

AN ATTEMPT
TO
DEHYDROGENATE COTTONSEED OIL

Thesis

by

ROBERT W. GILLIES

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INTRODUCTION.

It is now a well known fact that certain vegetable and animal oils can be hydrogenated or hardened, by heating them in an atmosphere of hydrogen, with a suitable catalyst, such as nickel or platinum. It is the purpose of this thesis to carry on an investigation of the reaction and to attempt to change the equilibrium conditions so that hydrogen is removed from the oil instead of being absorbed by it.

Removing hydrogen would give a more unsaturated oil, i.e. one containing less hydrogen and having more double bonds. Such a procedure would give an oil with different and interesting properties. For instance it should be more active chemically and should have better drying qualities.

Altho the exact mechanism by which the so called "drying oils" dry and become hard is not definitely known, it undoubtedly is an oxidation process in which the double bonds in the carbon chain unite with oxygen to give a hard elastic product. As a general rule the saturated oils are non-drying and as the number of double bonds increases, the ability of the oil to absorb oxygen also increases, and therefore the drying properties are improved¹

1. Lewkowitsch, Chem. Tech. & Anal. Oils, Fats & Waxes, (1913) P.466.

From this it can be expected that if an oil were to be dehydrogenated, it would dry better than the original oil which was less unsaturated and the treated oil could thus be used as a substitute for linseed and other drying oils.

The hydrogenation of an oil is extremely slow if no catalyst is present but if a suitable catalyst is used the reaction takes place readily. When nickel is used for the catalytic agent the hydrogenation takes place most rapidly at a temperature of 175 to 200°C. The speed of the reaction increases with rising temperature up to 180°C and then decreases as the temperature is raised further. This effect is an indication of an equilibrium condition. The speed of the reaction is also greater with increased pressure. Therefore by raising the temperature and reducing the pressure it might be expected that the equilibrium would be changed and that the reaction would reverse.

This view is supported by the following facts:

(1). Zelinski¹ dehydrogenated cyclohexane by heating it in contact with finely divided palladium black. The reaction commences at 170°C and proceeds rapidly at 200 to 300°C. At lower temperatures the reverse change occurs, passage of hydro-

gen and benzene over the catalyst at 100 to 110°C resulting in the hydrogenation of the benzene. Equilibrium is established at 200°C and above this temperature dehydrogenation occurs despite the presence of hydrogen.

(1). Sabatier¹ showed that although certain organic compounds are reduced at a temperature of 180°C by passing their vapors mixed with hydrogen thru tubes containing finely divided metals, especially nickel, at a temperature of 250°C the same metal brings about an oxidation of the compound, for example of alcohols to aldehydes and ketones.

(2). Shaw² found that distilling oleic acid thru fresh catalyst under a pressure of 100 mm. reduced the iodine number 5%, and that redistilling as before made no further reduction. Similar results were obtained at 150 and 200 mm. reducing the iodine number 13 and 20% respectively.

This seems to indicate that there is a definite equilibrium between stearic acid, oleic acid and hydrogen and that the amount of reduction was constant for any given pressure.

Wieland³ assumes that metallic hydrides unite as such with the unsaturated compound at the double bond and the labile addition product formed breaks down with the retention

1. C.A. 5, 702. (1911).
2. Seifer Stg. 1912, 713.
3. Ber. 45, 484. (1912).

of hydrogen and the elimination of the metal, the later then being in a condition to take up more hydrogen and again form the hydride. The following equation shows the assumed equilibrium using palladium as catalyst, but other metal would act similarly.



From a thermodynamic standpoint the equation appears to be a reversible one.

Sabatier¹ also believes that the activity of the catalyst is due to the formation of hydrides and that variations in the activity of the catalyst are due to different hydrides formed. Thus NiH₂ is more active than $\begin{array}{c} -Ni \\ H \end{array}$

If this assumption is correct it would appear as a consequence that nickel and other metals should not only effect a union of hydrogen but also that hydrogenating compounds should suffer a removal of their combined hydrogen, the metals acting as dehydrogenators. This actually proves to be the case. Between 200 and 300°C finely divided copper readily acts as a dehydrogenating catalyst, converting alcohols into ketones and aldehydes.

