformaldehyde). No yields are given and apparently other products were also obtained. This work seems to be worthy of a second look.

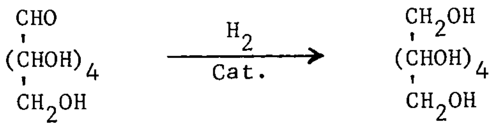
Finally, note must be taken of the possibility of the photochemical polymerization formaldehyde(251, 252, 254). The formation of reducing sugars has been observed when aqueous formaldehyde(252, 254) or CO_2(253) are exposed to sunlight(233) or ultraviolet radiation of 200-290 mu(248, 250). Little data are given and the products are poorly characterized. However, there is no indication that any lower sugars were produced. In an interesting patent(265), it is claimed that sunlight catalyzes formaldehyde condensation in the presence of lime! Since no evidence to the contrary is presented, it appears the true catalyst in this case is $Ca(OH)_2$.

In summary, the trimerization of formaldehyde followed by hydrogenation is a promising route to glycerol. The major drawbacks are the need for special catalysts and careful control of reaction conditions and the complex neutralization and recovery procedures, all designed to favor lower sugars. For these and other reasons outlined below, the hydrogenolysis of carbohydrates was considered slightly preferable and was selected for the engineering case study.

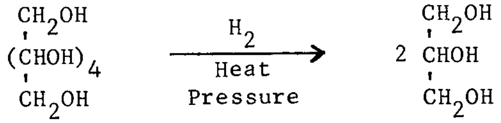
Hydrogenolysis of Carbohydrates

Crude mixtures of carbohydrates, such as those obtained by the base catalyzed polymerization of formaldehyde may be reductively cleaved to lower polyols by high pressure hydrogenation(197, 255, 263). Before and during World War II such a process was developed in Germany to give a glycerol substitute called "Glycerogen" (197, 264). Inverted beet sugar was hydrogenated over a nickel-on-pumice catalyst at 80-200°C. A high yield (92%) was realized of a product consisting of 40% glycerol, 40% propylene glycol and 20% of other polyhydric compounds including sorbitol, mannitol and ethylene glycol(264). It was used for non-food purposes. Since that time, the process has been studied in somewhat more detail(255-263).

The reaction normally proceeds in two stages. In the first, sugars are reduced to polyhydric alcohols. This is followed by cleavage of the carbon chain if the conditions are vigorous enough.

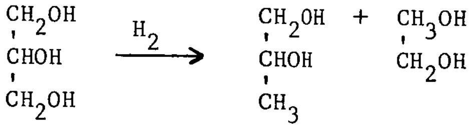
(1) 

$$\mathrm{CHO{-}(CHOH)_4{-}CH_2OH} \xrightarrow[\text{Cat.}]{H_2} \mathrm{CH_2OH{-}(CHOH)_4{-}CH_2OH}$$

(2) 

$$\mathrm{CH_2OH{-}(CHOH)_4{-}CH_2OH} \xrightarrow[\text{Heat Pressure}]{H_2} 2\ \mathrm{CH_2OH{-}CHOH{-}CH_2OH}$$

A major problem, if glycerol is the desired product, is the tendency for the reaction to continue to produce propylene glycol and ethylene glycol.

(3) 

$$\mathrm{CH_2OH{-}CHOH{-}CH_2OH} \xrightarrow{H_2} \mathrm{CH_2OH{-}CHOH{-}CH_3} + \mathrm{CH_2OH{-}CH_2OH}$$

Early studies of the hydrogenation of sugars were carried out under mild conditions and resulted in nearly quantitative yields of the corresponding polyol, reaction (1) (see reference 255 for a short review of work prior to 1943). Only at temperatures above 200°C is cleavage observed. The reaction was investigated in detail by Natta and his associates(255). They found that reaction (1) occurs much more rapidly than subsequent reactions. However, at temperatures above 200°C and hydrogen pressures of 100-200 atmospheres, cleavage is readily achieved. The best catalysts for the formation of mixtures of propylene glycol and glycerol and for suppression of ethylene glycol formation were copper compounds, especially copper chromite. In most runs with this catalysts, no ethylene glycol was observed. For glycerol alone, the best catalyst appeared to be nickel-chromium. However, the nickel catalysts were somewhat more active and produced some ethylene glycol. Natta claimed yields of 80% of propylene glycol-glycerol and of 50% of glycerol alone. Some of his results are summarized in Table 44.

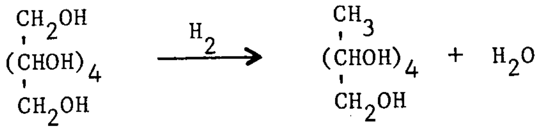
Catalyst	Solvent	Pressure (At.)	Temp.°C	Time	% Yield St. Mat.[1]	 Glycerol	 Glycol
Cu-Chromite	Alcohol	210	250	5 Hr.	36	21	29.5[2]
Cu-Chromite	Alcohol	175	250	5 Hr.	21.5	--	50[2]
Cu-Chromite	Alcohol	200	250	10 Hr.	10	8.5	62[2]
Ni-Cu (5-1)	Water	150	220	5 Hr.	54.4	5.9	18.8[3]
Ni-Cu (4-1)	Water	155	220	5 Hr.	29.0	19.4	19.5[3]
Ni-Cu (4-1)	Water-MeOH	150	220	5 Hr.	18.8	0	44.5[3]
Ni-Cu (3-2)	Water	160	230	5 Hr.	26.5	16.9	26.9[3]
Ni-Cr	Water	100	200	3 Hr.	3.0	47.5	10.5[3]
Cu-Ni (3-2)[4]	Water	160	160-250	3+2 Hr.	38.2	38.2	3.0[3]
Cu-Ni (3-2)[4]	Water	100	230	3 Hr.	78.3	--	12.1[3]
Cu-Ni (3-2)[4]	Water	160	230	3 Hr.	41.5	19.4	Trace
Ni	Water	100	240	3 Hr.	22.0	5.5	48.0
Ni	Water	160	220	5 Hr.	29.5	11.8	31.0

1. Could be recycled.
2. Exclusively propylene glycol.
3. Approximately 50-50 propylene and ethylene glycols.
4. Supported on kieselguhr.

Table 44 - Hydrogenolysis of Carbohydrates With Various Catalysts(255)

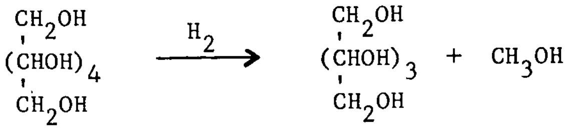
Natta found yields of glycerol were best in water solution at temperatures as low as possible and short contact times. He claims that better yields of glycerol result if the first stage hydrogenation is carried to completion before cleavage begins. According to Natta the second stage hydrogenation can proceed in four ways, reduction of the terminal hydroxymethyl group or splitting between bonds C_{1-2}, C_{2-3} or C_{3-4}.

(1)



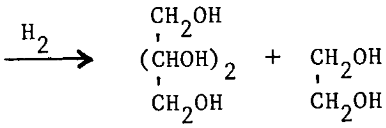
$$\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{(\mathrm{CHOH})_4}} \xrightarrow{H_2} \underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_3}}{(\mathrm{CHOH})_4}} + \mathrm{H_2O}$$

(2)



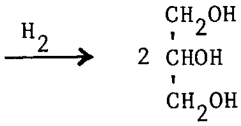
$$\underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{(\mathrm{CHOH})_4}} \xrightarrow{H_2} \underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{(\mathrm{CHOH})_3}} + \mathrm{CH_3OH}$$

(3)



$$\xrightarrow{H_2} \underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{(\mathrm{CHOH})_2}} + \underset{\mathrm{CH_2OH}}{\mathrm{CH_2OH}}$$

(4)



$$\xrightarrow{H_2} 2\ \underset{\mathrm{CH_2OH}}{\overset{\mathrm{CH_2OH}}{\mathrm{CHOH}}}$$

Further reduction of these initial compounds can and does occur. Some of the more likely products envisioned by Natta are given in Figure 41. He isolated all compounds except those in parentheses. The free energy relationships for some of the reactions are given in Table 45.

				ΔF°_{298} (Kcal)
1.	Glucose	$\longrightarrow$	"Hexite"	-6,800
2.	"Hexite"	$\longrightarrow$	2 Glycerol	-4,600
3.	"Hexite"	$\longrightarrow$	"Erythrite" + Ethylene Glycol	-3,800
4.	"Hexite"	$\longrightarrow$	"Pentite" + CH_3OH	-3,460
5.	"Methylpentite"	$\longrightarrow$	"Pentite" + CH_4	-10,300
6.	Glycerol	$\longrightarrow$	Ethylene Glycol + CH_3OH	-3,360
7.	"Hexite"	$\longrightarrow$	Methyl Pentite + H_2O	-22,060
8.	Glycerol	$\longrightarrow$	1,2-Propylene Glycol + H_2O	-21,560
9.	Glycerol	$\longrightarrow$	1,3-Propylene Glycol + H_2O	-18,160

Table 45 - Free Energy Calculations for the Various Hydrogenation Reactions(255)

The splitting of a 6-carbon "hexite" to 3-carbon fragments is favored relative to 4- or 5-carbon compounds. The most favorable reactions are those which produce water, but with suitable catalysts simple chain cleavage to form glycerol can be made the chief reaction.

