

THE EFFECT OF PRESSURE AND TEMPERATURE  
UPON THE HYDROGENATION OF  
CALIFORNIA SARDINE OIL

by

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# THE EFFECT OF PRESSURE AND TEMPERATURE UPON THE HYDROGENATION OF CALIFORNIA SARDINE OIL

## I. INTRODUCTION

### A. Development of Oil Hydrogenation

In the economy of fats and oils, nature has supplied a surplus of liquid oils but a comparatively small amount of the more useful, hence more valuable, solid fats. Attracted by the possibility of supplementing the supply of fats and of profiting from their greater value, both theoretical chemists and chemical technologists have devoted considerable effort to the conversion of oils to fat. Superficially, the problem appeared simple, being merely the conversion of linolenic, linoleic and oleic acids to stearic acid by the addition of 1 to 2% hydrogen. Actually these acids proved quite resistant to hydrogenation, and it awaited the development of effective hydrogen carriers and catalysts to give the process commercial practicability.

Before 1900, the attempts to convert olein to stearin were largely confined to chemical means.  
(13)  
Goldschmidt in 1875 reduced oleic acid by means of hydriodic acid and amorphous phosphorus at  $200^{\circ}$ - $210^{\circ}$  C.  
(9)  
This method was modified by de Wilde and Reyckler to involve the heating of oleic acid to  $280^{\circ}$  C. with 1% of iodine and subsequent recovery of the stearic acid and excess iodine. Similar attempts using chlorine and

bromine were also made. Tissier<sup>(38)</sup> in 1897 claimed to have reduced oleic acid by nascent hydrogen. Powdered metallic zinc was autoclaved with water and the fatty material. Other chemical methods involved the use of zinc chloride, sulfuric acid, caustic potash fusion, or the reduction of chlorinated oleic acid with zinc or iron.

All these chemical methods of reduction proved of little theoretical value and of no use commercially. For a more thorough discussion of such early attempts reference is made to the writings of Lewkowitsch<sup>(28)</sup> and Ellis.<sup>(10,11)</sup>

The real background of modern catalytic oil hydrogenation started with the work of Sabatier and Senderens.<sup>(35)</sup> Although they were not primarily concerned with the conversion of oleic to stearic acid, but with the general topic of the addition of hydrogen to unsaturated organic compounds, their work brought recognition of the effectiveness of Ni and certain other metals as carriers of hydrogen. By their exhaustive investigations they demonstrated that the promotion of the hydrogenation reaction by metallic catalyzers was one of widespread applicability.

The literature dealing with the specific use of the work of Sabatier and Senderens in oil hydrogenation is scanty, consisting mostly of patent notices. As is usually the case with patent literature, the number of

patents, claims and counter-claims becomes quite confused, therefore only a few of the more outstanding patents will be mentioned.

The first patent recognizing the possibilities of hydrogenating oils in the liquid state was a German patent granted to Le Prince and Siveke<sup>(27)</sup> in 1902. The Normann patent,<sup>(33)</sup> frequently held to be the fundamental and controlling patent for the hydrogenation of fatty oils generally, is in reality quite broad and rather vague. It provides for the hydrogenation of either vaporized fatty acids or liquid oil, offering two devices for accomplishing this end: (1) a cylinder containing a bed of granular pumice coated with a metal catalyzer through which the hydrogen and the oil vapors are passed, and (2) a container in which a mixture of the liquid oleic acid and a reduced nickel oxide catalyst is heated, and through which a stream of hydrogen is passed. Normann claimed complete conversion of oleic to stearic acid.

Following the caution given by Sabatier--that only the vapors of the material being hydrogenated should come in contact with the catalyzer--many early patents such as those of Schwoerer<sup>(37)</sup> and Bedford<sup>(5)</sup> attempted vapor phase hydrogenation. Erdmann<sup>(12)</sup> made earliest use of a spray tower system of hydrogenation in 1907, and Kayser<sup>(26)</sup> obtained a patent in 1911 for the use of an internally



agitated cylinder. Further mention will be made of these various industrial methods of hydrogenation under the heading of hydrogenation equipment. For a more thorough discussion of early hydrogenation equipment and patents, the writing of Ellis<sup>(10,11)</sup> is again recommended.

#### B. Hydrogenation of Pacific Coast Sardine Oil

Since the work of Sabatier and Senderens and the original patents just mentioned, the work on oil hydrogenation has been directed toward more efficient methods and wider application. Practically all unsaturated oils and fats have been hydrogenated experimentally and many have found commercial application. Among these, cottonseed, peanut, soybean, rapeseed, sesame seed, linseed, marine animal and fish oils have been hardened in sufficient quantity to be of commercial importance.

Though the possibility of converting the highly unsaturated, smelly, relatively worthless fish oils into clear tallows has been mentioned in numerous patents from those of De Hemptinne<sup>(8)</sup> in 1907 and the Badische Company<sup>(2)</sup> in 1914, on through a long list of others, the actual employment of this process, especially in the United States has just developed during the last decade.<sup>(7)</sup> Of the present 230,000,000 pounds of fish oils used annually in the United States, comprising 4 to 5% of our

total fat consumption, approximately two-thirds is hydrogenated for use in shortening, soap or stearic acid production.

On the Pacific Coast, the hardening of fish oil promises to be a small, but permanent part of the chemical industry. The reasons for this are (1) the obvious proximity of the source of supply of the raw oil, and (2) the abundance of cheap, pure hydrogen produced as a by-product of the electrolytic chlorine-caustic soda industry of the Puget Sound and California areas. The amount of oil thus processed here on the Coast has increased to about 30,000,000 pounds annually within recent years. The kinds of oils used for this purpose are in the order of their importance California sardine (*Sardinops caerulea*), sometimes called Washington or Oregon pilchard and sometimes described as *Sardina coerulea* under an older system of classification, and Alaska or Pacific herring (*Clupea pallasii*). Oil from the refuse of salmon canneries is sometimes used also.

### C. The Problem

For the best understanding and most satisfactory employment of the hydrogenation of fish oils, complete data on the course of hydrogenation should be available. These should include (1) hydrogenation control curves such as refractive index-iodine number, iodine number-

titer, and melting point-titer curves; (2) hydrogenation rate curves; (3) selectivity curves following the course of hydrogenation and showing the relative disappearance of the various unsaturated acids; (4) data showing the formation of iso-oleic acid, (5) of stearic acid, and (6) of free fatty acids. It is especially important that the relation of pressure and temperature of hydrogenation to the six items just mentioned be known. Because of the breadth of the subject, this paper will deal with the California sardine oil only.

#### D. Literature Review

Considerable work involving the hydrogenation of various fish oils has been done, but such works either have not been interested in the course of hydrogenation or have failed to recognize the effect of pressure and temperature. Of these, a few are of sufficient importance to be mentioned.

Control curves: A control curve represents graphically the relationship of an easily determined physical constant such as melting point or refractive index, to one of the common commercial specifications, usually iodine number or titer. Such curves are of basic importance in industrial oil hydrogenation and must be established by any company attempting to hydrogenate oil to the consumer's specification. A number of such relation-



ships have been established by industrial oil hydrogenators for their own use and have not appeared in the literature. Two examples of this type of work are the melting point-solidification point-titer tables of Haas<sup>(15)</sup> and the refractive index-iodine number-titer charts of Wojcik.<sup>(42)</sup> Both these works were prepared on California sardine and on Alaska herring, but they do not take into account the effect of the pressure and temperature of hydrogenation, nor the type of hydrogenation, nor the type of hydrogenation equipment. Maruta and Teruyama<sup>(30)</sup> have worked out a mathematical relationship between iodine number and refractive index in sardine oil as follows:

$$R.I.(50^{\circ}) = 1.4432 + ((2.085 \times 10^{-4})(I.No.) - (3.60 \times 10^{-7})(I.No.)^2)$$

where I. No. > 85, and

$$R.I.(50^{\circ}) = 1.4500 + .0001002(I.No.), \text{ where } I.No. < 85.$$

These expressions give results fairly consistent with the actual but again altered conditions of hydrogenation are not considered. Industrial experience has shown that such changes affect the iodine number-refractive index relationship beyond the limits of allowable error.

The fact that control curves are affected by temperature of hydrogenation has been observed by Moore, Richter and Van Arsdel<sup>(32)</sup> in their extensive study of

the course of hydrogenation of cottonseed oil. They noticed that while the ends of the melting point-iodine number curve remained fixed, there was considerable deviation in the central part of the curve, depending on the temperature of hydrogenation.

Hydrogenation rate curves: In a study of the rate of hydrogenation of an oil, it is obvious that the shape and, more particularly, the slope of the curve will change with the temperature and pressure. No data have been published on the variation in speed of addition of hydrogen to sardine oil, but Moore, Richter and  
(32)  
Van Arsdel have presented curves showing that increased temperature, pressure, and catalyst percentage and rate of agitation all accelerate the speed of hydrogenation in cottonseed oil.

The general conclusion is that for most oils the rate of hydrogenation is increased by raising the temperature up to the optimum for that particular oil. This temperature for many oils is about 180°C. The subject of optimum temperature is discussed at length  
(11)  
by Ellis. There are few examples of hydrogenation rate curves in the literature and none for sardine oil.

Selectivity curves: By selectivity in hydrogenation we mean the tendency for the more highly unsaturated acids or their glycerides (e.g. linoleic acid or linolein) to be singled out or selected for hydrogen-

ation in preference to the more nearly saturated acids or their glycerides (e.g. oleic acid or olein). To be completely selective, all linolic acid or linolein should be reduced to oleic acid or olein before any stearic acid is produced. Actually, such a condition is only approached, not reached. Most selectivity studies deal with the horizontal series of linolenic-linolein-oleic-stearic acids or their glycerides and it is to this series that this paper refers when selectivity is mentioned.

(21)  
Hilditch and Moore claim to have known as early as 1913 that hydrogenation is selective and since that time Hilditch and his co-workers have been prolific writers on the general subject of the composition of hydrogenated oils. They have determined the various acids after hydrogenation in the following oils:  
(21)  
(1) cottonseed, maize, soy and linseed, (2) olive  
(19, 20) (3) and cottonseed, (3) palm, (4) rapeseed,  
(14)  
whale, cod-liver and carp, and (5) antarctic whale  
(17)  
and north sea cod-liver. The object of their work has not been to follow the course of hydrogenation, but to study the composition of the original oil through an exhaustive examination of the hydrogenated material.

(16)  
Harper has demonstrated selectivity through a presentation of rates of conversion of one acid to another

for cottonseed, soy bean, whale and rapeseed, based on a compilation of the above works. His concern was with the vertical series  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$  and  $C_{20}$  acids. These works do not present selectivity curves nor mention the effect of pressure and temperature on selectivity.

The most complete discussion of the course of hydrogenation and of selectivity that has appeared to date is that of Moore, Richter and Van Arsdel.<sup>(32)</sup> Their work, done with cottonseed oil, presents triangular graphs showing the effect of temperature, pressure, catalyst percentage, rate of agitation, and size of hydrogenation equipment upon selectivity. These curves show that selectivity in hydrogenation of cottonseed oil varies (1) directly with temperature of the reaction; (2) inversely with pressure; (3) inversely with the percentage of catalyst; and (4) inversely with the rate of agitation.

No reference has been found to selectivity in the hydrogenation of sardine oil, but it may be assumed that much the same conditions hold as just described for cottonseed oil. Marcusson and Meyerheim<sup>(29)</sup> however, have reached the conclusion that fish oil does not hydrogenate selectively. They state that a certain percentage of the highly unsaturated fatty acids remain even after a large proportion of the oleic acid has been transformed into stearic acid.

It seems safe to assume that selectivity in the



hydrogenation of sardine oil is somewhat short of complete, but the statement that no selectivity is evinced is open to question.

