CORN OIL

A Study of Corn Oil, its Manufacture and Properties.

By
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A thesis submitted to the Department of Chemistry and Faculty of the Graduate School in partial fullfulment of the requirement for the Master's degree.

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PREFACE

Thru the suggestion of Prof. W. S. Long an investigation of the literature on corn and its products was begun in the Fall of 1919. The recent articles revealed that oil prepared form maize was of recent origin and not ~~prepared from~~ much was known about its reaction except those used in routine analysis of oils About this time an opportunity presented itself for the author of this paper to work in conjunction with the Aunt Jemima Milling Co., who were at this time extracting oil from corn and opened their plant for inspection as well as providing samples of their product. The author also feels indebted to the company for various suggestions and helps given during this study. Professors Long, Baily, and others of the Department of Chemistry, were of the greatest assistance in this work.

Literature of value in this research was not to be secured. The work done is mostly covered by patents of so called secret processes.

INTRODUCTION

That corn contains an oil in sufficient quantities for extraction, on a commercial scale was first revealed thru the brewing industry. The distillery residue contains 28% of oil if the germ is not removed and 10% if removed. Unless the residue are extracted they soon become unfit for stock food on account of rancidity. The residues are filtered dried in a drier and extracted in a suitable apparatus with volatile oils. Trichloroethylene is most extensively used. The oil obtained from this source contains from 30 to 70 per cent of free fatty acid, making them unfit for human food, and are thus largely converted into soap stock.

In the corn starch industry and its allies the oil in the corn kernel also proved and objectionable feature. Whole corn contains from 2 to 5% of fatty matter the greater portion of which is located in the germ. The pure germ yields upon extraction with ether from 15 to 30% of oil. To remove the germ without materially interferring with desired products led to what is known as the wet process of extracting the germ from corn. This consists of soaking the whole corn for several days in

water to which has been added a small quantity of sulphuric acid. The acid prevents fermentation. The water loosens the particles of the kernel, then by loosely grinding in water the germ is removed by flotation. The germ obtained by this method contains various amounts of bran which may after drying be removed by coarse seiving. The germ is again dried until it contains not more than three per cent of moisture and extracted with volatile oils or passed thru the Anderson Rotary Press.

The rapidity with which corn goods becomes rancid (often within one week under suitable conditions of temperature and moisture) led to the removal of the germ from such goods. This is accomplished by what is known as the short milling process. The corn is washed, tempered with steam, coarsely cracked and passed through a drier, over a seive, thru another roll somewhat finer, thru another drier, over another seive with the same mesh. and repeated for a third time. The material passing over the third seive consists mostly of germ with portions of bran and grits. This process if carefully manipulated will yield about 75% germ, 20% bran, and 5% starching matter, showing an oil content of about 20%. This

mixture is then dried to three percent of moisture and passed thru a continuous Anderson Rotary Press. An extraction of 15% of oil is obtained leaving about 5% in the oil cake.

The Effect of Bran upon the Extraction of Oil from the Corn Germ with the Anderson Press.

In a series of experiments on the Anderson Press the following results were obtained. Each is an average of ten experiments.

No.	Germ	Bran	Extract.	Oil Cake	Yield per bu.
1	98%	2%	19.68%	8.32%	0.75 lbs.
2	95%	5%	19.87%	7.13%	0.78 lbs.
3	90	10	19.29	6.41	0.85
4	80	20	19.43	3.32	1.10
5	75	25	19.63	2.00	1.25
6	60	40	10.15	4.11	0.73
7	50	---	-----	-----	----

The above results show with out a doubt that the greater extraction of oil from corn by means of the Anderson Press lies in the range of the 75% germ and twenty five percent bran. The above figures are merely indices as these experiments were performed on a commercial scale and without a doubt the germ was not uniform, however the separating and adding of bran was so regulated as to give a fair average of the percentages indicated.

A test for free fatty acid on the oil was made using the official agriculture method. Samples of each were tested.

No. 1	free fatty acid	0.88%
2		1.20
3		1.85
4		2.00
5		2.66
6		2.87

The free fatty acid content increases from .88% to 2.87% with an increase of bran from 2% to 40%. The curve shows a gradual increase in acid content with an increase in the bran, and leads to the conclusion that the free fatty acid content increases with the amount of bran mixed with the pure germ.

The Effect of Light on Corn Oil

The oil from the 98% germ was placed in 60 two ounce bottles tightly corked and set in a window where only the north light could reach it. These bottles were so placed that each would obtain maximum amount of light. One bottle was tested for free fatty acids about nine o'clock each morning for sixty consecutive days.

Days	free fatty acid	Days	free fatty acid
1	0.88%	31	1.62%
2	.89	32	1.68
3	.90	33	1.75
4	.91	34	1.82
5	.92	35	1.90
6	.92	36	2.10
7	.92	37	2.15
8	.93	38	2.24
9	.94	39	2.32
10	.95	40	2.40
11	.96	41	2.51
12	.97	42	2.62
13	.98	43	2.74
14	.99	44	2.86
15	1.01	45	2.98

16	1.03	46	3.10
17	1.06	47	3.25
18	1.09	48	3.02
19	1.10	49	3.68
20	1.13	50	3.94
21	1.20	51	4.09
22	1.23	52	4.25
23	1.26	53	4.50
24	1.30	54	4.75
25	1.34	55	4.98
26	1.39	56	5.32
27	1.42	57	5.60
28	1.45	58	5.91
29	1.50	59	6.18
30	1.56	60	6.32

A Control of which the original analysis was 0.89% was kept in a can from which both light and air were excluded. An analysis on the sixtieth day showed that the free fatty acid content had not changed.

