NASA CONTRACTOR REPORT

NASA CR-1104

NASA CR-1104

FACILITY FORM 602

(ACCESSION NUMBER)

(THRU)

(PAGES)

(CODE) 01

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

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

Final Summary

GPO PRICE $ ________

CFSTI PRICE(S) $ ________

Hard copy (HC) [redacted]

Microfiche (MF) [redacted]

ff 653 July 65

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

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1968

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Final Summary

Edited by John W. Frankenfeld

Prepared under Contract No. NAS 2-3708 by
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ACKNOWLEDGEMENT

The authors wish to express their appreciation for the assistance provided by Dr. Jacob Shapira of the Environmental Control Branch NASA/Ames. In addition valuable suggestions were received from Dr. E. Gilliland of M.I.T. and Drs. W. R. Kroll and J. Livingston, both of ESSO Research and Engineering Company, and are hereby gratefully acknowledged.

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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.	Energy Expenditure: 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.

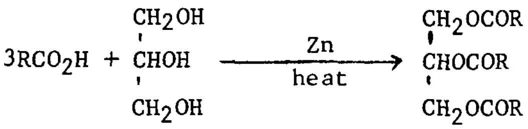
Historical - the German Process

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) $nCO + 2nH_2 \xleftrightarrow{\text{cobalt}} C_nH_{2n} + nH_2O$ 5-12%

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

(3)


$$3RCO_2H + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{heat}]{\text{Zn}} \begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array}$$ 80-90%

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).

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

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).

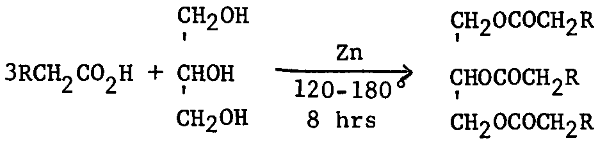
Acids	Boiling Range	Percent of Total
C_3-C_{10}	Up to 150°	7-15
C_{10}-C_{16}	150-240°	45-55
C_{10}-C_{25}	240-300°	2-5
Residue		5-20

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).



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

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.

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, Figures 2-4). 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.

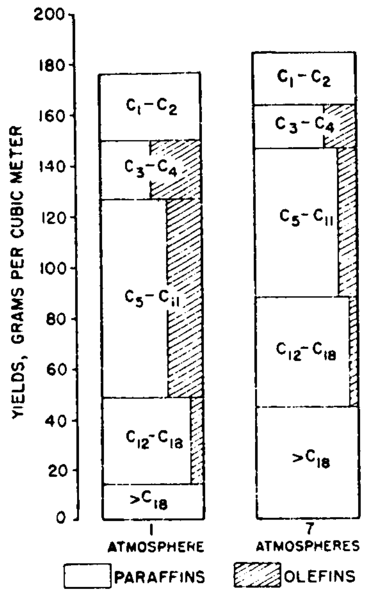
Catalyst	Temp. (°C)	Pressure (atm.)	Space-Time Yield[b] of C_{3+}, kg/cm^3/hr (bbl./1000 ft^3/day)	Liquid Product Distribution				Steel in Converter (ton/bbl/day)
				Gasoline	Diesel	Wax	Alcohol	
Ruhrchemie Process								
Co	175-200	1	8 (45)	56	33	11	[c]	2.7
Co	175-200	10	10 (57)	35	35	30	[c]	2.4
Lurgi 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.

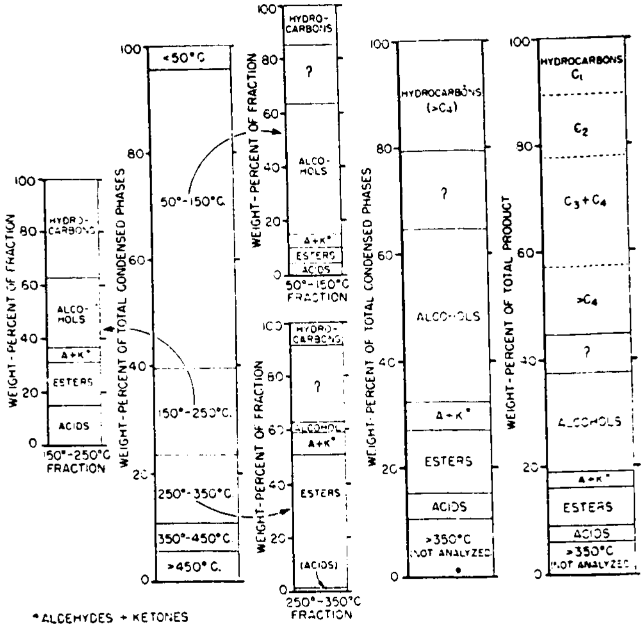
[c] Very small.

Table 7 - General Summary of Fischer-Tropsch Processes[a]



The C_1-C_2 and $>C_{18}$ fractions include small amounts of olefins.

2 - CO-ThO$_2$-MgO-Kieselguhr Catalyst



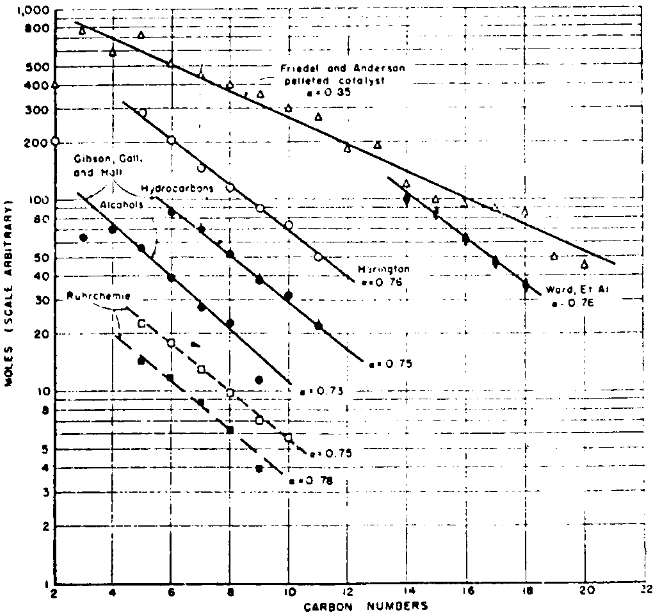
*ALDEHYDES + KETONES

A Distillation of condensed phases, exclusive of water, and composition of fractions

B Composition of condensed phases, exclusive of water

C Composition of total product, exclusive of water and carbon dioxide

3 - Nitrided Fused Fe$_3$O$_4$-Al$_2$O$_3$-K$_2$O Catalyst (a high oxygenate maker)



4 - Molecular Weight Range with Iron Catalysts

Figures 2-4 - F-T Processes Yield Complex Mixtures(33)

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 one 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 molecule 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:

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

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.

Effect of Reaction Variables and Type of Catalyst

Some partial generalizations on the effects of reaction variables are possible. These are illustrated in Table 8 and Figures 5-8. 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. 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. Formation of oxygenated products is favored by low temperatures and high pressures. Formation of olefin is favored by low pressure; temperature changes have irregular effects on olefin content of the product. 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. Iron also produces more oxygenated materials. However, these are of low molecular weight (e.g. ethanol). Either cobalt or iron catalyzed processes can be designed to give high yields of wax (up to 70%) but this is mostly hard, boiling above 450°C. The soft wax which might be used for fatty acid product runs to only about 20-30% of the total.

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). 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). Because of the expense involved ruthenium based processes have not been developed to the extent of cobalt or iron. However, the unusual properties of this type of catalyst suggested that it might be of special interest for spacecraft applications.

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 hydrogen 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 have been tested as F-T catalysts(49). Rhodium was the only other metal that was appreciably active. Difficulty-reducible metal oxides (thoria, CuO, Cr_2O_3 and Al_2O_3)have been examined. They require high temperatures and give primarily branched hydrocarbons.

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.

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 (alkalized 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.

The Fischer-Tropsch process has been researched so extensively that there seems to be little hope for finding a variant which might lead to useful intermediates. Examination of over 8,000 references in the Bureau of Mines Bibliographies (32) afforded no clues. Consequently the Fischer-Tropsch process is not recommended as a source of fatty acids or fatty acid intermediates on a spacecraft.

Catalyst: Composition Type Number	Fe_2O_3-CuO-K_2CO_3 Precipitated[b] P-3003.24		Fe_3O_4-K_2CO_3 Sintered[c] A-2101	A-2106.05	Fe_3O_4-MgO-K_2O Fused[c] D-3001			
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	20.0	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

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 8 - Effect of Operating Pressure on Activity and Selectivity in Fischer-Tropsch Synthesis(a)

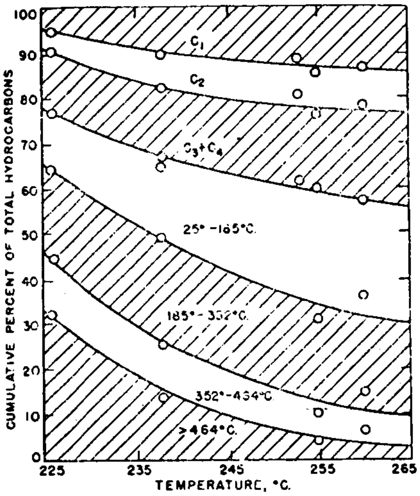


Figure 5 - Effect of Temperature on Hydrocarbon Distribution(33)

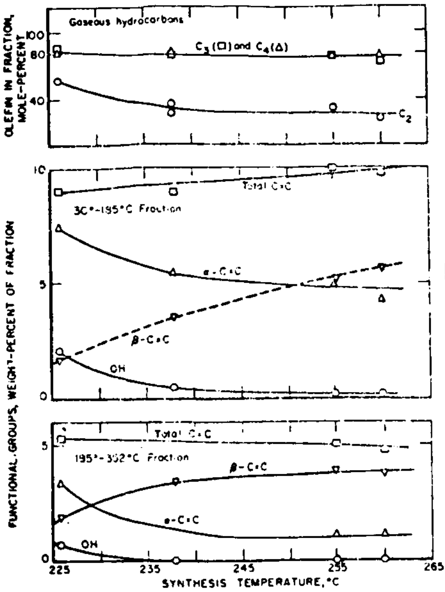


Figure 6 - Effect of Temperature on Functional Group Distribution(33)

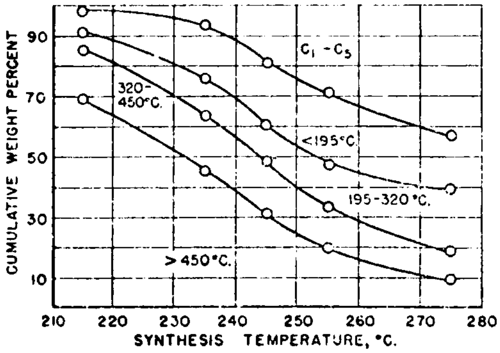


Figure 7 - Selectivity as a Function of Temperature with Precipitated Iron Catalyst, $1H_2 + 1CO$ Gas, Space Velocity 720 hr^{-1}, and 12 atm.(33)

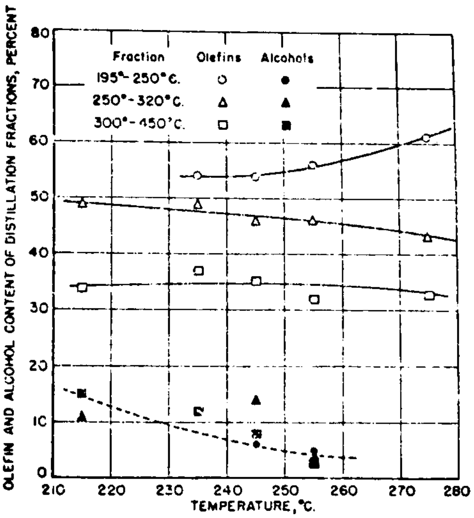


Figure 8 - Alcohol and Olefin Content of Distillation Fractions in Figure 9 (33)

Wax Cracking and Oxidative Dehydrogenation

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

$$RCH_2CH_2R \longrightarrow RCH{=}CH_2 + R'CH{=}CH_2$$

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 of 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. In addition, the molecular weight distribution of products is less favorable than that obtained by the Ziegler method (Figures 9 and 10). For these reasons, such processes were not given serious consideration.