1. Die Hydrierung durch Katalyse, Leipsic (1913), 17.

It is also known that the heat of combustion of carbon compounds increases with the unsaturation. According to a general principle compounds with high heats of combustion should be more stable at high temperatures, than ones with lower heats of combustion. Therefore an unsaturated oil might become more unsaturated by heating to a high temperature in the presence of a suitable catalyst.

On the other hand, according to Padoa and Fabis¹ under atmospheric pressure hydrogenation and dehydrogenation are distinct processes. In most cases nickel can effect either reaction, but on certain compounds the nickel acts in only one way. Under increased pressure the two limits of temperature are close together and under certain conditions the two reactions may proceed simultaneously, until equilibrium is attained².

METHOD.

The effect of heat alone upon the cotton seed oil was first studied and the effect of heat upon the oil mixed with various catalyzers. Samples of the oil were therefore heated over a range of temperatures varying from 175 to 340°C

1. J.S.C.I. (1908), 1083.

2. This may account for the failure to obtain any dehydrogenation.

for various periods of time, exposed to air and also in closed tubes, in order to determine if the oil was seriously darkened or decomposed. It was found that the oil was effected somewhat but not enough to interfere with the experiments to be performed later.

Several nickel catalyzers were then prepared, using the methods outlined by Mr. Trowbridge¹ and Mr. Zoul² respectively. In the preparation and use of the catalysts great care was taken to protect them from impurities that might poison them and reduce their activity³.

These catalysts together with a sample of catalyst obtained from the Globe Oil Mills, Los Angeles, were used in the experimental work. They were first tested out to make sure that they were active, by using them to hydrogenate samples of cotton seed oil. If they were found to be sufficiently active they were used for further experimentation in attempts to dehydrogenate the oil.

The hydrogenation tests were made at temperatures between 175 - 200°C, by passing hydrogen gas thru the heated oil and catalyst. The dehydrogenation was attempted at temperatures between 200 - 340°C by heating the oil and cataly-

1. Method used by the Globe Oil Mills, Los Angeles, to prepare their catalys for hydrogenating oils.
2. Of the Celite Products Co. previously with Proctor and Gamble.
3. There are many things that poison nickel, namely, Pb, Zn, Hg, S, Si, P, Cu(OH), As₂O₃, HCl, H₂SO₄, KOH, NaOH, and soaps of K, Na, Li, Mg, Ba, Fe, Cr, Zn, Cd, Pb, Hg, Zn, Sn, and Bi. C. A. Vol. 13, 383-4. (1913).

zer in special heating tubes. In some cases the outside air was excluded by closing the tube except for a piece of capillary tubing, in others the air pressure was reduced to about 0.5 atmosphere and in the remainder, carbon dioxide gas was bubbled thru the oil so as to displace the air.

METHODS OF ANALYSIS.

In determining the effect of the treatment, three tests were used, namely the iodine number, acid value, and refractive index. The physical appearance of the oil such as color, and viscosity was also useful in some cases.

The Iodine number is a measure of the unsaturation of the oil and was used to determine the amount of hydrogenation or dehydrogenation of the oil. However the oil can become saturated by the addition of oxygen as well as hydrogen, and the Iodine number does not differentiate between the two additions. Consequently another constant was needed, and was found in the refractive index. This value was found to increase if there was oxidation and decrease if there was reduction. A decrease in both the Iodine number and refractive index indicates hydrogenation, while a decrease in the iodine number accompanied by an increase in the refractive index indicates oxidation.

The acid value gives the amount of free fatty acid in the oil. This is normally very small but increases if there is decomposition, and so this test was used to determine if the oil was broken up into glycerine and free fatty acids by the treatment.

The Iodine number was determined by the Hanus method¹ taking the precautions given by Tuttle and Smith².

The Acid value was determined by the method advanced by Steele and Sward³. This is much faster than the older analyses and gives more reliable results.

The refractive indices were obtained by using an Abbe Refractometer.

APPARATUS AND MATERIALS.