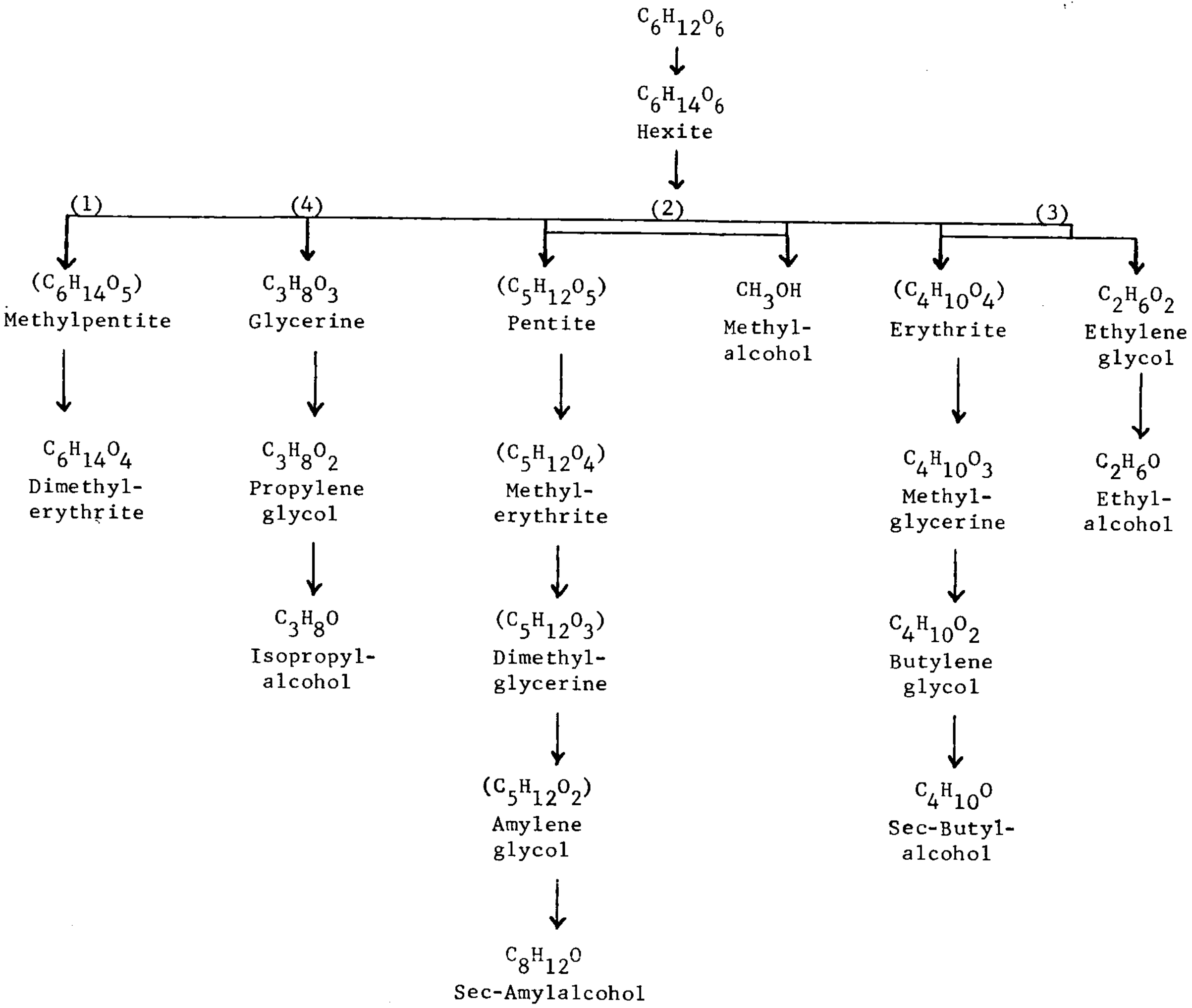
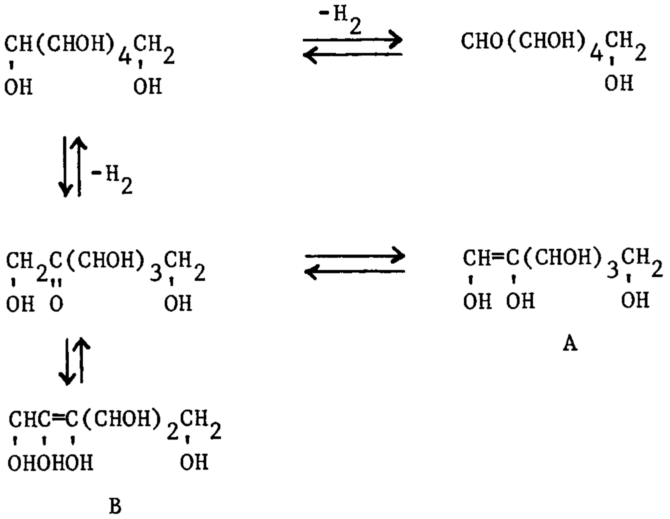


Figure 41 - Products of Sugar Hydrogenation According to Natta(255)

Material Hydrogenated	Temp. °C	Press. Atm.	Time	Glycol	% Yield	Mono-Alcohol	% Yield	% Yield
Ethylene Glycol	250	300	15 Hr.	--		Ethanol	10	72.5
Glycerol	205	300	15 Hr.	1,2-Propylene	74	*i*-Propyl	10	7.7
Erythritol	210	300	24 Hr.	1,2-Propylene 2,3-Butylene	23	*i*-Propyl *s*-Butyl	14 17	12.9
Xylitol	225	300	15 Hr.	Ethylene 1,2-Propylene	45 14	Ethanol *i*-Propyl	5	10.1
Sorbitol	220	300	15 Hr.	Ethylene 1,3-Propylene 2,3-Butylene	2 61 8	Ethanol *i*-Propyl	2 10	6.8
Manitol	205	300	15 Hr.	Ethylene 1,2-Propylene Butylene	2 55	*i*-Propyl	27	7.7
Dulcitol	195	300	15 Hr.	1,3-Propylene "Others"	64 --	*i*-Propyl	12	2.9
1-Methyl-Erythritol	210-215	300	15 Hr.	Ethylene 1,2-Propylene	6 78	Ethanol *i*-Propyl	15 8	7.6
1,4-Dimethyl-Erythritol	210-215	300	15 Hr.	1,2-Propylene "Higher Boiling"	43 24	*i*-Propyl	13	2.0
Rhamnitol (1-Methylxylitol)	210-215	300	15 Hr.	1,2-Propylene 2,3-Butylene	62 1	*i*-Propyl	16	4.0

Table 46 - Hydrogenolysis of Reduced Sugars According to Schmidt(257) (Cobalt-Zinc-Barium Catalyst)

The importance of using the proper catalyst is apparent, not only from Natta's work (Table 44) but also from a report by Schmidt that no glycerol resulted from hydrogenation of reduced sugars over cobalt-zinc-barium catalyst(257). Copper, which Natta found most useful for glycerol synthesis, was rigorously excluded by Schmidt. His results are given in Table 46. Schmidt's work confirms Natta's observations that 3-carbon fragmentation is favored. However, he visualizes the reaction mechanism differently. He postulates a prior dehydrogenation to the aldo or keto form of the sugar followed by enolization to form (A) and, to a much lesser extent (B). By analogy with his work on hydrocarbon cracking(258), Schmidt claims the weakest bond is allylic (i.e., the 3,4 bond) to the double bond.

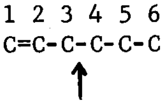


$$\begin{tikzcd}
\underset{OH}{CH}(CHOH)_4\underset{OH}{CH_2} \arrow[r, shift left, "-H_2"] \arrow[d, shift left] & CHO(CHOH)_4\underset{OH}{CH_2} \arrow[l, shift left] \\
\underset{OH}{CH_2}\underset{O}{C}(CHOH)_3\underset{OH}{CH_2} \arrow[u, shift left, "-H_2"'] \arrow[r, shift left] \arrow[d, shift left] & \underset{OH}{CH}{=}\underset{OH}{C}(CHOH)_3\underset{OH}{CH_2} \arrow[l, shift left] \\
\underset{OH}{CH}\underset{OH}{C}{=}\underset{OH}{C}(CHOH)_2\underset{OH}{CH_2} \arrow[u, shift left] &
\end{tikzcd}$$

A

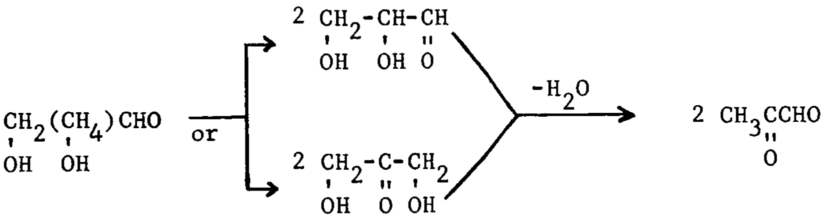
B

Splitting of the 3,4 bond would give rise to two 3-carbon fragments from (A) and explains the proponderance of such compounds in his reaction mixtures (Table 46).

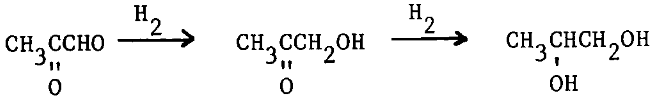


$$\overset{1}{C}{=}\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

Weidenhagen and Wegner isolated acetol from the hydrogenation of sucrose over nickel catalysis at 130°C(259). They postulated a splitting of the sugar to two moles of methylglyoxal followed by hydrogenation to acetol and, finally, to 1,2-propylene glycol.



$$\underset{OH}{CH_2}(\underset{OH}{CH_4})CHO \xrightarrow{\text{or}} \left\{ \begin{array}{l} 2\ \underset{OH}{CH_2}-\underset{OH}{CH}-\underset{O}{\overset{\|}{CH}} \\ 2\ \underset{OH}{CH_2}-\underset{O}{C}-\underset{OH}{CH_2} \end{array} \right\} \xrightarrow{-H_2O} 2\ CH_3\underset{O}{C}CHO$$



$$CH_3\underset{O}{C}CHO \xrightarrow{H_2} CH_3\underset{O}{C}CH_2OH \xrightarrow{H_2} CH_3\underset{OH}{CH}CH_2OH$$

Natta and others, however, found no splitting under these conditions but observed a rapid hydrogenation of the sugar to its reduced form(255, 257, 261, 263). This difference may be due to some special feature of Weidenhagen and Wegners' catalyst which was not described thoroughly.

