THE EXTRACTION OF OIL FROM COTTON SEED MEAL USING MIXTURES OF BUTANE AND OTHER ORGANIC SOLVENTS

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INTRODUCTION

The purpose of this research problem is to determine if as good a grade of oil or better grade of oil can be obtained from cotton seed meal by extraction using a mixture of commercial butane and a higher boiling solvent than can be recovered using butane alone.

A thorough search of the literature revealed no published data of any experiments in this field, and furthermore, no information was available regarding the recovery of oil by the extraction method, although considerable work has been done along this line. There are a few processes in use, but none have been successfully worked out. There is the Otto Wilhelm extraction system, the Bleil process, the Wurster and Sanger Rotary Solvent, and the Eddy process.[1] The last named is the only one that has been successfully operated on a commercial basis. On the other hand a relatively large amount of research has been done on the extraction of oil using gasoline and other petroleum products as the solvent. A process has been patented for the recovery of oil from oil bearing substances using a hydrocarbon solvent that is a gas at ordinary temperature and pressure, maintaining the solvent in a liquid phase while in contact with the material to be extracted.[2]

1. Manual of Operations for Cotton Oil Mills, Tri-States Cotton Oil Mill Superintendents Association. Ed. Service U. T. Eng. Exp. Station 124-40.
2. Reid, U. S. Pat. 1,802,533. (September 13, 1928)

GENERAL SURVEY OF FIELD

The solvent process for the recovery of oil has been experimented since the oil industry has been of any importance. During the World War the oil companies made extensive experiments with the solvent process, but after the war the price of oil did not warrant further investigation. There is no available information as to the solvents used, results obtained, or method by which the experimental work was carried on.

It has been only in the last few years that any intensive investigation has been made to improve the solvents. The solvent materials now in use are Benzene, Gasoline, or Petroleum Ether.

Dr. David Wesson at the annual convention of the American Chemical Society in Atlanta, 1930, made a statement regarding the present state of the oil recovery industry. Dr. Wesson said that only 85% of the oil is recovered by the present method of pressing; therefore it is quite evident that this falls far behind the chemical extraction by which practically 100% recovery is obtained.[1]

It is an interesting fact that often American cottonseed meal is reprocessed by chemical methods in Europe to remove the oil left in it by American oil mills.[2]

The possibilities of a continuous extraction process are limited. The necessities for a profitable commercial extraction is

1. Manual of Operations for Cotton Oil Mills, Op. Cit.
2. Ibid.

limited by the removal of oil from the meal, and the recovery of the solvent, therefore the chemical development is far in advance of the mechanical development.

In order that any solvent be acceptable it is necessary that:

1. The solvent dissolve oil and oil only; the darkening colors of hulls or meats should not be dissolved by solvent.
2. Solvent should extract oil efficiently.
3. Solvent should not have too low a distillation point.
4. A large portion of solvent used can be easily recovered.
5. The solvent offers reliable and uninterrupted operation.
6. The solvent used must operate without too much supervision to produce uniform results.
7. The initial cost is low.
8. The solvent used does not offer too great a fire hazard.[3]

It is at once obvious from the foregoing that the solvents used in the present extraction processes are not yet entirely satisfactory.

Butane has too low a distillation point; the loss of solvent is too great; the fire hazard is high. The apparatus necessary, when butane is used, is too expensive.

3. Manual of Operations for Cotton Oil Mills, Op. Cit.

APPARATUS

The construction of the apparatus is shown diagrammatically by Figure 1. A_1 is the condensing water intake. A_2 is the condensing water outlet. The charging tube is fastened to the extractor by means of unions D_1 and D_2. The extractor is evacuated by a vacuum connected at valve B_1. After the extractor has been evacuated valves E_1 and E_2 are opened to allow the liquid to drain into the extraction chamber. When enough liquid has drained into the extractor, valve E_1 is closed to prevent the liquid from backing into the charging tube when heat is applied; the proper amount of solvent is determined by the liquid level in the sight glass. Heat is applied by running steam through the steam coils VI. After running for a few minutes the extractor is vented out at valve B_1. IV and X are vapor by-passes. XI is a union by which the extraction chamber is taken from the remainder of the extractor for the purpose of putting in and removing the meal. At the end of the run the oil is taken out at valve B_2. The construction chamber was constructed of steel pipe 18 inches long and $2\frac{1}{2}$ inches in diameter.