The above figures show that light altho northern sky light will increase the free fatty acid content of corn oil. On the other hand oil excluded from light and air will not change.its free fatty acid content to any marked degree. In the above will be noticed a series of irregularities due to weather conditions.

The Effect of Decolorizing and Clarifying Agents on Corn Oil.

A quantity of crude corn oil was now obtained for the investigation of refining and decolorizing of the oil. In these experiments the official agriculture methods were used for analysis of resulting products. The effect of Fuller's earth, carbon (high grade), bone black, calcium oxide, and bleaching powder were tried with the following ratios and temperatures. Five mixes of each were made in small beakers and let stand for the required length of time, after which they were filtered and the determinations of their constants made.

The following table shows the effect of Fuller's earth upon the oil used.

Sample	Temp.	Quan. of Oil	Fuller's earth	Time Hours	Recovery
1	20	40 g.	2 g.	18	97.5%
2	20	40	5	18	92.5
3	20	40	10	18	85.
4	20	40	15	18	75
5	20	40	20	18	67.5

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %	Sample
1.4725	.8430	121.76	190.15	2.29	1
1.4725	.8431	121.32	190.10	1.57	2
1.4725	.8430	123.06	190.12	1.00	3
1.4725	.8432	120.96	190.16	.74	4
1.4725	.8432	122.00	190.75	.74	5

Sample	Temp.	Quan. of Oil	Fuller's earth	Time Min.	Recovery
1	20	40 g	2 g	5	98.00%
2	20	40	5	5	94.5
3	20	40	10	5	89.3
4	20	40	15	5	80.0
5	20	40	20	5	74.0

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %	Sample
1.4725	.8431	121.30	191.75	2.39	1
1.4725	.8432	121.45	191.90	2.00	2
1.4725	.8430	121.60	190.70	1.35	3
1.4725	.8430	121.90	191.20	1.00	4
1.4725	.8429	121.50	190.90	.74	5

Sample	Temp.	Quan. of Oil	Fuller's earth	Time Min.	Recovery
1	20	40 g	2 g	-	97.6%
2	20	40	5	-	95.6
3	20	40	10	-	89.
4	20	40	15	-	84.3
5	20	40	20	-	80

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4725	.8430	121.00	190.80	2.40	1
1.4725	.8430	121.35	190.91	2.10	2
1.4725	.8432	121.43	190.96	1.87	3
1.4725	.8431	121.00	190.98	1.50	4
1.4725	.8430	121.52	190.86	1.00	5

Sample	Temp.	Quan. of Oil	Fuller's earth	Time Min.	Recovery
4	20	40 g	15 g	3	85%
Original	20	40	--	-	--

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4725	.8431	121.42	190.86	1.50	4
1.4725	.8430	121.62	190.15	5.23	Original

Fuller's earth (XL English) used in the ratio of 40 grams of oil to 20 grams of earth gave the best results of color, taste, and reduced the free fatty acid content most. It will also be noticed that the time of action has no influence on the finished product. A thoro mixing and then filtering gave almost identical results with that of standing for some time. To completely remove the Fuller's earth from the oil it was necessary to filter twice and in some cases as high as three times. It takes between three and five minutes to clarify corn oil with Fuller's earth. The analysis also show that Fuller's earth at room temperature does not change the constants of the oil. The free fatty acid content cannot be completely removed from corn oil by the use of Fuller's earth at 20 degrees Centigrade.

The effect of Fuller's earth at 50 and 90 degrees, and at the fuming point of the oil were next investigated.

Sample	Temp.	Quan. of Oil	Fuller's earth	Time Hours	Recovery
1.	90	40 g	2 g	18	97 %
2.	90	40	5	18	91.5
3.	90	40	10	18	80
4.	90	40	15	18	77
5.	90	40	20	18	65
6.	Fuming	40	15	2 min	78

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4730	.8461	121.30	191.60	1.98	1
1.4730	.8464	121.28	191.00	1.50	2
1.4730	.8461	121.45	191.07	1.00	3
1.4730	.8462	121.12	191.13	.85	4
1.4730	.8465	121.50	191.18	.82	5
1.4735	.9195	121.03	191.22	.75	6

Sample	Tem.	Quan. of Oil	Fuller's Earth	Time Hours	Recovery
1.	50	40 g	2 g	18	97.5%
2.	50	40 g	5	18	92.0
3.	50	40	10	18	86.
4.	50	40	15	18	80.
5.	50	40	20	12	74.
Original	--	--	--	--	--

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4728	.9190	121.25	191.00	2.00	1
1.4728	.9190	121.30	191.09	1.63	2
1.4728	.9190	121.35	191.30	1.35	3
1.4728	.9192	121.30	191.16	.89	4
1.4728	.9191	121.30	191.27	.83	5
1.4725	.9218	121.88	------	1.998	Original

Corn oil treated with Fuller's earth at 20degrees Centigrade shows a refractive index of 1.4725,at 50 degrees Centigrade 1.4728, at 90 degrees Centigrade 1.4730, and at the fuming temperature 1.4735; also the specific changes respeciivelly from .8430 to .9190. This leads to the conclusion that the refractive index and specific gravity are influenced by the increase of temperature when corn oil is treated with Fuller's earth. This change is

probably due to the volatilization of the lighter oils. There is no change in the constants with the amount of Fuller's earth used at higher temperature. The only difference is with the variation of the temperature.

At this point a new sample of oil was taken and the action of charcoal was investigated, but as charcoal produced a product of greenish color, disagreeable odor, and taste the further study of charcoal and bone-black was abandoned. The results are given for comparison.