A number of patents concerning the hydrogenolysis of carbohydrates have appeared. Many of these were summarized by Natta(255). However, several more recent ones present some pertinent details worth discussing. Fuchs and Wolfram claim that the yield of glycerol may be increased relative to glycols and "hexites" by suppressing the primary reduction and causing the cleavage to occur on the sugar itself(256). This is accomplished by sintering or otherwise poisoning the hydrogenation catalyst so that it does not hydrogenate the sugar but is active enough to reduce the cleavage products, glyceraldehyde and dihydroxyacetone. A nickel catalyst on sodium carbonate was recommended. This could be further improved by addition of Na_2SO_3 or Na_2S. A summary of results with various catalysts is given in Table 47.

Conradin, Bertossa and Giesen found that, to a certain extent, any of three or four products could be favored by proper choice of reaction conditions(261). A summary is given below.

	Conditions Favoring					
				Catalyst Composition		
Product	Max. Yield	Temp.	Press.	Ni	Cu	Co
1,3-Propylene Glycol	70%	190-320°C	1-200 Atm.	10-14%	10-14%	1-5% (Optional)
1,2-Propylene Glycol	30%	180-210°C	10-50 Atm.	20-25%	2-5%	---
Glycerol + Ethylene Glycol	66%	200-220°C	100-200 Atm.	---	1-24%	1-24%

The catalysts were used in the form of hydroxides or oxalates with or without a carrier such as magnesium oxide and were pre-reduced prior to hydrogenation of the carbohydrates. Under the most favorable conditions, however, the yields of glycerol were only fair (Table 48). In general, the high conversion runs afforded large amounts of ethylene glycol.

					Products		
Catalyst-Additive	T°C	Press.	Time	% Conversion	% Glycerol[3]	% Glycols	Residue[4]
Ni^1-Untreated	108-130	200 Atm.	4-2 Hr.	2			98
Ni^1-Na_2CO_3	108-130	200	4-2 Hr.	32	27.5	4.5	68
Ni^1-Na_2CO_3+0.1% Na_2SO_3	108-130	200	4-2 Hr.	55	37	9	54
Ni^1-Na_2CO_3+0.4% Na_2SO_3	152	200	5 Hr.	77.5	62.5	15	22.5
Ni^1-Na_2CO_3+0.13% Na_2S + 0.13% NaOH	100-120	200	4.2 Hr.	67	57.5	9.5	33
Ni^1-Na_2CO_3+0.13% NaS +0.13% $NaHCO_3$	100-120	200	4-2 Hr.	14	5	9	86
Ni^2-Na_2CO_3 (300° Heat)	100-120	200	4-2 Hr.	--			
Ni^2-Na_2CO_3 (500° Sintered)	100-120	200	4-2 Hr.	79.5	68	10.5	21.5

(1) Supported on pumice.

(2) Supported on zinc oxide.

(3) Contains 20% methylglycerol.

(4) Mostly reduced sugars.

Table 47 - Increasing Glycerol Yields by Catalyst Poisoning(256)

Catalyst	Time	Press.	Temp.	% Conv.	% Glycerol	Glycols % 1,3	% 1,2	% Ethylene	Others
12.5% Ni-12.4% Cu	10 Hr.	150 Atm.	210°C	92	25	53	18	--	--
22% Ni-3% Cu	5 Hr.	150 Atm.	220°C	60	30	40	12	15	3
12% Ni-1% Cu-12% Co	20 Hr.	150 Atm.	195°C	45	39	44	11	--	--
Copper Chromite - Ag	20 Hr.	150 Atm.	200°C	66	20	51	10	6	3
Copper Chromite - Ag	10 Hr.	150 Atm.	200°C	58	23	60	8	7	2
5% Ni-20% Co	10 Hr.	150 Atm.	210°C	93	34	19	11	31	5
12% Ni-12% Co	10 Hr.	150 Atm.	210°C	96	34	19	15	32	--
23% Ni-2% Cu	10 Hr.	25 Atm.	210°C	83	19	20	32	10	19

Table 48 - Products from Hydrogenolysis of Sorbitol Over Various Copper-Nickel and Cobalt Catalysts(260) (Most catalysts supported on 75% MgO)

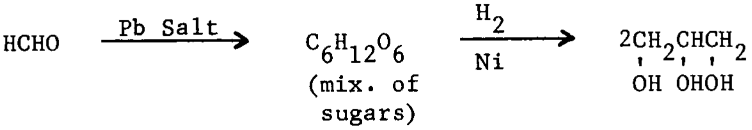
A British patent, assigned to Inventa A.G., claims good selectivity to glycerol (up to 57%) in the hydrogenolysis of sugar alcohols (e.g., sorbitol)(262). Increased hydrogen pressure was claimed to favor glycerol by suppressing losses due to side reactions and resinification. The catalyst was nickel on kieselguhr. The reaction mixture was kept basic (pH 8.4) by addition of CaO.

Pressure	Temperature	Residue*	Conversion	Glycerol	Glycols	Losses
100	200	3.7	96.3	19.5	36.0	44.6
600	220	47.6	52.4	45.4	43.0	11.5
800	220	64.5	35.5	57.0	38.2	4.8

* Starting material.

Giesen and Müller hydrogenated crude wood sugars and obtained glycerol in fair yields (30-50% with recycle)(261). This patent is noteworthy mainly because crude sugars are employed and an ion exchange method of purification of the product is described.

Finally, a process has been patented for the continuous production of polyhydric alcohols from formaldehyde <u>via</u> a carbohydrate intermediate(263).



$$\mathrm{HCHO} \xrightarrow{\text{Pb Salt}} \underset{\text{(mix. of sugars)}}{C_6H_{12}O_6} \xrightarrow[\text{Ni}]{H_2} 2\underset{\text{OH}}{CH_2}\underset{\text{OH}}{CH}\underset{\text{OH}}{CH_2}$$

The first step is similar to the formaldehyde condensations described above. An "enediol" initiator, glycose or a crude carbohydrate solution, was employed in the examples. The yield of the first step was claimed to be 86%. The crude mixture was hydrogenated over a Raney nickel catalyst to form various polyhydric alcohols. The overall yield of glycerol, based on formaldehyde consumed, was 47%.

Additional details for this process are given below. It was chosen as part of the basis for the engineering design since it provided the best details for a continuous process for glycerol formation starting with formaldehyde. In addition, the examples given appear to be real and are in agreement with the results of other investigators.

In summary, the hydrogenolysis of carbohydrates is a promising method for the synthesis of glycerol. This route has certain advantages to trimerization of formaldehyde: (1) comparable or better yields of glycerol relatively free from the objectionable ethylene glycol may be obtained with much simpler procedures; (2) the engineering is considerably less complicated; finally (3) since there is interest in carbohydrates as edible materials in their own right(5, 7, 251), this type of process could be integrated with an edible sugar synthesis. Much of the product of a non-selective carbohydrate condensation is not edible(251). This material, after separation of the valuable products, could be hydrogenolyzed to glycerol.

ENGINEERING DESIGN AND EVALUATION

It was originally planned to conduct a brief engineering survey of all candidate systems for fatty acid production which passed the original screen. The purpose of this survey was to evaluate each method from the standpoints of power, weight, volume and technical feasibility (reliability). These ratings, along with those based on chemistry (yield) and nutrition (value of the products) were to determine the most promising system or systems. It was apparent after the second phase of the literature search, however, that the choice could be made on the basis of chemistry and nutrition alone; only the Ziegler growth reaction with ethylene promised any reasonable selectivity to useful products. Consequently, the engineering phase of this program was devoted exclusively to this series of reactions. The major objective was to determine, in a semi-quantitative manner, the power requirements of the system, its reliability and complexity from an engineering standpoint. Such evaluations would serve as a basis for judgment of the feasibility of fatty acid synthesis from CO_2 on board a spacecraft and to point out areas for further research and development.

The production of synthetic fat along the lines described above involves a complex series of unit processes and unit operations. The chemistry of the fat synthesis has already been described. Briefly, the process involves (1) the production of C_2H_4 from CO and H_2, (2) polymerization of C_2H_4 to higher α-olefins, (3) production of glycerol, and (4) oxidation of the olefins to the fatty acids which are then esterified with the glycerol (5).

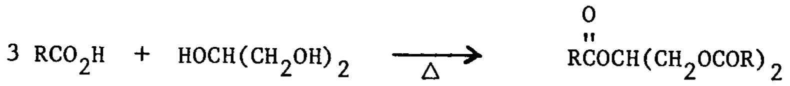
(1) $CO + H_2 \xrightarrow{\text{catalyst}} C_2H_4$

(2) $n\ C_2H_4 \xrightarrow{(C_2H_5)_3Al} RCH{=}CH_2$

(3) $6\ HCHO \xrightarrow{\text{base}} C_2H_{12}O_6 \xrightarrow{H_2} 2\ HOCH(CH_2OH)_2$

(4) $RCH{=}CH_2 \xrightarrow[H_2O]{O_3} RCO_2H + HCO_2H$

(5)



$$3\ RCO_2H + HOCH(CH_2OH)_2 \xrightarrow[\Delta]{} R\overset{\overset{O}{\|}}{C}OCH(CH_2OCOR)_2$$

Each of these five steps involves chemical reaction, separation and purification, fluid flow, heat and mass transfer. Although these are generally routine operations as carried out on earth, the absence of gravitational forces in space presents unique and difficult problems in the design of the necessary equipment. Furthermore, the commercial type equipment that would be needed for the production of only 5 lbs./day of fat would be so small that it is not now commercially available. There is little doubt that with continued R&D, small, low capacity equipment can be built to function as required in the absence of natural gravity. Since this equipment may be quite different from that to which we are accustomed, however, speculation of equipment size, volume, etc., is of little value and so has not been attempted. A brief, first approximation, estimate of power requirements has been made, however, along with a crude engineering design.