Iso-oleic acid: A definition of what acids are meant by iso-oleic acid is necessary. The isomerism of oleic acid may be of two types--position isomerism or stereoisomerism. Both types of isomers are included in the term "iso-oleic." Any oleic acid other than the normal 9:10 cis form falls into the category of iso-oleic acid. Thus, this grouping includes elaidic acid, ( the  $\Delta$ 9:10 trans form), the stereoisomer of normal oleic acids and petroselenic acid ( $\Delta$ 6:7 cis) and its stereoisomer. Iso-oleic acids with the unsaturation in the 7:8, 8:9, 11:12 and 12:13 positions have also been mentioned. In fact, the double bond may be between any two carbon atoms from the 2:3 to the 17:18, though the ones mentioned are the most common. All these acids are classed as iso-oleic acid. With the exception of the  $\Delta$ 12:13 cis acid, all are solids at room temperature, having melting points from  $33^{\circ}$  to  $54^{\circ}\text{C}$ . as compared with  $16^{\circ}\text{C}$ . for the normal oleic acid.

These iso-oleic acids are of interest here because of their appearance in the glycerides of hydrogenated oils. This accumulation of iso-oleic acid may come about in one of several ways: (1) by the saturation of the 9:10 but not the 12:13 double bond in linoleic acid,

(2) by the migration of the double bond of normal oleic acid, (3) by the conversion of oleic to elaidic acid under the conditions of the hydrogenation, and (4) by preferential hydrogenation of the oleic as against the elaidic acid.

From the industrial standpoint, the presence of iso-oleic acids in the hydrogenated fat is undesirable. (18)  
The presence of iso-oleic acids produces a fat of higher melting point than would be the case in a natural fat of the same iodine number. Iso-oleic acids lessen the value of hydrogenated fat in three important markets. First, the crystal structure of the solid iso-oleins, which is usually that of large, soft, waxy plates, tends to affect the appearance and consistency of edible fats in which they may be present and introduces some difficulties in cooling and preparing the final product. Second, the crystal structure of the iso-oleic acids are less tractable than that of palmitic and stearic acids, complicating the problem of utilizing fatty acids from hardened fats in the candle industry.

The third objection to the iso-oleic acids is in connection with the soap industry. Normal oleic acid yields an almost ideal soap by virtue of the relative ease of dispersion of its sodium salts and the low surface tension of these dispersions. The sodium salt of iso-oleic acids form dispersions less readily and of

higher surface tension. Their soaps then are inferior in lathering power and detergent power, to soaps made from natural fatty acids of the same degree of unsaturation.

Since these undesirable features exist, much effort has been devoted to the control of iso-oleic acid in the commercial hydrogenation of oils. However, the results of such works have been contradictory. Veno<sup>(41)</sup> found that the amount of iso-oleic acid produced is decreased<sup>(6)</sup> by higher hydrogenation temperatures, while Bloemen<sup>(31)</sup> and Mazume found the reverse to be true. Work with sunflower seed oil has demonstrated a gradual accumulation of iso-oleic acid up to 25-30% under all conditions of hydrogenation.

The presence and conditions of formation of iso-oleic acids have been reported for nearly all oils hydrogenated. Toyama and Tsuchrya<sup>(39)</sup> have studied iso-oleic acids in hydrogenated Japanese sardine oil. They suggest that it is produced by the partial hydrogenation of more highly unsaturated fatty acids. No comprehensive work dealing with the formation of iso-oleic acid during commercial hydrogenation of sardine oil appears to have been published.



## II. HYDROGENATION EQUIPMENT

To investigate the course of the hydrogenation of sardine oil a small scale hydrogenation unit for the production of the samples to be analyzed had to be constructed. Since these samples could not be obtained from a commercial hydrogenation plant, the model was set up in the basement of the chemistry building, following as closely as possible the conditions which would hold in a commercial plant. It had to be of about  $1\frac{1}{4}$  to 3 gallons capacity and so designed as to permit the withdrawal of samples at intervals during the hydrogenation. So that the work might have more importance commercially, it was desired to make the conditions of hydrogenation similar to those in an industrial process.

The equipment in use in industrial oil hydro-  
(18)  
genation falls loosely into three classes. The first is the agitation type, consisting of a cylindrical shell with a motor-driven agitator running horizontally through its length. Oil, with admixed catalyst is loaded into the unit, leaving  $\frac{1}{3}$  to  $\frac{1}{2}$  of the vacant space for gas. The oil is heated, and at the end of the process it is cooled, by means of internal coils. When the desired temperature has been reached, the gas space is filled with hydrogen, generally to a pressure of 50-100 pounds per square inch. Hydrogenation is accomplished by violent agitation of the oil, splashing a spray of oil-catalyst mixture into the hydrogen. This type of

equipment usually handles from 5 to 15 tons of oil per charge and is strictly a batch operation.

The second process in common use is also a batch process. Its equipment consists of an upright cylindrical shell, generally cone bottomed, which may be charged to  $1/2$  to  $2/3$  of its depth with oil and catalyst. This mixture is then withdrawn from the bottom and forced back into the top through some sort of spraying device. During actual hydrogenation the gas space above the oil charge is filled with hydrogen to a pressure generally not exceeding 100 pounds per square inch. Heating prior to and cooling during and after hydrogenation is accomplished by either an external heat exchanger built into the circulation line or by internal coils or by a combination of the two. In this equipment the bulk of the hydrogenation is done while the fine droplets of oil are descending through the gas space at the top of the vessel. This circulation hydrogenation system is usually built to handle from 10 to 25 tons of oil per charge.

The third system, one that is in less common use than the first two, differs from the others in that it is continuous in its operation. In it, the oil and hydrogen pass in countercurrent flow over a stationary catalyst on the surface of which the reaction takes place. Such a catalyst is frequently produced by the

anodic deposition of nickel oxide on a nickel framework. When this oxide is reduced with hydrogen at about 250°C., a nickel black of considerable surface is produced. This process has several advantages claimed for it, such as longer catalyst life, lower operating costs, and greater flexibility of operation.

Many variations of the three general types have been patented. Often some features of the first and second methods are combined. As early as 1913, Sachs (36) reported 183 patents on oil hardening methods, of which 33 were German, 22 French, 51 English, 33 American, 9 Belgian and 35 from other countries. This number has no doubt multiplied many times since 1913. Ellis (11) has made a very complete review of the methods of oil hydrogenation, which is recommended if a more thorough discussion is desired.

Examples of the first two types of equipment mentioned are in use in the hydrogenation of fish oils on the Pacific Coast. Of these, the second lends itself more readily to the construction of a laboratory model and was the type chosen for the production of the samples for this work. Such a hydrogenation unit was chosen in preference to the usual laboratory hydrogenation bomb, since (1) its capacity could be made large enough to permit the accumulation of 6 or 8 samples of 400-500 grams during the course of one run; (2) with it samples

can be withdrawn while the hydrogenation is in progress; and (3) as suggested before, its similarity to industrial equipment should give it more application in industry, while not detracting from its theoretical interest. The hydrogenation system used in the production of samples for this study is shown on the following page.

The reaction chamber was constructed from a three foot length of standard 6" steel pipe on either end of which was threaded six inch screw flanges. Six inch blank flanges drilled to accommodate circulating line, guage, vent and hydrogen inlet were used for the ends. Flanges were of extra heavy construction for greater safety. A 1/2 inch coupling welded through served as thermometer well. The circulation line was of 1/2 inch pipe with a 1/2 inch gear pump as the source of circulating power. This pump delivered approximately 3 gallons per minute. With the 5000 gram charge used, this rate of flow meant about two cycles per minute at the beginning of the run, or about twice that at the end, after the series of samples had been withdrawn.

About 3 1/2 feet of the circulation line was jacketed with a 1 1/4 inch pipe to serve as a heat exchanger. This jacket was connected to steam and cold water. In the actual operation, however, it was found that the steam pressure available did not supply sufficient heat to reach the desired temperature of hydrogenation and that radiation was sufficient to more than



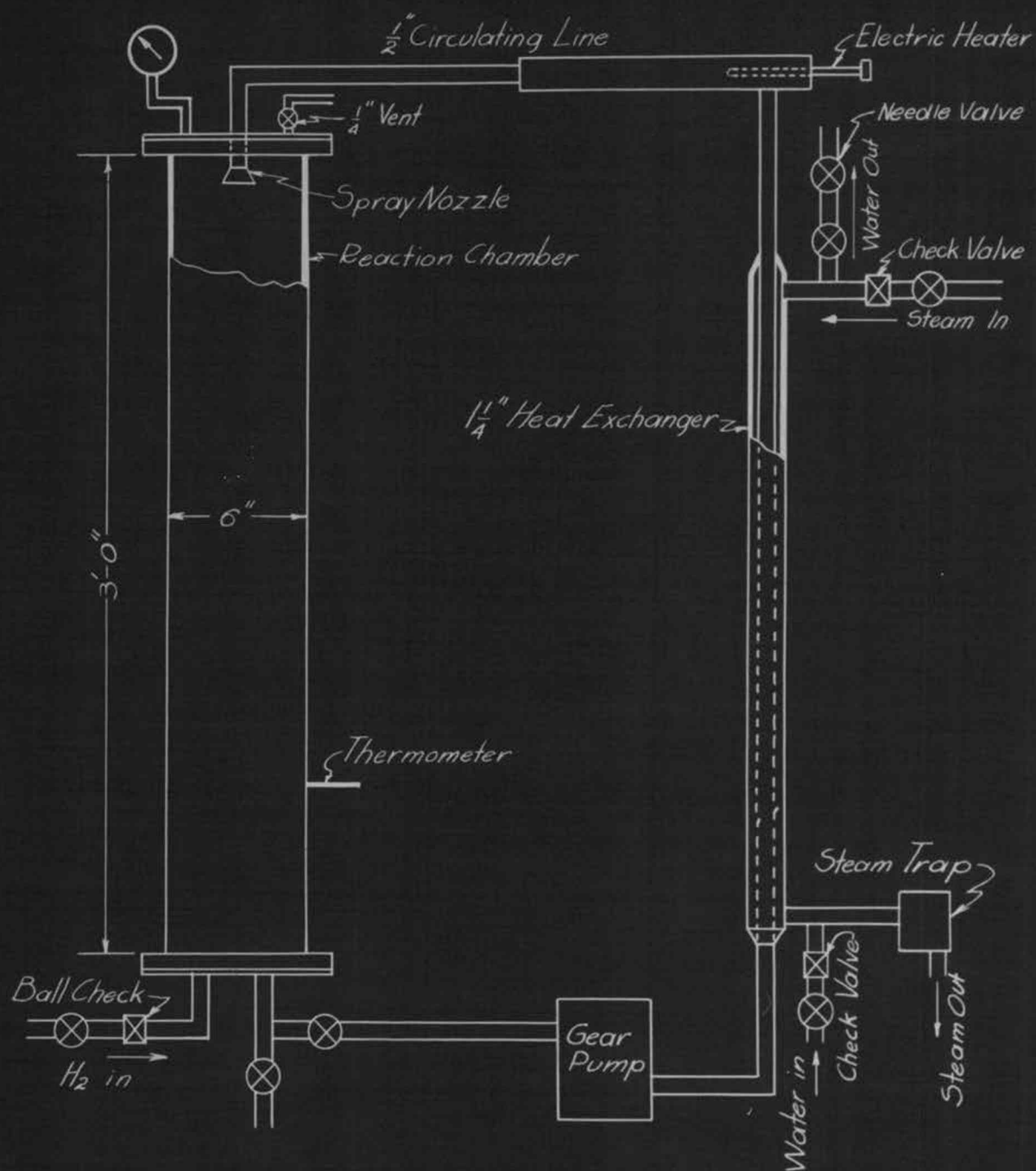


Fig. 1--Diagram of Hydrogenation Equipment

dissipate the heat produced by the exothermic hydrogenation reaction. Consequently, the heat exchanger was used but little. To obtain a sufficiently high temperature it was finally necessary to enlarge one part of the circulating line to 1 1/4 inch pipe and insert an electrical heating element. The entire system was insulated with inch magnesia lagging to conserve heat. With these alterations, an operating temperature of 140-195°C. was obtained without undue difficulty.

Temperature was determined by an ordinary 250° laboratory thermometer, graduated in degrees Centigrade, held in a packing gland so that the mercury bulb and about an inch of the stem were in direct contact with the oil. Pressure was read from a 0-100 pound gauge with 5 pound graduations, but on which pressure could be read to one pound. A check on the pressure was supplied by the low pressure gauge on the cylinder from which the hydrogen was obtained. Agreement in the two gauges was very close.