Sample	Temp.	Quan. of Oil	Carbon	Time Hours	Recovery
1.	20	40 g	2 g	18	-----
2.	20	40	.5	18	-----
Original	--	--	----	--	-----

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4743	.9218	90.5	--	1.22	1
1.4745	.9218	100.02	--	1.30	2
1.4725	.9218	121.88	--	1.998	Original

From the figures above it is shown that the iodine number has been reduced. The greater lowering of the iodine number is produced by the greater amount of carbon used.

Below are the results of the action of Calcium oxide on corn oil.

Sample	Temp.	Quan. of Oil	Calcium Oxide	Time Hours	Recovery
1.	20	40 g	1.0 g	18	-----
2.	20	40	.5	18	-----
Original	--	--	----	--	-----

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4744	.9219	122.74	xx	1.25	1
1.4743	.9220	126.94	--	1.18	2
1.4725	.9218	121.88	--	1.998	Original

Calcium oxide shows a slight reduction of the free fatty acid but an increase in the specific gravity and iodine number. At first it was supposed that filtering failed to remove any surplus calcium oxide or any of its products of reaction. The oil was then washed with water at 60 degrees Centigrade and dried. The results were not changed by this treatment. The iodine number is greater with .5 grams and the free fatty acid content is less than when one gram of oxide is used.. This bears out the fac

fact that the Calcium oxide forms compounds with the oil. These compounds cannot be removed by filtering or washing. They have an effect upon the refractive index and dissociate when the oil is treated with iodine; hence the increase in the iodine number. In this case the iodine unites with the Calcium forming Calcium iodide. This with the regular absorption would increase the iodine number.

Bleaching Powder;

Sample	Temp.	Quan. of Oil	Bleaching Powder	Time Hours	Recovery
1.	20	40 g	1.00 g	18	----
2.	20	40	.50	18	----
Original	--	--	-----	--	----

Refractive Index	Sp. G.	Iodine No.	Sap. No.	Free Fatty Acid %.	Sample
1.4745	.9225	122.62	--	.00	1
1.4745	.9225	115.36	--	.4	2
1.4725	.9218	121.88	--	1.998	Original

Bleaching Powder has no effeft upon the color of corn oil, but with the use of one gram to forty grams of oil the free fatty acid can be entirely removed. More logically speaking Clorine products are formed with the free fatty acids neutralizing the same. The iodine number is greater ~~than~~ with 1 grams than with .5 gram just the reverse with Calcium oxide. The reactions taking place were not analyzed and the explanation of this phenomenal remains in doubt.

Fuller's earth, carbon, calcium oxide and bleaching powder were tried in combination. These experiments were performed for the purpose of verifying the individual action of each in combination with Fuller's earth.

Sample	Temp.	Quan.	Fuller's Earth	Carbon	CaO	Bleaching Powder
1	20	40	2	5	--	--
2	90	40	2	.5	--	--
3	90	40	2	.5	.5	--
4	Fuming	40	2	.5	.5	--
5	90	40	2	.5	.5	.5
Original	--	--	-	--	--	--

Refractive Index	Iodine No.	Free Fatty Acid	Time Hours	Sample
1.4735	100.0	.86	18	1
1.4735	102.39	1.06	18	2
1.4725	103.79	.49	18	3
1.4730	103.19	.53	--	4
1.4735	106.52	.00	24	5
1.4725	121.88	1.99	--	Original

These combinations show the particular change when used separately. When ~~Extract~~ carbon is used with Fuller's earth we obtain the same greenish hue reduce the iodine number and increase the refractive

index. With the addition of Calcium oxide to Fuller's earth and carbon the iodine number is increased above that of carbon and Fuller's earth. This shows the ability of Calcium oxide to increase the iodine number. Bleaching powder in combination with the others does not show such a marked effect. In each experiment the individual effect can clearly be seen on the oil.

Neither of the above give an edible oil of the proper taste, odor, and color. Through the entire series Fuller's earth alone gave results which indicated value for the refining of the oil.

THE REFINING PROCESS

Fuller's earth, carbon, calcium oxide, and bleaching powder not producing a refined oil of the proper edible and keeping qualities without a low yield, it was decided to try neutralizing the free fatty acid of the oil with sodium hydroxide before treatment with Fuller's earth. The resulting product was one of strang soap-like taste indicating that a sodium compound had been formed of the free fatty acid. This soap-stock as it may be called was not removed by Fuller's earth. New Samples were taken tested for free fatty acid and enough sodium hydrate added to neutralize them. During the adding of the hydrate the oil was violently aggitated.

Oil Used	% Free Fatty Acid,	N-NaOH added
100 g	1.92	6.8
100	2.10	7.4
100	2.25	8.0

The resulting product was then placed in a separatory funnel thoroughly shaken and allowed to settle at a temperature of about 60 degrees Centigrade. The soap-stock settled to the bottom in twelve hours and was removed by being drawn from the funnel. 500 C.C. of sistilled water at sixty degrees Centigrade were added. The whole shaken

for five minutes, the oil and water allowed to separate and then the water was drawn off. This operation was repeated twice more. The oil was then analyzed for sodium, qualitatively traces of sodium were present, but none could be detected quantitatively. Quantitative determinations were made on both the oil and its ash. Analysis also showed no free fatty acid content. The color remained a light golden yellow.

The next thing was to remove the color. Fuller's earth having yielded the best results was tried in various quantities.