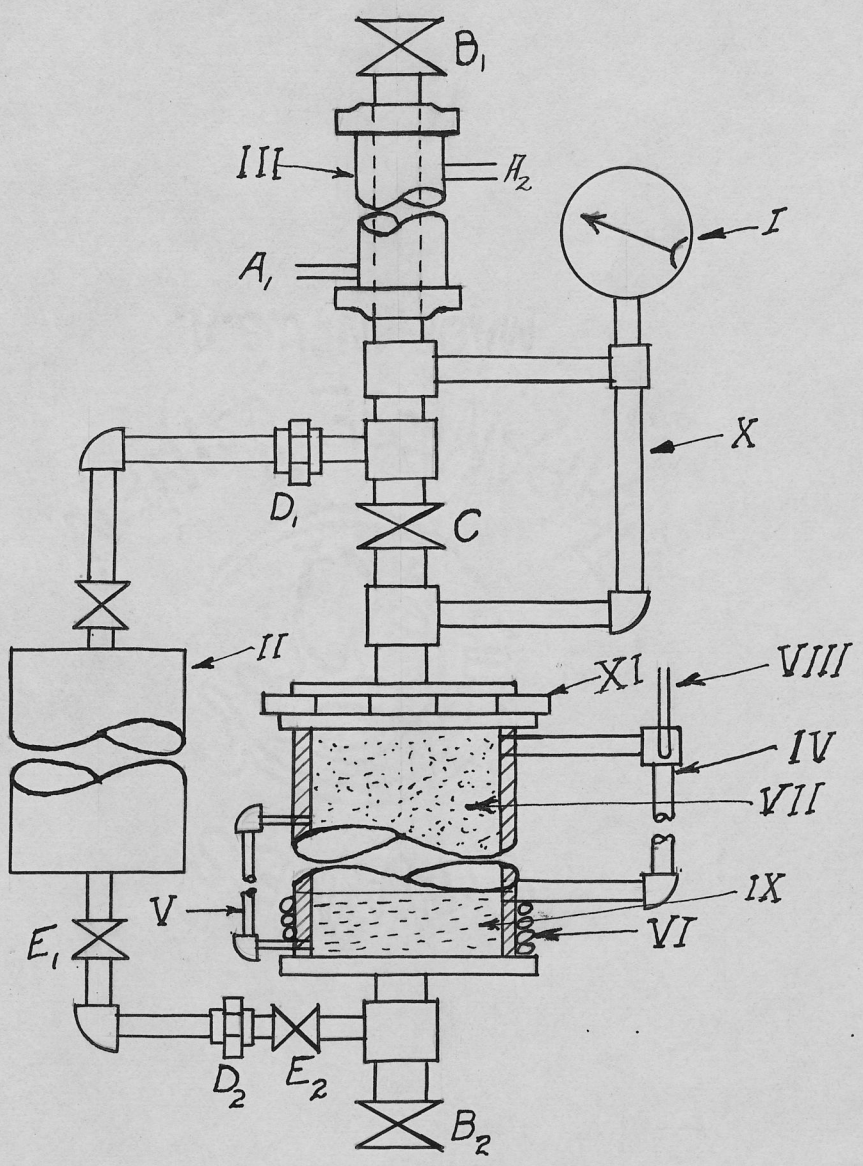


Figure I

I Pressure Gage
II Charging Tube
III Condenser
IV & X Vapor By-Passes
V Sight Glass
VI Steam Coils
VII Meal
VIII Therm. Well
IX Solvent
XI Union

TECHNIQUE

An extractor of design and construction as shown in figure 1 was used, because an extractor of this type is easily constructed, and has been found to be the most successful for pressure extraction.

In all samples taken, 300 grams of meal was used. The meal was placed in a filter bag and put in at the top of the extractor on lugs to hold the bag.

The charging tube was connected to a vacuum pump, and the pump allowed to run for several minutes to exhaust as much air as possible from the charging tube. Then the charging tube is connected to the butane drum and allowed to fill as much as possible by the vacuum created. It was found that it was necessary to heat the charging tube, and then suddenly cool to get a sufficient amount of butane in the charging tube.