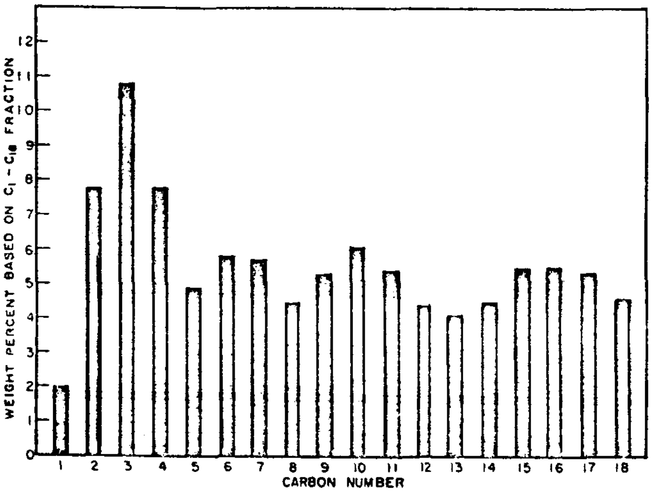


Figure 9 - Product Distribution from Typical Wax Cracking Run(80)

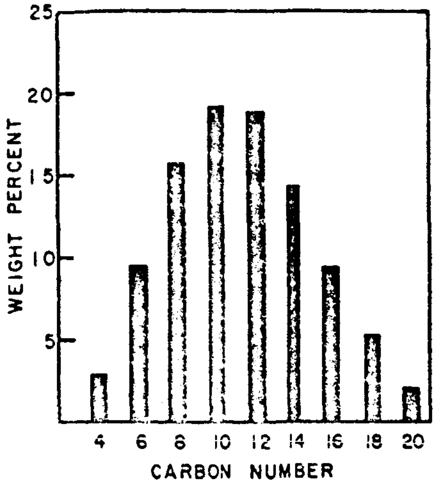


Figure 10 - Typical Distribution of α-Olefins from Ethylene Buildup (Ziegler)(80)

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.

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

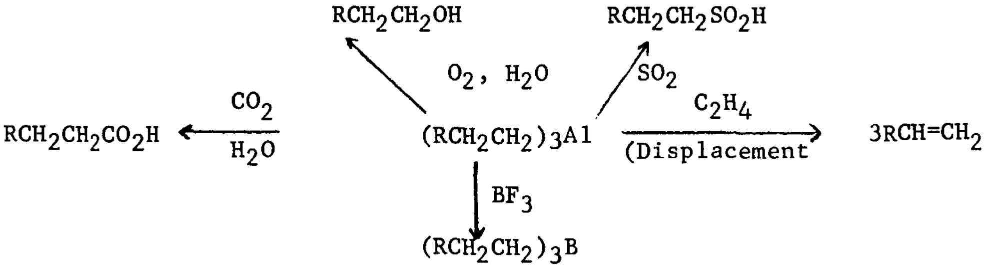
$$(2) \quad CH_2 = CH_2 \xrightarrow{Al\ (C_2H_5)_3} RCH = CH_2$$

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).



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):

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

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

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

$$\text{(d)}\quad nC_2H_4 \longrightarrow -(C_2H_4)_{\overline{n}}$$

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

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

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

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).

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

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

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 11. 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.

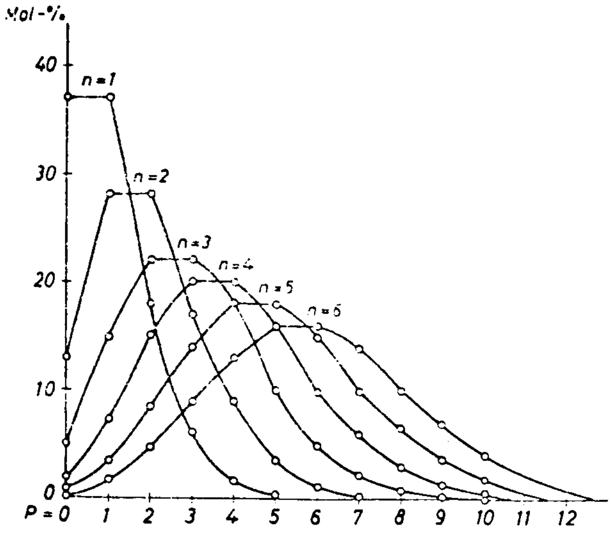


Figure 11 - Distribution of Alkyl Residues of the Form R-$(C_2H_4)_p$- on Aluminum in Growth Products from One Mole of R-Al and n Moles of Ethylene(78, 82)

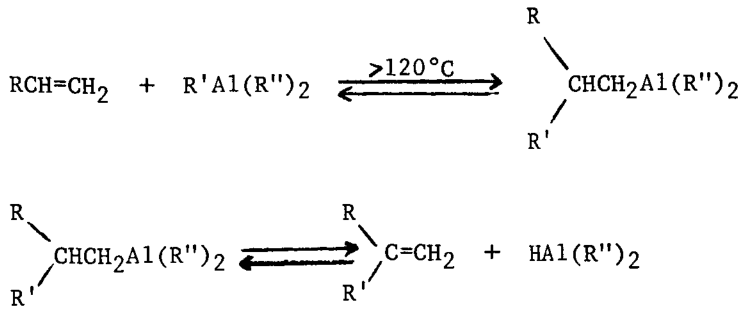
The Ziegler process as formulated above has two major drawbacks, (1) the growth reaction is very slow under the conditions shown (an hour is required to add one mole of ethylene to one equivalent of R-Al) and (2) the nickel catalyst employed in the displacement step greatly increases the recovery problems(76-83).

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).



$$RCH{=}CH_2 + R'Al(R'')_2 \underset{}{\overset{>120°C}{\rightleftharpoons}} \begin{matrix} R \\ \quad\diagdown \\ \quad\; CHCH_2Al(R'')_2 \\ \quad\diagup \\ R' \end{matrix}$$

$$\begin{matrix} R \\ \quad\diagdown \\ \quad\; CHCH_2Al(R'')_2 \\ \quad\diagup \\ R' \end{matrix} \rightleftharpoons \begin{matrix} R \\ \quad\diagdown \\ \quad\; C{=}CH_2 \\ \quad\diagup \\ R' \end{matrix} + HAl(R'')_2$$

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 12. 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).

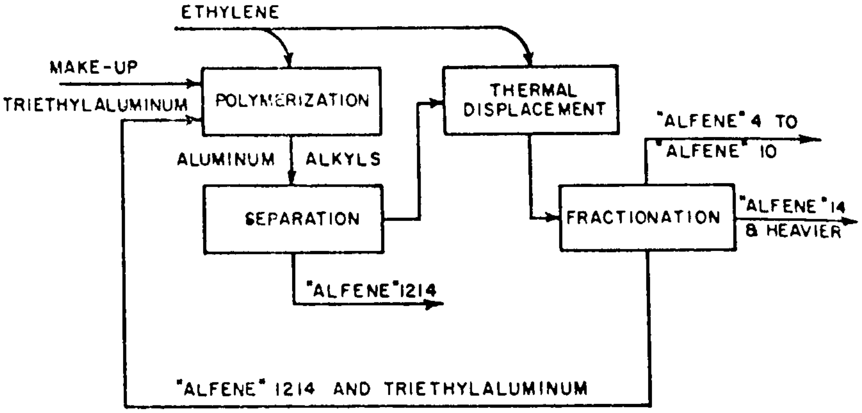


Figure 12 - Continuous Process for Production of α-Olefins via Ziegler Growth Reaction(80) ("Alfene" is α-Olefin)

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 $(\text{-}CH{=}CH\text{-})_n$ 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.

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

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

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

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 2200°F. The endothermicity of this reaction can be expressed by the following equation at 2258°F.

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

Complicating the whole situation are two further facts: methane does not begin decomposing to form acetylene until about 2250°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 2250°F or more, it is less stable than the elements, and so must be rapidly quenched to temperatures about 530°F 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. This 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. 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 can be used as synthesis gas. 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. 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. There are several minor differences in the advantage 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. 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, again, of the order of 2900°F. 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 over 6500°F. 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 gone commercial leading some observers to wonder about its utility(114). Acetylene has been observed in products of the action of silent discharge on various hydrocarbons. The silent discharge method is not considered a good process and has never been commercialized. In addition, methane is reported to be a poor feedstock. Better results are obtained with other light hydrocarbons(90).

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 2900°F, 100° 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(103).

Some data on the composition of product streams from various commercial acetylene processes is given in Table 9.

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 9 - 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 witn 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. Other catalysts have been described(111-113).

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, 133). 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).

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. Other reports have appeared(121-123). These workers used zinc and manganese as reducing agents.

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(124-133). 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). Akerloff has reported data on a modification of this process specifically designed for space applications(133).

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. This method recommends itself for spacecraft use. Chandler has worked out many of the details(116).

Conversion of Carbon Monoxide to Ethylene

$$2CO + 4H_2 \xrightarrow[\text{Heat, Pressure}]{\text{Cat.}} CH{=}CH_2 + 2\ H_2O$$

Under certain conditions, it is possible to achieve reasonable selectivity in the conversion of carbon monoxide 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. 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. 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.

Another Patent(138) issued in France and Austria, claims the preparation of ethylene from CO and H_2 over a partially reduced metallic catalyst. Data are sketchy. A product is claimed containing 95-100% ethylene (apart from inert gases).

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.

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.

Alumina gel is apparently inferior to silica gel if used alone, but is far more sensitive to the effects of promoters. Cu oxide, up to 3%, seems to be the best of the promoters.

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.

Tsutsumi also has a paper that appeared in 1956 in a Japanese journal,(143) 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. 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 <u>Table 10</u>.

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 10

DATA FROM PETERS PATENT ON CONVERSION OF CARBON MONOXIDE TO ETHYLENE

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.

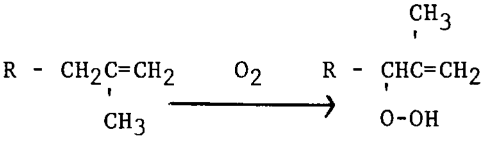
Oxidation of Paraffins

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

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 auto-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. Surprisingly the site of initial attack is allylic to the double bond:(145, 146, 148)



$$R - CH_2\underset{CH_3}{C}=CH_2 \xrightarrow{O_2} R - \overset{CH_3}{\underset{O-OH}{C}}HC=CH_2$$

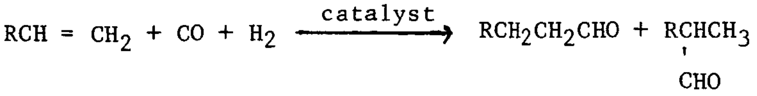
Gall investigated the air oxidation of olefins under conditions similar to those employed in paraffin oxidation and found significantly lower yields of the desired C_{10}-C_{20} acids(44).

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). In fact, about the only cases where the oxidation occurs cleanly are those in which the olefin contains no adjacent methylene groups. An example is the last step of the classical Barbier-Wieland degradation:(149)

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

The Oxo Reaction

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



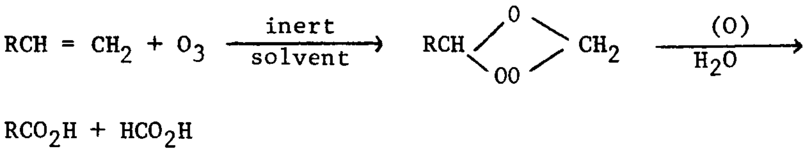
$$RCH = CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + \underset{\textstyle CHO}{RCHCH_3}$$

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 Oxo reaction, however, affords a high percentage of secondary aldehydes which would lead to undesirable branched-chain cacids. In addition, other by-products are formed including ketones, acids, acetols and polymeric compounds(163).