Quan. of Oil	% of Fuller's earth	Color
50 g	.25 g	Yellow tinge
50	.55	Colorless
50	1.0	"
50	2.0	"
50	5.00	"
50	10.00	"
50	15.00	"
50	25.00	"

The oil was agitated with Fuller's earth and then filtered twice. These experiments were carried out at room temperature. On this particular sample one half of one per-cent of Fuller's earth will clarify and decolorize the oil.

An excess of Fuller's ~~oil~~ *earth* will not effect the product only in so far as lowering the yield. The product was a clear colorless oil free from fatty acids with the characteristic odor of corn.

Super heated steam known as the best deodorizing agent for corn goods was tried with the following results.

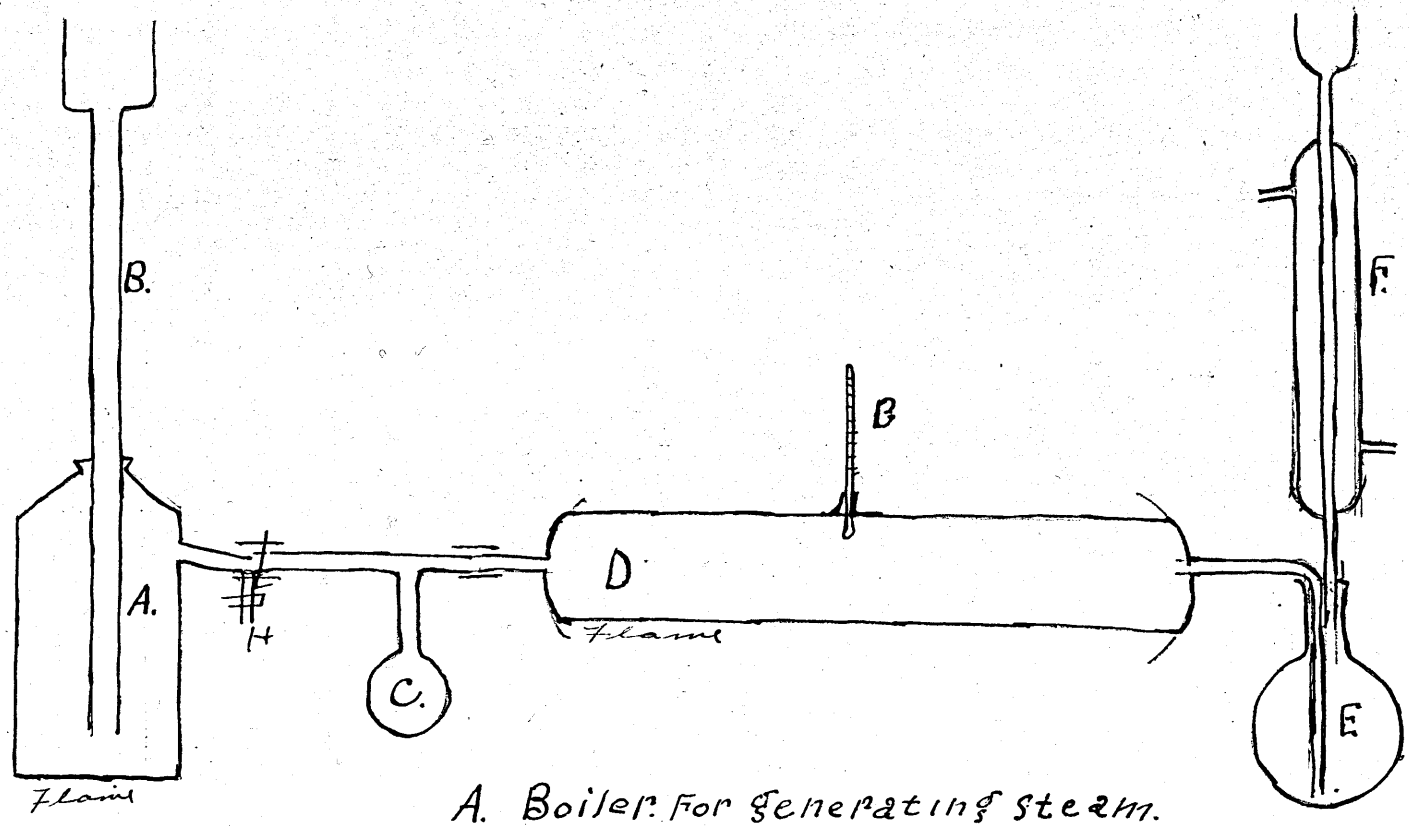
No. of Samples	Amount of Oil	Temp. of Steam	Time of Action	Change of odor
1	100 g	150 C	1 Hr.	None
1	100	150	2	"
1	100	150	5	"
1	100	200	1	Slight
1	100	200	2	"
1	100	200	5	"
1	100	225	1	Greater
1	100	225	2	"
1	100	225	5	"
1	100	250	1	Better
5	100	280	1	Removed
1	100	280	1/2	Slight
1	100	280	1/4	Less

From the above data it is evident that steam at the temperature of 280 degrees Centigrade is required

for the deodorization of corn oil. At this temperature the steam must act for one hour. Less time will not remove the odor. In the above experiments apparatus and condensers illustrated in the accompayning diagram were used.