It should be pointed out that although the process selected for producing the fatty glycerides is believed to be the best of all those available today, it nevertheless is a very complex one. There is, in fact, no commercial integrated process or plant today of which we are aware that is as complex as that proposed for this synthesis. In addition, much less complicated plants require maintenance and supervision. Completely automatic push button operation and control is still an unrealized goal for the great majority of chemical operations.

A simple line-diagram of the fat synthesis is shown in Figure 42. The process will be discussed in four sections:

I Ethylene Synthesis
II Ziegler Growth and Displacement Reactions
III Synthesis of Glycerol
IV Acid Synthesis and Esterification

These sections correspond to the major divisions shown in Figure 42 and in the more detailed engineering design (Figure 43).

General Considerations

The system was designed to produce 5 lbs. of fat continuously over a 24 hour period. This was deemed sufficient for 10 men. The total electrical power requirement is given in Tables 49-52. It does not appear to be excessive. The total theoretical power is only about 136 watts. The actual requirement would be considerably greater mainly because of the extremely low efficiencies of the miniaturized equipment needed. This is estimated at 2465 watts (Table 49). Expressed another way it is 12 KWH/lb. Thermal power requirements have not been determined. These, however, would not be great. Each step of the reaction sequence is exothermic with the exception of ozone formation and it is anticipated that the process would be heat integrated to make economical use of excess heat. Since none of the reaction temperatures are excessive, this should not be a major problem. Obviously complete heat balance is not possible. Some heat rejection will be necessary. It was assumed that this could be accomplished by space radiation. At any rate, the amount of excess heat would not be large.

Although the power needed appears reasonable and even weight and volume requirements would probably not be inordinate (at least compared to biological systems), this process suffers from other disadvantages. The major of these is complexity and along with it the inevitable reduced reliability of an extremely intricate system. This is exemplified by the data in Table 52. At least 77 control loops are required. Since this is neglecting redundancy, it is anticipated that considerably more actually will be needed. This will become even more apparent from the descriptions of individual parts of the system below. The material balances for the entire system are given in Table 54. This complete engineering design comprises Figure 43.

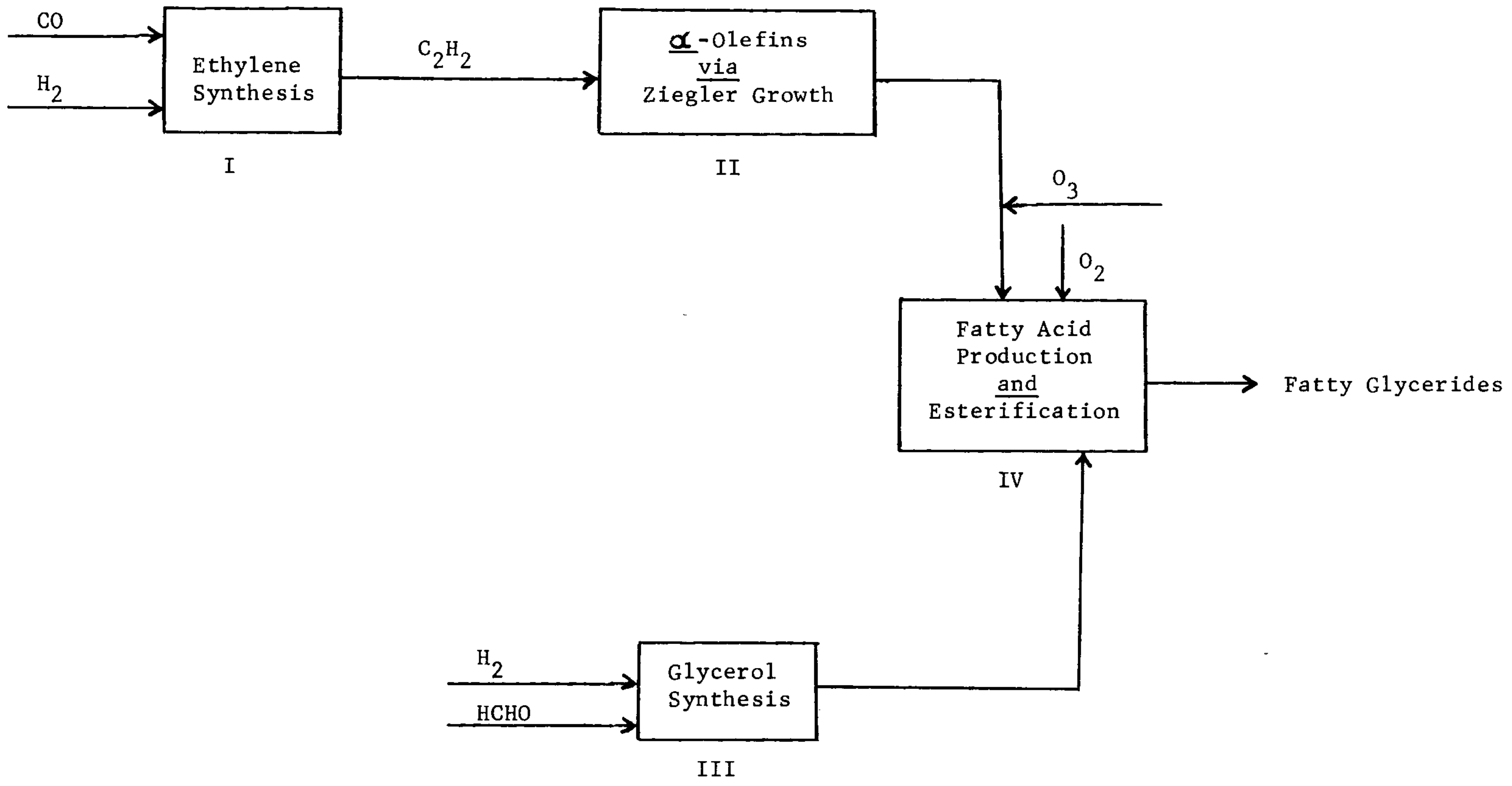


Figure 42 - Glyceride Synthesis via Ziegler Growth Reaction

For 5 lbs./day - Sufficient for 10 Men

	Total Watts Theoretical	Total Watts Estimated Actual
Pumps (21)	1	380
Compressors (7)	104	1786
Controls (77)	---	128
Ozonizer	30	171
Totals	135	2465

OR: 12 KWH/lb.

Table 49 - Electrical Power Requirements for Fat Production *via* Ziegler Growth Method

Pump	Appears in Div. --- of Fig. 43	ΔP (Atm.)	Flow (Gm./Min.)	Theor. Watts	Est. Actual Watts
1	I	100	0.0007	0.444	45
2	II	10	0.0004	0.0292	20
3	II	1	0.0005	0.0032	15
4	II	100	0.0002	0.157	40
5	IV	1	0.0005	0.0029	15
6	IV	1	0.0001	0.0007	15
7	IV	1	0.00009	0.0006	15
8	III	1	0.0001	0.0009	15
9	III	1.5	0.0001	0.0095	15
10	III	100	0.0002	0.156	40
11	III	1	0.00006	0.0004	15
12	III	2	0.0001	0.0018	15
13	IV	0.2	0.0007	0.0009	5
14	IV	0.2	0.0067	0.0087	5
15	IV	1	0.00008	0.0005	15
16	IV	1	0.0005	0.0032	15
17	III	1	0.00003	0.0002	15
18	III	1	0.00007	0.0005	15
19	II	1	0.0002	0.0011	15
20	III	1	0.0002	0.0016	15
21	I	2	0.0004	0.0046	15
	Totals			.8284	380

Table 50 - Pump Data

Compressor	Appears in Div. --- of Fig. 43	ΔP (Atm.)	Std. Cu. Ft./Day	Theor. Watts	Estimated Actual Mech. Eff.	Elect. Eff.	Watts
1	I	20	678	91	30	50	606
2	II	5	117	3.2	10	15	214
3	II	70	30	1.6	10	15	107
4	I	1			--	--	(300)[2]
5	IV	0.3	500	5.2	10	15	347
6	III	100	11.4	2.5	10	15	167
7[1]	IV				--	--	(45)[2]
		Totals		103.5			1786

(1) Handles 0.42 lbs. H_2O/day.

(2) No data for estimation; rough guess only.

Table 51 - Compressor Data

Type	No.	Estimated Power Req. (Watts) Each	Total
Level	2	2	48
Flow	10	2	20
Pressure	16	-	--
Temperature	24	2	48
Timer	3	4	12
	77		128 Watts

Table 52 - Control Breakdown

Ethylene Production (Figure 43, I)

The first step in the production of fat involves the synthesis of C_2H_4 from CO and H_2 as described by Peters(139). The CO and H_2 are combined and compressed to about 20 atmospheres, and catalytically reacted at about 735°F, to obtain partial conversion to C_2H_4 (and H_2O). The reaction is exothermic so that once started, it will be self-sustaining and will even supply the heat needed to bring the reactants to the conversion temperature.

The reactor effluent is cooled and then refrigerated to remove the first by-product water (as ice) and next liquidified ethylene. It has been assumed that refrigeration can be supplied by a space radiator thereby eliminating the requirement for supplying power to a compressor-operated device.

The liquified C_2H_4 is pumped up to 100 atmospheres and used as the refrigerant to cool the reactor effluent. The C_2H_4 is then used in the polymerization to αolefins. Unconverted CO and H_2 is also used as a coolant and then recycled back to the reactor.

α-Olefins Via Ziegler Growth (Figure 43, II)

This process design was based on references 77-81 and 85. Most of the C_2H_4 that has been produced is fed to the Ziegler growth reactor where it combines with triethylaluminum (TEA). The TEA is carried in a stream of C_{12} to C_{14} α-olefins since its vapor pressure is intermediate between these olefins and separation from them is difficult.