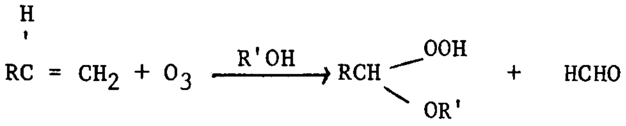
Ozonolysis

The most reliable method for degradation of an olefin to a carboxylic acid is ozonolysis followed by oxidative decomposition of the ozonide.

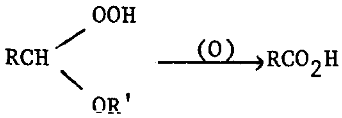


Ozone attacks the double bond selectively and no rearrangements occur. As a result this method is commonly used as an analytical tool for determining the position of double bonds(145, 153-157).

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



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



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

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. Ozonolysis is a very high yield reaction. Asinger obtained acids in 95-98% selectivities(156). 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.

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.

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 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

$$O_2 \longrightarrow 2O\cdot$$

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

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.

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

$$O^*_2 + O_2 \longrightarrow O_3 + O\cdot$$

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

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.

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

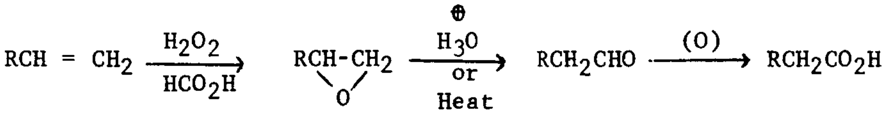
$$RCHO \xrightarrow[H_2SO_4]{KMNO_4} RCO_2H$$

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.

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

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.



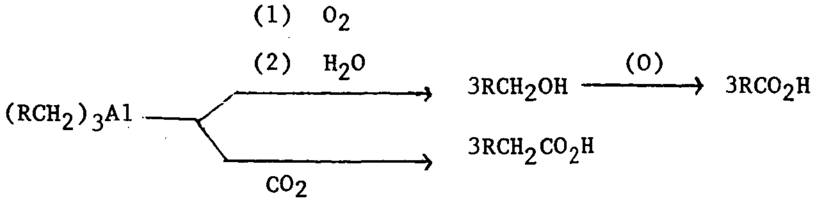
Such acids would correspond exactly to the Ziegler olefins and, hence would contain only even numbers of carbon atoms.

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).

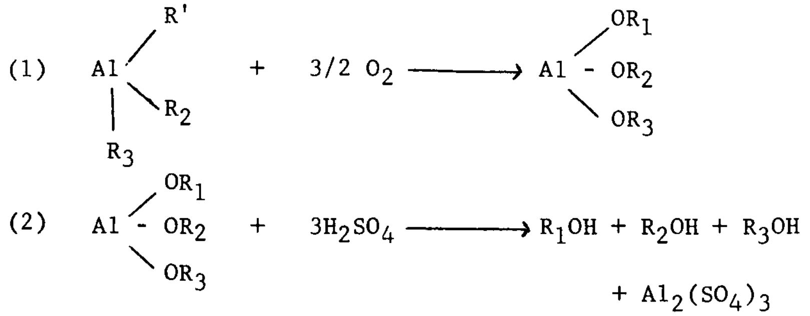
Oxides of α-olefins would be expected to yield aldehydes by analogy with earlier work(166, 168, 169). However, high molecular weight compounds (above C_3) have not been studied extensively and considerable amounts of ketones might also be formed.

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.



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:



Considerable processing is required. This sequence would have to be greatly 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:

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

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

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

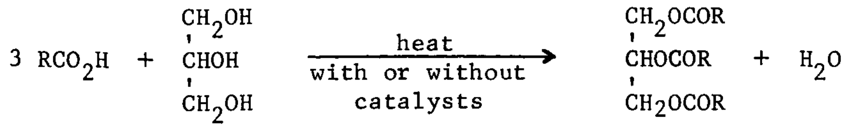
This sequence was examined and found to be too costly in terms of power, weight and complexity to be considered.

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. In addition Ziegler and others(175-178) have found that the maximum yields of acids by this process is 60% and then only under forcing conditions (see, especially, reference (178). However, the most serious objection is, again, the need to regenerate triethylaluminum from the salt.

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

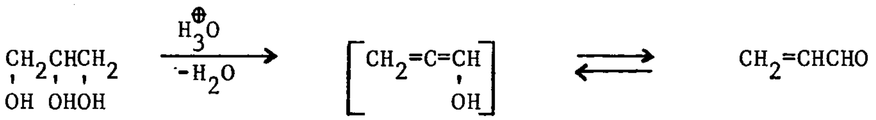


$$3\ RCO_2H + \begin{array}{l} CH_2OH \\ \,| \\ CHOH \\ \,| \\ CH_2OH \end{array} \xrightarrow[\text{with or without catalysts}]{\text{heat}} \begin{array}{l} CH_2OCOR \\ \,| \\ CHOCOR \\ \,| \\ CH_2OCOR \end{array} + H_2O$$

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, 186-191) 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:



$$\underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2} \xrightarrow[-H_2O]{H_3O^{\oplus}} \left[CH_2{=}C{=}\underset{OH}{CH} \right] \rightleftarrows CH_2{=}CHCHO$$

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 difficult.

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 studies by several workers including Hartman(192) and Feuge(187, 189). The reaction proceeds in two stages and follows second order kinetics.

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 *via* 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 than glycerol.

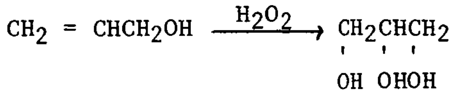
The only published information concerning this reaction is contained in a series of patents by Gresham(199-204). He employed cobalt catalyst (but also claimed nickel, ruthenium, copper, chromium and manganese salts) at high temperatures and pressures to obtain ethylene glycol and its formate esters(199, 200). Glycerol was obtained, as triacetin, only when acetic acid was the solvent and yields were poor.

Synthesis from Acetylene or Ethylene

Glycerol may be produced from acetylene by this series of reactions:(205-228)

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

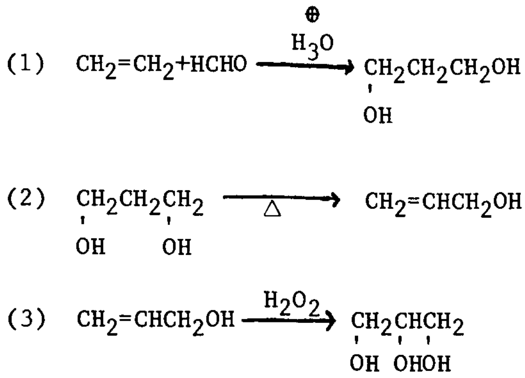
(2) $HC\equiv CCH_2OH \xrightarrow{H_2} H_2C = CHCH_2OH$

(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.

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) $CH_2{=}CH_2{+}HCHO \xrightarrow{H_3O^{\oplus}} \underset{OH}{CH_2}CH_2CH_2OH$

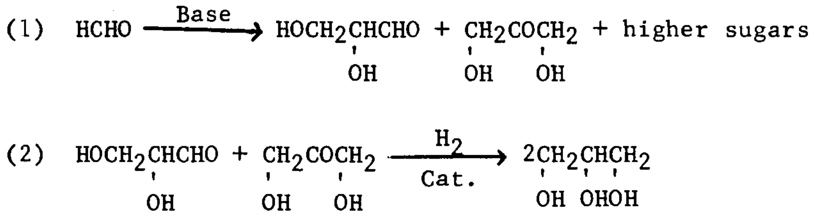
(2) $\underset{OH}{CH_2}CH_2\underset{OH}{CH_2} \xrightarrow[\Delta]{} CH_2{=}CHCH_2OH$

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

Ethylene, however, reacts very sluggishly under normal Prins conditions,(229, 230) requiring elevated temperatures, strong acid catalysts and affording poor yields of diol.

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) $HCHO \xrightarrow{Base} HOCH_2\underset{OH}{CH}CHO + \underset{OH}{CH_2}CO\underset{OH}{CH_2}$ + higher sugars

(2) $HOCH_2\underset{OH}{CH}CHO + \underset{OH}{CH_2}CO\underset{OH}{CH_2} \xrightarrow[Cat.]{H_2} 2\underset{OH}{CH_2}\underset{OH}{CH}\underset{OH}{CH_2}$

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 misture 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). The reaction is autocatalytic and has a long induction period. Pfeil and Ruckert(241) formulated the reaction as shown in Figure 13.

The condensation is 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), who found that TlOH was quite effective in suppressing this undesired side reaction (see Figure 14).

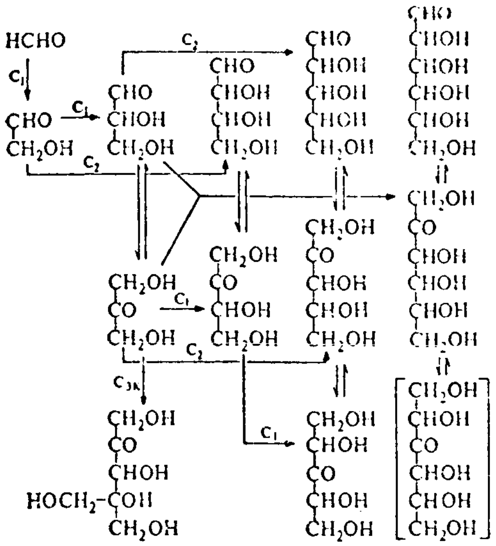
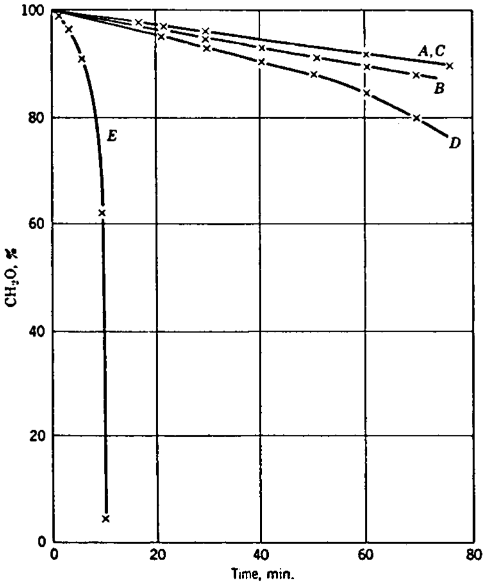


Figure 13 - Condensation of Formaldehyde under the Influence of Alkali (Pfeil and Ruckert)(241)



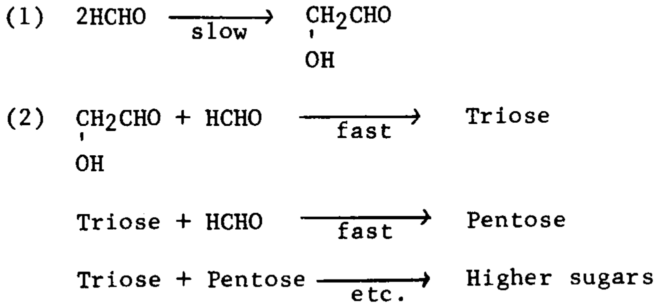
Curve	Catalyst		CH_2O conc.	CH_2O/ alkali ratio	Cannizzaro reaction
A	NaOH	0.070*N*	0.583*M*	8.3	100%
B	$Ba(OH)_2$	0.082	0.514	6.4	100
C	LiOH	0.076	0.491	6.5	100
D	$Ca(OH)_2$	0.046	0.351	7.6	62
E	TlOH	0.082	0.553	6.7	9

Figure 14 - Course of Reaction of Aqueous Formaldehyde with Alkaline Catalysts at 60°C(240)

The same effect was obtained by addition of a salt containing the Tl$^{(+)}$ Cation. The Cannizzaro reaction was greatly reduced at low formaldehyde concentration, and more significantly, it was completely repressed by the addition of dihydroxyacetone to the reaction mixture. Dihydroxyacetone 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).