After the initial difficulties were overcome, the equipment operated very satisfactorily. As it was constructed, hydrogenation could be conducted at pressures between 0 and 100 pounds and temperatures up to 200° or 225°C., and with a charge of 2000 to 6000 grams of oil. In addition to being of value in following the course of hydrogenation, as in a study of this type, this app-

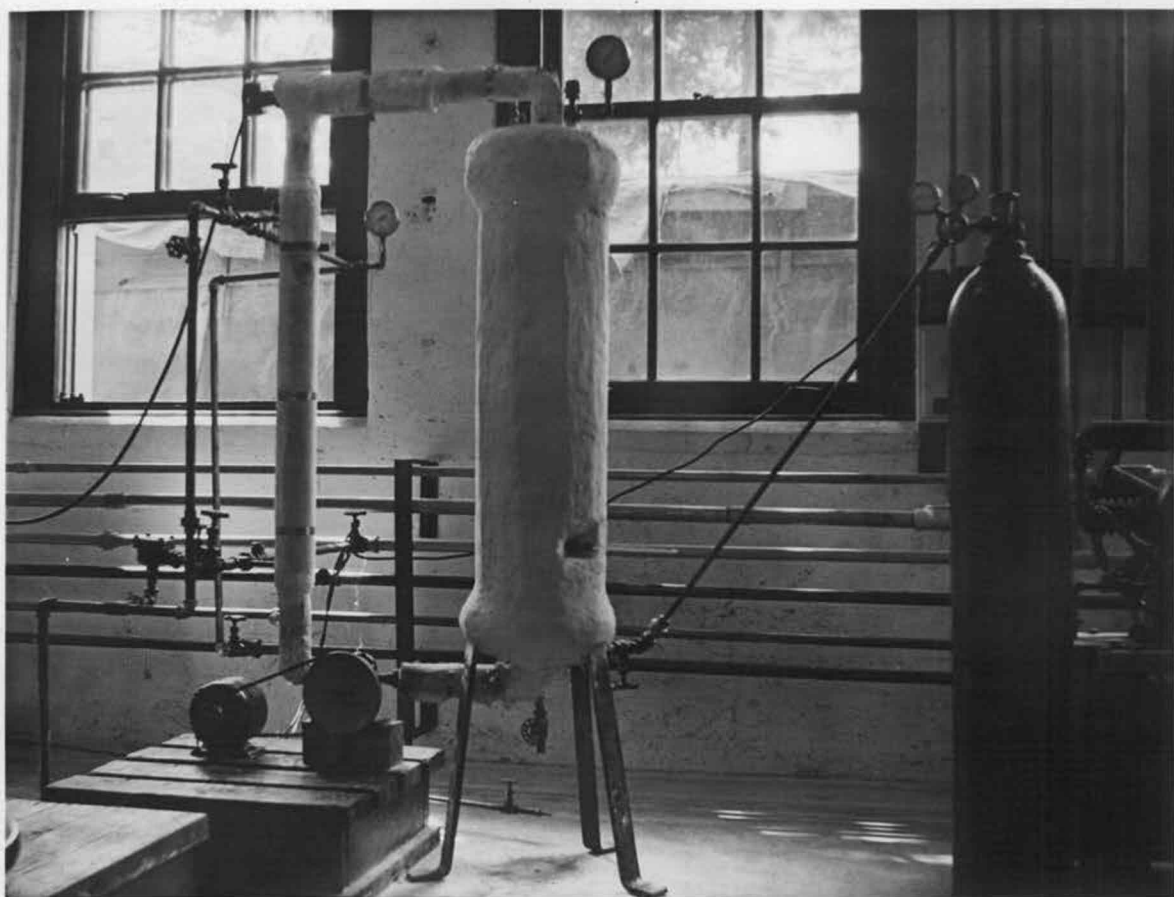


Fig. 2--Photograph of Equipment



aratus is suitable for use in an industrial laboratory in determining whether an oil is capable of hydrogenation to a desired product, or in the production of special samples which differ from the current plant output.

### III. PREPARATION OF SAMPLES

#### A. Materials Used

The following materials were used in the preparation of the hydrogenated samples:

Oil: The oil used was a pre-treated California sardine oil supplied by the Hooker Electrochemical Company of Tacoma, Washington, taken from oil to be used by them in industrial oil hydrogenation. Pre-treatment consisted of vacuum drying, bleaching with activated clay and activated carbon, and filtering. The analysis of the oil used was as follows: Iodine number--181.0; saponification number--188.0; thiocyanogen number--104.8; refractive index--1.4656 at 60°C.; free fatty acid content--1.14%; solidification point of fatty acids--33.10; solid fatty acids--23.1%.

Catalyst: The catalyst used was a wet-reduced nickel carbonate suspended in hydrogenated fish oil, produced by the Seymour Manufacturing Company of Seymour, Conn. It is handled by the Rufert Chemical Company of New York, brokers, from which it takes the name of Rufert catalyst. The sample used was supplied by the Hooker Electrochemical Company from their regularly purchased stock. By the Seymour Company's analysis, the catalyst contained 21.8% of Ni.

In the industrial oil hydrogenations, the usual method of using catalyst is to use .15 to .25% of Ni

the first time that the catalyst is used, and on subsequent recyclings to add small amounts of new catalyst until the total percentage of Ni reaches .5 to .8. The catalyst may then be discarded or re-worked for its nickel content.

In the hydrogenator used for this work, .25% Ni was found to give too slow a rate of hydrogenation. .75% Ni was finally found to give the most satisfactory results and was kept as the catalyst content throughout the work.

Filter aid and Bleach: To improve the ease of filtration and the appearance of the oil samples, .25% each of Johns-Manville Filter Cel (a diatomaceous earth) and bleaching clay, a product of the Filtrol Corporation, called Super Filtrol ( an activated clay) were added to the charge. These material were likewise secured from the Hooker Company.

#### B. Operation of Hydrogenator

117 g. of catalyst, 12.5 g. filter aid and 12.5 g. Filtrol were heated to 60°C. with about 700 g. of oil, with occasional stirring, until the catalyst had melted and was suspended in oil. All solids in the catalyst mixture were rinsed into the hydrogenator with sufficient 40° oil to bring the total charge of oil to 5000 g.

The charge was heated with circulation, using both the steam in the heat exchanger and the electrical heating unit.

When the temperature reached  $110^{\circ}\text{C}.$ , circulation was stopped briefly while the reaction chamber was purged with hydrogen. No pressure was introduced, but merely an atmosphere of hydrogen established. Circulation of the oil was then resumed. At about  $135^{\circ}\text{C}.$ , the steam to the heat exchanger was shut off and heating continued with the electrical unit. The proper pressure of hydrogen was introduced at a temperature  $15^{\circ}$  below the temperature to be maintained for the run. The gas was vented to atmospheric pressure shortly after being admitted. This removed any traces of moisture or inert gasses.

### C. Hydrogenation Data

The summary of the pressure, temperature, hydrogenation time, etc. are given in Table I.

Maximum pressure variation was 3 pounds except while samples were being removed when for 15 or 20 seconds pressure dropped below that limit. Temperature was maintained at the figure given,  $\pm 3^{\circ}$ .

Each charge consisted of 5000 g. of oil, 172 g. catalyst (3.44% catalyst or .75% Ni), 12.5 g. (.25%)

filter aid and 12.5 g. (25%) bleaching clay. In Table I, overall time is time from completion of loading until after the last sample had been removed. Hydrogenation time is figured from the first introduction of hydrogen until the last sample was finished. Six samples were taken on each run.

TABLE I

Run	Temperature Centigrade	Pressure lb.	Overall time	Hydrogenation time
A.	145 <sup>0</sup>	65	4 hrs. 40 min.	2 hrs. 50 min.
B.	170 <sup>0</sup>	65	4 hrs. 40 min.	2 hrs. 40 min.
C.	195 <sup>0</sup>	65	3 hrs. 40 min.	2 hrs.
D.	170 <sup>0</sup>	40	4 hrs. 25 min.	2 hrs. 45 min.
E.	170 <sup>0</sup>	90	4 hrs. 30 min.	2 hrs.
F.	170 <sup>0</sup>	65	5 hrs. 15 min.	2 hrs. 45 min.

Runs A, B and C were primarily for the purpose of studying the effect of temperature and runs D, E and F were for noting pressure effect. Runs B and F are duplicates. This was done to give a check on whether the results obtained could be reproduced. However, since B was the first run made and was used throughout as a trial run, it has not agreed in all respects.



#### IV. ANALYSIS OF SAMPLES

The tests used in the examination of oils are fairly well accepted, but a review of the literature on these tests shows a great many variations and modifications. Among the books giving a thorough discussion of the analytical constants of hydrogenated oil are those of Ellis, <sup>(11)</sup> Hilditch <sup>(18)</sup> and Jameison. <sup>(48)</sup>

In addition to these standard reference works, innumerable journal articles are devoted to minor alterations in technique and procedure. To have established analytical procedure from among these would have meant a lengthy series of trial determinations. This has been quite thoroughly done by the various committees of the American Oil Chemists Society and it was decided to use their methods, as published in their handbook, <sup>(1)</sup> throughout all laboratory work.

The following analytical determinations were made:

##### A. Free Fatty Acid

This is customarily reported as the percentage of free fatty acid calculated to oleic acid except in oils where lower molecular weight fatty acids predominate, such as palm, cocoanut and palm kernel oils. In this work, all free fatty acid percentages are as oleic acid. The error which this introduces is very small, not exceeding  $\pm 5\%$  of the percentage reported.

Determination: Weigh between 7 and 10 g. oil into a 250 c.c. erlenmeyer flask and dissolve with heating in 50 c.c. of neutral 95% alcohol, freshly distilled from NaOH and neutralized to phenolphthalein with .25 NaOH, and titrate with .25 N NaOH, using phenolphthalein as indicator.

Calculation:

$$\frac{N \times \text{c.c.} \times 282.3 \times 100}{1000 \times \text{sample weight}} = \% \text{ F.F. A.}$$

The .25 N NaOH was standardized against .25 N HCl with  $\text{Na}_2\text{CO}_3$  as primary standard.

B. Titer Test

This test is the one most frequently used in describing the hardness of a fat. It is the solidification point of the fatty acid portion--not that of the glyceride--of the oil determined under definitely described conditions.

The standard titer thermometer described by the AOCS handbook was not available but one very similar was substituted for it. This was an A.S.T.M. thermometer of 27-71°C. range, graduated in .2° and designed for 79 m.m. immersion.

Determination: Heat 80 c.c. of glycerol-caustic



solution (250 g. KOH in 1000 c.c. glycerine) and add 50 g. of the melted fat. Stir the mixture well and continue heating until the melt is homogeneous, at no time allowing the temperature to exceed  $150^{\circ}\text{C}$ . Allow to cool somewhat and carefully add 50 c.c. of 30 per cent sulfuric acid. Add hot water and heat until the fatty acids separate out perfectly clear. Draw off the acid water and wash the fatty acids with hot water until free from mineral acid, then decant from residual water. Heat to  $130^{\circ}\text{C}$ . as rapidly as possible while stirring. Transfer the fatty acids when cooled somewhat, to a 2.5 x 10 mm. (1 x 4-inch) titer tube, placed in a 450 c.c. (16 oz.) salt-mouth bottle of clear glass, fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly with a circular motion in one plane at about 100 r.p.m. until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids.

The titer should be made at about  $20^{\circ}\text{C}$ . for all fats having a titer above  $30^{\circ}\text{C}$ . and at  $10^{\circ}\text{C}$ . below the titer for all other fats. Any convenient means may be

used for obtaining a temperature of  $10^{\circ}\text{C}.$  below the titer of the various fats.

### C. Refractive Index

The refractive index is a constant commonly used in the identification of oils and one that changes quite characteristically during hydrogenation. In hydrogenation it is frequently used as a control constant, being quickly determined and having a fairly constant relationship to the iodine number and titer. During the course of the hardening of the oil, the refractive index drops. In the case of sardine oil this change in refractive index is between the limits of 1.4660 and 1.4475.

For this work, determinations were made on an Abbe refractometer with water jacketed prisms for temperature control. All readings were reported at  $60^{\circ}\text{C}.$  and were made between  $57^{\circ}$  and  $63^{\circ}\text{C}.$ , using a temperature correction of  $.00036^{(34)}$  per degree. The refractometer was adjusted against  $\alpha$ -bromnaphthalene and all readings are correct to  $\pm .0002$ .

