

THESIS

THE DEHYDROGENATION OF COTTON SEED OIL

BY

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INTRODUCTION

It is well known that vegetable oils can be hydrogenated by passing hydrogen thru them when they contain a proper catalyst such as finely divided nickle. This thesis represents an attempt to reverse the above reaction so that hydrogen would be removed instead of added to the oil. The object of dehydrogenation would be to form an oil having greater unsaturation and hence more chemical activity, which might render it useful in the preparation of other compounds and might also increase its drying properties.

Since hydrogenation with finely divided nickle as a catalyst proceeds best at a fairly low temperature there was some likelihood that the reaction might reverse by simply heating the oil at a higher temperature in the presence of the same catalyst. The following facts also support this view:

1 Zelinski¹ dehydrogenated cyclohexane by means of heating the latter in contact with finely divided platinum black.

2 Sabatier² showed that certain organic compounds are reduced by passing their vapours mixed with hydrogen thru tubes containing finely divided metals, especially Nickle, at a temperature of about 180 degrees, and that at 250 degrees the same metal brings about an oxidation, for example, of alcohols to aldehydes or ketones.

1, A, 1911,1,958.

2. A, 1911,1,702.

3 The heat of combustion of carbon compounds increases with the unsaturation. According to a general principle, a compound which has a high heat of oxidation should be more stable at a high temperature than one which has a low heat of oxidation for it is difficult to give off heat to surroundings at a high temperature. Therefore an unsaturated oil might become more unsaturated by heating to a high temperature in the presence of a catalyst which would assist the reaction.

 Since the iodine number of an oil is an index of its saturation, it was decided to determine the iodine numbers of the various samples worked with. The object of the experimentation then became to increase the iodine number of the oil. The Hanus¹ method was used. Precautions given by Smith and Tuttle² were observed. Saponification values were also taken by the method given in Leach, p.379.

METHOD

 It was decided to try first to prepare a nickle catalyst by reducing a salt or oxide of nickle in a stream of hydrogen, following a general method used in the preparation of nickle for hydrogenation, such as given by Ellis.³ Samples of oil were then heated without a catalyst for certain lengths of time to determine the effect of heat alone upon them. Some samples were protected from the air and some were not. Samples were then heated at similar temperatures and for similar lengths of time in the presence of catalysts with or without the passing of hydrogen. In this

1. Leach, Food Inspection and Analysis, , p. 383.
2. Tech. paper, Bur. Stand. No. 37, "Iodine Number of Linseed and Petroleum Oils", Smith and Tuttle.
- 3 Ellis, Hydrogenation of Oils, p. 54-58.

way the effect of the heat alone would be known, and could be differentiated from the effect of the catalyst.

APPARATUS

It was first necessary to obtain a source of hydrogen which would contain no trace of arsenic, chlorides, sulphur, phosphorus, ammonia, or oxides of nitrogen, as these substances would poison the nickel.¹ To this end an electrolytic hydrogen generator was constructed consisting essentially of three U-tubes joined together in parallel, and in each side of which was an electrode of sheet iron made from tin-can material. Each electrode was soldered to an iron wire which in turn was soldered to a platinum wire. The latter was sealed into the side of the U-tube and connected to the outside source of current. Ordinary solder gave a mirror test for arsenic, so could not be used. Silver solder, however, was used without analysis.

The cathode arms of the U-tubes were joined by a manifold so that all the hydrogen generated was brought together into one stream. A vertical glass tube about a meter long was sealed to the anode arm of each U-tube so that the electrolyte could be forced up until its hydrostatic pressure would force the hydrogen thru the rest of the apparatus.

In series with the hydrogen manifold was a stop-cock tube, two wash tubes containing alkaline pyrogallol solution, a tube containing soda-lime, and a bulb containing cotton. The stop-cock was used to form a constant resistance to the flow of hydrogen so that the variable resistance to the flow of hydrogen was constant. ¹ Catalysis in Industrial Chemistry. Henderson, p.103. part of the total resistance, which would make the flow of hydrogen

occurring thru the apparatus would be only a small percent of the total resistance, which would make the flow of hydrogen more steady thruout the apparatus. The alkaline pyrogallol was placed in the path of the hydrogen in order to absorb the oxygen which might diffuse over from the oxygen electrode into the hydrogen. The soda lime and cotton were to remove moisture and suspended impurities. The various parts of the apparatus were sealed together so that all joints were of glass and all the parts were made of glass. This was done to prevent traces of impurities from the apparatus itself contaminating the hydrogen. An approximately 25% solution of sodium hydroxide was used for the electrolyte. The generating current was taken from a storage battery having an e.m.f. of twelve volts.