Catalysts to Favor Lower Sugars

The major problem in the trimerization 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:



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

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

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

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

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 15).

Varying the amounts of lead hydroxide or benzoylcarbinol had little effect on yield of lower sugars (Figures 16 and 17), 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.

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 Benzoylcarbinol. 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

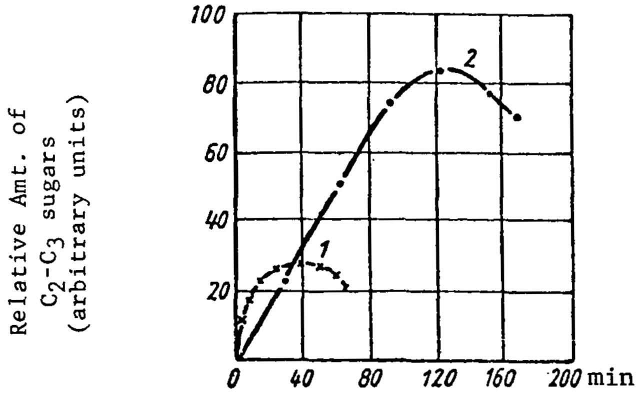


Figure 15 - $Pb(OH)_2$ vs. $Ca(OH)_2$ Catalysis; Both curves 4% HCHO Soln.; Curve 1: 1/400 M benzoylcarbinol, 1/100 M $Ca(OH)_2$; Curve 2: 1/400 M benzoylcarbinol, 1/100 M $Pb(OH)_2$(235)

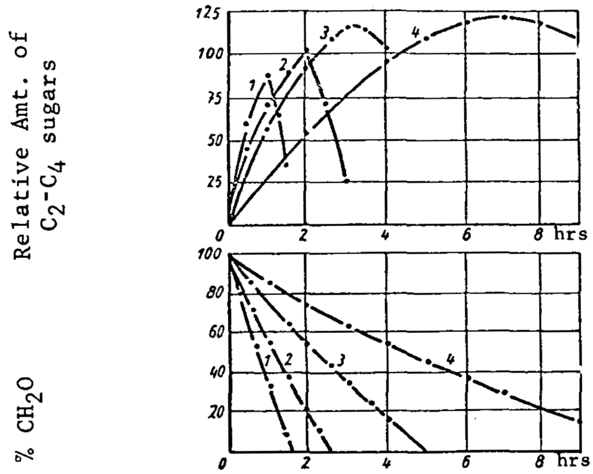
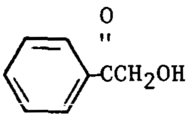
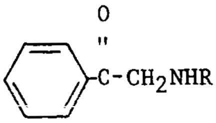


Figure 16 - Effect of $Pb(OH)_2$ Concentration on Yield of Lower Sugars and Rate of CH_2O Disappearance; 100 ml 20% CH_2O Soln. and 1/100 M Benzoylcarbinol; Curve 1: 4% $Pb(OH)_2$; Curve 2: 2% $Pb(OH)_2$; Curve 3: 1% $Pb(OH)_2$; Curve 4: 0.5% $Pb(OH)_2$; T = 25°C(235)

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



Benzoylcarbinol



a Phenacylamine

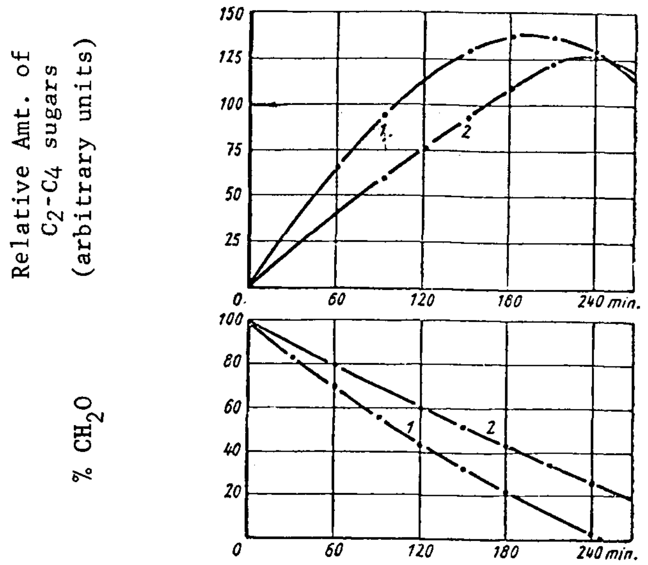


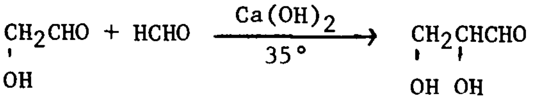
Figure 17 - Effect of Increased Benzoylcarbinol Concentration of Yield of Lower Sugars and Rate of CH_2O Disappearance; 100 mls 10% CH_2O soln.; 0.5% $Pb(OH)_2$; Curve 1: 1/100 M Benzoylcarbinol. Curve 2: 1/200 M Benzoylcarbinol(235)

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 18. 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%

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



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

isolation of glyceraldehyde is apparently rapid neutralization of the basic solution with oxalic acid before higher sugars can be formed. However, this claim is fairly well documented. Kuzin also prepared glycolaldehyde 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.

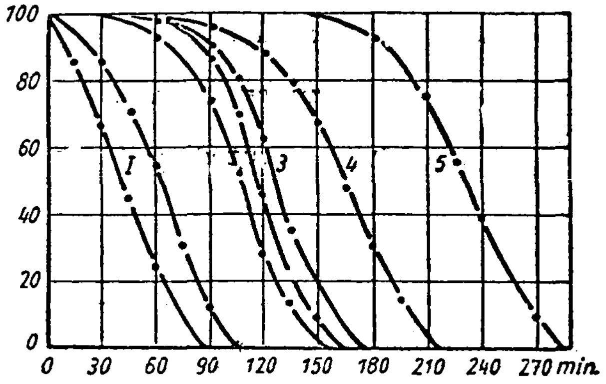
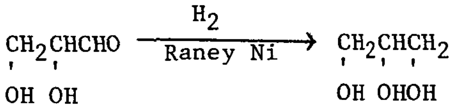


Figure 18 - Phenacyl-ionexchange Resins as Catalysts for the Formaldehyde Condensation. 4% CH_2O, 2% $Pb(OH)_2$, 2,5 m-valence catalyst, 75°C. I: benzoylcarbinol; II: p-acetamido-benzoylcarbinol; 1: acylamino compound of Amberlite XE64 and p-aminobenzoylcarbinol acetate; 2: phenacyl-polyaminostyrene; 3: phenacyl-Wofatite MD; 4: phenacyl-Wofatite N; 5: no catalyst(235)

Hydrogenation to Glycerol

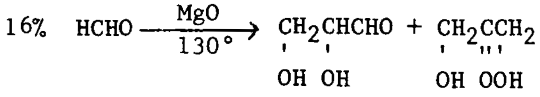


$$\underset{\text{OH}}{\text{CH}_2}\underset{\text{OH}}{\text{CH}}\text{CHO} \xrightarrow[\text{Raney Ni}]{H_2} \underset{\text{OH}}{\text{CH}_2}\underset{\text{OH}}{\text{CH}}\underset{\text{OH}}{\text{CH}_2}$$

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 glyceraldehydes and/or glycerol 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.

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



$$16\%\ \text{HCHO} \xrightarrow[130^\circ]{\text{MgO}} \underset{\text{OH}}{\text{CH}_2}\underset{\text{OH}}{\text{CH}}\text{CHO} + \underset{\text{OH}}{\text{CH}_2}\underset{\text{O}}{\text{C}}\underset{\text{OH}}{\text{CH}_2}$$

patent claims that higher temperatures and pressures increase the rate of reaction and represent a significant 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.

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 obtained as well.

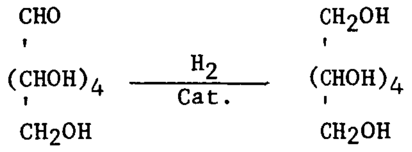
Finally, note must be taken of the possibility of the photochemical polymerization formaldehyde(251, 252, 254). The formation of reducing sugars has been observed when aqueous formaldehyde(252, 254) or CO_2(253) are exposed to sunlight (253) or ultraviolet radiation of 200-290 mu(248, 250). Little data 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 preferably and was selected for the engineering case study.

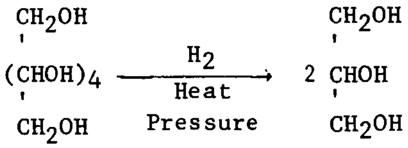
Hydrogenolysis of Carbohydrates

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.

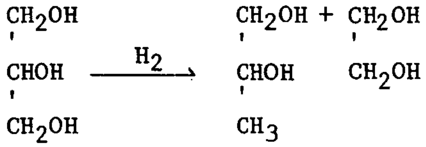
(1) 

$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow[\text{Cat.}]{H_2} \begin{array}{c}CH_2OH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}$$

(2) 

$$\begin{array}{c}CH_2OH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} \xrightarrow[\text{Heat Pressure}]{H_2} 2\ \begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

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) 

$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \xrightarrow{H_2} \begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_3\end{array} + \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

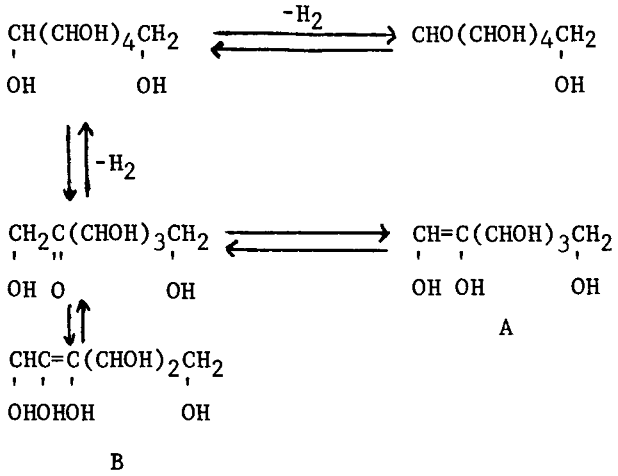
Early studies of the hydrogenation of sugars were carried out under mild conditions and resulted in nearly quantitative yields of the corresponding polyol, reaction (1) (see reference 255 for a short review of work prior to 1943). Only at temperatures above 200°C is cleavage observed. The reaction was 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 11.

Catalyst	Solvent	Pressure (At.)	Temp. °C	Time	St. Mat.[1]	% Yield Glycerol	% Yield 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.

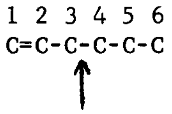
Table 11 - Hydrogenolysis of Carbohydrates With Various Catalysts(255)

The importance of using the proper catalyst is apparent, not only from Natta's work 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. 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.



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

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.



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

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. 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.

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.

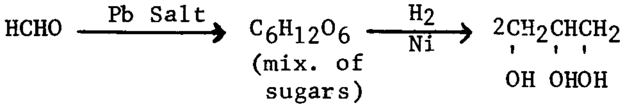
	Conditions Favoring					
				Catalyst Composition		
Product	Max. Yield	Temp.	Press.	Ni	Cu	Co
1,3-Propylene Glycol	70%	190-320°C	1-200 Atm.	10-14%	10-14%	1-5% (Optional)
1,2-Propylene Glycol	30%	180-210°C	10-50 Atm.	20-25%	2-5%	---
Glycerol + Ethylene Glycol	66%	200-220°C	100-200 Atm.	---	1-24%	1-24%

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. In general, the high conversion runs afforded large amounts of ethylene glycol.

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.

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, glucose 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

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) $6\ HCHO \xrightarrow{\text{base}} C_6H_{12}O_6 \xrightarrow{H_2} 2\ HOCH(CH_2OH)_2$

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

(5) $3\ RCO_2H + HOCH(CH_2OH)_2 \xrightarrow[\Delta]{} R\overset{\overset{O}{\|}}{C}OCH(CH_2OCOR)_2$

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 19. The process is divided into 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 19 and in the more detailed engineering design (Figure 20).