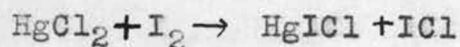
### D. Iodine number

The degree of unsaturation of many unsaturated organic compounds can be determined by reacting the

compound with one of the halogens, usually iodine. The iodine adds at the double bond or point of unsaturation and for many compounds this reaction is quantitative.

In the analysis of fats and oils, such a reaction gives rise to the quantitative expression of unsaturation commonly called the iodine number. Numerically, this value is the number of centigrams of iodine absorbed by 1 gram of oil or fat, i.e. the percentage of iodine absorbed.

Three methods of determination of the iodine number are in common use. These differ mainly in the halogen solution with which the sample of oil or fat is treated. These are (1) Wijs method in which the oil is treated with a .1 N solution of iodine monochloride in glacial acetic acid. This solution may be made either by chlorinating a solution of iodine in glacial acetic acid until the thiosulfate titration is doubled, or by dissolving iodine trichloride and iodine in acetic acid; (2) the Hanus method is similar to that of Wijs except that a .1 N solution of IBr is used instead of ICl; (3) the Hubl method involves the use of two solutions-- (a) iodine in 95% alcohol and (b) mercuric chloride in 95% alcohol. In this method, the active halogen is ICl, the same as in the Wijs solution. When the two solutions mentioned are mixed, the reaction



takes place, liberating  $\text{ICl}$  which attacks the double bonds of the oils. Even when kept separately, the solution of iodine in alcohol is not permanently stable, while if mixed prior to use the actual Hubl solution of iodine-mercuric chloride in alcohol undergoes slow but progressive change. The Hubl solution requires much longer contact with the oil or fat to insure complete addition than does the Wijs solution. Wijs solution has the drawback that with some types of organic compounds it shows a slight tendency to substitute for hydrogen as well as add at the double bond.

The Hanus solution is frequently preferred to that of Wijs because of its ease of preparation, but the Wijs method is used most often in commercial oil analysis and is the method adopted by the AOCS.

The following directions for the determination are from the AOCS handbook.

Preparation of Wijs iodine solution: Dissolve 13.0 g. of resublimed iodine in 1 liter of C.P. glacial acetic acid and pass in washed and dried chlorine gas until the original thiosulfate titration of the solution is not quite doubled. Preserve the solution in amber glass-stoppered bottles, sealed with paraffin until ready for use. Mark on the bottles the date on which the solution is prepared and do not use Wijs solution that is more than 30 days old.



There should be no more than a slight excess of iodine, and no excess of chlorine. When the solution is made from iodine and chlorine, this point can be ascertained by not quite doubling the titration.

Determination: Weigh accurately from 0.10 to 0.50 gram (depending on the iodine number) of the melted and filtered sample into a clean, dry, 250 c.c. glass-stoppered bottle containing 15 to 20 c.c. of  $\text{CCl}_4$ . Add 25 c.c. of iodine solution from a pipet, allowing to drain for a definite time. The excess of iodine should be from 50 to 60 % of the amount added--that is, from 100 to 150% of the amount absorbed. Moisten the stopper with a 15% KI solution to prevent loss of iodine or chlorine, but guard against an amount sufficient to run down inside the bottle. Let the bottle stand in a dark place for 30 minutes at a uniform temperature, and then add 20 c.c. of 15% KI solution and 100 c.c. of distilled water. Titrate the iodine with 0.1 N sodium thiosulfate solution, added gradually with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in the solution in the tetrachloride may be taken up by the potassium iodide solution. Conduct two determinations on blanks which must be run in the same

manner as the sample except that no fat is used in the blanks. Slight variations in temperature quite appreciably affect the titer of the iodine solution, as acetic acid has a high coefficient of expansion. It is therefore essential that the blanks and determinations on the sample be made at the same time. The number of c.c. of standard thiosulfate solution required by the blank, less the amount used in the determination, gives the thiosulfate equivalent of the iodine absorbed by the amount of sample used in the determination.

The .1 N sodium thiosulfate used in the titration of the excess iodine was standardized against a carefully prepared solution of  $K_2Cr_2O_7$ .

Calculation:

$$\frac{126.9 \times N \text{ (thio)} \times \text{blank-titration} \times 100}{\text{Sample weight} \times 1000} = \text{I No. \% I}_2 \text{ (absorbed)}$$

E. Thiocyanogen number

This is a newcomer among the analytical constants of fats and oils. It depends upon the fact that  $(SCN)_2$  radical behaves like a halogen and can, with limitations substitute itself in the double bonds of an unsaturated carbon chain. The  $(SCN)_2$  can be liberated from the thiocyanate by bromine if the reaction is done in an entirely anhydrous medium. Usually  $Pb(SCN)_2$  is treated

with bromine in anhydrous acetic acid containing an excess of acetic anhydride.

(24)  
H. P. Kaufman first employed the thiocyanogen solution in the analysis of oils in 1926. The method was later improved by Kaufman and Keller (25) and with minor changes, the test is still carried out as described by them.

The thiocyanogen number may be reported as the number of centigrams of  $(\text{SCN})_2$  absorbed by one gram of oil, but is more frequently reported as the iodine equivalent to this amount of  $(\text{SCN})_2$ . This keeps both iodine number and thiocyanogen number in terms of the same units. This is the value referred to as SCN number throughout this paper. More strictly it should be called the thiocyanogen-iodine number, but the first is used for reasons of brevity.

As stated above, there are exceptions to the ability of the  $(\text{SCN})_2$  to react with the unsaturations in fatty acids. These are of importance. Whereas the iodine in the iodine number determination reacts with all the double bonds, the thiocyanogen reacts quantitatively with oleic acid but with only one double bond of acids of the linoleic acid type (2 double bonds) and with only two double bonds of acids of the linolenic acid type (three double bonds). By the use of the I. No. and SCN No. jointly, it is possible to calculate the

component acids of a mixture of three acids or their glycerides.

The following formulas illustrate this important use of the constant.

		I No.	SCN No.
Linoleic acid glyceride	(X)	173.27	86.635
Oleic acid glyceride	(Y)	86.04	86.04
Saturated acid glycerides	(Z)	000	00

$$(1) X + Y + Z = 1000$$

$$(2) 173.27X + 86.04Y + Z = 100 \text{ Iodine No.}$$

$$(3) 86.635X + 86.04Y + Z = 100 \text{ SCN No.}$$

The following formulas are derived by solving the above equations:

$$(4) X = 1.154 (\text{Iodine No.} - \text{SCN No.})$$

$$(5) Y = 1.162 (2\text{SCN No.} - \text{Iodine No.})$$

$$(6) Z = 100 - (X + Y)$$

It must be remembered that Z also includes the percentage of unsaponifiable matter.

The formulas for the free fatty acids are:

$$(7) X(\% \text{ linoleic acid}) = 1.104 (\text{I. No.} - \text{SCN No.})$$

$$(8) Y(\% \text{ oleic acid}) = 1.112 (2\text{SCN No.} - \text{I No.})$$

$$(9) Z(\% \text{ saturated acids plus unsaponifiable matter}) = 95.7 - (X + Y)$$

The application of the method to oils which contain linolenic acid is the same as that already given, except that it is necessary to know the correct percents of the saturated and unsaturated acids. The equations



used for the calculation of the percent of linolenic, linoleic and oleic acids in the oil are as follows:

Acids	% in oil	Theoretical I No.	Theoretical SCN I No.
Linolenic	X	273.7	182.5
Linoleic	Y	181.1	90.5
Oleic	Z	89.9	89.9

$$(10) \quad 273.7X + 181.1Y + 89.9Z = 100 \text{ (iodine number)}$$

$$(11) \quad 182.5X + 90.5Y + 89.9Z = 100 \text{ (SCN number)}$$

$$(12) \quad X + Y + Z = 100$$

By the solution of these equations simultaneously the following formulas are derived:

$$(13) \quad X(\text{linolenic acid}) = 1.080 \text{ SCN No.} - 97.8$$

$$(14) \quad Y(\text{linoleic acid}) = 98.5 \text{ (1.112 I No.} - 2.708 \text{ SCN No.)}$$

$$(15) \quad Z(\text{oleic acid}) = 100 - (X + Y)$$

The procedure used in this work and given here is from the AOCS handbook. Another, but slightly modified, (23) is given by Jamieson.

#### Reagents:

- (1) Lead thiocyanate
- (2) Anhydrous glacial acetic acid
- (3) Bromine

(1) Preparation of lead thiocyanate: Dissolve 250 grams of the finest C.P. neutral lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ) in 500 ml. of distilled water. Dissolve likewise 250 grams of C.P. KSCN in 500 ml. of water. Add the lead acetate solution to the potassium thiocyanate solution slowly and with stirring. Filter

off the precipitated lead thiocyanate on a Buchner funnel and wash successively with distilled water, alcohol and ether. Dry the  $\text{Pb}(\text{SCN})_2$  as much as possible by drawing air through it. Remove from the funnel and dry on a watch glass in a  $\text{P}_2\text{O}_5$  desiccator for 8-10 days before using. This  $\text{Pb}(\text{SCN})_2$  should be a greenish or yellowish-white crystalline material; if it is at all discolored it must be discarded. Precipitated  $\text{Pb}(\text{SCN})_2$  may be kept for a period not exceeding two months.

(2) Preparation of Acetic acid: Acetic acid is conveniently and suitably dehydrated by refluxing with acetic anhydride. Into a 3 liter Florence flask, with a large test tube set in the neck and through which cold water is passed to serve as a condenser, are placed 2 liters of C.P. glacial acetic acid (99.5-100.0%) and 100 ml. of acetic anhydride (90-100%). This mixture is refluxed over an oil bath for three hours at approximately  $135^\circ\text{C}$ . After the anhydrous acid has cooled to room temperature, it should be placed in cleaned and dried glass-stoppered bottles.

(3) Preparation of a 0.2 N solution of  $(\text{SCN})_2$ : For the preparation of one liter of solution: Suspend 50 g. of the dry  $\text{Pb}(\text{SCN})_2$  in 600 ml. of anhydrous acetic acid in a round-bottomed 2 liter flask, equipped with a mechanical stirrer and a dropping tube. Slowly add with agitation 5.1 ml. of C.P. bromine suspended in

200 ml. of dry acid in the dropping tube. The acetic acid-bromine solution should be added at a rate such that the liquid in the reaction flask remains only faintly tinged with brown. When the entire bromine-acetic acid solution has been added, the dropping tube is rinsed out with an additional 200 ml. of the dry acid which is added immediately to the reaction mixture. When the bromine has all reacted, as indicated by the color of the reaction mixture, the agitation is ceased, the precipitated lead bromide allowed to settle, and filtered rapidly. A 13 cm. Buchner funnel and qualitative filter paper together with two 2-liter pressure flasks are used for the filtration. They are previously dried for one hour at  $105^{\circ}\text{C}$ . The entire solution is filtered by suction into the one flask, when the funnel, containing the paper and some cake, is transferred to the second flask and the solution refiltered. It should be perfectly clear upon the second filtration. The solution should be stored in glass-stoppered brown bottles and kept in a cool place ( $60-70^{\circ}\text{F}$ .).

Determination: Weigh 0.1-0.3 g. oil accurately into a dry 125 ml. glass-stoppered erlenmeyer flask. Add from a pipet 25 ml. of  $(\text{SCN})_2$  solution and allow to stand for 24 hours in the dark. The storage place should be from  $65-70^{\circ}\text{F}$ . in temperature and should not exceed  $70^{\circ}\text{F}$ . for any length of time. The size of the

sample is governed largely by the expected thiocyanogen absorption. The excess  $(\text{SCN})_2$  should be at least 100% and preferably less than 150% of the amount absorbed by the oil, although a greater excess seems to do no harm. At the end of 24 hours, 1 g. of dry powdered KI is added and the flask swirled rapidly for 2 minutes. It is advisable to agitate the blank determination for 3 minutes. Then add 30 ml. of distilled water and titrate the liberated iodine with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch as an indicator. At least three blanks should be run with the samples. The solution should also be titrated at the beginning of the 24 hour period. If the drop is more than 0.2 ml. on the blank titrations, the solution is decomposing too rapidly and erratic and low figures will be the result.