The charging tube was then connected to the extractor and the joints screwed tight. With all connections made air tight the extractor was connected to a vacuum pump, and the pump allowed to run not less than five minutes. While the pump was running the connecting valve was closed. Water was started through the condenser. Then the valve connecting the charging tube and extractor was opened, sufficient solvent to be used was allowed to siphon off. If the extractor was warm it was necessary to heat the charging tube and drive over enough solvent.

When enough solvent has been driven into the extractor, determined by the solvent level in the sight glass, the connecting valve was closed, and heat applied to the bottom of the extractor. After heating for some time the valve at the top of the extractor was opened and the apparatus allowed to vent out. As the butane vapor is heavier than air, it carried out any air that may be left. The steam was so regulated that the temperature would be between 80 and 90 degrees F. At these temperatures the pressure was between 50 and 60 pounds per square inch.

After the end of the run valve (C) was closed, and the valve at the top of the charging tube was opened; the vapor by-passed through X, and was condensed to liquid; the liquid was then allowed to run back into the charging tube. The connecting valve was then closed, and the oil drawn off at the bottom of the extractor.

The free fatty acid was determined by taking 7.05 grams of oil, from a pipette calibrated to deliver that amount of oil, and adding 50 cc. of methyl alcohol containing .05% of phenolphthalein and sufficient amount of NaOH solution to give the alcohol a faint pink color. The alcohol must be made faintly pink just before adding to the oil. The oil was titrated with .25 N NaOH solution until a permanent pink color was produced, that could not be removed by violent shaking. The oil was titrated to the same shade of pink as the alcohol solution was before it was

added to the oil.[1]

After the amount of free fatty acid was determined, the amount of 14° Baumé caustic to refine the oil was found in tables provided by the National Cottonseed Products Association. For any percent of free fatty acid the required amount of caustic is given in grams of caustic per hundred grams of crude oil. After the proper amount of caustic had been added, the container holding the oil and caustic was heated in a water bath to approximately 70° F. The oil was agitated for 15 minutes at high speed with a mechanical agitator. The water bath was then heated quickly to about 150° F. and stirred for 12 minutes at slow speed. The agitator was stopped, and the oil allowed to settle in the water bath for one hour at 150° F. The oil was then allowed to settle for 24 hours at atmospheric temperature. The soap stock was then filtered from the oil.[2]

The refined oil was then graded in an enclosed Wesson type Tintometer with Lovibond's standard color glasses. The Tintometer is a light-proof box with dull black interior, and a white reflecting surface set at a proper angle to reflect light vertically upward through the tube containing the sample of oil, and through the standard color glass. An eyepiece fits over the oil tube and color glasses so that the light passing through both may be observed simultaneously. Two identical tubes were placed side by side one contained oil and the other water, both tubes

1. Rules of the National Cottonseed Products Association, P. 138.
2. Ibid.

were filled with the same volume of liquid; the color glasses were adjusted over the tube containing water until the same shade of light was transmitted through both tubes. Lovibond's standard color glasses are standardized by the Bureau of Standards.[3]

The best grade of crude oil is called prime crude cotton seed oil. Prime crude cotton seed oil must be sweet in flavor and odor, must be free from water and settlings, and must produce when refined, prime summer yellow oil. Prime summer yellow oil must be clear, sweet in flavor and odor, free from water and settlings, and of no deeper color than the combined standard glasses of 35 yellow and 7.6 red on Lovibond's equivalent color scale, and must not contain more than 1/4 of one percent free fatty acid.[4]

3. Ibid.
4. Ibid.

OPERATING OBSERVATIONS

The greatest difficulty encountered in the construction of the extractor was getting the apparatus to hold the gas pressure encountered at the temperature at which the extraction was run. The only method of over-coming the leaks was welding and brazing all joints.

The first two times that extraction was tried no oil was obtained, and from the appearance of the meal it was evident that no refluxing had taken place. Then it was found necessary to evacuate the extractor. In the next run not enough oil was obtained to make the refining test. The only thing which could be wrong was that not enough or too much solvent was present. Then a sight glass was put on the extractor to determine the liquid level.

After the proper amount of solvent was in the extractor and the heat applied, complete extraction was not obtained. It was found that the solvent collected in the cool parts of the extractor. It was found necessary to heat all of the extractor except the condenser.