The electric furnace used for maintaining the necessary temperatures consisted of a silica tube of $2 \frac{1}{4}$ " inside diameter and 15" long surrounded with resistance wire and magnesia and asbestos insulation. This tube was placed in a vertical position and arranged so that it could be placed at any desired height. Its lower end was closed with asbestos. Heating current was furnished at 110 volts. A thermostat was constructed and used during most of the experimentation which kept the temoerature at any point desired within a variation of about 10 degrees.

EXPERIMENTAL

Samples of oil were first heated in the furnace to determine the effect of heat alone upon them. Catalysts were then prepared and attempts were made to hydrogenate and dehydrogenate samples of oil. A semi-tabular statement of the experiments carried on and the results obtained follows on the next page. This will in turn be followed by a more detailed discussion of the work done, and by a summary of results.

Remarks about catalyst	Temp. C	Time hrs.	Remarks about oil	Temp. C	Time hrs.	I no.	Sap. K
0 No catalyst			Untreated oil			108.3	195.4 195 193
1 No catalyst			Heated, covered with glass wool	320	4.5	71.8 74.4	
2 No catalyst			Heated, covered with cork, held by small springs	360	5	94.5 96.7	
3 No catalyst			Same as above	290	5	104.9 105.9	
4 No catalyst			Same as above	250	5	106.7 106.9	
5 No catalyst			Same as above	350	5	104.9 105.0	
6 Reduced Ni(OH) ₂ made from NaOH and Ni(NO ₃) ₂	320	5	Tt. half full. Passed H ₂	200	5	93.3 93.9	
7 Reduced Ni(OH) ₂ on pumice	240	6	Passed H ₂	170- 180	3	106.6 106.6	
8 Ni(NO ₃) ₃ changed to basic carbon- ate with Na ₂ CO ₃ and reduced	300- 320	9	Oil heated with cat. Covered w glass wool. Con- sistency vaselene.				Not anal.
9 Basic carbonate pptd. from very dilute sol'n	310- 320	5	Covered with slit cork.	220- 240	2.5	107.3 106.4	
10 Cu soap prep'd in dil. sol'n, cold. Light blue ppt.			Most of sample spattered out, due to H ₂ O	320	5 min,	109.1 103.2	
11 Cu soap prep'd as above			Small amt. soap dried and dis. in oil. Dec. on heat., leaving fine suspension.	350- 360	5	90.7 90.3	
12 Prepared Ni soap as above			Ni soap in oil decomposes, fine suspension	350- 360	6	88.8 88.3	

All the heating of catalysts and oil samples was done in five inch test tubes suspended vertically in the furnace. The various precipitates which were reduced were placed in the test tubes and hydrogen passed over them while in the furnace at the temperatures indicated. The test tube used with samples 6 and 7 had the hydrogen tube sealed to its lower end from whence the latter was bent around and upward, passing out of the top of the furnace. The hydrogen therefore bubbled up from the bottom. The oil was added to the same tube that the catalyst was prepared in. Between samples the hydrogen tube was broken near the furnace and the oil-tube removed from the furnace for cleaning, after which it was sealed back onto the apparatus. Because of the inconvenience of this method, the rest of the experiments were carried on by placing the catalyst or oil into an ordinary test tube and passing hydrogen by the use of a straight glass tube leading down into the test tube and nearly touching the bottom. Samples 10, 11, and 12 did not require the passing of any hydrogen and were kept from exposure to the air by being covered with round disks of ground glass. The top of each test tube was also ground to a plane surface so that a tight joint was made simply by the glass disk resting upon the top of the test tube. This joint was made especially air-tight by the oil itself.