Calculation:

$$\frac{(\text{Blank-Titration}) \times N(\text{Thio}) \times 125.9 \times 100}{\text{Sample weight} \times 1000} = \text{SCN No.} \\ (\text{expressed as iodine equivalent to } (\text{SCN})_2 \text{ absorbed})$$

The same thioisulfate used on the iodine number was used on the thiocyanogen determination, making this determination also dependent upon the same dichromate solution as primary standard.

As applied to the harder samples of hydrogenated oils, this procedure has the handicap of giving results too low with the harder samples. The fat is not soluble



in the acetic acid and despite attempts to get the material into small particles, some of the fat was not attacked and the reaction did not go to completion. An attempt to use dried and redistilled carbon tetrachloride as a solvent to bring about a better contact was not successful. Results were erratic and high, and the decomposition displayed by the blank was excessive. No explanation for this behavior could be found at once and lack of time prohibited further investigation.

#### F. Separation of Solid and Liquid Acids

In the analysis of oils and fats, it is frequently of interest to know the percentages of solid and liquid acids and to be able to analyze the two independently. This separation is useful in determining iso-oleic acids since these acids are the only 18 carbon acids which are solid and yet unsaturated. It is essential that this separation be made in the determination of selectivity for one index of selectivity is the graph of iodine number of the oil of the mixed fatty acids against the percent of solid fatty acid. Finally, with the saturated fatty acids removed, an iodine number and thiocyanogen number on the liquid portion permits the calculation of the percentages of oleic, linoleic and linolenic acids in the original oil.

Several methods for such a separation have been proposed. All depend upon the relative solubilities of the lead salts of the liquid and solid fatty acids. The methods of Varrentrop and Grossfeld for the determination of solid fatty acids by the insolubility of their lead salts in ether have been improved by Baughman and Jamieson. <sup>(4, 23)</sup> The method of Twitchell, <sup>(40)</sup> using alcohol as the solvent, is in most common use in this country.

This method, as adopted by the AOCS was used in this study. It follows:

(1) Preparation of mixed fatty acids: Saponify in a 600 ml. beaker about 25 grams of the melted oil sample with about 15 grams potassium hydroxide dissolved in a small amount of water and 25 ml. of 95% alcohol. Bring to dryness on a steam bath or hot plate. (Care should be taken not to burn the soap.) Add to the soap about 200 ml. distilled water; heat on steam bath until soap is dissolved; add concentrated hydrochloric acid while stirring until soap is completely broken up. A small strip of litmus will show when mixture has been acidulated. Heat the solution containing curds of fatty acids on steam bath or hot plate until they, together with the entire contents of beaker, will pour freely into a 500 ml. separatory funnel. Transfer should be aided with 100 to 150 ml. of ethyl ether. Fatty acids-ether solution must then be washed free of acid with

distilled water. Usually three washings are sufficient, but tests of wash water with methyl orange indicator should be made. Separation of water from fatty acid-ether solution should be made as close as possible to insure no water getting into the mixed fatty acid sample. After washing free of acid filter fatty acid-ether solution through paper into a 250 ml. Soxhlet. Evaporate all trace of ether on steam bath under a current of inert gas. (Note: Use precaution to prevent oxidation of fatty acid.)

(2) Separation of solid from liquid fatty acids: From the ether-free mixed fatty acids, weigh accurately into a 250 ml. beaker a sample that will give approximately  $1.2 \pm 0.3$  grams of solid fatty acids. The sample weight should never exceed 5 grams. Weigh 1.5 grams powdered lead acetate into another beaker. Add to each about 50 c.c. of 95% alcohol, cover with watch glasses, and bring both to boil on hot plate or steam bath. Transfer the alcoholic lead acetate to the alcoholic fatty acids, stirring continually with a glass stirring rod which may be left in sample to aid later in filtration. Cool to room temperature and place in ice bath at  $15^{\circ}\text{C}$ . overnight. Filter through 3-inch Buchner funnel which has filter paper cut to fit snugly. Suction should be used to aid filtration. Use 150 c.c. of 95% alcohol cooled to  $15^{\circ}\text{C}$ . to transfer lead soaps from beaker to

Buchner funnel and in washing. After alcohol has filtered from the lead soaps, transfer them quantitatively back to the original beaker, using about 100 c.c. warm 95% alcohol to aid the transfer. Make one-half per cent acetic acid with glacial acetic acid.

Before discarding filtrate, make a test for excess lead acetate by adding a few drops of concentrated sulfuric acid to about 50 c.c. of the filtrate. Absence of cloudiness shows the sample of fatty acids was too large and present sample is of no value; therefore, it will be necessary to weigh a smaller sample of mixed fatty acids and apply the same procedure. If there is an excess of lead acetate, continue with present sample by bringing it to a boil on hot plate, stirring occasionally to assure the lead soaps dissolving. Cool to room temperature, then in ice bath at 15°C. for two hours or ice box over night. Filter through Buchner, using suction and 200 c.c. 15°C. 95% alcohol as in first filtration. After lead soaps are drawn free of alcohol, transfer them quantitatively to original beaker, using ethyl ether to aid (about 75 c.c.). Break up lead soaps by adding 20 c.c. of 1 to 3 nitric acid. Transfer to a 500 ml. separatory funnel, using ethyl ether to aid. An extra 5 c.c. of 1 to 3 nitric acid may be used to advantage in removing the last trace of sample from the beaker. Wash ether with distilled water until



neutral to methyl orange. Transfer ether to a tared 150 ml. Soxhlet and wash all traces of solid fatty acids into the Soxhlet with ether. Evaporate ether on steam bath under a current of inert gas. Dry in an oven at  $103^{\circ}\text{C}$ . for one hour, remove, cool and weigh. See that no water is in sample. It is well to be sure of constant weight by returning to oven a second time for 30 minutes.

## V. TABULATION AND CORRELATION OF RESULTS

Analytical results are given in the following tables. Table II shows the analysis of the whole oil at the various stages of hydrogenation. As would be expected, the iodine number, refractive index and thiocyanogen number decrease during hydrogenation and the titer and free fatty acid increase over the run as a whole, though in a few cases decreasing temporarily.

The rate of hydrogenation, as shown by the fall in iodine number, decreases as the oil becomes more saturated. Fig. 3 and Fig. 4 show the hydrogenation rate curves and the effect of temperature and pressure upon them. It is most interesting to note that for both temperature and pressure, but most particularly for temperature, there is a critical point above which reaction rate increases rapidly. For hydrogenation at 65 pounds the critical temperature is about  $180^{\circ}\text{C}$ . and for hydrogenation at  $170^{\circ}$  the pressure is about 75 pounds. Such curves may be of value in commercial work to determine the point of economic balance between prolonged operation periods and the detrimental effects of higher temperatures such as free fatty acid accumulation. It is of interest to note that at  $170^{\circ}\text{C}$ . the same effect may be obtained by increasing the pressure 25 pounds as by increasing the temperature  $25^{\circ}$ , but without the detrimental effect of considerably increased free fatty acid.

Figures 7, 8 and 9 give control curves from which the titer may be predicted by determining either iodine number or refractive index. As stated earlier, this relationship is not ironclad. Iodine number-titer points are scattered considerably but showed so little correlation between temperature or pressure and position of the curve that only one curve was drawn. The important things to note from this curve are that titer has no significance as a specification for oil whose iodine number is above 90, and that the curve is made up of two distinct portions, an uncertain portion in which titer stays approximately the same and a second, well-defined portion in which the usual I No.-titer change is apparent. The point of break is approximately at an I No. of 90 which corresponds to the point at which the remaining unsaturated oil is made up principally of oleic acid glycerides.

The relationship between R.I. and titer is even less definitely defined than that between I No. and titer, but no significant relationship is noticeable. It may be stated that this curve is not materially affected by the pressure at which the hydrogenation is conducted but that in the range where such a curve is most often used, i.e. above a titer of  $34^{\circ}$ , the higher the temperature of hydrogenation the lower will be the

titer for a given refractive index.

Table III gives the percent solid fatty acids present in the samples and the iodine number of such solid acids. Using this iodine number, the percentage of solid unsaturated fatty acids has been calculated and reported as iso-oleic acid and the solid saturated acid has been reported as stearic acid. It is of interest that the original oil, although having an iodine number of 181, still contains 23.1% of solid fatty acid of which .8% is solid unsaturated acid and 22.3% is stearic acid. Were the hydrogenation to be completely selective, the percentage of stearic acid would remain constant until all acids less saturated than oleic were hydrogenated to oleic. The courses that would be taken by the stearic acid-I No. curve for both 100% selectivity and complete absence of selectivity are shown by the dotted lines in Fig. 10 and Fig. 11. By comparing these with the actual curves, it may be seen (1) that the degree of selectivity in all cases is fairly great; (2) that selectivity varies directly as the temperature of the hydrogenation; (3) that selectivity varies indirectly as the pressure of hydrogenation.

Fig. 12 and Fig. 13 show the effect of conditions of hydrogenation upon the accumulation of iso-oleic acid. These curves show that in all cases the iso-oleic builds



up to a maximum at about an iodine number of 50 on the original oil and then drops off as the iso-oleic acid itself is hydrogenated; also that the maximum amount of iso-oleic varies directly with the temperature of hydrogenation, but is not materially affected by the pressure.

Table IV gives the percent liquid acids and the analysis of these acids. It is interesting that despite the degree of selectivity of the hydrogenation, some liquid acids more unsaturated than oleic remain even below an iodine number of 45.

## VI. SUMMARY

The following work has been done:

(1) A vertical circulation type hydrogenator, suitable for either an industrial laboratory or for a research laboratory, has been designed, built, and successfully operated.

(2) This equipment has been used in the preparation of six samples on each of six hydrogenation runs of California sardine oil.

(3) These samples have been analyzed and the analysis presented in tabular form.

(4) The analytical constants have been correlated graphically.

(5) From these the following conclusions have been drawn:

- a. The course of hydrogenation is affected by the temperature and pressure of hydrogenation.
- b. A critical pressure and temperature in the hydrogenation reaction are apparent at approximately 75 pounds and 170°C.
- c. The relationship of iodine number and titer is not noticeably affected by temperature or pressure of hydrogenation.
- d. Pressure has no noticeable effect upon R.I.-titer relationship but above a titer of 34°, the titer for a given R.I. varies inversely as the

temperature of hydrogenation.

e. Selectivity in hydrogenation of California sardine oil varies directly as the temperature of the hydrogenation; varies indirectly as the pressure; and is quite apparent in all cases.

f. Increasing temperature causes an increase in the amount of iso-oleic acids produced but pressure has no conclusive effect.

g. The rate of liberation of free fatty acids is not affected by changes in the pressure of hydrogenation. Increasing temperature causes a considerable increase in the rate of formation of free fatty acids, especially above the critical temperature of 170°C.

h. Two observations on oil analysis are made:

1. The titer on hydrogenated California sardine oil is without significance for oil of I No. lower than 90. Such oil should be described by its iodine number.

2. The thiocyanogen number determination does not work satisfactorily on hard oil samples (above a melting point of 35°C.).

The use of  $\text{CCl}_4$  as a solvent does not lead to satisfactory results.