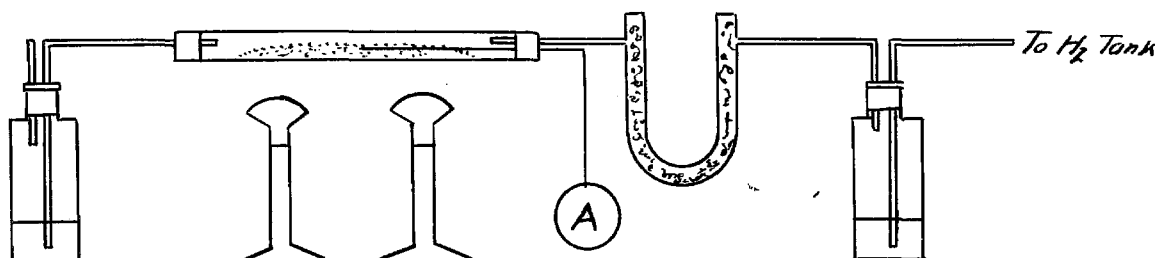
All of the heating was done in an electric heating unit consisting of a porcelain tube wound with resistance wire, and insulated with magnesia and asbestos. The heater was placed in a vertical position and the ends closed with asbestos plugs. The temperature was regulated with a mercury thermostatic regulator that kept the furnace within 10°C of any desired temperature.

1. Leach Food Inspection and Analysis, p 383.
2. Tech. Paper, Bur. Stand. No. 37, Iodine Number of Linseed Oil.
3. Jour. Ind. Eng. Chem., 14, 57 (1922).

The oil was contained in a special heating tube of pyrex glass made as shown in the drawing. This tube could be connected to the vacuum line and the pressure on the oil reduced, or a gas could be bubbled thru the oil, or the tube closed with stoppers and the outside air excluded.



The nickel catalyst was reduced in the tube as shown below. The tube was of pyrex glass 25 mm. by 300 mm. closed at each end with cork stoppers, protected by glass wool. The heating was done with two fish tail burners. Hydrogen gas was led from a cylinder thru a flask containing oil, to act as a bubble counter, and then thru a calcium chloride drying tube, and to the pyrex tube. The used gas was passed thru another flask partially filled with oil to act as a safety device. The temperature was measured by means of a thermo-couple placed inside of the pyrex heating tube.



Cottonseed oil was used in this work because it is a semi-drying oil, it is fairly inexpensive, and a pure supply could be easily be obtained from the Globe Oil Mills, Los Angeles. Winter oil, bleached, but with the stearin not removed was used, for the first experiments. Later, this was removed by cooling in ice water, and filtering off the precipitated stearin. This oil is used by the Globe Oil Mills to hydrogenate commercially and so it did not contain anything liable to poison the catalyst.

The hydrogen gas used was obtained in cylinders from the California Compressed Gas Co., Los Angeles, and is manufactured by electrolytic process. It contained about 0.5% oxygen. The nickel was obtained from the Globe Oil Mills and is the same as is used by them. It is electrolytic and is claimed to be practically 100% pure. The kieselghur was obtained from the Celite Products Co. and was their best grade. The carbon dioxide gas was obtained in cylinders from the Liviti Distilled Water Co., Los Angeles, and contains about 3% air.

RESULTS.

It was found that heating samples of cottonseed oil decreased the Iodine number and increased the acid value

and refractive index. The oil was also darkened and became more viscous. A precipitate was formed when the oil was heated above 275°C.

The magnitude of these effects depended upon the temperature, the time of heating and the amount of air in contact with the oil. Nickel oxide and the reduced nickel oxide catalyzers were found to increase this effect, the former to a greater extent than the latter.

The nickel catalyzers prepared and used in the experiments were tested and found to be as active as a sample of catalyzer obtained from the Globe Oil Mills, Los Angeles, which was known to be catalytically active.

Cottonseed oil was successfully hydrogenated to a hard oil.

Heating under diminished pressure of about $\frac{1}{2}$ atmosphere the oil darkened considerably and the viscosity increased more than when the oil heated under atmospheric pressure. The effect was greater when nickel was present.

From the oils heated to temperatures above 275°C there was obtained flocculent precipitate which came down after the oil had stood for a day or two. This appeared to be stearin, but it was not definitely proven to be so. If it were stearin, it may have been already present as such, and

precipitated by the heat treatment, or it may have been freshly formed by two molecules of olein reacting with each other in such a way that one molecule gave up part of its hydrogen to the other, forming as a result one molecule of stearin, and one of linolic tri-glyceride.

No dehydrogenation of the cottenseed oil was obtained in any of the experiments performed.

A tabular statement of the procedures and the results is given and will be followed by a more detailed account of each, and a discussion of the results.

TABULATED RESULTS.