The catalyst of sample 6 was made by reducing nickle-hydroxide formed by adding normal sodium hydroxide to a solution of 10 cc. nearly saturated nickle nitrate solution

in 100 cc. water. The precipitate was filtered off, placed in test tube and reduced in electric furnace by a stream of hydrogen from the generator. The temperature was maintained at 200 degrees and hydrogen passed 5 hours. The test tube was stoppered with glass wool. A fair suspension of nickel was obtained but the particles were large enough to be easily seen with the naked eye. There were undoubtedly some finer particles present, however. The oil used in this experiment was partially solidified the day after hydrogenation. It was warmed and centrifuged before its iodine number was obtained.

In sample 7, 7 grams of powdered pumice stone were added to 600 cc. water, and the suspension so formed was boiled and decanted. 30 cc. nickel nitrate solution and 600 cc. more of water were added to this decanted pumice stone. The nickel was then precipitated with $1/5$ normal sodium hydroxide, which gave an intimate mixture of nickel hydroxide and pumice. This was filtered with suction, dried in an evaporating dish, and a considerable amount poked into the test tube.

Silver nitrate was then used to test the sodium hydroxide and nickel nitrate for chlorides. The sodium hydroxide contained enough chloride to make a light milky silver chloride precipitate. Some sodium bicarbonate and sodium carbonate was then tested. Of these the sodium carbonate gave the faintest test, which was much fainter than the test given by the sodium hydroxide formerly used. This sodium carbonate was thereafter used in precipitating the nickel.

After finishing the work on sample 7, a basic nickle-carbonate precipitate was prepared in the following manner, using dilute solutions to prevent the occluding of impurities, especially chlorides, as much as possible. Dissolved 5 grams sodium carbonate in 300 cc. water, added to a solution of 20 cc. nickle nitrate in 300cc. water, slowly with stirring. A very fine precipitate separated which was filtered with suction. Dried the above over sulfuric acid in a dessicator for six days, placed in tube and in furnace, and passed hydrogen. Later, during the heating of the oil, the thermostat broke which allowed the temperature of the furnace to go high enough to boil off and char all the oil and distil the mercury of the regulator to the outside of the furnace. After this the temperature was adjusted by regulating a lamp-bank resistance by hand, which method gave a control of temperature which was sufficiently accurate.

The catalyst used in sample 8 was prepared in the same manner as that used in sample 7, except that the precipitate stood in the dessicator only one day. The catalyst in its final form was black, in small chunks in the bottom of the test-tube. An attempt was made to grind up these chunks with the end of the hydrogen tube. This turned the nickle into a fairly fine powder, but not fine enough to form the kind of suspension desired. Oil was added to within one inch of the top of the test tube, and hydrogen was passed during the addition. The hydrogen tube was then removed and the test tube stoppered with glass wool which was saturated with the oil so as to exclude the air better. After heating this sample for 14 hours at 310-320 degrees, it was dark brown, nearly opaque, and when

cool of about the same consistency as vaselene. From this it appeared that in spite of precautions taken, the oxygen of the air had oxidized the oil, for sample 2 which had been heated even up to 360 degrees for a period of five hours, when stoppered with a cork, showed almost no change in physical appearance. The iodine number of this sample, therefore, was not taken as it was bound to be very low due to oxidation, just as in the case of sample 1. The possibility that the great increase in the viscosity of the oil could have been due to the action of the catalyst and not to the air is eliminated by the failure of other samples to thicken when heated with a catalyst and well protected from the air.

The catalyst used in sample 9 was prepared with much more dilute solutions than formerly used in order to get a purer precipitate. Dissolved 5 grams sodium carbonate in 2 L water, and also 20 cc. nickel nitrate in 4 L water. Added the sodium carbonate solution to the nickel nitrate solution slowly with stirring. Decanted, added 2 L water, stirred, decanted again, filtered and stood over night on filter. Filled test tube about half full of the voluminous precipitate so obtained, covered with a slit cork thru which the hydrogen tube protruded, and left in furnace for a week. Then passed hydrogen, 310-320 degrees, 5 hours. Black solid in small lumps settled to bottom, with some fine dust mixed in. Added a half test tube of oil, passed hydrogen at 220-240 degrees for 2 1/2 hours. Centrifuged before obtaining iodine number. The iodine number showed the oil to be saturated to practically the same

extent as the untreated oil, so the catalyst evidently had no effect in increasing the unsaturation.