The Ziegler growth reaction is carried out at about 100 atmospheres and 320°F. The reaction is exothermic and use is made of the heat evolved for maintaining the growth reaction at temperature as well as for effecting some subsequent separations. Contact time is 10-20 minutes. This time was chosen to provide a consumption of 18 moles of C_2H_4 per mole of TEA (6 moles per R-Al bond). This was predetermined as the ratio yielding the best product distribution (Table 53). The product from the growth reaction is first flash distilled at 30 atmospheres (320°F) to remove unreacted ethylene which is recycled. A second distillation is then conducted to remove the C_{12} and C_{14} olefins which are passed to the ozonolysis chamber. The higher boiling trialkylaluminums (TAA) are contacted with ethylene at about 535°F and 10 atmospheres to displace the α-olefins and regenerate TEA. The contact time is short (around 0.8 seconds). After the excess ethylene is flashed and recycled, the product mixture is separated by distillation. Three fractions are obtained: (1) C_4-C_{10} olefins, (2) triethylaluminum (TEA) and C_{12}-C_{14} olefins, and (3) olefins higher than C_{14}. Cuts (1) and (3) are combined with the C_{12}-C_{14} olefins separated earlier and passed on to be ozonized. Fraction (2) is recycled to the growth reactor to complete the continuous process. By proper choice of pressures the three flash distillations may be conducted at a common temperature (320°F). This is the temperature of the Ziegler growth reaction. Thus, all four unit processes may be integrated to make use of waste heat generated by the Ziegler reaction.

Synthesis of Glycerol (Fig. 43, III)

This is a two step process involving condensation of formaldehyde to sugars followed by hydrogenative cleavage to glycerol. The process design was based mostly on a patent of Maclean and Heinz(263) but also incorporates the reports of Langenbeck (235, 243) and Natta(255). No attempt was made to optimize the synthesis conditions; the design is only illustrative. However, any changes would be expected to be minor as far as the engineering aspects are concerned.

A mixture of formaldehyde, water and lead acetate is allowed to react for an hour at 210°F and 2 atm. pressure. The products are fractionated, water and formaldehyde are recycled and a mixture of crude sugars and the catalyst are passed successively through a cationic and anionic exchange resin to remove lead and acetate ions. The crude sugars are then hydrogenated over a nickel catalyst (copper compounds may also be used; Natta(255) suggests they are superior) at 100 atm. and 400°F (3 hours). Hydrogen is flashed off and recycled and the crude glycerol is purified by fractional distillation. The glycols and higher boiling residues are burned and the pure glycerol is pumped over to the esterification chamber.

Olefin	Corresponding Acid*	Wt. %
C_4	C_3	0.4
C_6	C_5	1.9
C_8	C_7	5.2
C_{10}	C_9	9.6
C_{12}	C_{11}	13.9
C_{14}	C_{13}	16.1
C_{16}	C_{15}	15.7
C_{18}	C_{17}	13.4
C_{20}	C_{19}	10.6
C_{22}	C_{21}	6.4
C_{24}	C_{23}	3.7
C_{26}	C_{25}	2.1
C_{28} and higher	C_{27} and higher	1.0
		100.0

* Obtained by ozonolysis with loss of one carbon.

Table 53 - Distribution of Olefins and the Corresponding Acids from the Ziegler Growth Reaction ($C_2H_4/(C_2H_5)_3$ Al = 6)

Conversion of Olefins to Acids and Esterification (Fig. 43, IV)

This process is based upon data in references 155, 156, 158. The α-olefins from the Ziegler reaction are dissolved in Freon 11 (fluorotrichloromethane; "Freon" is a duPont trademark), cooled to 30°F and ozonized with 2% O_3 in O_2. The ozone is produced in a "Welsbach" ozonizer(155). The freon solution of ozonides is mixed with recycle formic acid and oxidized at 250°F with O_2 containing a trace of O_3. The actual oxidizing agent is probably performic acid. The products are then separated into an overhead stream of Freon 11, most of the formic acid, O_2 and a little water which is recycled. The bottoms are filtered to remove trace solids (mostly Al_2O_3 which is carried along from the Ziegler reaction) and fractionated. The middle fraction, which contains the purified fatty acids is passed on to be esterified. The bottoms are burnt. The overhead, containing about one pound/day of formic acid and trace non-condensables, is also burnt. It is necessary to dispose of this amount of formic acid, equal to the amount produced on ozonolysis, to prevent its build-up in the system.

The pure fatty acids are mixed with glycerol and converted to glycerides at 500°F and about 5 mm pressure (compare reference 193). The glycerides are purified by steam distillation. The overhead is burnt. It is recognized that the degree of purification necessary to yield an edible product can be determined only by experimentation. It is very unlikely that a more sophisticated separation and refining procedure would be necessary.

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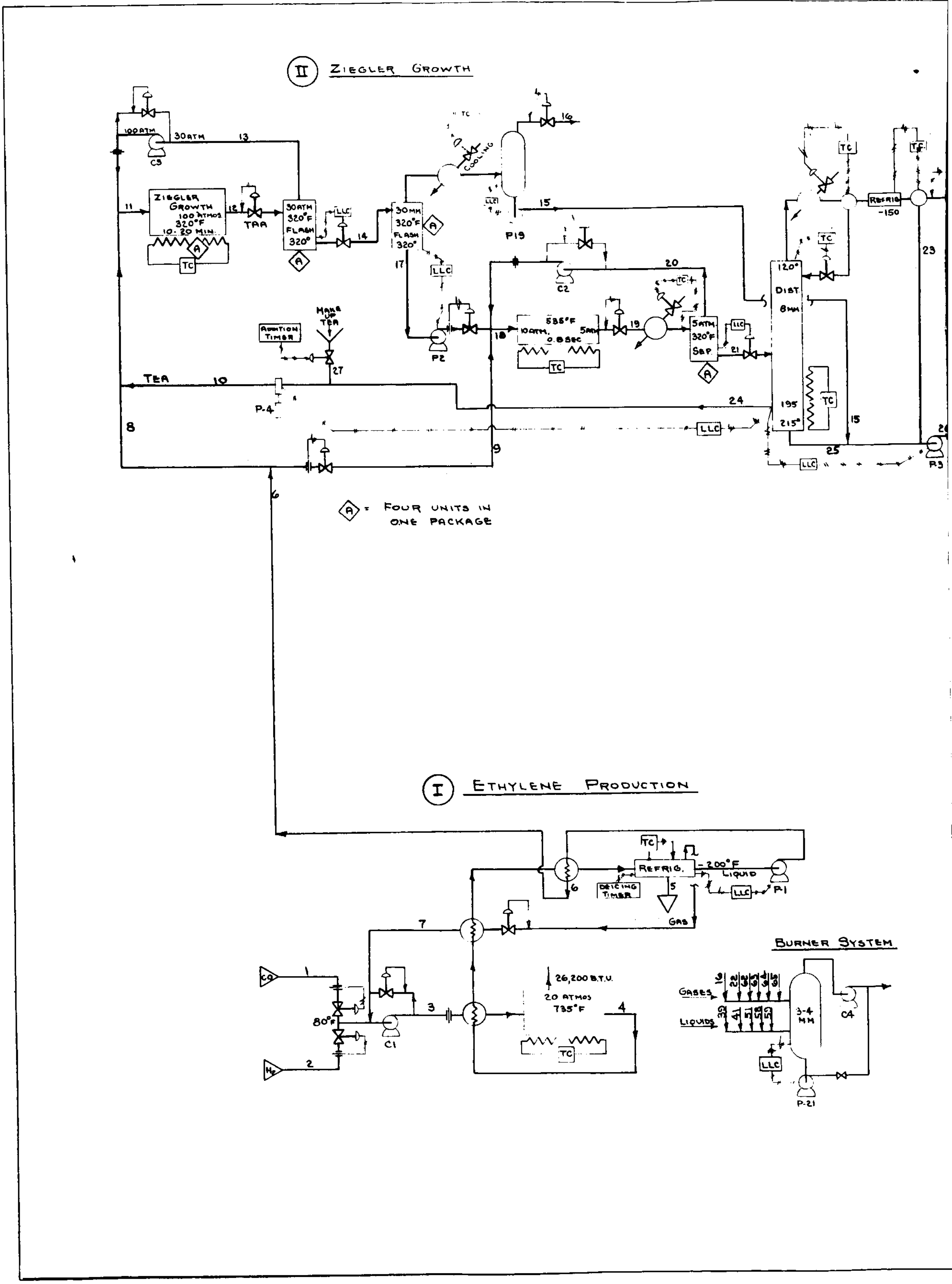