No.	Temp.	Time	Condition	Cat. 1 No	Refract Index	Acid No.	Remarks.
0			Raw oil	105.0	1.4680	0.1053	Clear, light yellow
0'			" " Stearine removed	105.3	1.4679	0.1141	No change
1	215	1	Heated exposed to air	104.5	1.4680	0.1264	No change
2	215	1) 2	"	102.7	1.4680	0.1281	No change
	260	1)	"				
3	260	2	"	102.4	1.4679	0.2285	No change
4	320-35	2½	"	84.0	1.4706		Much darker, more viscous
5	320-35	"	"	4 76.1	1.4736		About the same as No. 4.
6	315-55	½	"		1.4685		Clear, light yellow
7	315-35	1	"		1.4692		Slightly darker than No. 6
8	315-35	1½	"		1.4695		Slightly darker than No. 7
9	315-35	2	"		1.4704		Slightly darker than No. 8
10	315-35	2½	"		1.4712		Slightly darker than No. 9 small ppt.
11	315-35	3	"		1.4725		Slightly darker than No. 10, small ppt.
12	320	2	Heated in test-tube closed with cork.	98.5	1.4691	5.60	No change
13	220-50	2½	Heated in Heat tube closed with capillary.	102.9	1.4680		" "

No.	Temp.	Time	Condition	Cat.	l No	Refract Index	Acid No.	Remarks
14	315-30	2½	Heated in Heat. tube closed with capillary.	5	101.1			Darkened, flocculent ppt. more viscous.
15	"	2½	"	6	95.0			" "
16	175	1½	Passed H ₂ thru.	1	102.9	1.4678		No change.
17	175	1½	" " "	2	102.9		0.274	" "
18	175	2	Heated in flask H ₂ A & M.	2	91.2			" "
19	175-195	2	H ₂ passed thru	3	82.1	1.4679		Hardened oil completely.
20	175-200	6	Heated in flask H ₂ A & M.	3	36.3			" " "
21	220-50	2½	CO ₂ passed thru	3	105.9	1.4660		No change.
22	195-215	2	" " "	3	102.7	1.4686		Little darker, more viscous, small ppt.
23	195-215	2	" " "		103.5	1.4682		Little darker, less viscous, no ppt.
24	315-35	2½	" " "	3	98.0	1.4693		Still darker, more viscous, small ppt.
25	270-85	6	" " "	3	97.1			Slightly darker and more viscous.
26	290-310	2½	½ Atm. press.	3 (used)	76.6	1.4716	9.56	Very dark, viscous, oil hardened on standing.
27	315-35	2½	½ " "		92.6	1.4692		Some darker, viscous, small ppt.
28	315-25	2½	½ " (thru cap.)		91.4	1.4704		Very dark, and viscous, large ppt.

EXPERIMENTAL WORK.

The first experiments made were to heat the raw oil in 7 inch test-tubes exposed to the air, to various temperatures in order to ascertain how heating alone effected the oil. No. 1, 2 & 3 were heated to a temperature of 175°C and showed that the oil was not effected very much at this temperature. There was however a small decrease in the Iodine number showing that there was some oxidation, and a small increase in the acid value showing that there was a little decomposition. These effects were too small to be shown by the refractive index. There was no change in the physical appearance of the oil.

In No. 4 and 5, the oil was heated to a higher temperature, in the first case without, and in the second case with a catalyzer. Both were heated exposed to air, for the same time and at the same temperature. The Iodine number was lowered and the refractive index raised, but the effect was greater in the one containing the catalyzer than in the other one. The only difference in the conditions of the two was the catalyzer and so it appears that it helped in the oxidation of the oil¹.

1. The oxidizing effect of the catalyst may be due to the oxygen in the catalyst. If 2% catalyst is used, there would be 0.4 gm. of nickel, which if entirely oxidized, would furnish 0.109 gm. of oxygen. This would be sufficient to reduce the Iodine number to 53.8. Assuming that the reduced catalyst contained 20% oxygen, there would be sufficient to decrease the Iodine number to 94.5.

Experiments 6, 7, 8, 9, 10 and 11 were made by heating the oil in open test-tubes at a temperature of 315 to 335^o C and taking samples every half hour.

The refractive index of these samples showed a gradual increase showing that the amount of oxidation depends upon the length of time that the oil is heated.

