THE TECHNOLOGY AND CHEMISTRY
OF SOYBEAN OIL

BY

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P R E F A C E

Soybeans have been only recently introduced into this country. As yet they are still planted on an experimental scale, and much work must be done in order to determine the variety best suited to the soil and climate of this part of the world. Very few farmers know about it, and it is only when we can make sufficiently good use of it that the farmer will accept to plant it, and thereby come to appreciate both its nutritive and its soil - improving qualities.

This paper is mainly a study of the chemistry of Syrian soybean oil. Its technology, which is briefly discussed in the first part, gives a general idea of the methods used for its processing. The third part, dealing with catalytic hydrolysis, is a separate problem by itself. The critical study of a solvent-extraction plant, given in Appendix "B", is also a separate problem, dealing with oil technology.

I wish to thank all the personnel of the Chemistry Department, especially Professor Nicholas D. Constan, who has kindly consented to act as advisor to me on the work undertaken during this academic year.

CONTENTS

INTRODUCTION

Taxonomy and ecology

The soybean belongs to the family "Leguminosae", sub-family "Papillionaceae", and genus "Glycine" or "Soja". It is a plant indigenous to China, Manchuria, Korea, Japan, and Indo-China. That it has been known for a long time is shown by the fact that it was described in a "materia medica", written by the Chinese Emperor Shen-Nung in the year 2838 B.C., as a plant possessing no less than three hundred medicinal properties. Therefore it must have been used as a staple food for a long time before that date.[1] The Chinese and Japanese prepare a large variety of foods from the bean, which they consume in great quantities. To them milk, butter, cheese, and meat have never meant cows but soybeans.

It has been found that poorer types of soil suit the bean better than rich ground, which weakens the plant's resistance to frost. The bean requires nitrifying bacteria which, if absent from the soil, can be introduced by inoculation of the seeds prior to sowing.

Morphology[2]

The soybean (Soja max) is a summer leguminous annual. Pods are from 2.5 to 6.5 centimeters long and contain from 2 to 4 seeds. The stems, leaves, and seed pods are covered with short reddish-brown or gray hairs. The root tubercles are large and abundant.

(1) Borth, pp. 208-9   (2) Burlison, pp. 3-4

The flowers are small and inconspicuous, either white or purple, and are clustered in the axils of the leaves. The stems are branched, rather woody, and grow from 5 to 8.5 centimeters or more in height.

The oil (approximately 18%) is contained mainly in the cotelydons, which make up fully 90% of the seed and contain 20-21% oil. The germ constitutes only 2% of the seed and contains approximately 10% oil. The remaining 8% is the hull, containing only 0.6% oil.[1]

Uses of the Soybean

The soybean has been called by some "the ubiquitous bean" due to the immensity and diversity of its uses, as shown in the table on the following page.[2]

Fig.1. SOYBEANS PLANTED
AT AL-ABDEH, 1944
(courtesy of the Office
Economique de Guerre)

(2) Reference 17, p.2

(1) Goss, p.12.

		Breakfast foods	
		Diabetic foods	Breads
	Celluloid substitute	Flour	Cakes
	Stock feed	Infant foods	Pastry
	Fertilizer	Macaroni	
Meal	Human food	Crackers	
	Glue	Soy milk	
	Vegetable casein	Bean curd	
	Water paints	Soy sauce	
		Bean powder	

	Glycerin	Butter substitutes
	Enamels	Lard substitutes
	Food products	Edible oils
	Varnish	Salad oils
	Waterproofing goods	
	linoleum	
	Paints	
Oil	Soap stock	Hard soaps
	Celluloid	Soft soaps
	Rubber substitutes	
	Printing inks	
	Lighting	
	Lubrication	
	Lecithin	

Green Beans	Green vegetables Canned vegetables Salads

		Sheep	
	Stock feed	Cattle	
	Soy beans	Poultry	
	Boiled beans	Hogs	
Dried	Baked beans		Fresh
Beans	Soups	Bean curd	Dried
	Coffee substitute	Condensed milk	Smoked
	Vegetable milk	Fresh milk	Fermented
	Breakfast foods	Confections	
		Soy casein	Paper sizing
		Milk powder	Paints
			Textile dressing
	Green manure	Hay	and waterproof-
Plant	Forage	Silage	ing
	Pasture	Soilage	Plastics.

SOYBEAN   UTILIZATION

PART I

THE TECHNOLOGY OF SOYBEAN OIL

THE TECHNOLOGY OF SOYBEAN OIL

A. Methods of Processing:

Soybean oil can be obtained by three methods, all of which are widely used:

(a) Continuous pressing in expellers and screw presses.

(b) Hydraulic pressing.

(c) Solvent extraction.

(a) Expeller method:[1] This is the oldest and most widely used method of extracting soybean oil. The beans are crushed, dried to a moisture content of about 3 per cent, and passed through a steam-jacketed trough which heats the beans to about 65°C, before they reach the pressing cage or expeller. This treatment renders the product more mobile without injuring the quality of the oil or impairing the digestibility of the nutrients in the meal. The ordinary working pressure is about six tons per square inch. The oil is pumped through a rotary strainer on its way to storage, while the cake emerges in thin sheets that are broken up on a re-volving cake breaker at the discharge end.