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 12-15. 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 12). 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

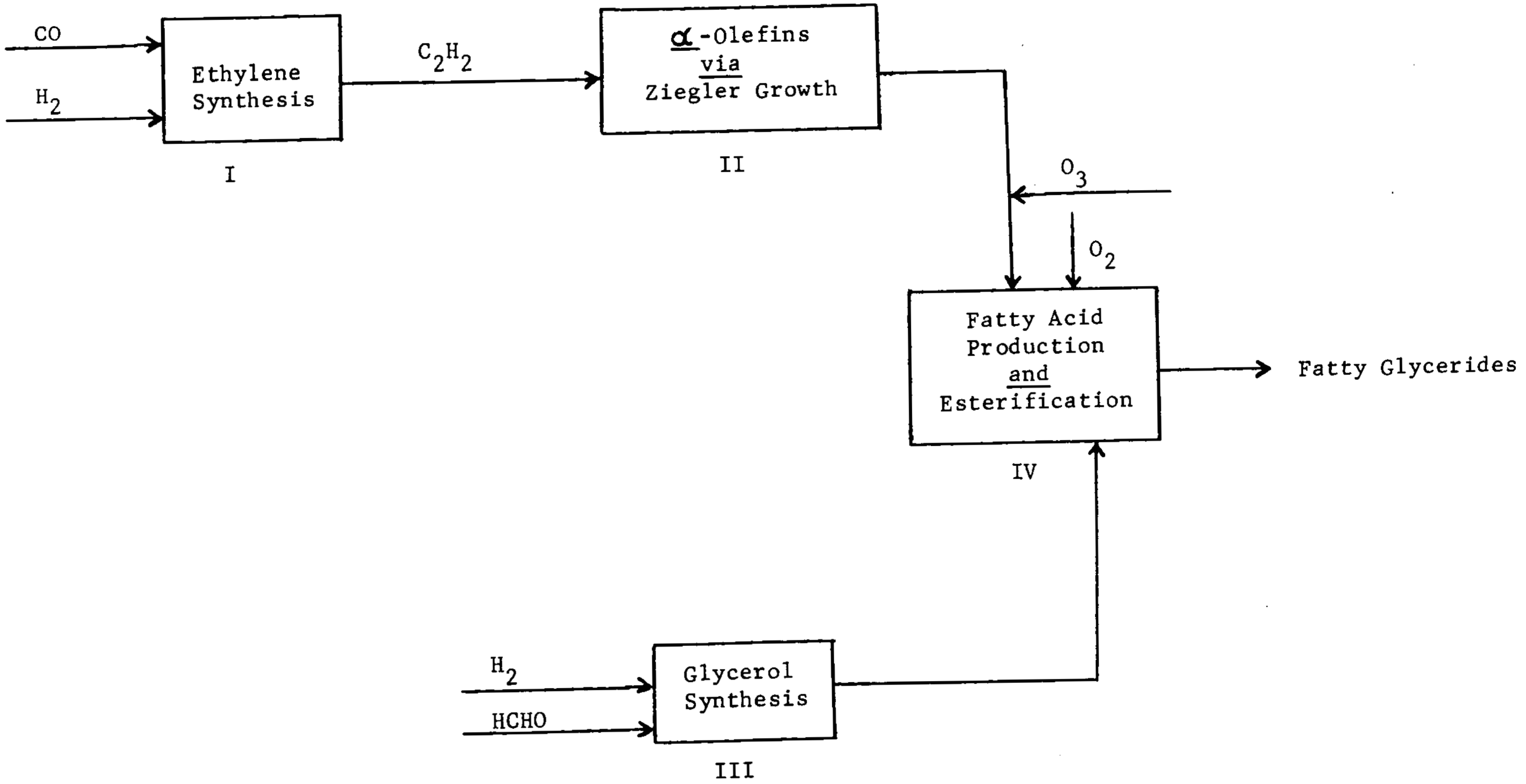


Figure 19 - Glyceride Synthesis *via* Ziegler Growth Reaction Schematic

For 5 lbs./day - Sufficient for 10 Men

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

OR: 12 KWH/lb.

Table 12 - 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 13 - Pump Data

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 15. At least 77 control loops are required. Since this is neglecting redundancy, it is anticipated that considerably more actually will be needed. The material balances for the entire system are given in Table 17.

An analysis of the carbon numbers of the acids to be expected is given in Table 16.

					Estimated Actual		
Compressor	Appears in Div. --- of Fig. 43	ΔP (Atm.)	Std. Cu. Ft./Day	Theor. Watts	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 14 - Compressor Data

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

Table 15 - Control Breakdown

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

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All Figures Given as lb./day

Process Stream[1]	Appears in Part of Fig. 20	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				0.92											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 20.

(2) Triethylaluminum.

(3) Trialkylaluminums.

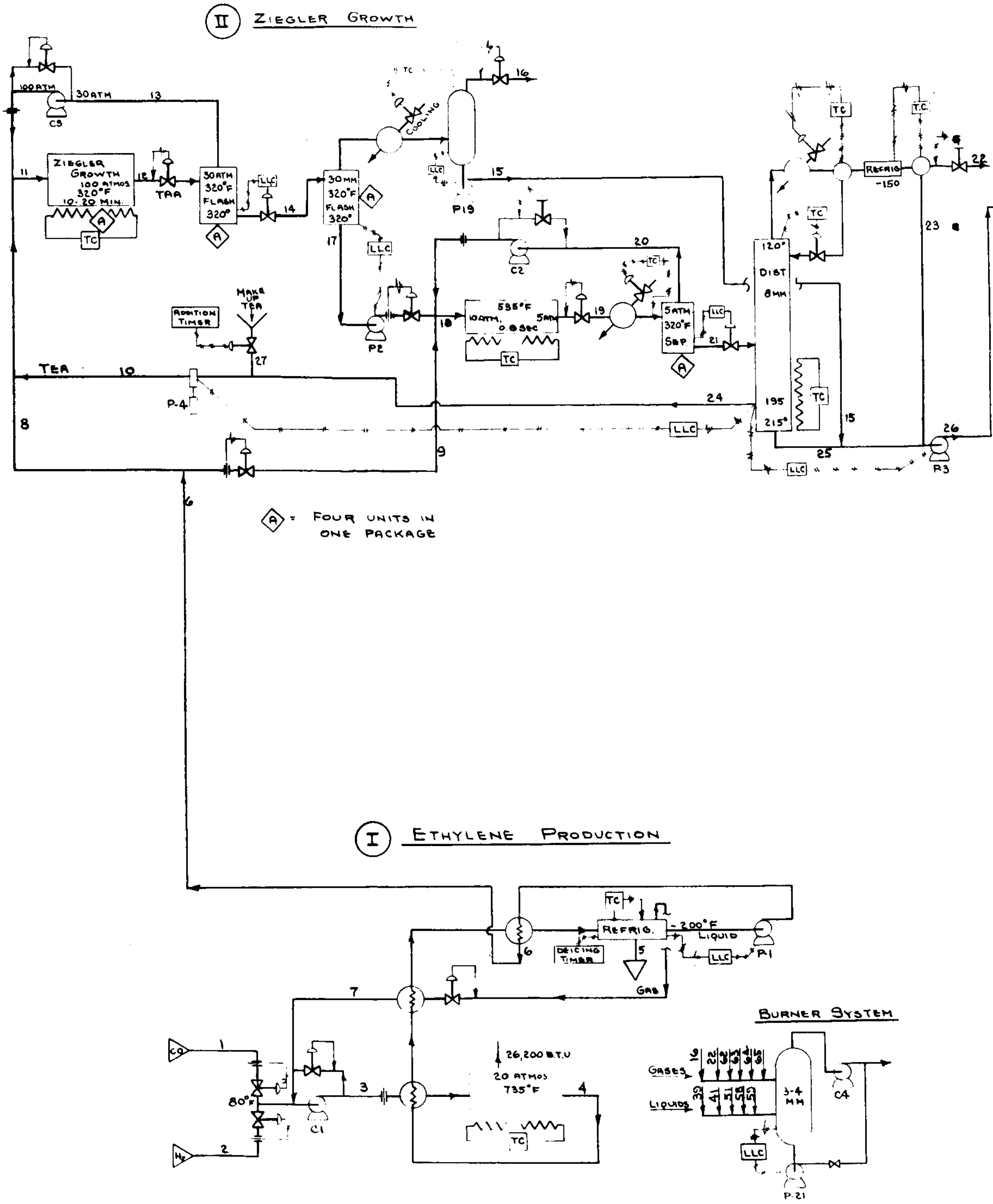
(4) By-product streams to be burnt.

(5) Fluorotrichloromethane (duPont).

(6) Make-up fresh.

(7) By-product to be discarded.

Table 17 - Material Balance for Fatty Glyceride Synthesis


II ZIEGLER GROWTH
100 ATM
30 ATM
13
C5
11
ZIEGLER GROWTH 100 ATMOS 320°F 10-20 MIN.
12
TAA
A
TC
30 ATM 320°F FLASH 320°
LLC
14
30 MM 320°F FLASH 320°
17
COOLING
TC
LLC
P19
16
15
C2
20
TC
585°F
10 ATM.
0.8 SEC
5 ATM
19
5 ATM 320°F SEP.
21
18
P2
MAKE UP TEA
ADDITION TIMER
27
TEA
10
P-4
8
9
6
24
LLC
120°
DIST 8 MM
195
215°
TC
REFRIG -150
T.C.
22
23
15
25
26
P3
A = FOUR UNITS IN ONE PACKAGE
I ETHYLENE PRODUCTION
TC
REFRIG.
-200°F
LIQUID
DEICING TIMER
5
6
P1
LLC
GAS
7
CO
1
80°F
H2
2
C1
3
26,200 B.T.U.
20 ATMOS
735°F
4
TC
BURNER SYSTEM
GASES
LIQUIDS
3-4 MM
C4
LLC
P-21