TABLE II

## ANALYSIS OF WHOLE OIL

Sample	Elapsed time	F.F.A.	R. I.	I. No.	Titer	SCN No.
<hr/>						
A--145 <sup>0</sup> , 65# Minutes						
0	0	1.147	1.4656	181.0	33.10	104.8
1	15	1.069	1.4633	156.3	32.25	102.6
2	35	1.076	1.4606	134.3	32.15	96.6
3	65	1.021	1.4568	104.7	32.70	87.3
4	95	.992	1.4543	81.9	34.80	76.0
5	125	1.035	1.4527	65.1	38.50	
6	170	1.002	1.4512	46.2	43.20	
B--170 <sup>0</sup> , 65#						
0	0	1.147	1.4656	181.0	33.10	104.8
1	15	.980	1.4634	156.0	31.35	94.8
2	35	.996	1.4600	132.8	32.15	90.0
3	55	1.012	1.4571	108.4	32.25	84.0
4	85	1.176	1.4543	81.8	33.85	
5	115	1.210	1.4527	66.4	37.80	
6	160	1.306	1.4509	51.4	41.55	
C--195 <sup>0</sup> , 65#						
0	0	1.147	1.4656	181.0	33.10	104.8
1	15	1.074	1.4626	150.1	32.80	97.6
2	30	1.219	1.4590	119.6	32.05	90.4
3	45	1.075	1.4555	92.7	32.10	82.7
4	60	1.370	1.4538	74.9	34.90	68.6
5	90	1.600	1.4505	45.5	42.65	
6	120	1.984	1.4488	25.8	48.00	



TABLE II CON'T

Sample	Elapsed time	F.F.A.	R.I.	I. No.	Titer	SCN No.
Minutes						
D--170°, 40#						
0	0	1.147	1.4656	181.0	33.10	104.8
1	20	1.030	1.4636	157.3	33.00	103.3
2	40	1.100	1.4614	139.0	32.40	95.9
3	60	1.105	1.4590	120.6	31.55	93.3
4	90	1.048	1.4559	96.2	32.15	80.1
5	120	1.062	1.4539	79.0	34.40	
6	165	1.167	1.4520	58.6	39.20	
E--170°, 90#						
0	0	1.147	1.4656	181.0	33.10	104.8
1	15	1.150	1.4615	143.3	32.50	97.5
2	30	1.020	1.4576	112.0	32.30	89.4
3	45	.960	1.4552	91.1	32.80	82.7
4	60	1.007	1.4534	74.3	35.70	
5	90	1.061	1.4506	45.1	43.45	
6	120	1.173	1.4486	23.8	48.80	
F--170°, 65#						
0	0	1.147	1.4656	181.0	33.10	104.8
1	20	1.088	1.4629	152.8	32.60	93.1
2	40	1.060	1.4601	131.8	32.40	89.8
3	60	1.147	1.4578	112.0	32.10	84.0
4	90	1.187	1.4551	88.3	32.75	78.5
5	120	1.205	1.4532	71.6	35.80	
6	165	1.318	1.4510	49.1	42.00	

TABLE III

## Analysis of Solid Acids from Twitchell Separation

Sample	Cond.	% Solid acids	I No.	% Iso- oleic	% Stearic
Original oil		23.1	3.22	.8	22.3
A1	145°	26.2	6.04	1.8	24.4
2	65#	28.2	7.90	2.5	25.7
3		30.0	11.14	3.7	26.3
4		38.9	13.89	6.0	32.9
5		46.0	13.96	7.1	38.9
6		59.6	11.96	7.9	51.7
B1	170°	27.4	5.86	1.8	25.6
2	65#	30.3	10.80	3.6	26.7
3		34.2	15.53	5.8	28.4
4		38.2	16.72	7.1	31.1
5		47.2	16.94	8.9	38.3
6		55.4	15.15	9.3	46.1
C1	195°	26.4	5.65	1.6	24.8
2	65#	27.8	10.30	3.2	24.6
3		33.5	17.90	6.7	26.8
4		40.0	19.30	8.6	31.4
5		60.5	15.10	10.2	50.3
6		79.7	9.06	8.4	71.3
D1	170°	24.3	6.35	1.7	22.6
2	40#	25.4	7.78	2.2	23.2
3		26.8	11.10	3.2	23.6
4		30.0	15.54	5.2	24.8
5		38.8	19.40	8.4	30.4
6		39.8	19.10	8.5	31.3
E1	170°	26.9	6.66	2.0	24.9
2	90#	30.8	11.18	3.8	27.0
3		34.6	17.05	6.6	28.0
4		41.1	17.60	8.1	33.0
5		60.8	13.05	8.8	52.0
6		79.6	7.65	6.8	72.8
F1	170°	25.5	7.78	2.2	23.3
2	65#	27.8	10.05	3.3	24.5
3		29.0	11.04	3.6	24.4
4		33.0	15.82	5.8	27.2
5		39.8	16.70	7.4	32.4
6		54.0	14.90	8.9	45.1

TABLE IV

## Analysis of Liquid Acids from Twitchell Separation

Sample	% liquid acids	I No.	SCN No.
Original oil	76.9	212.3	125.3
A-1	73.8	186.0	125.0
2	71.8	173.1	123.9
3	70.0	142.2	117.6
4	61.1	120.4	109.3
5	54.0	108.5	102.9
6	40.4	88.9	85.4
B-1	72.6	195.5	130.6
2	69.7	188.4	117.4
3	65.8	146.2	118.8
4	61.8	122.0	110.8
5	52.8	97.8	94.0
6	44.8	94.4	90.0
C-1	73.6	181.5	122.2
2	72.2	155.0	116.0
3	66.5	128.1	113.1
4	60.0	111.8	107.3
5	40.3	92.8	90.0
6	20.3	90.5	89.4
D-1	75.7	180.3	118.0
2	74.6	173.3	119.7
3	73.2	151.5	118.8
4	70.0	132.8	115.8
5	61.2	117.6	111.8
6	60.2	117.5	109.7
E-1	73.1	178.0	120.6
2	69.3	148.6	119.6
3	65.4	128.7	117.0
4	58.9	116.0	108.6
5	39.2	92.0	90.1
6	20.4	90.0	-
F-1	74.5	-	-
2	72.8	168.0	120.0
3	71.0	146.0	117.5
4	67.0	128.0	113.4
5	60.2	110.5	106.3
6	46.0	93.7	90.9