It was then thought that a much more finely divided form of nickel might give the result desired so it was decided to try to decompose a nickel soap in solution in the oil. This experiment was first carried on with the copper. A potassium soap was first made by saponifying 30 grams of cottonseed oil, (the same oil as that used thruout the experiment), with 7 grams of potassium hydroxide dissolved in water. The mixture was stirred and heated until a nearly solid mass was formed. There was considerable unsaponified oil left, altho the amount used was calculated from the saponification constant of the oil. This unsaponified oil was drained off and the soap dissolved in 300 cc. water and heated to boiling. Dissolved 24 grams copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, which is equivalent to 6 grams potassium hydroxide, in 200 cc. water, added slowly with stirring to the soap solution which was still hot. A black, tarry precipitate separated out and floated on top. Poured out the water and placed 20 drops of the tarry matter in a test tube half full of oil and placed in furnace, in which the temperature was about 400 degrees. In about half a minute there occurred violent boiling and slight gas explosions inside the furnace. It was thought at first that these explosions might be due to gaseous decomposition products of the oil and possibly even to hydrogen, but subsequent experimenting showed that the phenomena was probably due to the vaporization and burning of the oil as it spattered onto the hot furnace.

A similar soap solution to the above was again prepared, but dissolved in 800 cc. water instead of 200 cc. 50 cc of this solution was then diluted to 500 cc. with cold water. To this was added slowly, with stirring, a solution of 2 grams copper-nitrate in 300 cc. water. This time a beautiful light blue precipitate was obtained, which coagulated well. After decanting and filtering, about $1/2$ cc. of this precipitate, undried, was smeared around the inside of a test tube, oil was added until the tube was $2/3$ full, and the precipitate was caused to dissolve by being stirred into the oil with a glass rod. Heated this sample, which was number 10, five minutes at 320 degrees, during which time most all the oil spattered out because of the water which was introduced with the precipitate. The oil which was left was dark greenish brown and opaque.

For sample 11 a perfectly dry test tube was used. About $1/10$ cc. of the same precipitate was smeared around the inside of the test tube and slightly heated to drive off some of the moisture. A few cc. of oil was then added, the precipitate dissolved, and the solution heated over a bunsen flame until all the popping due to evaporation of water had ceased. The test tube was then nearly filled with oil and covered with a disc of ground glass as previously described, making an air tight joint. Heated to 350-360 degrees for five hours, after which the oil was observed to contain a very fine copper suspension. The suspension had the same color as copper itself, the particles could not be seen with the naked eye, and the suspension was nearly opaque. The iodine number of this oil

showed that there was a decrease in the unsaturation rather than an increase.

Several attempts were then made to prepare a nickle soap using the nickle carbonate which had been precipitated for use with sample 9, as it was thought that this precipitate was especially pure. The nickle solutions thus prepared gave emulsions when added to the soap solutions. This was probably due mostly to acidity of the nickle solutions so prepared, which liberated the fatty acid from the soap. A nickle soap was finally prepared from a very dilute solution of nickle-nitrate which coagulated in the same manner as the copper soap previously prepared. Similar amounts of solution were used as when the copper precipitate was prepared. The nickle precipitate was decanted and filtered. About 1/10 cc. of it was smeared around the inside of a perfectly dry test tube, heated, dissolved in a small amount of oil and heated over a bunsen burner until all water was driven off, in the same way as the last copper precipitate was treated. The test tube was then nearly filled with oil, covered with a glass disk, and heated at 350-360 degrees for six hours. The nickle soap did not decompose as rapidly as did the copper soap, but finally gave nearly as good a suspension, which was black and nearly opaque. There were some larger particles than in the case of the copper and these settled to the bottom of the test tube, but most of the nickle remained in a fine suspension. The iodine number of this sample, however, was even less than that obtained from sample 11, showing that no dehydrogenation had taken place, or else that whatever dehydrogenation that may have taken place

was more than counteracted by other actions of an opposite nature.

In connection with these last two samples containing the copper and nickle suspensions, which were heated to 350-360 degrees for 5 and 6 hours respectively, it is interesting to note that their iodine numbers were reduced to about 90 and 88 respectively by the treatment, whereas sample 2 which contained no suspension had its iodine number lowered only to 95 and sample 5 which also contained no suspension and which was heated to 350-360 degrees for 5 hours did not have its iodine number changed appreciably at all. It seems therefore probable that the presence of the copper and nickle suspensions in the oil must have assisted chemical changes within the oil, resulting in lowering the iodine number to a greater extent than when no suspension was used.