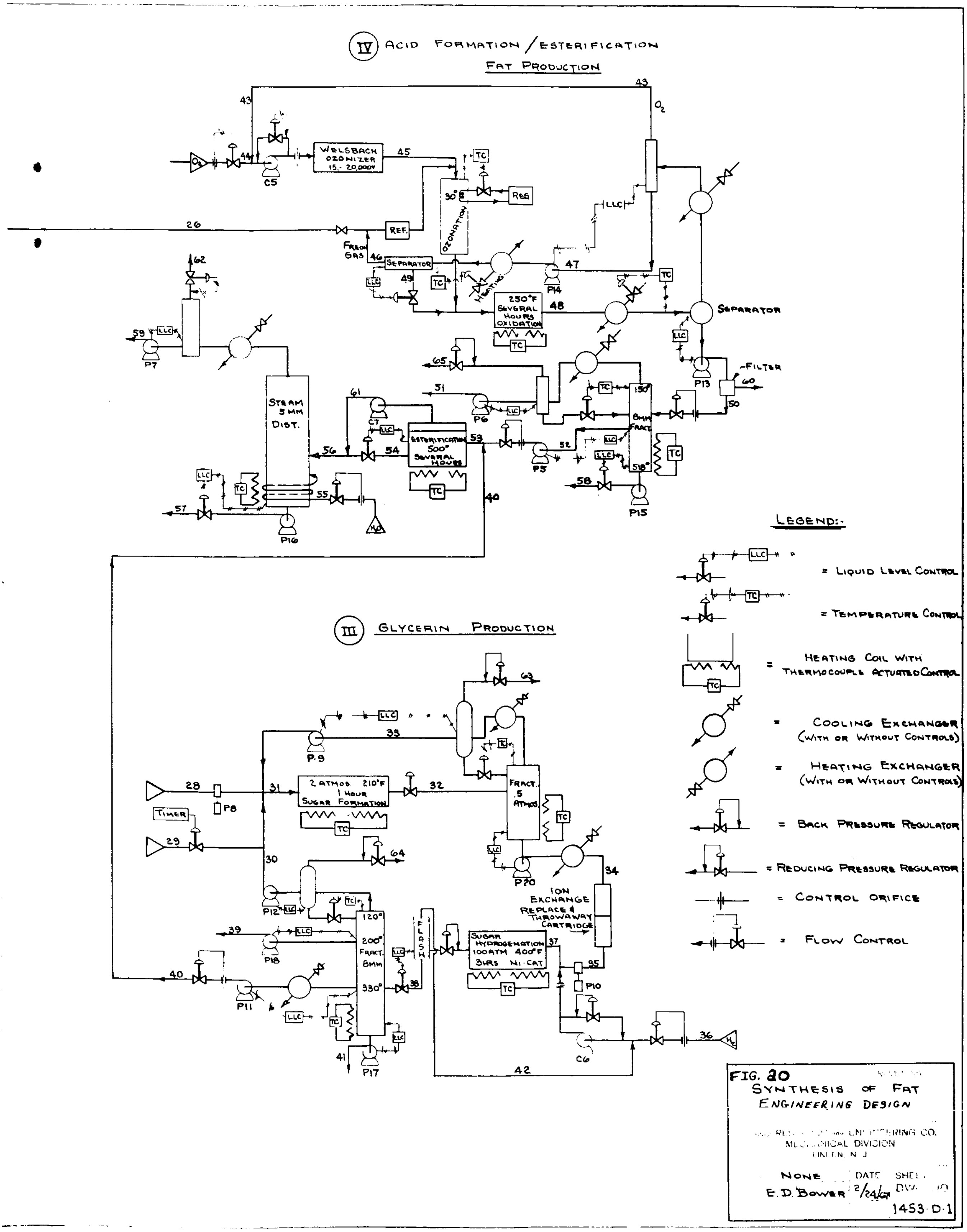


FIG. 20
SYNTHESIS OF FAT
ENGINEERING DESIGN

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 16) 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.

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.

REFERENCES

The presence of an asterisk (*) indicates that a reprint of the reference is on file at the Ames Research Center. A double asterisk (**) indicates a translation of a foreign article has been made and is on file. Foreign language papers are indicated by a parenthetical symbol at the end of the reference:

(G) = German
(F) = French
(R) = Russian
(Cs) = Czechoslovakian
(It) = Italian

1. Mason, J. L.: Proc. AIAA 2nd Ann. Space Flight Meeting (1963).

2. Hine, C. H.: Symposium on Toxicity in the Closed Ecological System (1963) p. 33; DDC # AD 440942.

3. Myers, J. E.: Conference on Nutrition in Space and Related Waste Problems, NASA SP-70 (1964) p. 283.

4. Borisov, V. and Gorlov, O.: Life in Space, FTD-MT-63-200, DDC # AD 608650.

5. Jagow, R. B. and Thomas, R. S.,eds.: Study of Life Support Systems for Space Missions Exceeding One Year in Duration, Final Summary Report, Lockheed Missiles and Space Company, January 1966.

6. Wilks, S. S.: Conference on Nutrition in Space and Related Waste Problems, NASA SP-70 (1964) p. 305.

7. Drake, G. L., et al.: Study of Life Support Systems for Space Missions Exceeding One Year in Duration, Final Summary Report, General Dynamics, Convair Division (1966).

8. McDowell, M. E. and Leveille, G. A.: Conference on Nutrition in Space and Related Waste Problems, NASA SP-70 (1964) p. 317.

9. Smylie, R. E. and Reumont, M. R.: Manned Spacecraft: Engineering Design and Operation, P. E. Purser, M. A. Faget and N. F. Smith, eds., Fairchild Publications, Inc, New York (1965) Ch. 15.

10. Gerathewohl, S. J.: Ch. 11 in Principles of Bioastronautics, Prentice-Hall, Inc. Englewood Cliffs, N. J., (1963).

11. Fox, S. W.: Food Technology, 17, 22 (388) (1963).

12. Fox, S. W., et al.: Conference on Nutrition in Space and Related Waste Problems, NASA SP-70 (1964) p. 331.

13. Dymza, H. A., Stoervsand, G. S., and Swift, S. M.: Army Science Conference, West Point (1966) DDC # AD 634673.

14. Miller, S. A., et al.: Final Report No. AMRL-TR-64-121, Aerospace Medical Division, Wright-Patterson AFB, Ohio (1965) DDC # AD 623 615.

15. Miller, S. A.: Conference on Nutrition in Space and Related Waste Problems, NASA SP-70 (1964) p. 343.

16. Calloway, D. H.: 46th Ann. Mtg. of Am. Dietetic Soc., Philadelphia (1963).

17. Kirk, R. E. and Othmer, D. F.: Encyclopedia of Chemical Technology, Interscience Publishers Inc., New York (1951) Vol. 6.

18. See, for example, King, C. G.: J. Am. Oil Chemists Soc., 34, 559 (1957)

19. Casal, J. J. and Holman, R. T.: J. Am. Oil Chemists Soc., 42, 1134 (1965).

The German Process

*20. Anonymous: Publication No. 1, The Division of Nutrition of FAO, Nutritional Studies Series (1949).

**21. Pardun, H.: Seifen-Ole-Fette-Wachse, 74, 25, 49 (1948). (G).

*22. Williams, P. N.: Chem. and Ind. (London), 19, 251 (1947).

23. Wachs, W. and Reitstotter, J.: Angew, Chem. B, 20, 61 (1948). (G).

*24. Schiller, G.: Z. Lebensm.-Utersuch, u. - Forsch., 88, 174 (1948). (G).

25. Kroll, W. R., Esso Research and Engineering Company, Personal communication to J. W. Frankenfeld and S. M. Kaback (1966).

26. Anonymous: FIAT Final Rept. 426 (1945). (Bur. of Mines Bulletin 544: Abst. 1495, p. 195).

*27. Stossel, E.: Oil and Gas J., (8/18/45) p. 146.

*28. Carlin, G. T.: Food Technology, 1, 404 (1947).

*29. Baldeschwieler, E. L.: OPB Rept No. 225 (1945).

30. Daily News Record, January 26, 1967, p. 28; Chemical Horizons, 6, (5) NA-18 (February 2, 1967).

The Fischer-Tropsch Synthesis

31. Storch, H. H., Golumbic, N., and Anderson, R. B.: The Fischer-Tropsch and Related Syntheses, Wiley (1951).

32. Anderson, H. C., Wiley, J. L., and Newell, A.: U.S. Bureau of Mines Bulletin 544, Part I: Literature (1954); Part II: Patents (1955).

33. Emmett, P. H. ed.: Catalysis, Volume IV (1956).

34. Emmett, P. H. ed.: Catalysis, Volume V, (1957).

35. Pichler, H. and Hector, A.: pages 446-489 in Kirk-Othmer Encyclopedia of Chemical Technology, Volume IV, Interscience (1964).

36. Pichler, H.: Chemische Technik, 18, 392 (1966).

37. Pichler, H.: Advances in Catalysis, 4, 271 (1952).

38. Nefedov, B. K., and Eidus, Ya. T.: Russian Chemical Reviews, 34, 272 (1965).

39. Russell, W. W. and Miller, G. H.: J. Am. Chem. Soc., 72, 2446 (1950).

40. Fischer, F. and Pichler, H.: Brennst.-Chem., 14, 306-9 (1933).

41. Köbel, H., and Ackermann, P.: Brennst.-Chem., 31, 10 (1950).

42. Pichler, H., et al.: Brennst.-Chem., 45, 215 (1964).

43. Koch, H. and Titzenthaler, E.: Brennst.-Chem., 31, 212 (1950).

44. Gall, D. and Hall, C. C.: Fuel, 27, #5 155 (1948).

45. Igonin, P. G., et al.: Khim. i Tekhnol. Topliv i Masel, 11, #5, 19 (1966).

46. Schlesinger, M. D., et al.: Ind. Eng. Chem., 46, 1322 (1954).

47. Fischer, F., Tropsch, H., and Dilthey, P.: Brennst.-Chem., 6, 265 (1925).

48. Fischer, F., Bahr, Th., and Meusel, A.: (see also similar articles in Ber., 69, 183 (1936); Ges. Abhandl. Kenntnis Kohle, 12, 263 (1937)), Brennst.-Chem., 16, 466 (1935).

49. Pichler, H.: Brennst.-Chem.: 19, 226 (1938) (G).

50. Fischer, F. and Pichler, H.: ibid., 20, 247 (1939) (G).

51. Pichler, H. and Buffleb, H.: ibid., 21, 257, 273, 285 (1940) (G).

52. Guyer, A., Guyer, P., et al.: Helv. Chim. Acta, 38, 798 (1955) (G).

53. Guyer, A., Jutz, J., and Guyer, P.: ibid., 38, 971 (1955) (G).

54. Guyer, P., Thomas, D., and Guyer, A.: ibid., 42, 481 (1959) (G).

55. Kölbel, H. and Bhattacharyya, K. K.: Ann., 618, 67-71 (1958) (G).

56. Kölbel, H., Ger.: 1,092,458, f. 7/27/56, i. 11/10/60 (G).

57. Kölbel, H., et al.: Makromol. Chem., 70, 1 (1964) (G).

58. Pichler, H. and Firnhaber, Angew. Chem.: 75, 166 (1963) (G).

59. Pichler, H., et al., Brennst.-Chem.: 44, 337 (1963) (G).

60. Pichler, H., et al., Makromol. Chem.: 70, 12 (1964) (G).

61. Pichler, H.: S. Af. Pat. Appl., 64/207, f. Ger. 1/22/63.

*62. Howk, B. W. and Hager, G. F.: U.S. 2,549,470 (4/17/51).

*63. Gresham, W. F.: U.S. 2,535,060 (12/26/50).

*64. Gresham, W. F.: U.S. 2,632,014 (11/31/51) (contin.-in-part of U.S. 2,535,060 (6/15/49).

*65. Karn, F. S., Shultz, J. F., and Anderson, R.B.: Ind. Eng. Chem. Prod. R&D, 4, 265-9 (1965).

*66. Worsham, C. H. and Holder, C. H.: U.S. 2,521,436, f. 9/3/48, i. 9/5/50.

Wax Cracking

*67. Anonymous: Chem. Week, 91, 57 (7/7/62).

68. Gerasicheva, Z. V., Botnikor, Y. A. and Osipora, E. V.: Khim. i. Tekhnol. Toplic i Masel, 11, #9, 1 (1966) (R).

69. Zhorov, Y. M., Kuznetsov, O. I. and Panchenkav, G. M.: Neftekhimiya, 6, #3, 396 (1966) (R).

*70. Anonymous: C.&E.N., 39, #32, 56 (8/7/61).

71. See Kearby, K. K.: Vol. 2 of Petroleum Hydrocarbons, Brooks, B. T., Kurtz, S. S. Jr., Boord, C. E. and Schmerling,`L. eds., Reinhold, N.Y. (1955) for a review.

72. Morrell, C. E.: Ch. 3 in Synthetic Rubber, Whitby, G. S., Davis, C. C. and Dunbrook, R. F., eds., Wiley and Sons, N.Y. (1954).

73. Plate, A. F. and Tarasova, G. A.: Zh. Ob. Khim., 13, 21 (1943) (R).

74. Mattox, W. J.: Paper, A.C.S. 107th Meet., Div. Org. Chem., Cleveland (1944); A.C.S. Abs. of Papers, 54 M.

75. Monsanto Co.: Netherlands Appl., 65, 17031; 65, 17032; 65, 17033 (filed 12/28/64).

Ziegler Growth Reaction

**76. Ziegler, K.: Nobel Prize Lecture, December 12 (1963); Angew. Chem., 76, 545 (1964) (G).

77. Ziegler, K.: Angew. Chem., 68, 721 (1956) (G).

*78. Ziegler, K.: Angew. Chem., 72, 829 (1960) (G).

**79. Zosel, K.: Address at the Annual Meeting of the German Society for Petroleum Science and Coal Research, Karlsruhe (1962) (G).