EXPERIMENTAL DATA

Table No. 1

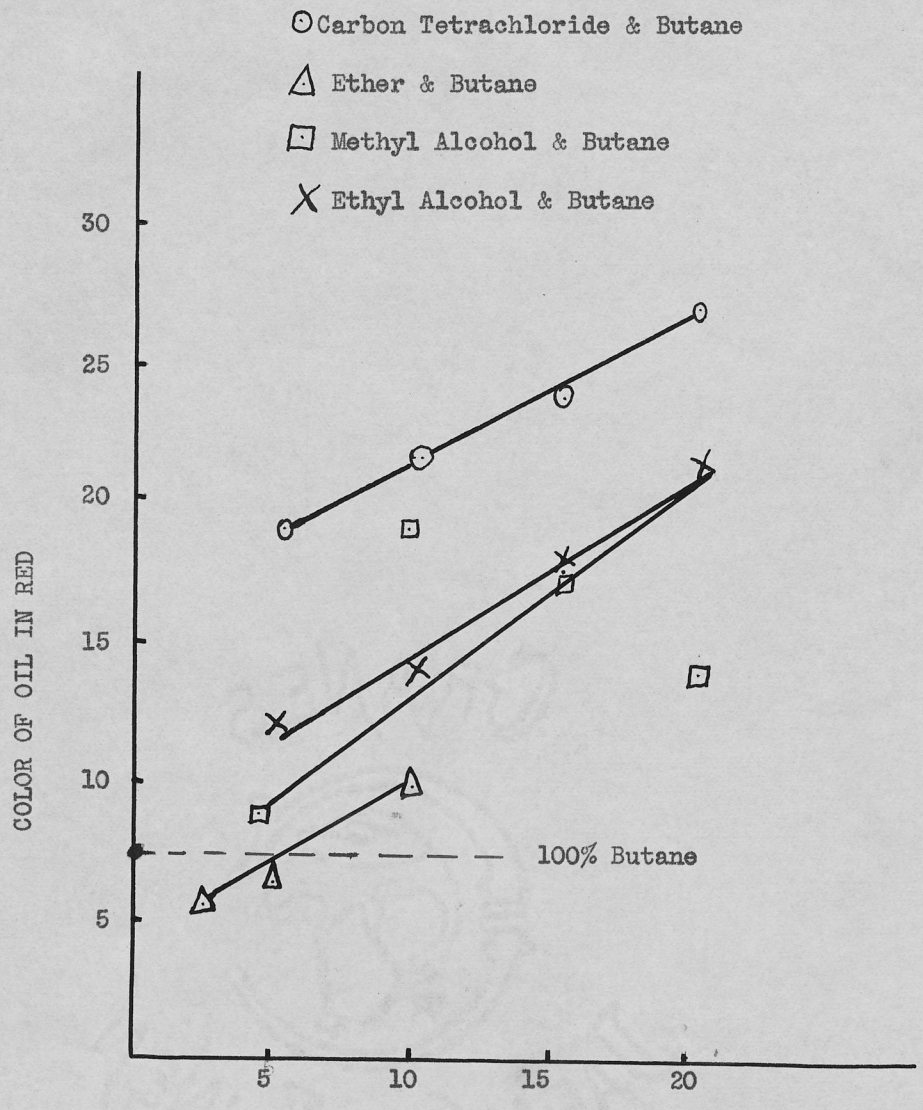
	Fatty Acid %	Color	Time Hours	Oil Extracted Grams
100% Butane	1.2	35 Y 19 R	12	85
100% Butane	1.6	35 Y 7 R	5	86
100% Butane	1.8	35 Y 7.3 R	12	85
95% Butane 5% Carbon Tetrachloride	1.0	35 Y 19 R	12	82
90% Butane 10% Carbon Tetrachloride	1.1	35 Y 21.5 R	12	83
85% Butane 15% Carbon Tetrachloride	1.4	35 Y 24 R	12	81
80% Butane 20% Carbon Tetrachloride	2.3	35 Y 27 R	12	83

Table No. 1
(Continued)