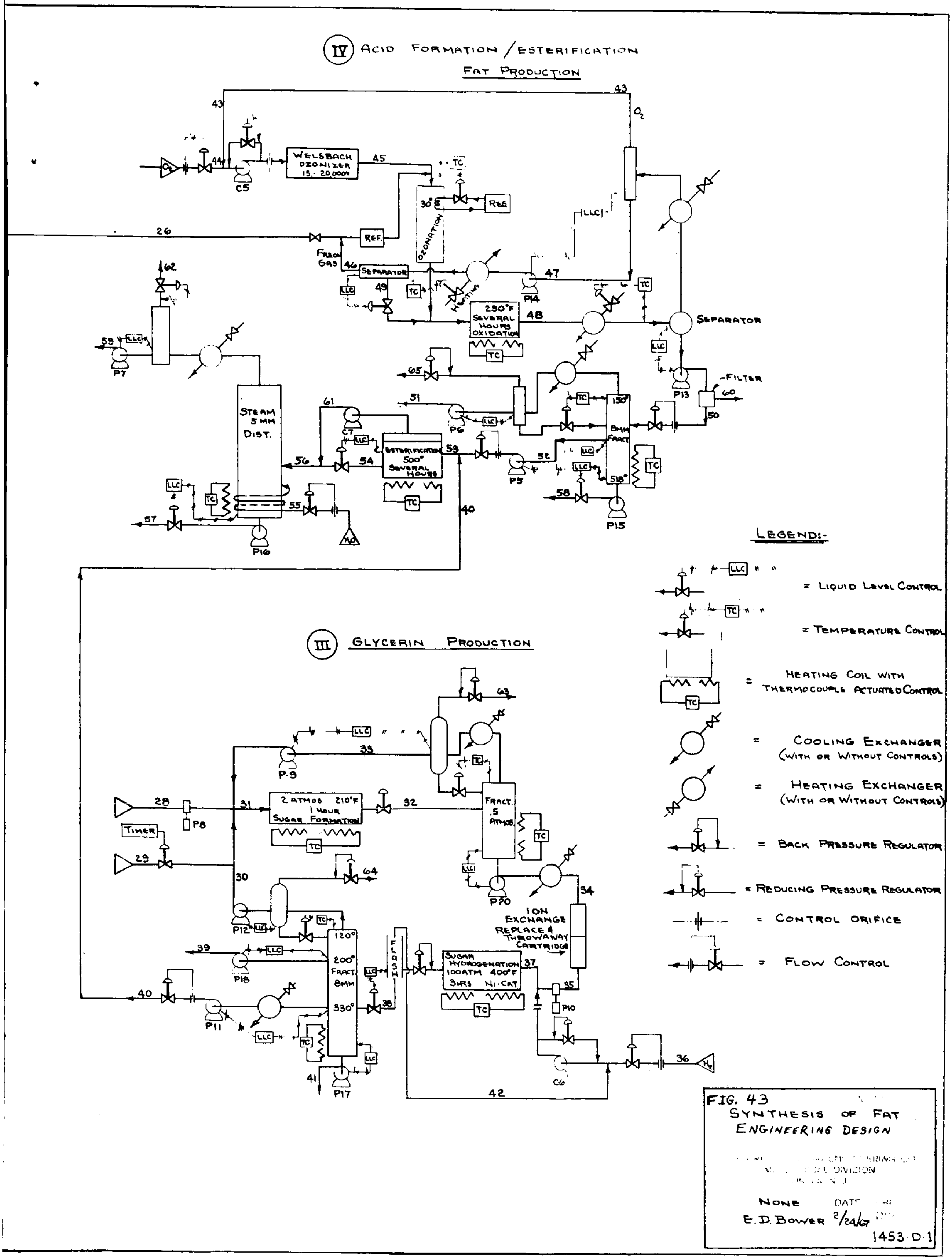

FIG. 43
SYNTHESIS OF FAT
ENGINEERING DESIGN

All Figures Given as lb./day

Process Stream	Appears in Part of Fig. 43	CO	H_2	C_2H_4	H_2O	TEA[2]	TAA[3]	C_{12}-C_{14} Olefins	C_2-C_{30} Olefins	HCHO	$Pb(Ac)_2$	Sugars	Glycerol Residue	Glycols	Glycerol	Al_2O_3	O_2	O_3	Freon 11[5]	C_3-C_{29} Acids	Acid Residue	Pure Fat	Fat Over-Head	HCO_2H
1	I	10.50																						
2	I		1.51																					
3	I	28.80	1.54	0.038																				
4	I	18.30	0.034	5.22	6.66																			
5	I				6.66																			
6	I, II			5.22																				
7	I	18.30	0.034	0.028																				
8	I			4.49																				
9	I			0.73																				
10	I					0.98		~1.5																
11	I			6.74		0.98		~1.5																
12	I			2.30			5.43	~1.5																
13	I			2.24																				
14	I			0.056			5.43	~1.5																
15	I						0.060	~1.5																
16[4]	I, II			0.056																				
17	II						5.37																	
18	II			9.55			5.37																	
19	II			8.81		0.96	0.050		5.07															
20	II			8.81																				
21	II					0.96	0.050		5.07															
22[4]	I, II			Tr.																				
23	II								~0.87															
24	II					0.96		~1.5																
24	II						0.050		2.70															
26	II, IV						0.11		5.07															
27	II					0.02																		
28	III									1.28														
29	II										0.022													
30	II				1.70																			
31	II				13.4					1.49	0.022													
32	II				11.7					0.21	0.022	1.28												
33	II				11.7					0.21														
34	II				1.7						0.022	1.28												
35	II				1.7							1.28												
36	II		0.030																					
37	II		0.060		1.7							1.28												
38	II				1.7								0.37	0.22	0.72									
39[4]	I, III													0.22										
40	III, IV														0.72									
41[4]	I, III												0.37											
42	III		0.030																					
43	IV																41.07							
44	IV																42.77							
45	IV																41.50	1.27						
46	IV																		30.00					
47	IV				12.5														40.00					50.00
48	IV				12.5											0.01	41.07		40.00	4.98	0.89			51.0
49	IV				12.5														10.00					50.00
50	IV																			4.98	0.89			1.00
51[4]	I, IV																							1.00
52	IV																			4.98				
53	IV														0.72					4.98				
54	IV																					5.00	0.29	
55	IV				0.50																			
56	IV				0.42																	5.00		
57	IV																					5.00		
58[4]	I, IV																				0.89			
59[4]	I, IV				0.32											0.01							0.29	
60[6]	IV																							
61	IV				0.42																			
62[4]	I, IV				Tr.																			
63[4]	I, III				Tr.																			
64[4]	I, III				Tr.																			
65[4]	I, IV				(trace non-condensables)																			

(1) Numbers correspond to those in Figure 43.

(2) Triethylaluminum.

(3) Trialkylaluminums.

(4) By-product streams to be burnt.

(5) Fluorotrichloromethane (duPont).

(6) Make-up fresh.

(7) By-product to be discarded.

Table 54 - Material Balance for Fatty Glyceride Synthesis

NUTRITIONAL EVALUATION OF SYNTHETIC FATS

The importance of the fats to nutrition has always been considered to be principally as an energy source. Until recently, the type of fat, or, more specifically, the nature of the fatty acid with the exception of the so-called essential fatty acids, and polyhydric alcohol moiety was not considered of importance. Current opinion, however has begun to emphasize other factors in the utilization of fats above and beyond those associated with energy. For example, the nature of the dietary fat has been shown to influence cholesterol transport and thus presumably play a role in the development of artherosclerosis. Chain length has been shown to determine rates of oxidation and thus usefulness of the fatty acid. At the subcellular level, the nature of the fatty acid has been shown to play an important role in the maintenance of the molecular mechanisms associated with energy metabolism, i.e. ATP and electron transfer. Thus it is apparent that the fats play a unique role in metabolism and nutrition and that this is not only related to the energy function and the fat soluble vitamin transport function of these nutritional factors but to many other more fundamental subcellular functions.

To understand the possible role of synthetic lipoid material and their possible significance in human nutrition, it is first necessary to develop some concepts of the basic role of the fats in nutrition and the ways in which they are metabolized. Moreover, the interrelationship of the fats with each other and with other dietary constituents must also be recognized. Finally the potential toxicity of the synthetic lipid mixtures must be evaluated. The following review is not meant to be exhaustive but rather it attempts to define the problems associated with the use of synthetic fat mixtures.

The Nutritional Importance of the Fats

In a classic paper(266), Burr and Burr demonstrated for the first time that the fats had a specific nutritional function above that of an energy source. More recently(267) Deuel and his colleagues have reemphasized and expanded this positive significance of the fats. For example, not only is the time of sexual maturity delayed(268) in rats fed a low-fat diet, but there is also a decreased fertility and increased neonatal mortality(269). Work capacity(270) and resistance to cold(271) are also influenced by the level and type of dietary fat. Many other examples can be given but it is apparent from these few that the fats have many different physiological roles other than those associated with energy.

The interrelationship of the fats to other nutrients has also been well defined. In an extensive review, Munro(272) concluded that the fats had a specific sparing action on nitrogen retention and that this action, while in large measure could be associated with the energy density of the fats, had components specific for the fats. The thiamine sparing action of the fat is well known and dates from the early classic experiment of Evans and Lepkovsky(273). This work has never been challenged and represents an important factor in considering fat levels in diets. A number of reports have appeared in the literature which indicates that the level and type of fat in the diet can markedly influence the utilization of calcium and vice versa(274, 275). Similar relationships (but less clear) can be found for other dietary constituents.

The specific action and interrelationships among the fatty acids have also been demonstrated to be of importance. At the subcellular level, a number of papers have emphasized the varying ability of the fatty acids to cause mitochondrial swelling and to influence ATP synthesis. For example, medium chain length fatty acids (C_{10}-C_{14}) decrease the lag phase in this phenomena(276) while in another study(277) unsaturated, medium chain length fatty acids were shown to produce the greatest swelling of mitochondria. This is important when one considers the fact that the phenomena of swelling is a necessary precursor of electron transport. Confirmation of this has been reported(278) in a paper which demonstrated that long chain acids tended to inhibit the synthesis of ATP while medium chain acids tended to stimulate the synthesis. Further evidence for the importance of chain length of fatty acid is obtained in a series of papers involving whole animal studies. Alfin-Slater et al(279) concluded that several metabolic pathways and physiological responses affected by essential fatty acid deficiency can be modified by the type of non-essential fatty acid present in the diet with the greatest detrimental effect produced by short chain acids. Similar results were obtained by Kaunitz et al(280) who concluded that long chain fatty acids increased essential fatty acid requirement while medium chain acids did not. These authors also reported(281) that the beneficial effect of triglycerides on body weight can be correlated with the melting point of the fat involved with the peak effect by fatty acids in the C_{10}-C_{15} range. Similar beneficial results of medium chain acid use has been noted in humans by Uzawa et al(282). Not much additional data is available in human subjects. Van de Kamer and Weijers(283) reported that smaller chain length acids and those with significant unsaturation were absorbed more readily than other types of fatty acid. In contrast, Dawson et al(284) claim that greater absorption was noted with long chain acids than with short chain and that "n" homologs were absorbed more readily than "iso" homologs. To make matters more confusing Schwabe et al(285) using C^{14}-labeled octonoate report no difference in the rate of utilization between rats and humans in contrast to the previous report. Some of these differences may be explained by the report of Spining et al(286) who demonstrated that feeding free fatty acids and methyl esters of fatty acids produced pathological tissue changes as well as decreased adsorption patterns when compared to triglyceride feeding.