*80. Acciarri, J. A., Carter, W. B. and Kennedy, F.: Chem. Eng. Progr., 58, 85 (1962).

**81. Zosel, K.: Brennst.-Chem., 41, 321 (1960) (G).

**82. Ziegler, K.: Brennst.-Chem., 45, 194 (1964) (G).

83. Ziegler, K. et al: Ann., 629 1-256 (1960) (G).

84. Kroll, W. R.: Doctors Thesis, U of Aachen (1958).

*85. Zosel, K. and Holzkamp, E.: Brit., 908, 032 (10/10/62).

86. Kroll, W. R., Esso Research and Engineering Company: Personal communication to S. M. Kaback and J. W. Frankenfeld (1966).

87. Walling, C.: Free Radicals in Solution, Wiley and Sons, N. Y. (1957).

88. Gaylord, N. G. and Mark, H. F.: Polymer Reviews, Mark, H. F. ed. Vol. 2, pp. 219-220.

89. Oser, B. A., Food and Drug Research Labs., and Miller, S. A., M.I.T.: Personal Communcation to J. W. Frankenfeld, (1966).

Ethylene Synthesis

90. Miller, S. A.: Acetylene--Its Properties, Manufacture and Uses, Volume I, Academic Press (1965), pages 371-475.

*91. Goldstein, R. F. and Scarffe, D. R.: Svensk Kem. Tidsk., 75, 350 (1965).

*92. Beller, H. and Wilkinson, J. M., Jr.: Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edition, Volume I, pages 178-193 (1963).

93. Hydrocarbon Processing, 44, No. 11 (1965).

94. Hardie, D. W. F.: Acetylene, Manufacture and Uses, Oxford (1965).

*95. Stobaugh, R. B.: Hydrocarbon Processing, 45, No. 8, 125-136 (1966).

*96. Chemical Week, November 21, 1964, pages 89 and 90.

*97. Othmer, D. F.: Hydrocarbon Processing, 44, No. 3, 145 (1965).

*98. Hydrocarbon Processing, 44, No. 11, 162 (1965).

99. Oil and Gas Journal, June 20, 1966, p. 181.

*100. Happel, J. and Kramer, L.: U.S. 3,156,733 (12/2/60).

*101. Happel, J.: U.S. 3,156,734 (11/10/64).

*102. Happel, J. and Kramer, L.: U.S. 3,227,771 (1/4/66).

103. Brewer, A. K. and Kueck, P. D.: J. Phys. Chem., 35, 1293 (1931).

*104. Nieuwland, J. A. and Vogt, R. R.: The Chemistry of Acetylene, Reinhold (1945), pages 95-98.

105. Bond, G. C.: in Catalysis, Emmett, P. H., ed., Vol. III, Reinhold (1955), pages 109-148.

106. Bond, G. C. and Wells, P. B.: Advances in Catalysis, 15, 91-226 (1964).

*107. Bond, G. C. and Wells, P. B.: J. Catalysis, 5, 65-73 (1965).

108. BIOS Surveys Report 30, London (1951).

109. Copenhaver, J. W. and Bibelow, M. H.: Acetylene and Carbon Monoxide Chemistry, Reinhold (1945).

110. Reppe, J. W.: Acetylene Chemistry; PB 18852s, pages 18 and 19.

111. Bond, G. C., Dowden, D. A., and MacKenzie, N.: Trans. Faraday Soc., 54, 1537 (1948).

112. Frevel, L. K. and Kressley, L. J.: U.S. 2,802,889 (6/1/54).

113. Shcheglov and Sokol'skii, D. V., Trudy Inst. Khim. Nauk, Akad. Nauk Kazakh. SSR, 2, 150-157 (1958); CA 53, 196g (1959).

114. Gilliland, E., M.I.T., Personal Communication to S. M. Kaback (1967).

115. Van Patten, R. E.: Annotated Bibliography on Bio-medical (Animal) Satellite Vehicles, Life Support Systems, and Related Technology, AD 433,237, December 1963.

*116. Chandler, H.: Solid Electrolyte CO_2 Reduction System, AD 625, 482, October 1965; also, AD 603,357, May, 1964.

117. Foster, J. F. and McNulty, J. S.: Study of a Carbon Dioxide Reduction System, AD 269,507, August, 1961.

118. Smith, J. M. and Thomas, R.S.: pages 285-303 in Symposium on Toxicity in Closed Ecological System, AD 440,942 (1963).

119. Hollander, J. and Spialter, L.: J. Chem. Educ., 35, 446 (1958).

120. Quinn, E. L. and Jones, C. L., Carbon Dioxide, Reinhold (1936).

121. Weinhouse, S.: J. Am. Chem. Soc., 70, 442 (1948).

122. Senegavnik, Comm. Energie Atomique (Fr.) Rappt., 726, 82 pt. (1957); CA, 52, 19368h (1958).

123. Campbell, A. N. and Brown, E. A.: J. Am. Chem. Soc., 60, 3055 (1938).

124. Storch, H. H., Golumbic, N., and Anderson, R. B.: *The Fischer-Tropsch and Related Syntheses*, Wiley (1951) page 28.

125. Bahr, H.: Ges. Abhand. Kenntnis Kohle, 8, 219 (pub. 1929).

126. Bahr, Th.: *ibid*., 12, 292 (1937).

**127. Farben, I. G., Knobloch, W., and Schiller, G.: Ger., 730,409.

128. Holder, C. H.: U.S. 2,514,282, Standard Oil Development Co., (7/4/50).

129. Barkley, L. W., *et al*.: Ind. Eng. Chem., 44, 1066 (1952).

130. Brit. Pat. 851,108, Esso Research and Engineering Co., pub. 10/12/60.

131. Frey, U.: Brit. 654,404, pub. 6/20/51.

132. Peters, K. and Küster, H.: Z. phys. Chem., A148, 284 (1930).

133. Akerlof, G. C.: "The Generation of Formaldehyde from Carbon Dioxide as a Route to Edible Sugars," Part I of "A Study of the Feasibility of the Regeneration of Carbohydrates in a Closed Circuit Respiratory System," FMC Corp. (1953) NASA N64-11801.

134. Orlow, G.: Berichte, 42, 893 (1909) (Originally in Zhur. Russ. Khim. Obschch. 40, 1588 (1909), with author's name given as E. I. Orlov).

135. Fester, G.: Brennst.-Chem., 3, 244 (1922); Fester, G. and Brude, G.: *ibid*., 5, 49 (1934) (G).

136. Nonnenmacher, H. and Oettinger, W.: Ger., 922,883, BASF (1/27/55) (G).

*137. Nonnenmacher, H., Oettinger, W., and Göhre, O: Ger., 896,338, BASF (11/12/53) (G).

*138. Asboth, K.: Fr., 1,026,398, f. Austria 7/21/50, deliv. 2/4/53; also Austrian, 171,701, issued 6/25/52.

*139. Peters, K.: U.S. 2,960,518 (11/15/60); also Brit., 833,976; Fr., 1,223,311; Austrian, 204,018.

140. Tsutsumi, S.: Jap. 4172/58, issued 5/28/58, CA, 54, 293g (1960).

*141. Hayashi, T. and Tsutsumi, S.: U.S. 2,973,384, f. Jap. 8/4/56, i. 2/28/61; also Jap., 3214/59.

142. Tsutsumi, S., Jap.: 319/60, issued 1/19/60, CA, 54, 17852f (1960).

143. Tsutsumi, S.: J. Fuel Soc. Japan, 35, 560 (1956); CA, 51, 18562d (1957).

Conversion of Hydrocarbons to Acids

*144. Wagner, R. B. and Zook, H. D.: Synthetic Organic Chemistry, Wiley and Sons, N Y. (1953) p. 422.

145. Royals, E. E.: Advanced Organic Chemistry, Prentice-Hall, N. J. (1956) Ch. 4.

146. Farmer, E. H., et al: Trans. Faraday Soc., 38, 348 (1942); ibid., 38, 340 (1942); J. Chem. Soc., 121 (1942).

147. Ellis, C.: The Chemistry of Petroleum Derivatives, Reinhold, N. Y. (1937) Vol. 2, Ch. 39.

148. Frank, C. E.: Chem. Revs., 46, 155 (1950).

149. House, H. O.: Modern Synthetic Reactions, W. A. Benjamin, N. Y. (1965) pp. 92-100.

*150. Hickinbottom, W. J., Peters, D. and Wood, D.G.M.: J. Chem. Soc., 1360 (1955).

151. Water, W. A.: Quart. Revs., 12, 277 (1958).

152. Franz, J. E., Herber, J. F. and Knowles, W. S.: J. Org. Chem., 30, 1488 (1965).

153. Bailey, P. S.: Chem. Revs., 58, 925 (1958).

154. Long, L. Jr.: Chem. Revs., 27, 437 (1940).

155. Maggiolo, A.: Welsbach Corp., 4th revision (1962).

*156. Asinger, F.: Ber., 75, 656 (1942) (G).

157. Livingston, J. R., Esso Res. & Eng. Co., Personal Communication to J. W. Frankenfeld.

*158. Bailey, P. S.: Ind. Eng. Chem., 50, 993 (1958).

159. Bailey, P. S.: J. Org. Chem., 22, 1548 (1957).

160. Greenwood, F. L.: J. Org. Chem., 10, 415 (1945).

*161. Goebel, C. G. _et al_.: U.S. 2,813,113 (11/12/57).

*162. Thieme, C.: Ger., 767,841 (1/18/54) (G).

163. Voorhies, A. Jr., Owen, J. J., and Johnson, J. F., _Advances in Petroleum Chemistry and Refining_, Interscience, N. Y. (1958) Vol. 1, Ch. 10.

164. Bird, C. W.: Chem. Revs., _62_, 283 (1962).

*165. Roos, L. and Orchin, M.: J. Org. Chem., _31_, 3015 (1966).

166. Parker, R. E. and Isaaca, N. S.: Chem. Revs., _59_, 737 (1959).

*167. Malinovskii, _Epoxides and Their Derivatives_, Davey and Co., N. Y. (1965) pp. 316-345.

168. Weissberger, A.: Heterocyclic Compounds with Three-and Four-membered Rings, Interscience, N. Y. (1964) part 1, pp. 230-261.

169. Winstein, S. and Henderson, R. B. in _Heterocyclic Compounds_, Elderfield, R. C., ed., Wiley and Sons, N. Y. (1950) Vol. 1, pp. 47-52.

*170. Levy, J. and Sfuas, M.: Compte Rend., _184_, 1335 (1927) (F).

171. Wagner, R. B. and Zook, H. D.: _Synthetic Organic Chemistry_, Wiley and Sons, N. Y. (1961) p. 419.

172. Royals, E. E.: _Advanced Organic Chemistry_, Prentice-Hall, N. J. (1956) Ch. 7.

173. Fuson, R. C.: _Advanced Organic Chemistry_, Wiley, N. Y. (1950) p. 226.

*174. Lobo, P. A. _et al_.: Chem. Eng. Progr., _58_, 85 (1962).

*175. Mirviss, S. B. and Inchalik, E. J.: U.S. 2,827,458 (3/18/58).

*176. Zakharkin, L. I. and Gavrilenko, V. V.: Dokl. Akad. Nauk SSSR, _118_, 713 (1958) (R); _CA_, _52_, 11738f (1958).

177. Zakharkin, L. I. and Gavrilenko, W.: USSR, 112, 349, 6/25/58 (R); _CA_, _53_, 2093f (1959).

*178. Ziegler, K. _et al_.: Ann. _629_, 251 (1960) (G).

179. Reference _74_, pp. 834-835 (G).

180. Marshall, D. W.: U.S. 3,168,570 (2/2/65).

*181. Johnson, W. K. and Wygant, J. C.: U.S. 3,057,900 (10/9/62).

*182. Ardon, M.: Oxygen, W. A. Benjamin Inc., N. Y. (1965) pp. 51-66.