Fig. 3--Rate of Hydrogenation  
Effect of Temperature

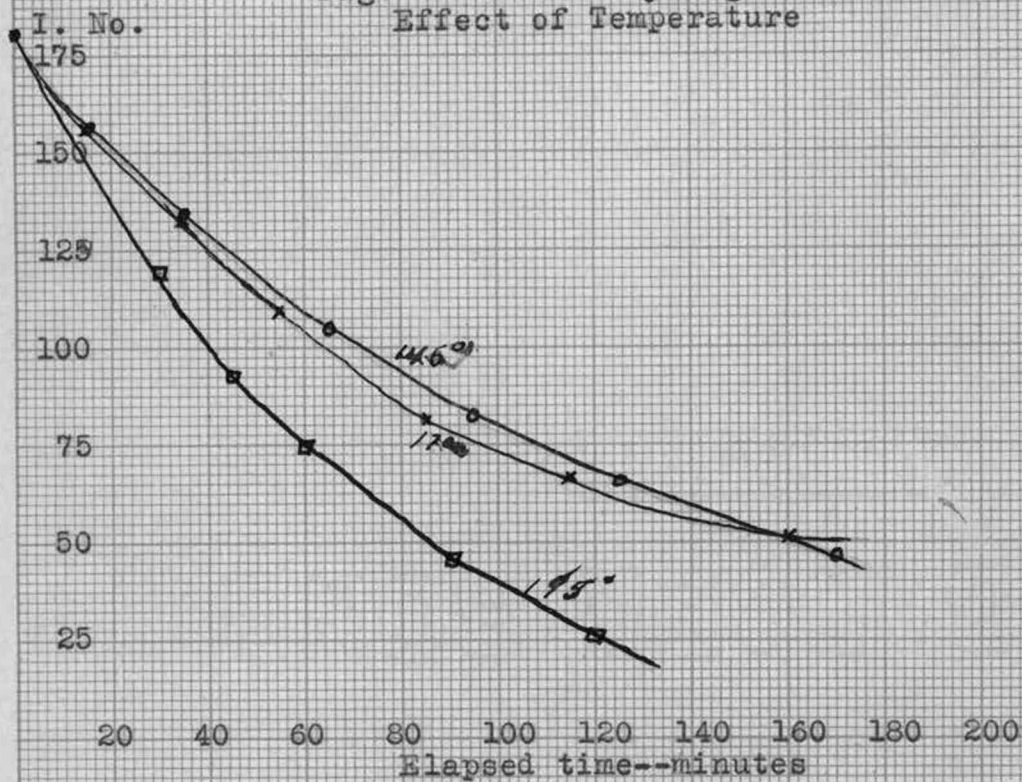


Fig. 4--Rate of Hydrogenation  
Effect of Pressure

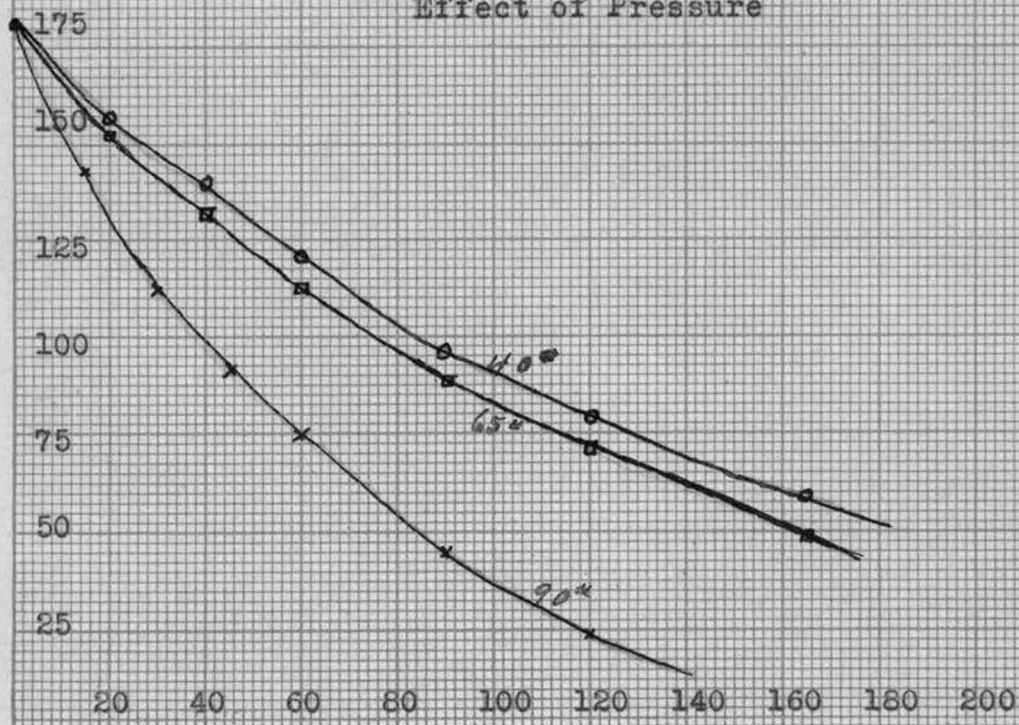




Fig. 5--Average Reduction in Iodine Number per Minute  
Effect of Temperature

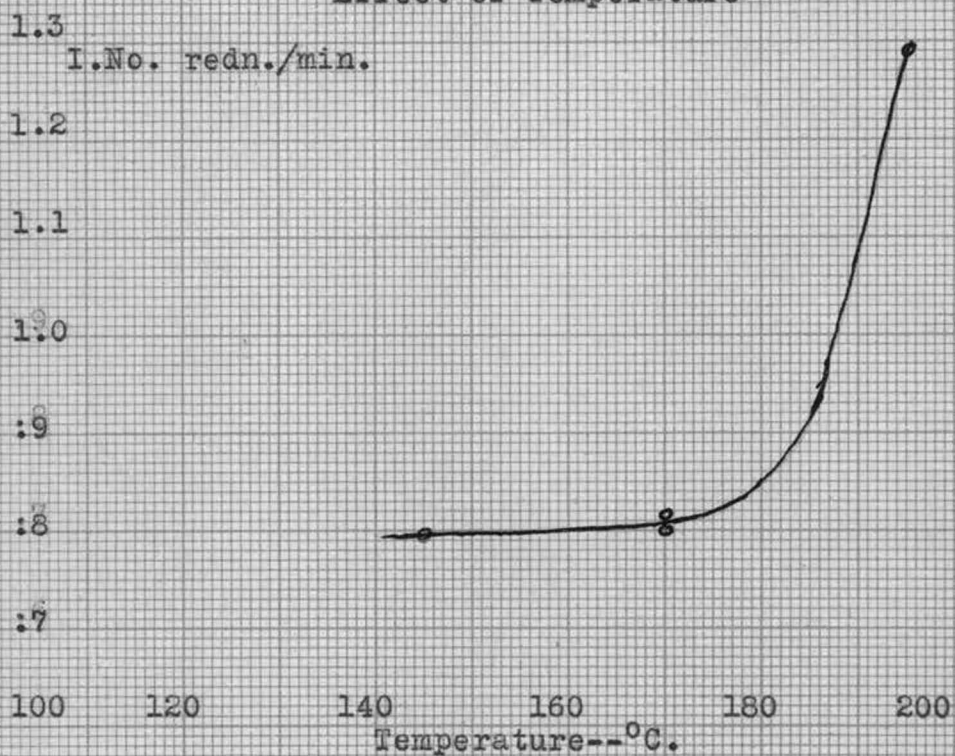


Fig. 6--Average Reduction in Iodine Number per Minute.  
Effect of Pressure

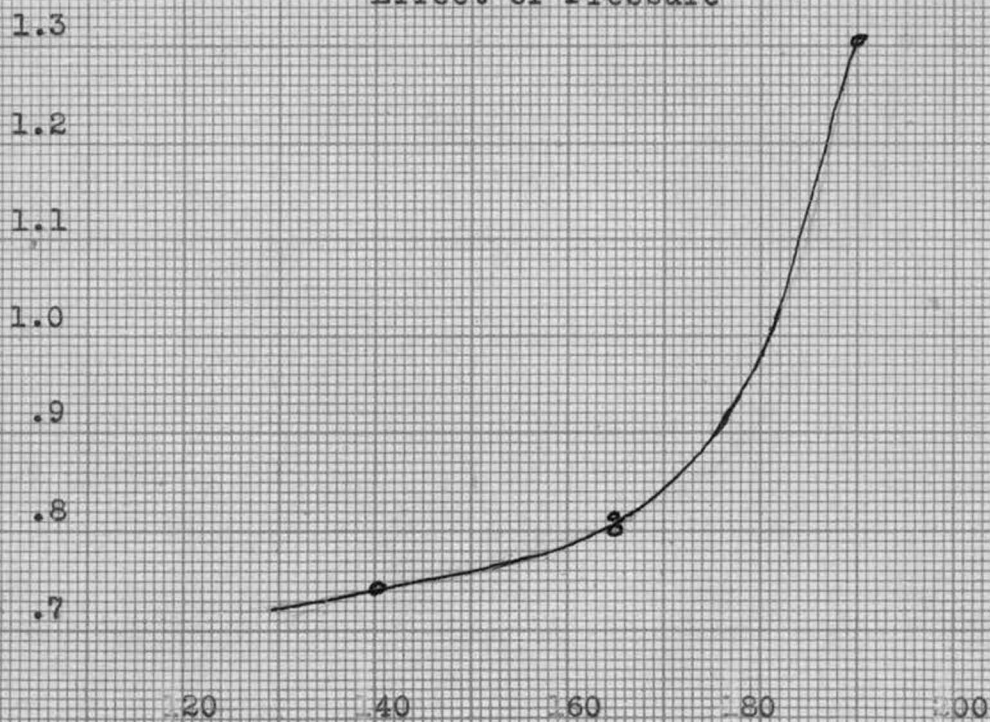
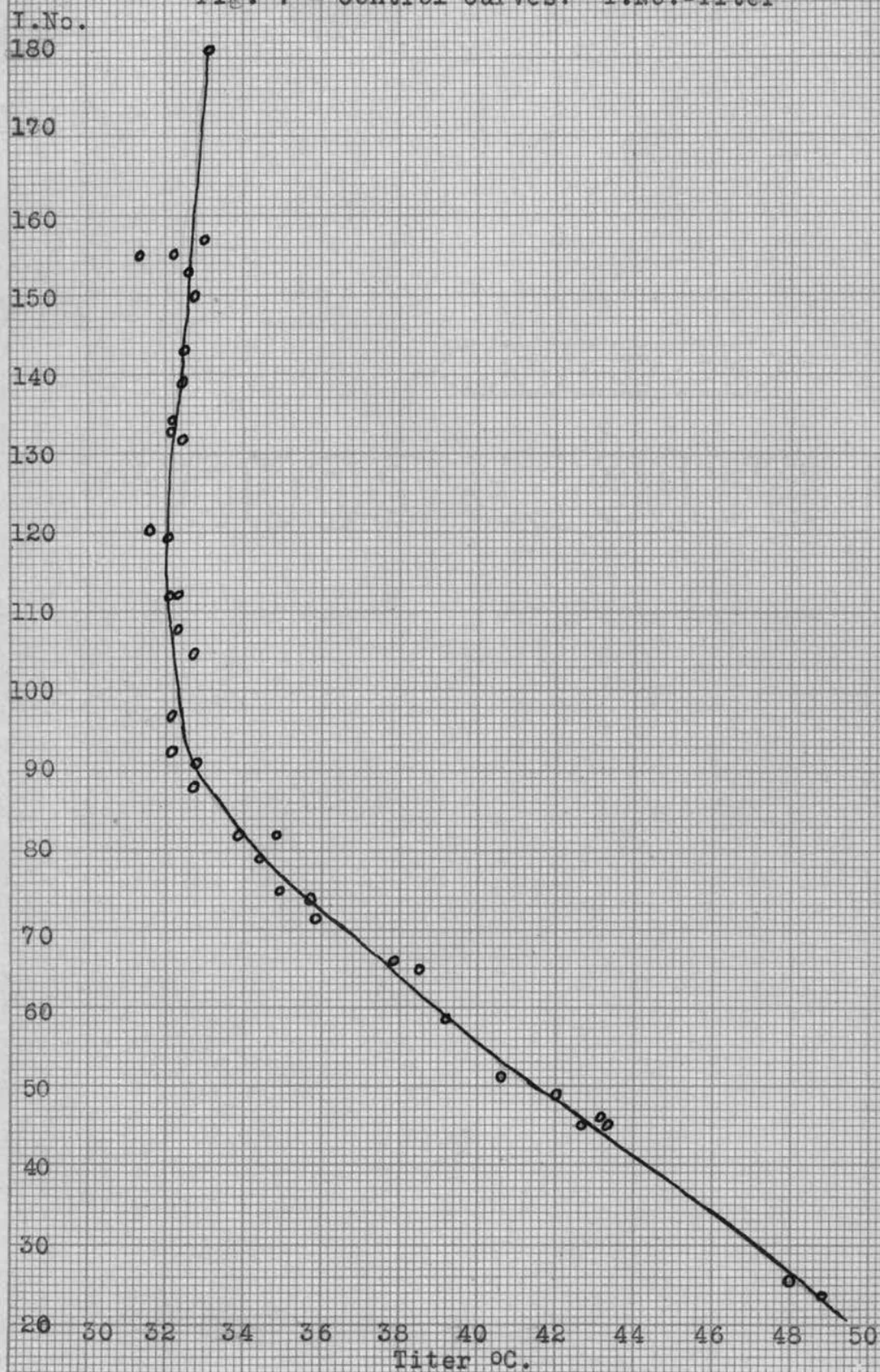
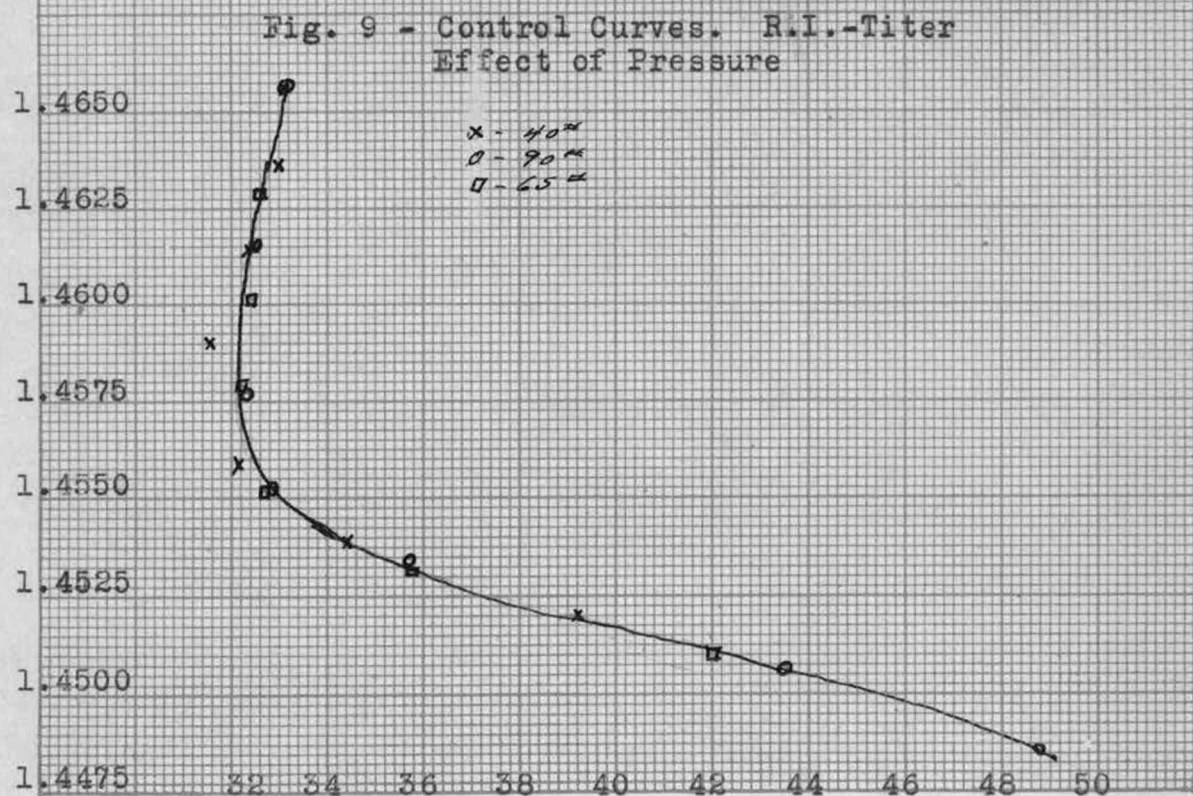
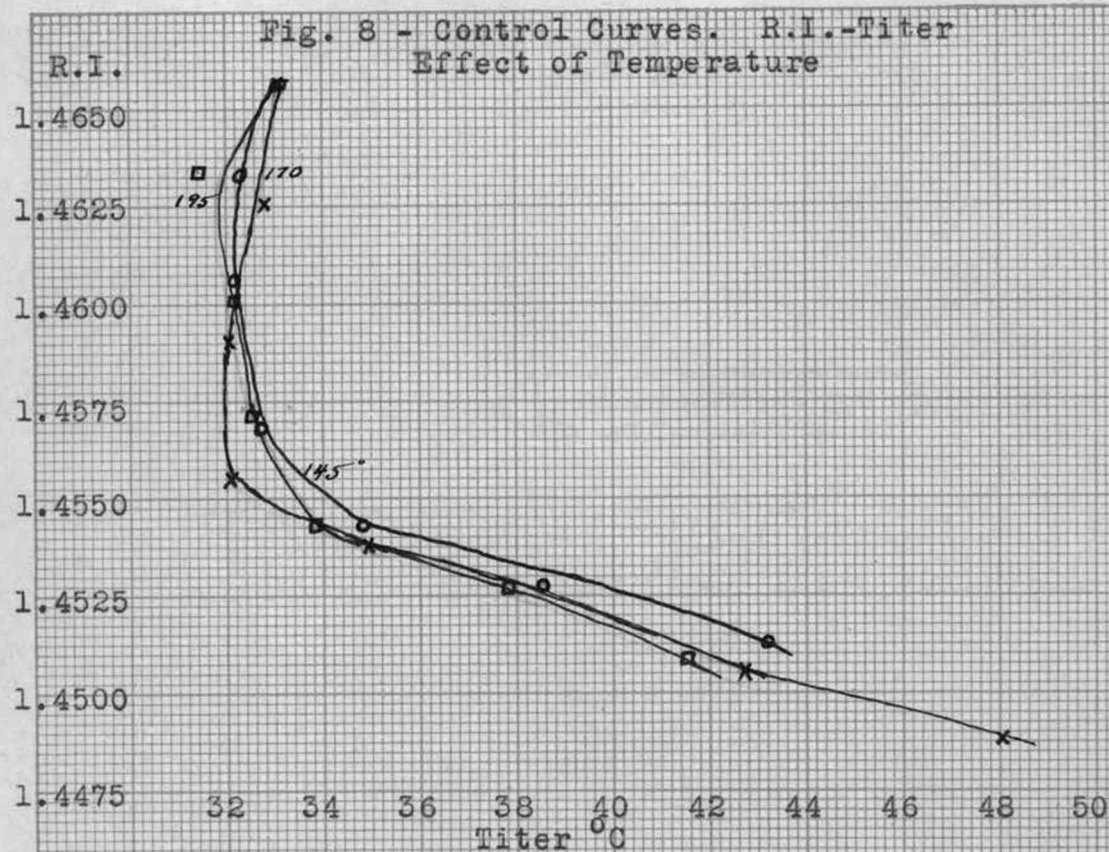