In summary, therefore, it is apparent that there is a specific quantitative need for lipids in the diet. Moreover, the type and quantity of fat in the diet can influence the requirement and utilization of other nutrients. In addition, optimum utilization of the fats themselves require a specific pattern of fatty acids presented in a specific form and not as free fatty acids or methyl esters. Thus, any consideration of synthetic fats must keep these requirements in mind.

The Metabolism of Fatty Acids

The metabolism of fatty acids has been reviewed by Deuel(287). In general, the even carbon fatty acids are oxidized sequentially into two carbon acetate fragments. These, in turn, after being combined with oxaloacetate to form citrate are oxidized to carbon dioxide, water and energy. If, for some reason, the final oxidative steps are inhibited, the two carbon fragments accumulate and recombine to form acetoacetate which in turn forms acetone or beta-hydroxy-butyric acid, the ketone bodies. The rates of oxidation of each fatty acid has been reported to be a function of chain length(288). This, however, may also be due to differential rates of absorption as well as rates of oxidation. A somewhat different pattern occurs when the fatty acid has an odd number of carbons. In this case the terminal oxidation gives rise to a three carbon propionate fragment which, in turn is metabolized to succinate. In this way it enters the Krebs cycle and can be used to form glycogen. The three carbon fragment is not ketogenic and will not form ketone bodies. The metabolism of propionate has been reviewed in detail by Kaziro and Ochoa(289). The metabolism of branched chain fatty acids is somewhat more difficult to interpret. Coon et al(290, 291) studied the metabolism of alpha methyl butyric acid in rat liver slices. Their results showed that carbons 3 and 4 contribut to acetoacetate production while the residue is converted to propionate. Furthermore, they demonstrated that the beta-oxidation of the molecules proceeds down the main chain without oxidation of the alpha methyl group. Tryding and Westoo(290-293) performed similar studies with alpha methyl substituted stearic acids. Their results indicated that the branching did not affect adsorption and distribution of the fatty acids. In contrast, when the branching consisted of dimethyl substitution on the alpha carbon, beta-oxidation was inhibited while no effect was noted with monomethyl substitution. When substitution on the beta carbon occurs(294) or when the branch is more than one carbon in length(295), beta oxidation is inhibited. The urinary products of such substitution include dicarboxylic acids and glucouronides of the compounds administered.

It would appear therefore that the presence of an odd number of carbons or mono-methyl substitution in the alpha methyl position does not significantly inhibit beta-oxidation. Moreover, such compounds give rise to propionate rather than acetate and thus are glycogenic rather than ketogenic, a characteristic of great value.

The Utilization of Synthetic Fats

During the past twenty years a great deal of work has been done in attempting to produce utilizable fats from petroleum by-products. Most of this work is German in origin and suffers, at least in the nutritional and physiological studies, from a lack of proper control, poor analytical methods and statistical analysis. Thus, it is difficult to interpret the results of these studies and to draw meaningful conclusions from them. The following comments, however, represent an attempt to do so.

Most, if not all of the pertinent literature has been reviewed(296). The product produced by the Fischer-Tropsch process consists of at least 50% odd carbon fatty acids and a small proportion of iso and branched chain acids. In addition, these products also contain significant amounts of hydroxy, keto and dicarboxylic acids as well as alcohols and ketones. It is no wonder, therefore, that these products produce toxic effects when fed and, at least, a reduction in caloric density of the product. It is claimed however that by judicious selection of catalysts and production parameters, many of the deleterious products can be removed. In spite of this, however, careful work with these products has indicated (297) that only up to 10-20 g a day can be tolerated by the human. Other work in animals tends to confirm this finding. What is clear however is that these products must be better defined and their composition controlled before meaningful evaluation of their potential can be made. It is interesting to note that a paper reporting the use of mannitol as a substitute for glycerol in triglycerides was published in 1919(298). These authors report that such synthetic fats were as well utilized by the rat as natural fats.

Summary of Requirements for Dietary Fat

The data available thus far is clear on the specific dietary requirement for fat. Not only does there appear to be a need for fat itself for specific metabolic function but the nature and amount of fat in the diet can determine the need for a number of other nutrients. The nature of the fat used is also of significance. The data appears to indicate that, in addition to the essential fatty acids (linoleic, linolenic and arachadonic), the medium chain fatty acids, C_{10}-C_{14} are best utilized. Moreover, the extent of unsaturation also appears to play a role. In addition evidence is available which indicates that free fatty acids and methyl esters of these acids are not well utilized. The evidence is also clear that odd carbon fatty acids are also utilized. Moreover, there may be some advantage in the use of these compounds in that they tend to be glycogenic rather than ketogenic. When branching is considered, only branches of one carbon on the alpha position of the fatty acid apparently can be tolerated. Branches of greater size or in the beta position tend to inhibit oxidation. The data available thus far on synthetic fats is not good. Contamination with branched chain, keto, hydroxy and dicarboxylic acids tends to lower the utilization of these products. Unfortunately, pure products of this type are not yet available.

Thus it would appear that any synthetic fat should have the following characteristics:

(a) The fatty acids should be mostly of chain length C_{10}-C_{16}.

(b) They should be fed as triglycerides or esters of higher alcohols.

(c) At least 1% of the total fat should be essential fatty acids.

(d) Odd carbon number acids can be tolerated but the level of branching and other types of substitution must be low and well controlled.

(e) Although the extent of unsaturation of these acids does not seem to be of first importance, some degree of unsaturation is desirable although excessive amounts can cause problems of autoxidation

Theoretical Evaluation of Product from the Ziegler Reaction

In the process based on the Ziegler reaction (Table 53) the distribution of fatty acids is such as to provide a significant peak at C_{11} to C_{21}. This distribution is satisfactory when compared to the hypothetical requirements suggested above. On the other hand, these are all odd carbon fatty acids for which there is another problem. Although the data suggests that the feeding of odd carbon fatty acids produces no deleterious effect, no long-term studies in which these fatty acids were fed at high levels in the diet have been done. The basic question involves the capability of the enzyme systems converting propionate to succinate to handle this load. If this was possible, the use of odd carbon fatty acids may prove valuable in reducing the carbohydrate requirement in that propionate is glycogenic and odd carbon acids would, in effect, carry their own carbohydrates. A more serious problem exists when contaminants are considered. About 1-2% of the fatty acids produced are branched. Depending upon the position and nature of the branching, the possible toxic and inhibitory effects must be considered. Also, around 10% of the fatty acids are oxy and keto acids, certain of which are known to be toxic. Problems due to other possible contaminants such as catalysts and solvents are difficult to evaluate at this time. There is no question, however, that, from a metabolic point of view, synthetic fatty acids of the pattern suggested by the Esso Research group could probably be utilized in a normal diet. However, before such use is contemplated a great deal more information would be required. If, for example, it could be determined that odd carbon acids could, in fact, be utilized for extensive periods of time, then some means of removing branched chain and other substituted acids would probably have to be developed. In addition, it must not be overlooked that these fatty acids would of necessity have to be fed in the form of polyhydric alcohol esters since, as discussed earlier, free fatty acids and monoesters of methanol are relatively toxic. Thus it would appear that, while the product proposed above is a good start towards a synthetic fat, much more information is required before any reasonable evaluation of the product in terms of nutrition and metabolism can be made.

Suggestions for Research

As indicated in the earlier sections of this report, much more information is needed for the evaluation and design of new products. This work must of necessity include better controlled and more detailed investigations of the specific needs and more detailed investigations of the specific needs for fatty acids, i.e., whether or not a specific group of fatty acids such as the medium chain length acids can substitute for the whole spectrum of naturally occuring fatty acids. Moreover, the importance of unsaturation must also be determined since a completely saturated product offers some advantage in terms of product stability and storage. For the odd carbon fatty acids, some emphasis must be placed in determining the extent to which they can be used in terms of amount and time of exposure. At this point, such data is not available and is required before any use of them can be made. The question of branching also has to be settled since at this time, the amount of branched chain acids that the organism can tolerate is essentially unknown. Finally, some thought must be given to the nature of the compound with which the fatty acids must be esterified. For example, other, simpler polyhydric alcohols such as 1,3 butanediol may be of use in this problem since the synthesis of such compounds may prove easier than that of glycerol. It must be remembered, however, that the use of such compounds would develop other problems.

Conclusions

The development of procedures to synthesize fats involves criteria in addition to those of chemistry and engineering. The fats have a unique and specific role in nutrition and metabolism. The need for these dietary constituents is not only quantitative but also qualitative demanding specific patterns of fatty acids presented to the organism in specific ways. The inability of any process to deliver the pattern will be reflected not only in an increased need for fat but also in abberations of utilization of other nutrients. Moreover, the presence in the fat of potentially toxic compounds of low utilization offers additional problems. On the other hand, there is a distinct possibility of providing new forms of fat of greater efficiency of use such as the odd carbon fats as well as developing new compounds which may ultimately provide a new base for nutrition. Thus, this work has importance greater than that of providing a synthesis of a natural product and on this basis must be considered of vital importance.

CONCLUSIONS

The synthesis of fatty acids and lipids from simple waste materials such as CO_2 appears feasible chemically. Of a large number of candidate methods, the Ziegler growth reaction of ethylene to give α-olefins followed by oxidative ozonolysis to acids appears to be the most feasible. Only by this route can reasonable selectivities to materials having desirable properties be obtained. However, from the engineering standpoint, the synthesis of fatty acids appears to be very complex and not to be considered seriously as a source of food on board a spacecraft.