An interesting experiment was done with the cottonseed oil which did not have any particular bearing upon the problem of this thesis but which may be worth reporting. 100 cc. oil was placed in a 250 cc. distilling flask which was provided with an air-cooled Leibig condenser. Compressed air was forced thru the condenser from the compressed air line. The oil was heated with a bunsen burner and three fractions were distilled off. During the distillation large quantities of acrolein were evolved due to the decomposition of glycerine in the oil. The oil began to give off "steamy" vapors at 303 degrees, bubbled slightly at 350 degrees, and started to boil at about 360 degrees. The thermometer bulb in the above instances

was immersed in the oil, and the readings are not corrected. The following readings were taken with the bulb just below the outlet of the distilling flask. The temperature remained at 350 degrees during practically the whole of the distillation. Three portions of distillate were collected, as follows:

Fraction	Volume	Color	Physical state	Saponification K
I	12cc	cream	like solid cooking fat	166.6 - 166.1
II	25cc	straw	"	176.3 - 176.2
III	20cc	amber	"	171.3 - 172.8
Residue	25cc	green-black	tarry	83.4 - 89.6

It was very difficult to titrate the residue in getting its saponification value, due to the very dark color of the solution. The most interesting result of the above experiment was that each distillate crystallized on cooling into a solid fat. This may have been due to an increase in the percentage of free fatty acid, due to decomposition of the glycerides, which would raise the melting point, and also to polymerization. Free fatty acids would raise the saponification value, however, but since the latter value was considerably less in the distillates than in the original oil, there is an indication that most of the change was due to polymerization, since only the latter explanation will account for the decrease in the saponification value. This also would explain the very low saponification value of the residue, for polymerization products occurring in the

distilling portion would have a higher boiling point than the rest of the oil and hence remain over in the residue. Unsaponifiable decomposition products may also have been formed.

SUMMARY

1 Samples of cotton seed oil were heated in test tubes protected from air, each for a period of five hours. At temperatures of 250, 290, and 350 degrees the iodine number was but very slightly lowered. At 360 degrees it was lowered about 5 per-cent. It was also shown that at 360 degrees distillation and decomposition of oil begins; but at temperatures below 350 degrees heat alone has but little effect. (Samples 2, 3, 4 and 5.)

2 Sample heated 4 1/2 hours, 320 degrees, not protected from air (stoppered with glass wool) had iodine number reduced to about 73. (Originally 107). Since the introduction of air was the only variation between this and the samples heated while protected from the air, this reduction of the iodine number must have been due to oxidation. (Sample 1).

3 No satisfactory hydrogenation and no dehydrogenation was obtained by heating the oil in the first case with and in the second case without the passage of hydrogen, using nickle catalyst prepared by reduction of basic nickle carbonate in stream of hydrogen. (Samples 6. 7. 8. 9.)

4 Very fine suspensions of copper and nickle were obtained by making cotton seed oil soaps of copper and nickle respectively, dissolving these in the oil, and decomposing by heating. These samples were well protected from air and heated to 350-360 degrees for 5 and 6 hours respectively. The iodine numbers of the oils were lowered to about 90 and 88. Since oil containing no suspension and heated to 360 degrees continuously for 5 hours (sample 2) had iodine number lowered only to about 95 and the iodine number of oil heated to ^{360?} 350 degrees, 5 hours (sample 5) was not affected, the presence of the copper or nickle suspension in the oil must have assisted chemical changes within the oil, resulting in lowering the iodine number to a greater extent than when no suspension was used. *May be reduction of Ni. salt by oil, which would be oxidized, ∴ the iodine number would be lower.*

5 A sample of cottonseed oil distilled with decomposition at 350 degrees, giving off large quantities of acrolein. The saponification constants of the fractions distilled increased slightly as the distillation progressed, but the saponification constant of the residue was very low. This result may have been due to decomposition of the glycerine, giving rise to a higher proportion of free fatty acids in the distillate and a lower proportion in the residue, to polymerization, and to formation of unsaponifiable decomposition products in the residue.