The product now is a sweet oily odorless and tasteless fatty substance, in many ways superior to other salad oils. The constants of the oil had not changed from the original sample and were:

Specific gravity ----------	0.9218
Refractive index ----------	1.4725
Iodine number ----------	121.88



A. Boiler for generating steam.
B. Pressure Gauge
C. Flask for collecting condensed Steam.
D. Super Heater
E. Flask containing oil.
F. Condenser for volatilized oil
G. Thermometer

APPARATUS

The diagram on page 20 is the apparatus used for the deodorizing of the corn oil. A consists of a plain water boiler for the generation of steam. Into the boiler is placed a long glass tube to serve as a presure gauge. C is a water trap and used for the collecting of any condensed water vapor which may form before the steam reaches the super-heater D. The superheater consists of a large gas pipe, two inches in diameter, five feet long and closed at the ends with the exception of 1/8 inch hole to which is supplied a small iron tube. The end carrying the longer tube is bent at an angle of nineth degrees and extends into a pyrex glass flask E. Into the 1,000 C. C. flask is placed a charge of one hundred grams of oil. Here some difficulty was experienced in the oil foaming but not to such an extent as to materially interfere with the experiment. The foaming of the oil increased with an increase of temperature. F the condenser serves to return any oil which may volatilize and permit the steam to excape. The cooling water was found to give the best results at a temperature of about

sixty degrees centigrade. Care must be taken to prevent the condensing steam from returning to the oil as this has a tendency to lower the temperature.

The temperature of the superheated steam is produced by increasing or diminishing the number of burners in a series under the large gas pipe. These burners may be so regulated as to produce the desired temperature. To the flask E is applied a small flame in order to keep it at the proper temperature.

All other apparatus consisted of beakers, flasks, buretts, etc. and other apparatus used in routine work.

CONCLUSIONS

1. Corn germ gives the greatest yield of oil extracted by means of the Anderson Press when it contains 25% of bran.
2. Corn oil when exposed to the light will increase it's free fatty acid content. This increase will become greater the longer the oil is exposed to the light.
3. Fuller's earth will clarify and decolorize corn oil when used in the ration of 2 to 4.
4. Carbon, Calcium oxide, and bleaching powder show no value for the refining of corn oil.
5. Superheated steam at 280 degrees centigrade gives best results for deodorizing corn oil.
6. A very palitable oil can be produced from corn oil by neutralizing the free fatty acid washing several times with warm water, treating with Fuller's earthl filtering, and subjecting to superheated steam.

BIBLIOGRAPHY

1. Manufacture and Utilization of corn oil from distillery residue

B. Lack---Seifensieder Ztg. No. 40

2. Corn oil. Seifensieder Ztg. No. 40.

3. Corn oil-Its possible use as an adulterant in lard and its detection.

J. Am. Chem. Soc. Vol. 29----921 to 26.

4. Degerminatiog of corn--A. Woolner Jr.

U. S. patent 1,258,076, March 5, 1918.

5. Separating the germ from the starchy kernel of corn. --- H. Wulkan.

U. S. Patent, 1,045,490.

6. Conditioning corn for degerminationg and milling.

U. S. Patent, 944,013.

7. The Hydrogenation of oils. --- Ellis

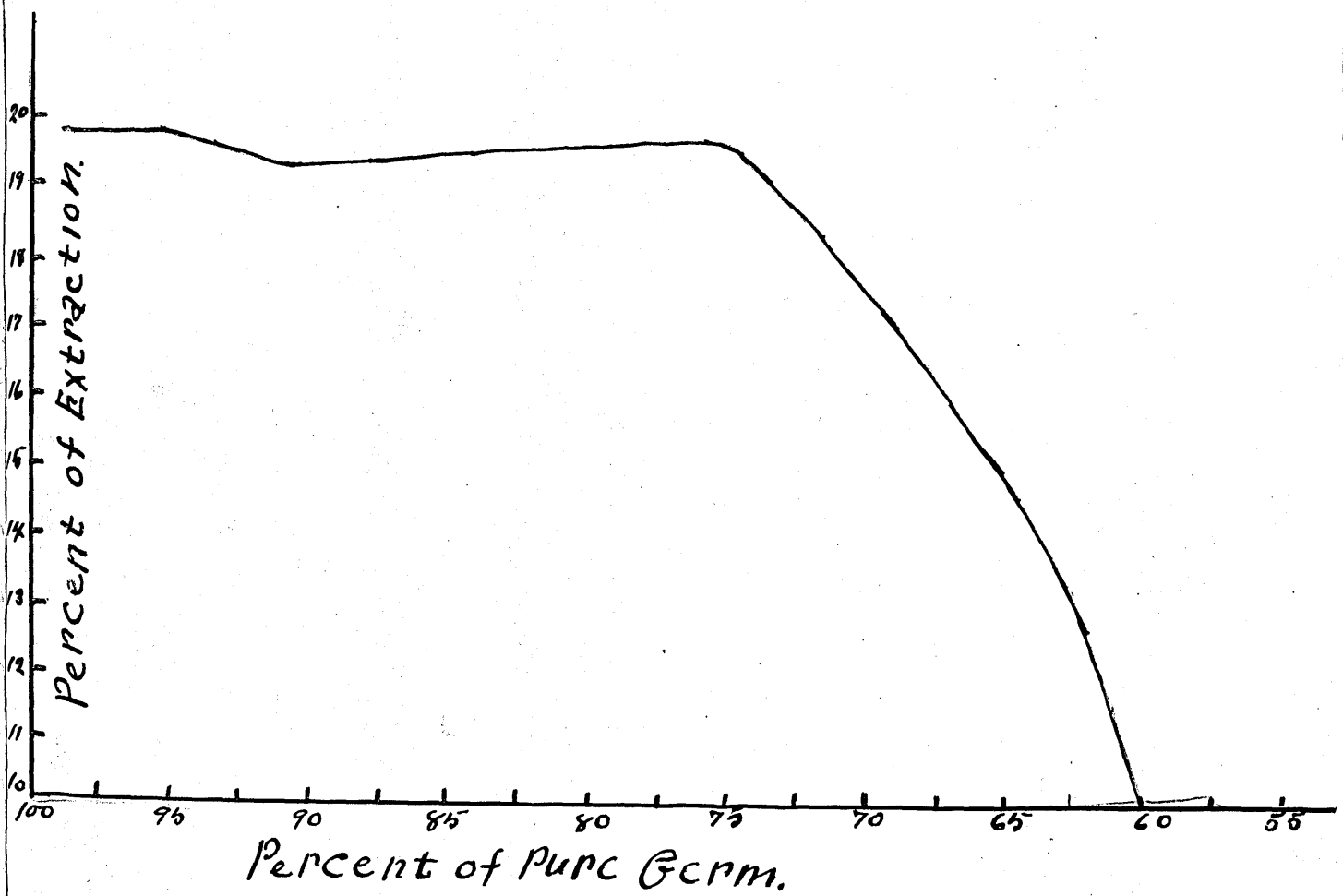
8. Process of the manufacture of corn products.