The previous tests were all made with the oil exposed to the air but as the attempts to dehydrogenate would be made in a closed tube a series of experiments were next made by heating the oil in tubes with only a small amount of air present.¹

Experiment 12 was made by closing a test-tube with a cork to prevent oxidation from exposure to the air. The high temperature charred the cork so much that another method of excluding the air was necessary. Wrapping the cork in asbestos paper, and covering the surface with a coating of ground asbestos in sodium silicate, helped somewhat, but was not entirely satisfactory.

To overcome this difficulty a special heating tube was made as previously described, and used for the remaining procedures except where otherwise stated.

1. When the tube was filled there was about 20 cc. of air left in it. For an oil with an Iodine number of 105 it would take 443 cc. of air to completely oxidize the oil. Thus 20 cc. of air would lower the Iodine number about 2.5 points. Heating in closed tubes with out any catalyst gave a reduction of the Iodine number of about this magnitude.

In experiment 13, the tube was closed by fastening a piece of capillary tubing having a bore of imm. and about 20 cm long, to the ends of the heating tube. This allowed the air to expand upon heating but prevented the diffusion of the outside air into the tube to take the place of that which might be absorbed by the oil. As shown by the Iodine number and refractive index, the capillary tube prevented oxidation more than the cork did.

The experiments so far showed that heating in the air as high as 330°C caused some oxidation, and a little decomposition with liberation of free fatty acids, but that if the air was excluded the oxidation was small. The next step was to prepare a catalyzer.

The first catalyzer made was prepared from directions given by Mr. Trowbridge. The formula used was:

- 1 part nickel (Electrolytic, approximately 100%)
- 4 parts nitric acid (C. P Concentrated)
- 4 parts distilled water (Free from chloride)
- 3 parts kieselghur (Best grade and washed with acid)

The nickel was dissolved in the nitric acid, diluted with the 4 parts of water, and the kieselghur (previously washed for two days in 2% nitric acid) and 4 liters of water added in a 6 liter flask. C. P. ammonia hydroxide was then added until the nickel dissolved and the solution turned a deep blue color.

The flask was then heated at a temperature of 80°C and

air blown thru until the nickel was precipitated on the kieselghur. The precipitate was then washed thoroly with hot water and dried until it turned dark gray. It was then ground to a fine powder with a mortar and pestle, and reduced in the reduction tube (previously described) at a temperature of 500°C in a stream of hydrogen gas. The reduced nickel was allowed to cool in an atmosphere of hydrogen was then poured directly into cottonseed oil so that 10 gm. of the mixture contained 1 gm. of the nickel.

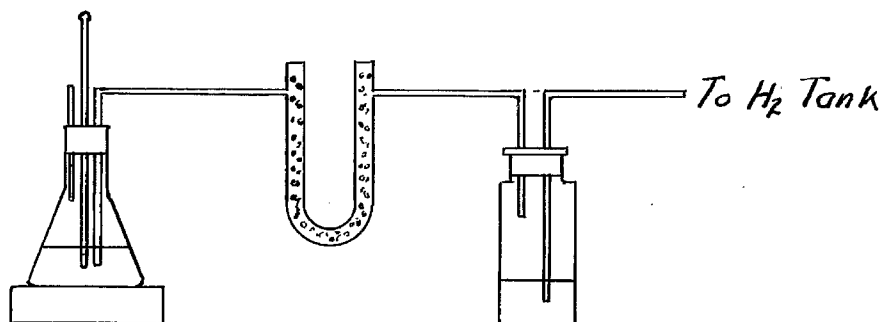
A solution of nickel nitrate was made up, and this was used for making various batches of catalyst as described above. In the case of a later batch, the nickel was precipitated by sodium carbonate instead of by ammonium hydroxide. The precipitated nickel carbonate was treated as before.

Catalysts No. 1 and 2 were prepared from the same nickel hydroxide but were reduced at different times. No 3 was prepared from the nitrate solution. No. 4 was obtained from the Globe Oil Mills No. 5 was prepared from the nickel carbonate precipitate. No. 6 was a sample of nickel oxide prepared from the carbonate by heating. It was not reduced.

Experiments 16 to 20 were made to test the catalyzers for activity. The tests were made in the heating tube and in a special flask.

As was shown by the Iodine number catalysts No. 1 and 2 were only very slightly active. No 3 and 5 were as active as No. 4 which was obtained from the Globe Oil Mills and was known to be active. In experiments 19 and 20 catalyst No. 3 reduced the oil to a hard fat.