	Fatty Acid %	Color	Time Hours	Oil Extracted Grams
97½% Butane 2½% Ether	2.4	35 Y 6 R	12	84
95% Butane 5% Ether	2.4	35 Y 10.5 R	4	85
95% Butane 5% Ether	1.8	35 Y 6.5 R	12	86
95% Butane 5% Ether	2.0	35 Y 6 R	12	86
90% Butane 10% Ether	1.7	35 Y 10.2 R	12	87
95% Butane 5% Methyl Alcohol	3.2	35 Y 11.5 R	6	84
95% Butane 5% Methyl Alcohol	2.2	35 Y 9.3 R	12	84
90% Butane 10% Methyl Alcohol	1.4	35 Y 19 R	12	80

Table No. 1
(Continued)

	Fatty Acid %	Color	Time Hours	Oil Extracted Grams
85% Butane 15% Methyl Alcohol	1.8	35 Y 17 R	12	84
80% Butane 20% Methyl Alcohol	2.2	35 Y 14 R	12	85
95% Butane 5% Ethyl Alcohol	1.8	35 Y 12 R	12	84
90% Butane 10% Ethyl Alcohol	2.0	35 Y 14 R	12	84
85% Butane 15% Ethyl Alcohol	2.2	35 Y 17 R	12	83
80% Butane 20% Ethyl Alcohol	2.8	35 Y 22 R	12	85
Petroleum Ether	1.8	35 Y 10.5 R	12	86



RELATION BETWEEN COLOR OF OIL

AND

SOLVENT MIXTURES

(After 12 hours extraction)

DISCUSSION OF RESULTS

It is concluded from the results that the solvent passes through the meal at a rapid rate, and that complete extraction takes place in a relatively short time. From 3 to 4 hours should be time enough for complete extraction. Samples were taken from some of the samples run, and extracted on a steam bath with petroleum ether to determine if all of the oil was out of the meal. There was less than 0.05% of the total amount of oil left in the meal, and the oil remaining was the same for the samples run less than 12 hours. It is evident that after 3 or 4 hours, the probable time for complete extraction, the solvent is only removing coloring matter from the hulls.

The results obtained using butane and carbon tetrachloride was too dark for practical use. The dark color may have come from the coloring matter in the hulls, or from the attack of the carbon tetrachloride on the iron pipe. This would be especially true if there was a slight amount of water present, as the carbon tetrachloride reacts with water to form a slight amount of hydrochloric acid. The dark color may have come from the foreign matter in the apparatus; as the carbon tetrachloride mixtures were the first run.

There was not any great difference in the results obtained by using butane and methyl alcohol or ethyl alcohol. A relation plotted between the percent of alcohol used and the

color obtained shows that the color increases rapidly with the increase of amount of alcohol used. From the results obtained it is concluded that only dilute solutions of the alcohols can be used with any degree of efficiency. Another difficulty with the use of alcohols is the loss of the alcohol as solvent.

From a study of the graph, it is at once apparent that the only solvent mixtures, extracting oil of a better quality than butane alone, are the butane-diethylether mixtures containing somewhat less than 5% of ether. The best result was obtained with a solvent composed of 97.5% butane and 2.5% ether, which extracted an oil refining to a color of 35 yellow and 6 red.

From the results obtained no accurate relation or explanation can be given for the amount of free fatty acid in the crude oil. The amount of free fatty acid varies with the samples used, and the amount of moisture present.

SUMMARY

1. Extractions were run using mixtures of Butane and Carbon Tetrachloride, Methyl Alcohol, Ethyl Alcohol, Diethyl Ether.

2. The Carbon Tetrachloride mixtures did not give good results; the oil extracted was too dark for commercial use.

3. The Ethyl and Methyl Alcohol mixtures gave practically the same results, and the oil extracted was too dark for commercial use.

4. The best results obtained were from using 5% or less of Diethyl Ether, the remainder of the mixtures being Butane. The color of the oil from the extractions using $2\frac{1}{2}$% and 5% Ether was 35 yellow and 6 red.

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1. Manual of Operations for Cotton Oil Mills, Tri-States Cotton Oil Mill Superintendents Association. Ed. Service U. T. Eng. Exp. Station 124-40.

2. Reid, U. S. Pat. 1,802,533. (September 13, 1928)

3. Rules of the National Cottonseed Products Association. Published by the Association.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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