The food value of synthetic fats has not been fully established; considerable contradictory evidence is available. However, indications are good that such materials, if sufficiently free of undesirable impurities, are non-toxic and may be nutritionally useful. Synthetic fats might be used to provide 50-60% of the total calories in spacecraft diets. Fats are the most efficient sources of calories on a weight basis and are highly acceptable and satisfying as foods.

The synthesis of glycerol is considerably less complicated. The estimated power requirement, 800 watts for 10 lbs. of glycerol (20,000 Kcal) is only about 1/3 of that required to produce 5 lbs. (20,000 Kcal) of fats. Consequently, glycerol synthesis appears feasible. Several methods are available. The most promising involve polymerization of formaldehyde followed by hydrogenation or hydrogenolysis of the sugars obtained. Natural glycerol is a promising nutrient, at least in mixed diets. The value of synthetic glycerol, which may contain ethylene and propylene glycols remains to be established.

Regardless of the type of material selected, considerable additional research will be required. In the case of fatty acids, the most pressing needs are engineering and nutritional studies; for glycerol synthesis research into the chemistry of the system is also indicated.

Finally, it must be pointed out that, on any permanent or semi-permanent installation, such as an orbital laboratory or a moon base, especially where there may be partial gravity, the process would become more attractive. For such applications the advantages of fats as food, appetite satisfaction and resemblance to natural materials might be of considerably greater importance.

RECOMMENDATIONS FOR FURTHER RESEARCH AND DEVELOPMENT

Based upon the results of the literature survey described above and upon the best judgment of all who have been involved in this project, the following suggestions for further research and development are offered. After some general comments, more detailed recommendations are made concerning each of the various aspects of fatty acid and glycerol synthesis. These are only summarized. The rationale governing the suggestions should be clear from the preceding suggestions.

General

The synthesis of compounds, modeled after natural fats, from CO_2 on board a spacecraft is not recommended. Although the chemistry appears sound and power and weight requirements are not excessive, the complexity and questionable reliability of such a process combine to make the probability of success in a fail safe completely automated system extremely small. Consequently, it would be preferable to devote research efforts and funds to investigations of other systems. A more rational approach would be to synthesize lower molecular weight compounds (e.g., glycerol, butanediol, sugars or glycerides of lower acids) where the processes are simpler and the possibilities of undesirable isomers greatly reduced.

The synthesis of glycerol from CO_2 is especially recommended. Glycerol is promising nutritionally and any reasonable route is much less complex than fatty acid production.

Any chemical process will have several unit processes in common. In the opinion of the engineers involved in this study, the best approach to solving engineering problems would be to work out the unit processes, including equipment design and testing under zero gravity conditions, separately rather than trying to engineer an entire system. In fact, the results of such studies might have considerable bearing on the choice of the system.

Synthesis of Glycerol

This is recommended as more feasible than the synthesis of fatty acids. Four methods show promise:

(1) Direct hydrogenation of carbon monoxide
(2) Synthesis from acetylene and formaldehyde
(3) Trimerization of formaldehyde
(4) Hydrogenolysis of carbohydrates

Methods (3) and (4) are most highly recommended; (1) is simple but poorly documented and gives considerable ethylene glycol; (2) involves several steps and requires a large energy input.

There is little to choose between (3) and (4). Both involve condensation of formaldehyde and hydrogenation of the products to glycerol. In the trimerization reaction, the major problem lies in stopping the condensation at the three carbon (glyceraldehyde or dihydroxyacetone) stage. A wide variety of catalyst combinations are possible for this reaction. Almost any compound of the "enediol" type in conjunction with an alkaline earth hydroxide is effective so that considerable research in catalyst selection is indicated. The mechanism of the formaldehyde condensation is not clearly understood. Many variants have been suggested. Consequently, a brief mechanism study is recommended. Based on the results of this study, the development of a successful synthesis of three carbon sugars might be based on:

- A physical separation by selective chelation or precipitation of the three carbon compounds as formed
- Proper catalyst selection to promote triose formation
- Reducing the reaction rate sufficiently to permit controlled addition of formaldehyde

It appears preferably to search for methods to go directly to the triose rather than to form glycol aldehyde and then add a third mole of formaldehyde.

Hydrogenolysis of carbohydrates (method (4)) may have some slight advantage over the trimerization reaction. This is the fact that three carbon fragments are distinctly favored in chain splitting reactions. The major impurities found are the relatively non-toxic propylene glycols rather than ethylene glycol which is encountered in the trimerization method. Relatively little is known about its hydrogenolysis reaction so that a fertile field for further study exists. Again a wide variety of catalyst and reaction conditions are possible and seem to have a great effect on yield and product distribution. Research is recommended on:

- Kinetics
- Catalyst composition
- Hydrogen pressures and temperatures
- Solvents
- Product isolation and purification

Finally, the reaction must be verified on crude sugar mixtures. Most reported experiments employed a single, pure hexose. It should be noted that the possibility exists of integrating this process with the synthesis of edible carbohydrates. After separation of the edible portion, the remainder might be hydrogenolyzed to glycerol.

Synthesis of Fatty Acids and Glycerides

Despite the difficulties expressed above, it is recognized that, if other, simpler methods fail, this area may require further consideration. Consequently, some specific recommendations will be made. In general, the problems, and they are formidable, are ones of engineering rather than chemistry. The chemical aspects of each step of the most promising synthesis are well worked out (with the possible exception of ethylene synthesis) and extensive additional research would not be needed.

Reduction of Carbon Dioxide

The electrolytic reduction of CO_2 has been carefully worked out by the Air Force and reduction by hydrogen in a silent and glow discharge by NASA. The latter is simply the reverse water gas shift reaction which, in the present study, was deemed the most promising of the methods examined. There appears to be no need for a great deal of additional work in this area.

Reductive Polymerization of Carbon Monoxide

The only feasible, documented, method is the Ziegler growth reaction. The foregoing statement is qualified by the few reports, in patent art, of the direct synthesis of alcohols by the Fischer-Tropsch reaction with ruthenium catalysts in hydroxylic media. This work is not convincing but it cannot be ruled out and, if fatty acids must be synthesized, it is recommended that the ruthenium route be examined further. The Ziegler reaction, on the other hand, is extensively documented. High yields of linear compounds, nearly 100% of which is in an acceptable molecular weight range may be expected. It is recommended that the displacement reaction with ethylene be used to produce α-olefins. Although this adds a step, it preserves the catalyst, the loss of which appears to be prohibitive. Any method which yields alcohols or acids directly from the aluminum alkyls would destroy the catalyst. The basic parameters for the Ziegler reaction have all been established. The only further work envisioned would be in equipment design and testing and in nutritional evaluation.

For the synthesis of ethylene the direct hydrogenation of carbon monoxide is recommended. An alternate route is the pyrolysis of methane to acetylene followed by selective hydrogenation. The direct route is simpler and requires much less energy. Selectivities of 80% at 36% conversion have been claimed for this reaction. It appears that higher selectivity is possible at lower conversion. The catalysts used are complex and some further research is indicated to find the best ones.

Conversion of Olefins to Acids

The recommended procedure is ozonolysis followed by oxidative cleavage of the ozonide. Direct oxidation of the olefin is so non-selective that its inherent simplicity is outweighed by the complicated recovery scheme. The ozonolysis reaction requires research for proper choice of conditions and solvent. The freons are potentially useful as the inert medium required to dilute the ozonide. The oxidative cleavage of the ozonide should be investigated in order to avoid using a non-regenerable oxidant. Air or oxygen with a trace of ozone is the simplest but performic acid gives the best results.

Ozonolysis leads to strictly odd-carbon acids. If nutritional testing indicates these are unacceptable, epoxidation and rearrangement of the Ziegler olefins or direct synthesis of even-carbon alcohols (by oxidation of the aluminum alkyls) represent the most promising alternatives. They would, of course, yield exclusively even-carbon acids.

Glyceride Formation

This step should not prove difficult. The Germans used zinc dust as a catalyst and this is superior to acids which often give colored products. It appears, however, that no catalyst is necessary. Numerous reports of successful esterification under conditions of high temperatures and low pressures (to drive off water) have been found. Some work on the refining of the products will be necessary, however, Glycerides are difficult to purify.

Engineering Recommendations

This area requires an immense amount of work if the fatty acid process is to be used. It is recommended that development of certain unit processes, common to any chemical synthesis, be completed before an attempt is made to engineer the entire system. These include:

- Fractionation under zero gravity conditions.
- Other gas-liquid separators ("knock-out" units).
- Compressors developing high pressures at low rates.
- Multi-phase heat exchange equipment.
- Pumps which can handle very small amounts of materials at reasonable power efficiencies and which have long life times.
- Liquid level sensors (controls).

As far as the system as a whole is concerned, instrumenting and automating the process present extremely difficult problems. Because of the external controls required, it is not recommended that the entire unit be spun to create an artificial gravity field. Certain portions of it, however, especially fractionators, might have to be rotated.

Nutrition

A considerable effort will be necessary in nutritional evolution irregardless of which system is chosen for further study. The nutritional value of synthetic fats has not been firmly established. The German work indicates they are non-toxic if carefully refined and fed in a mixed diel but considerable controversy exists as to their actual food value. In the case of synthetic glycerides, therefore, testing would be necessary to establish:

- Acute and long range toxicity of the mixture actually obtained.
- Nutritive value and metabolic fate of odd-numbered fatty acids.
- Limits of toleration of branched chain and oxygenated acids.
- Molecular weight range of acceptable materials.
- Maximum levels at which the synthetic material may be incorporated in the diet.

For glycerol synthesis, special attention must be given to the effects of varying amounts of propylene and ethylene glycols on the toxicity and nutritive value of the product. The maximum tolerable levels of these impurities would play a considerable part in designing the synthetic process.

Acceptance

It has frequently been pointed out that this may be the ultimate limiting factor in utilization of synthetic foods. Considerable research is recommended in formulation of synthetic foods to approximate customary diets as closely as possible. The combination of fats and high-protein materials into "baked" goods of pleasing flavor and consistency is one intriguing possibility.

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