The flask used in experiments 18 and 19 for testing the catalysts was a conical 300 cc. flask fitted out with a 3-hold stopper carrying a long tube for bubbling gas thru the oil, a thermometer and a shorter tube for an outlet with a ballon attached to the end.



The flask containing the oil and catalyst to be tested was put on an electric hot-plate and heated to a temperature of 180°C (temperature of maximum hydrogenation). Hydrogen was then bubbled thru the oil from the cylinder until the ballon was partially filled and assumed the position shown by the dotted lines. The flask was then shaken and the ballon would collapse, due to the hydrogen being absorbed by the oil, if the catalyst were active.

Experiments 21 - 26 were heated at the same temperature bubbling carbon dioxide thru the oil. This served to stir

up the catalyst and prevent it from settling out at the bottom. It also displaced the air and prevents oxidation and the bubbles going up thru the oil might tend to drag hydrogen along with it if any were liberated from the oil.

In all cases the Iodine number was increased to only a slight extent and the refractive index was only slightly reduced. There did not appear to be any dehydrogenation of the oil, or if there was it was obscured by the oxidation.

Experiments 16 and 17 were each carried out by heating the oil at the same temperature, for the same time, but 16 had a catalyst, and 17 did not. In this case again the catalyst seemed to have assisted in the oxidation of the oil as shown by both the Iodine number and the refractive index.

Experiment 25 was carried out by heating a sample of the oil to a temperature of 270 - 285°C for 6 hours, bubbling carbon dioxide gas thru the oil while heating. Even by heating for this length of time there was no appreciable dehydrogenation, altho the oxidation was not very large.

Experiments 26 - 28 were heated under $\frac{1}{2}$ atmosphere pressure. In all of these a precipitate was obtained that appeared to be stearin but it was not definitely proven to be so. In experiment 20 the Iodine number was reduced to 76.6 by heating to a lower temperature than in experiments 27 and 28. This was because a catalyst was used that had already been used in hydrogenating and some of the hardened

oil still remained in the nickel. This sample hardened upon standing.

These last three oils all became very viscous and it is thought that this was due to oxygen diffusing back thru the vacuum line. To test this out a capillary tube of 1mm. bore and 20 mm. long was placed in the vacuum line to prevent this. However practically the same changes occurred as when this was not used, thus disproving the assumption.

At temperatures above 300°C the oil fumed considerably in air,

SUMMARY.

1. Samples of cottonseed oil were heated with and without a catalyst and it was found that the Iodine number decreased, the acid value and the refractive index increased, and that the oil darkened and became more viscous. This showed that there was oxidation and some decomposition, with a liberation of free fatty acids.
2. At temperatures below 260°C the effect was very small on all of these properties.
3. As the temperature increased the oil darkened and the Iodine number decreased, and the acid value and refractive index increased. These effects increased more rapidly above 260°C .
4. As time of heating increased the above effects increased.

5. In closed tubes the change in Iodine number and refractive index was less than in open tubes. The other changes (increased) regardless.
6. The addition of reduced nickel or nickel oxide appeared to increase the oxidation of the oil. The later had more effect than the former.
7. Catalysts were prepared and found to be catalytically active as shown by their ability to harden the cottensed oil.
8. Attempts were made to dehydrogenate the oil by heating to a high temperature and passing carbon dioxide thru the tube. They were unsuccessful however and oxidation took place, probably caused by the oxygen (3%) in the carbon dioxide gas.
9. The oil heated in the carbon dioxide atmosphere was not oxidized as much as if heated in air or in a closed tube. This was because the carbon dioxide gas displaced the air.
10. Samples were heated under a pressure of about $\frac{1}{2}$ atmosphere and it was found that the Iodine number was reduced, and the acid value and refractive index increased to a greater extent than in the other experiments.
11. Inserting a capillary tube $\frac{1}{16}$ mm. in diameter and 20 cm. long into the vacuum line did not give different results than when it was not used.
12. At temperatures above 200°C the oil fumed and it is probably that under reduced pressure part of the more volatile portions of the oil distilled off. This would account

for the large changes in the Iodine number and the very large increase in the acid value as well as the increase in viscosity.

13. Samples heated to high temperatures were found to gradually form a precipitate upon standing. This appeared to be stearin but this was not definitely proven to be so.

14. It was found that the oil was oxidized and decomposed before a high enough temperature could be reached to bring about a dehydrogenation of the oil or else that any hydrogenation obtained was obscured by the oxidation.