American Manufactures Association of Products from Corn.

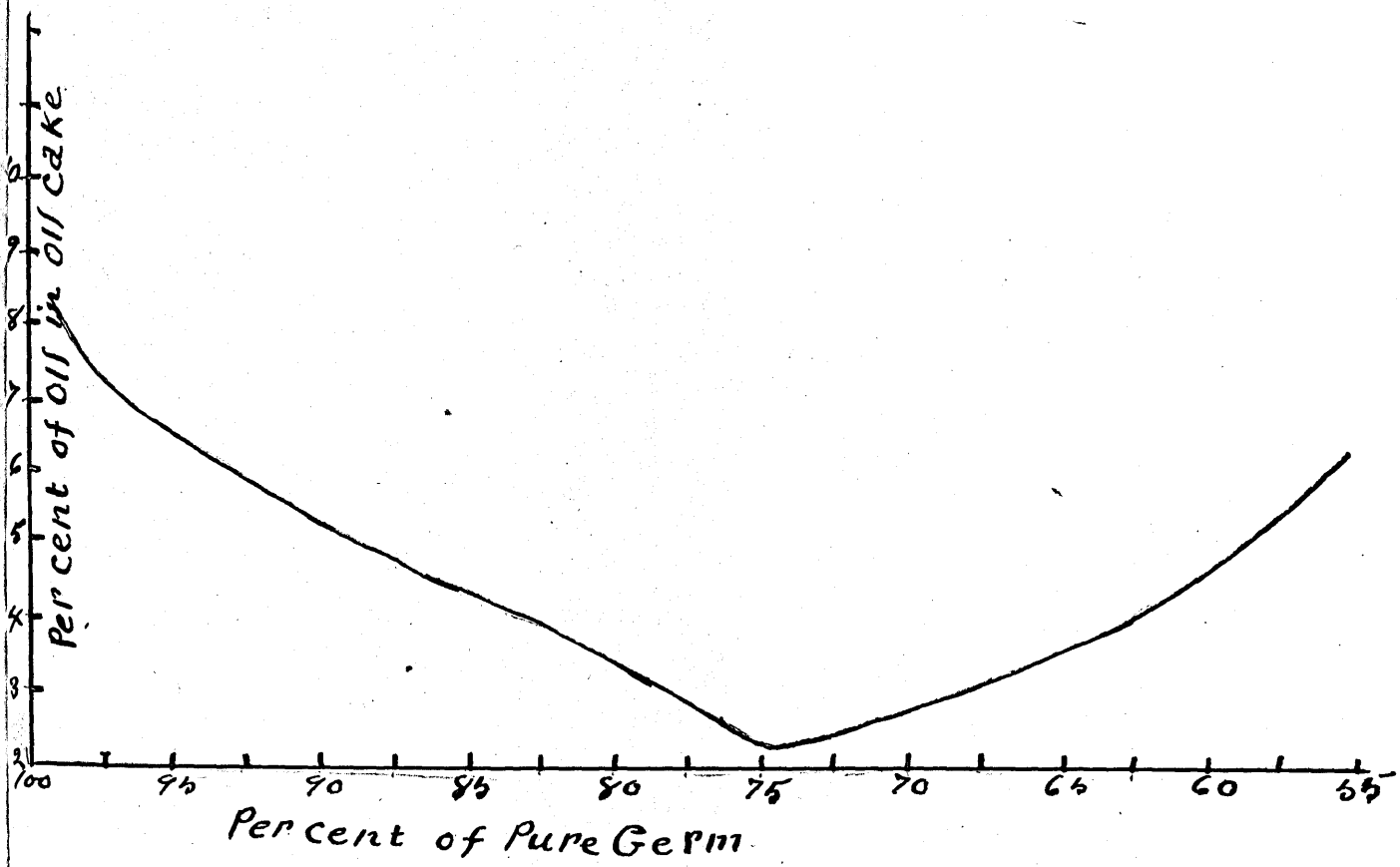
9. U. S. Bulletins No. 769 and 215.