183. Ewell, A. W.: J. App. Phys., 13, 759 (1942).

184. Am. Chem. Soc.: Advances in Chemistry Series #21, Washington, D. C. (1959).

Conversion to Glycerides

185. Berthelot: Ann. Chim., 41, 238 (1854) (F).

186. Hartman, L.: Chem. Revs., 58, 845 (1958).

*187. Feuge, R. O., Kraemer, E. A. and Bailey, A. E.: Oil and Soap, 22, 202 (1945).

*188. Hilditch, T. P. and Rigg, J. G.: J. Chem. Soc., 1774 (1935).

*189. Feuge, R. O.: J. Am. Oil Chemists Soc., 39, 521 (1962).

190. Ivanoff, N.: Chim. et. ind., 53, 41 (1945) (F).

191. Patrick, T. J., Jr. and Johnson, K. G.: U.S. 3,060,224 (10/23/62).

*192. Hartman, L.: J. Am. Oil Chemists Soc., 43, 536 (1966).

**193. Bellucci, I., et al.: Gazz, Chim. Ital., 42 II, 283 (1912). (It.)

194. Bellucci, I.: atti accad. Lincei, 20 I, 235 (1911). (It.); C.A., 5, 2100.

*195. Bellucci, I. and Mangetti, R.: atti accad. Lincei, 20 I, 125 (1911). (It.); C. A. 5, 1587 .

*196. Spaght, M. E.: CIOS Report #1667 on the German Fat Industry. #1667 on the German Fat Industry.

Synthesis of Glycerol

*197. Machell, G.: Ind. Chemist., 535 (Nov. 1960).

198. Fieser, L. F. and Fieser, M.: Organic Chemistry, Heath and Co., Boston (1944).

*199. Gresham, W. F.: Brit., 655,237 (12/9/48).

*200. Gresham, W. F.: U.S. 2,636,046 (10/16/48).

*201. Gresham, W. F. and Schweitzer, C. E.: U. S. 2,534,018 (12/12/50).

*202. Gresham, W. F.: U. S. 2,570,792 (10/9/51).

*203. Gresham, W. F., and Brooks, R. E.: Brit., 625,909 (7/6/49).

*204. Gresham, W. F., and Brooks, R. E.: U.S. 2,451,333 (10/12/48); Virtually identical to above British patent.

*205. Reppe, W. et al.: Ann., 596, 25 (1955) (G).

*206. Reppe, W. and Keyssner, E.: U.S. 2,232,367 (2/25/41).

*207. Reppe, W. et al.: U.S. 2,300,969 (11/3/42).

208. Suzuki, K.: Rev. Phys. Chem. Japan, 23, 57 (1953); CA, 49, 3007^{f}.

*209. Hecht, O. F.: U.S. 2,768,215 (10/23/56); Stanley, H. M., Sandsbury, H. and Minkoff G., Austral., 124,926 (7/9/43).

*210. Kigama, R., Osugi, J. and Suzuki, K.: Rev. Phys. Chem. Japan, 22, 22 (1952).

*211. Part II, idem. ibid., 22, 59 (1952).

*212. Johnson, A. W.: J. Chem. Soc., 1014 (1946).

213. Campbell, K. N. and Campbell, B.: Chem. Revs., 31, 77 (1942): See also Augustine, R. L.: Catalytic Hydrogenation, M. Dekker Inc., N. Y. (1965) pp. 69-71.

214. Crombie, L.: Quart. Revs., 6, 128 (1952).

215. McQuillin, F. J. and Ord, W. O.: J. Chem. Soc., 2902 (1959).

216. Ishida, E.: Japan, 2272 (1952); CA, 48, 2083^{g}.

217. Bal'yan, Kh. v.: Zhur, Obshchei Khim., 31, 28 (1961) (R); CA, 55, 2453^{b}.

218. Martinet, P. and Doupeux, H.: Compte. Rend., 259(14), 2241(1964) (F); CA, 62, 2726^{c}.

219. Marvel, C. S. and Young, C. H.: J. Am. Chem. Soc., 73, 1066 (1951).

*220. Broadbent, H. S. and Selin, T. G.: J. Org. Chem., 28, 2343 (1963).

221. Schnabel, R., Schmidt, W. and Heinz, K.: U.S. 2,300,598 (11/3/43).

222. Reference 92 pp. 178-179.

*223. Anonymous: Petroleum Refiner, 38, (11) 254 (1959).

224. Wallace, J. G.: Hydrogen Peroxide in Organic Chemistry, Monograph A-11387, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

*225. Uddeholms Aktiebolag Co.,: Brit., 917,747 (2/6/63).

*226. N. V. De Bataafsche Petroleum Maatsch.: Brit., 634,118 (3/15/50).

*227. Milas, N. A., Kurz, P. F. and Anslow, W. P., Jr.: J. Am. Chem. Soc., 59, 543 (1937).

228. A few of the German patents concerning this process: Ger., 890,943; 892,589; 907,774; 908,135; 921,446 (G).

229. Arundale, E. and Mikeska, L. A.: Chem. Revs., 51, 505 (1952).

*230. Baker, J. W.: J. Chem. Soc., 89 (1948).

231. Olsen, S.: Fr., 933,182 (4/13/48).

*232. Olsen, S.: Z. Naturforsch., 1, 676 (1946) (G).

*233. Olsen, S.: Chem. Ber., 81, 540 (1948) (G).

234. Butlerow, A.: Ann., 120, 295 (1861) (G).

**235. Langenbeck, W., et al.: J. Prakt. Chem., (4)3, 196 (1956) (G).

*236. Langenbeck, W.: Tetrahedron, 3, 190 (1958) (G).

*237. Langenbeck, W.: Angew. Chem., 66, 151 (1954) (G).

238. Furukawa, J. and Saegusa, T.: Vol. 3 of Polymer Reviews, Mark, H. F. and Immergut, E. H., eds. Interscience, N. Y. (1963).

*239. Breslow, R.: Tet. Letters, 21, 22 (1959).

*240. Pfeil, E. and Schroth, G.: Ber., 85, 293 (1952) (G).

*241. Pfeil, E. and Ruckert, H.: Ann., 641, 121 (1961).

*242. Hanford, W. E. and Schreiber, R. S.: U.S. 2,224,910 (12/17/40).

**243. Langenbeck, W.: Angew. Chem., 61, 186 (1949) (G).

**244. Kuzin, A.: Zh. Obschei Khimii, 8 (7), 592 (1938) (R).

245. House, H. O.: Modern Synthetic Reactions, W. A. Benjamin Inc., New York (1965) Ch. 1.

246. Wagner, R. B. and Zook, H. D.: Synthetic Organic Chemistry, Wiley & Sons, New York (1953) p. 149.

247. Tomilo, A. P., Sergo, A. A. and Varshavskii, S. L.: Elektrokhimiyo, 1 (9), 1126 (1965) (R).

*248. Mayer, R. and Jäschke, L.: Ann., 635, 145 (1960) (G).

**249. Binko, I. and Kolar, J.: Czech., 92, 198 (10/15/59) (Cz).

*250. Seyewetz, A. and Gibello: Bull. Soc. Chim. (Paris), 3 31, 434 (1904) (F).

251. Mitchell, P. W.: The Preparation and Evaluation of Sugars from Formaldehyde, Part II of A Study of the Feasibility of the Regeneration of Carbohydrates in a Closed Circuit Respiratory System, FMC Corp. (1953) NASA N64-11801. This reference contains a good literature review.

252. Baly, E. C., Heillron, I. M. and Barker, W. F.: J. Chem. Soc., 1025 (1921).

253. Moore, B. and Webster, T. A.: Proc. Roy. Soc. (London), B87, 163, 556 (1914); B90, 168 (1918).

254. Vogel, H.: Z. Zuckerind, 49, 1953 (1924).

**255. Natta, G., Rigamonti, R. and Beati, E.: Ber., 76, 641 (1943) (G).

**256. Fuchs, O. and Wolfram, A.: Ger., 1,004,157 (7/6/55) (G).

**257. Schmidt, O.: Z. Physik Chem., 159, 349 (1932) (G).

258. Schmidt, O.: Z. Physik Chem., 159, 337 (1932) (G).

*259. Weidenhagen, R. and Wegner, H.: Ber., 71, 2712 (1938) (G).

*260. Conradin, F., Bertossa, D. and Giesen, J.: U.S. 2,852,570 (9/16/58).

*261. Giesen, J. and Müller, F.: U. S. 3,011,002 (11/28/61).

*262. Inventa A. G. (Swiss): Brit., 834,771 (5/11/60).

*263. Maclean, A. F. and Heinz, W. E.: U.S. 2,760,983 (8/23/56).

264. Godfrey, T. M.: Glycerol, ACS Monograph 117, Miner, C. S. and Dalton, N. N. eds., Reinhold, N. Y. (1953), pp. 79-80.

*265. Prudhomme, E. A.: U.S. 2,121,981 (6/28/38).

Nutrition of Fatty Acids

266. Burr, G. O. and Burr, M. M.: J. Biol. Chem., 82, 345 (1929).

267. Schur, B. T. et al: J. Nutr., 33, 641 (1957).

268. Deuel, H. J. et al: J. Nutr., 33, 579 (1957).

269. French, C. E. et al: J. Nutr., 43, 91 (1952).

270. Samuels, L. T. et al: J. Nutr., 36, 639 (1948).

271. Ershoff, B. H.: J. Nutr., 53, 439 (1954).

272. Munro, H. N.: Physiol. Rev., 31, 449 (1951).

*273. Evans, H. M. and Lepkovsky, S.: J. Biol. Chem., 83, 269 (1929).

274. Cheng, A.L.S. et al: J. Nutr., 37, 237 (1949).

*275. Steggerda, F. R. and Mitchell, H. H.: J. Nutr., 45, 201 (1951).

*276. Avi-Dor, Y.: Biochem. Biophys. Acta., 39, 53 (1960).

*277. Zborowski, J. and Wojtcak, L.: ibid., 70, 596 (1963).

278. Falcone, A. B. and Mao, R. C.: ibid., 105, 233 (1965).

*279. Alfin-Slater, R. B. et al: J. Nutr., 87, 178 (1965).

280. Kaunitz, H. et al: J. Nutr., 71, 400 (1960).

*281. Kaunitz, H. et al: J. Nutr., 20, 521 (1960).

*282. Uzawa, H. et al: Am. J. Clin. Nutr., 15, 365 (1963).

*283. Van de Kamer, J. J. and Weijers, H. A.: J. Clin. Invest., 41, 488 (1962).

*284. Dawson, A. M. et al: Proc. Soc. Exptl. Biol. Med. 117, 97 (1964).

285. Schwabe, A. D. et al: J. Appl. Physiol. 19, 335 (1964).

*286. Spining III, A.M. et al: Proc. Soc. Explt. Biol. Med., 117, 774 (1964).

287. Deuel, H. J. Jr.: The Lipids, Vol. III, Interscience Publishers, New York, (1957).

*288. Kirschner, S. L. and Harris, R. S.: J. Nutr., 73, 397 (1961).

289. Kaziro, Y. and Uchoa, S.: Adv. in Enzymology, 283 pp. (1964).

*290. Coon, M. J. and Abrahamsen, N. S. B.: J. Biol. Chem., 195, 805 (1952).

*291. Coon, M. J. et al: J. Biol. Chem., 199, 75 (1952).

292. Tryding, N. and Westoo, G., in Biochem. Prob. of Lipids, Interscience Publishers, New York (1956).

*293. Tryding, N. and Westoo, G.: Acta Chem. Scand, 11, 427 (1957).

294. Asano, M. and Yamacawa, T.: Chem. Abstr., 44, 2626 (1950).

295. Dziewiatkowski, D. D. and Lewis, H. B.: J. Biol. Chem., 158, 77 (1945).

*296. Ref. 20, p. 2.

*297. Lang, K. and Adickes, F.: Z. Physiol. Chem., 269, 236 (G) (1942).

298. Halliburton, W. D. et al: Biochem. J., 13, 302 (1919).

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