Fig. 7 - Control Curves. I.No.-Titer







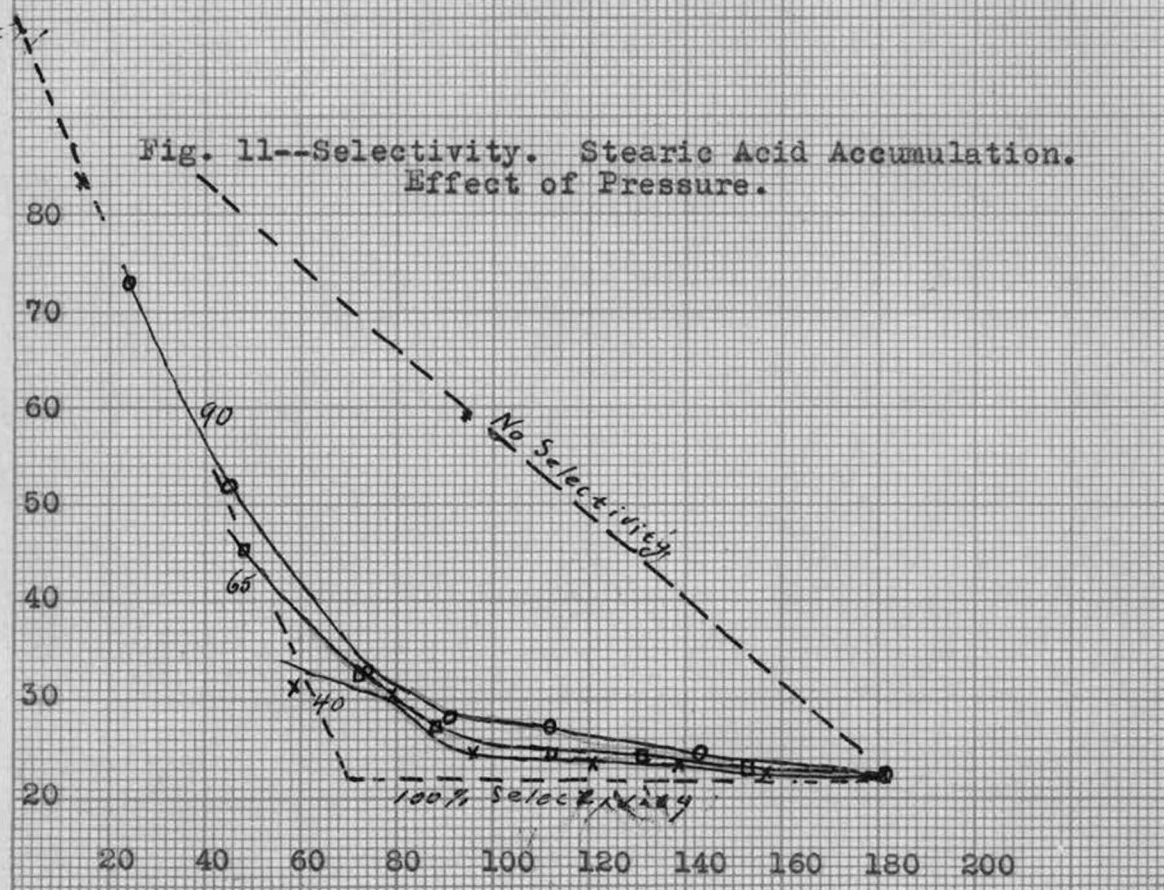
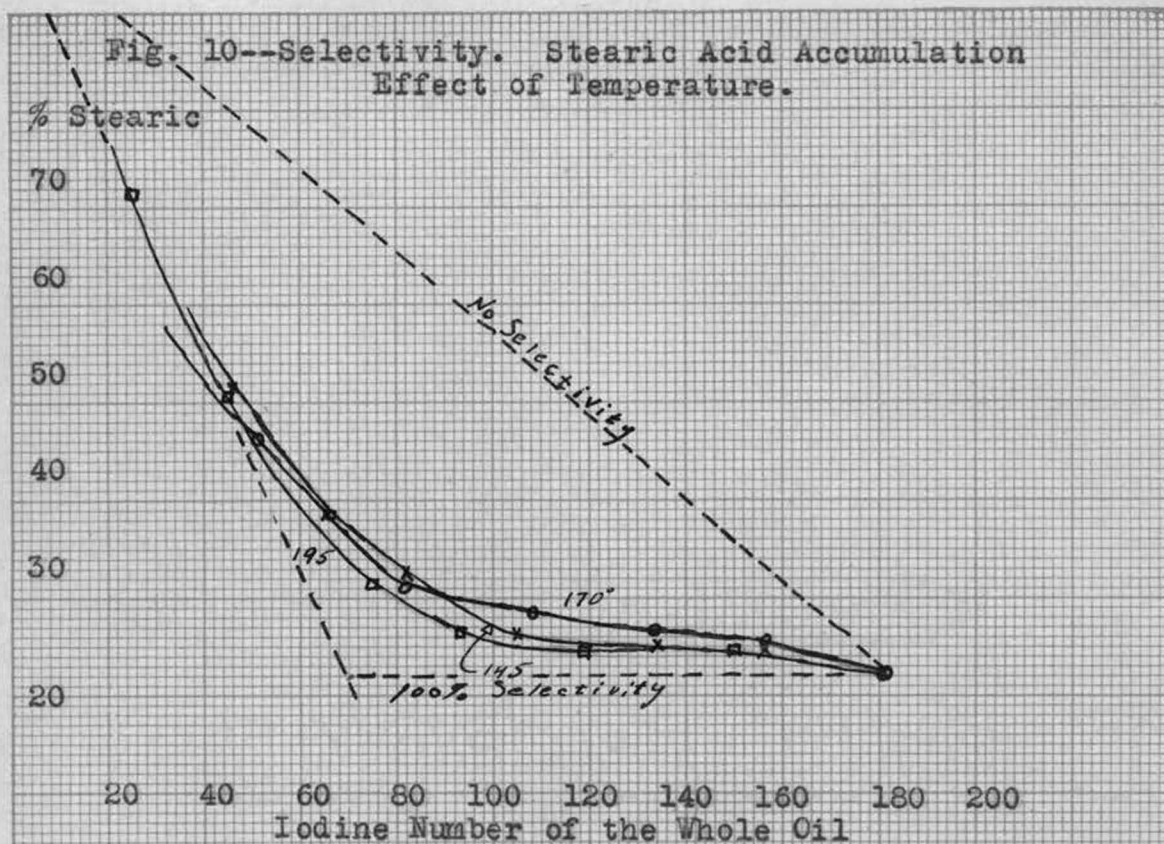




Fig. 12--Selectivity. Iso-oleic Acid Formation.  
Effect of Temperature.

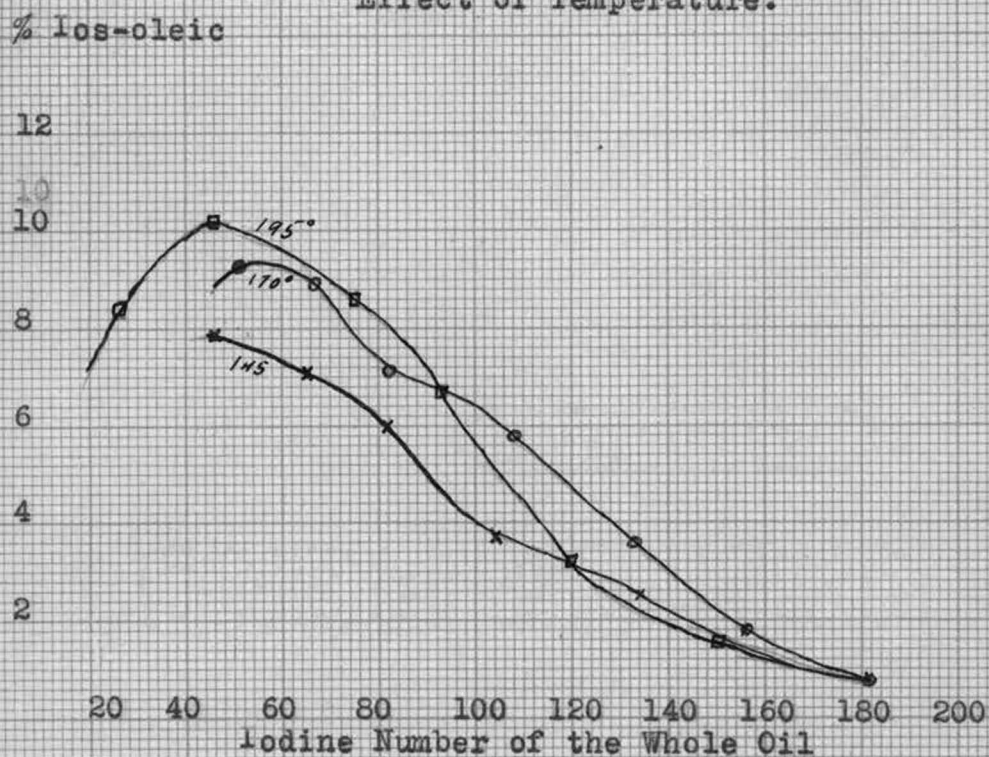
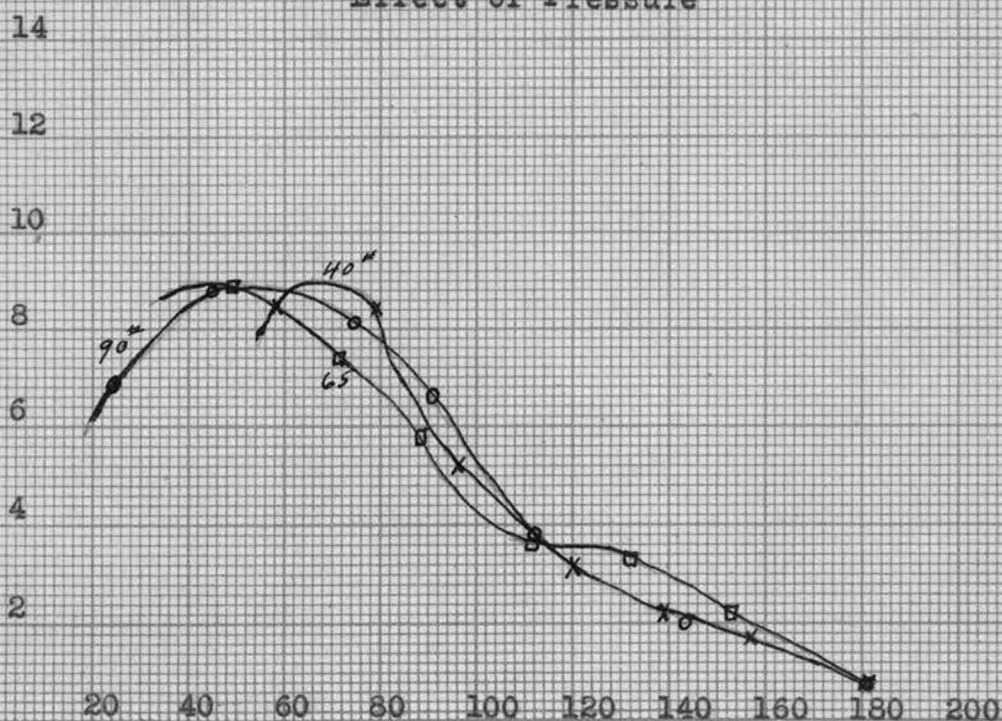


Fig. 13--Selectivity. Iso-oleic Acid Formation.  
Effect of Pressure



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