10. Chemical Abstracts.

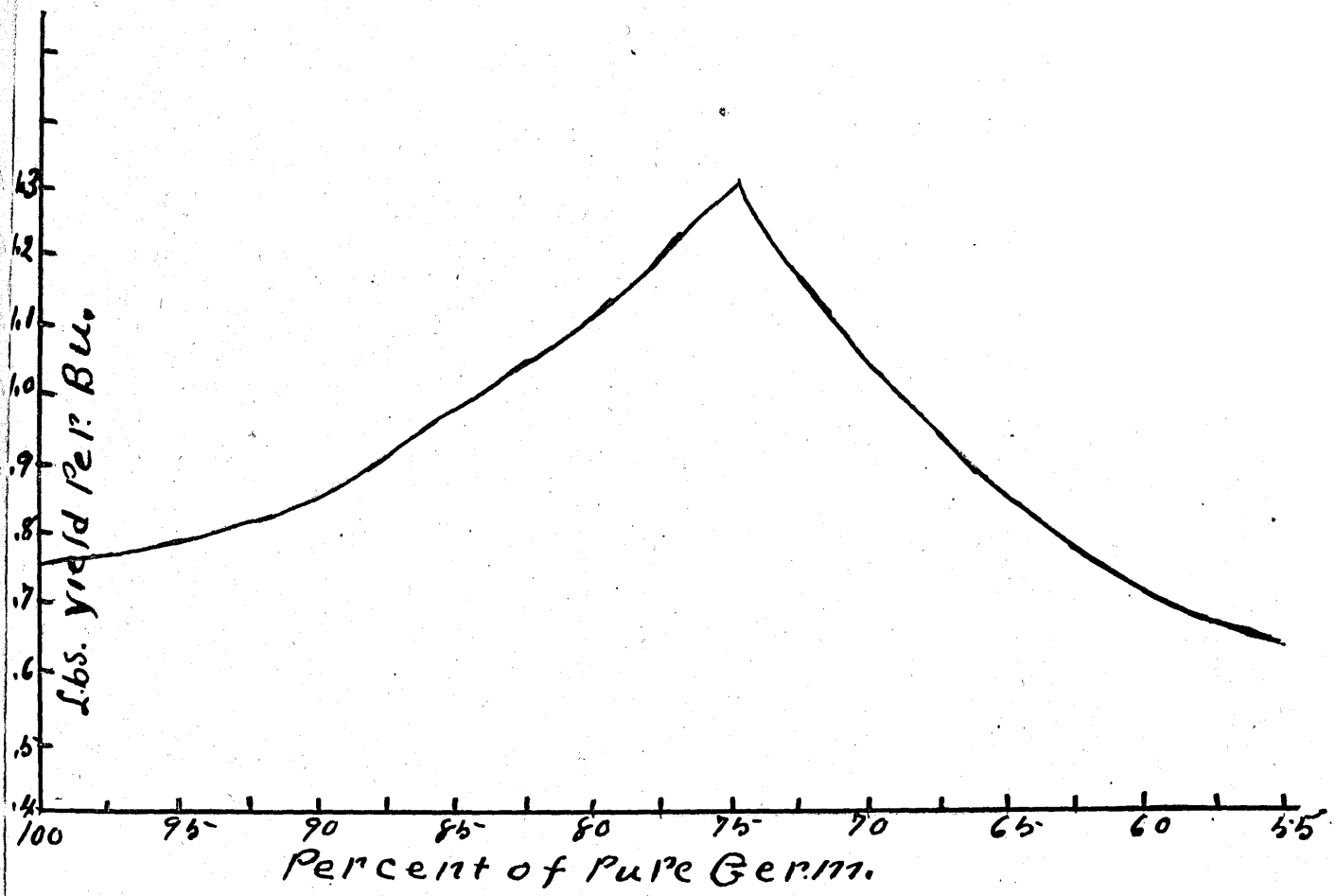
Diagram showing yield of Extraction.



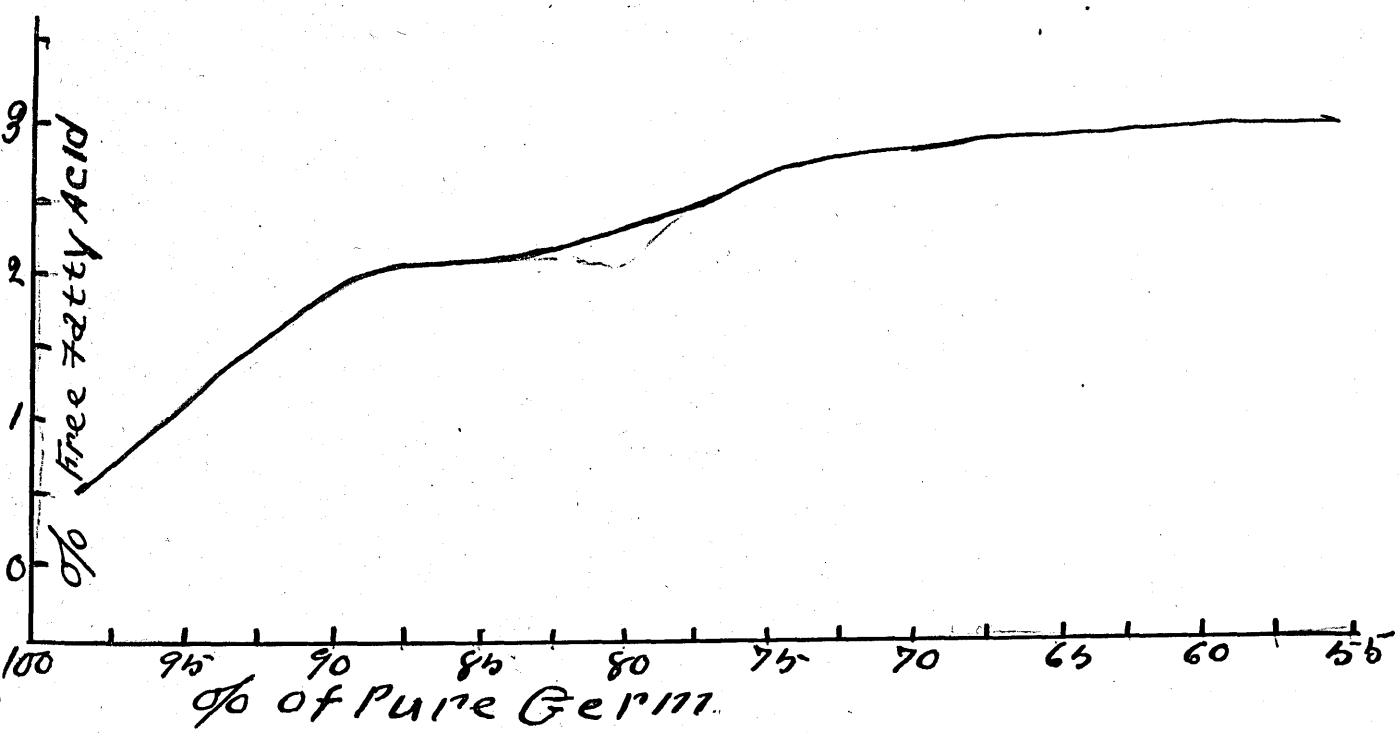
Curve Showing fat remaining in oil cake compared with percentages of Germ

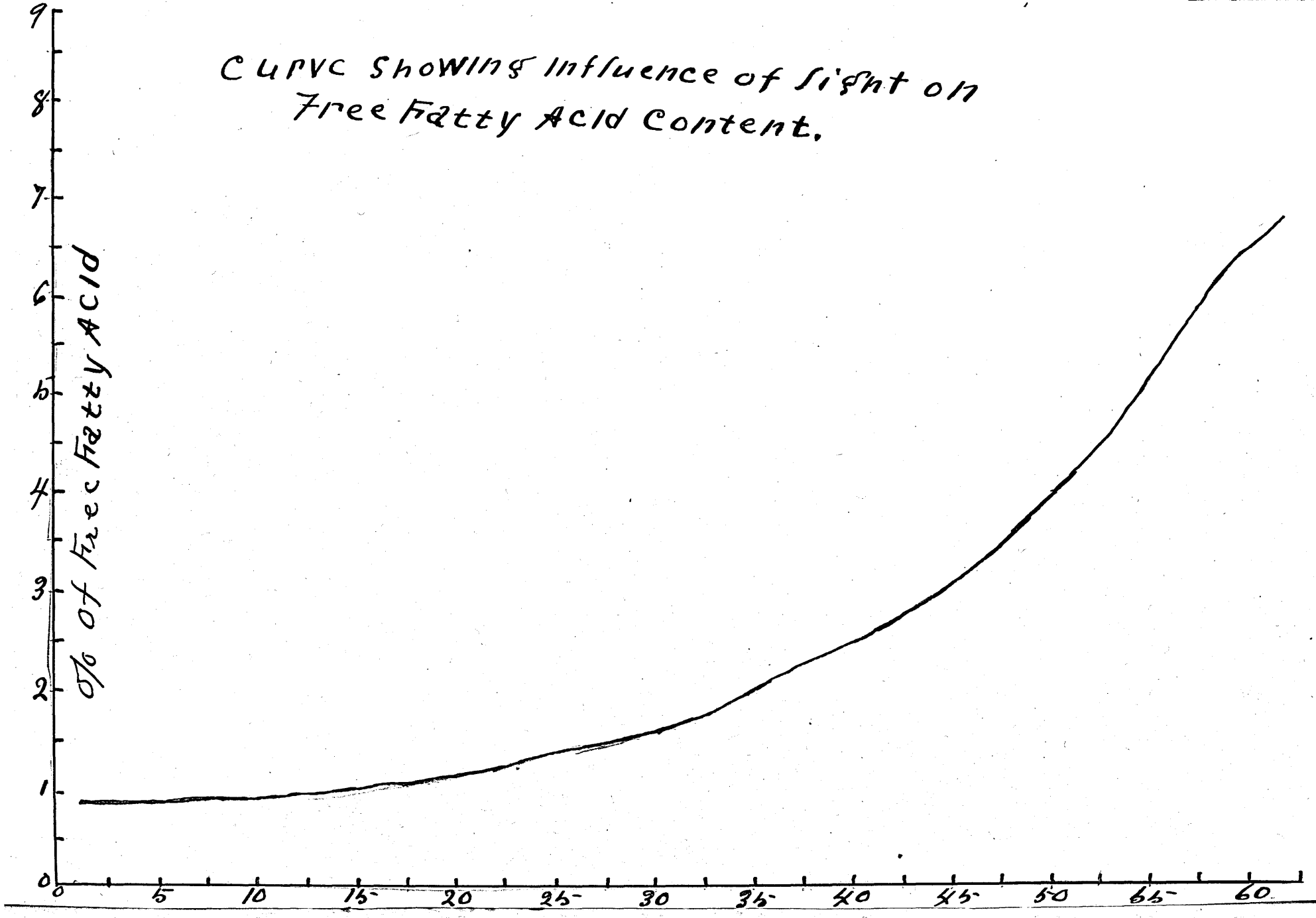


Curve Showing yield of oil per Bushel



Curve Showing Free Fatty Acid Content
In Extraction.




Curve Showing Influence of Light on Free Fatty Acid Content.
% of Free Fatty Acid
0
1
2
3
4
5
6
7
8
9
0
5
10
15
20
25
30
35
40
45
50
55
60