(b) Hydraulic pressing: The beans are prepared in the same way as above, except that they must be heated to a higher temperature before being pressed. As this process is not continuous it requires much hand labor for loading and unloading the presses.
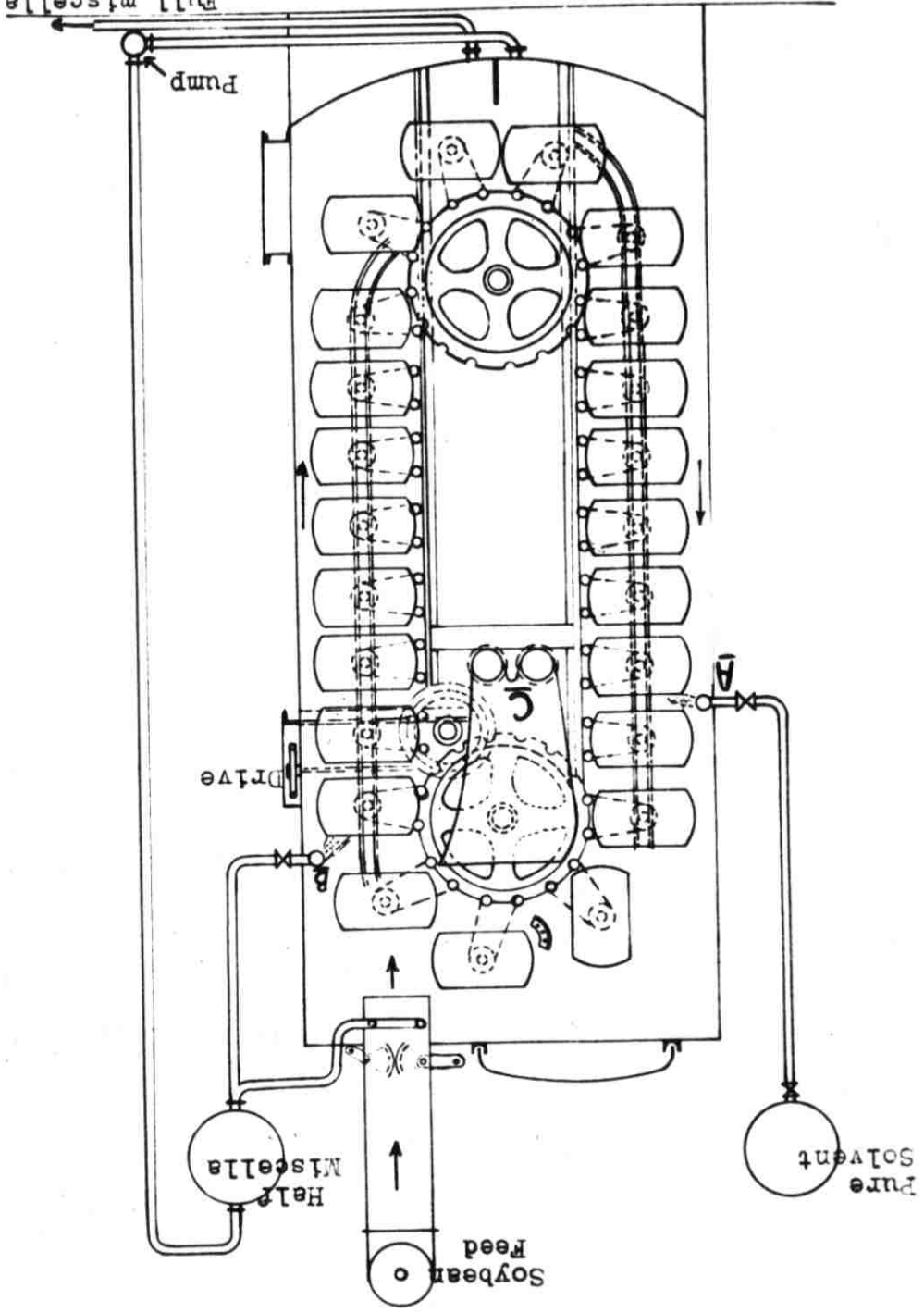
(c) Solvent-extraction: This process has been extensively used in Europe. It consists in dissolving the oil in a suitable solvent,

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(1) Burlison, p.9

Figure 2
The Bollmann or 'paternoster' system
of continuous solvent extraction

such as benzine, and later evaporating the solvent, leaving the oil behind. Soybean oil obtained by this method is claimed to possess superior bleaching qualities and shows less refining loss. Likewise the meal becomes less susceptible to rancidity and shows better adhesive properties for utilisation in the glue industry.

Solvent extraction methods operate under three different forms:

1. The independent extractor process.

2. The semicontinuous or series process.

3. The continuous process.

In the first process each extractor has its own still, condenser, and solvent tank, and is a unit by itself, independent in every way from other extractors. This form of solvent-extraction is the least complicated, and one that is claimed to prove more profitable in the long run.[1]

The semicontinuous or series process uses a battery of four to six extractors working in series, so that the hot solvent from one is used in the next, thereby reducing the amount of steam necessary to heat the otherwise cold solvent. The oil-laden solvent is then either distilled off in each extractor's individual still or else it is collected and distilled off in a common evaporator.[2]

Continuous extraction processes operate on the counter-current principle. In figure 2, the Bollman or "paternoster" system is shown.[3] A pair of conveyer chains encircle upper and lower sprocket wheels and have attached a large number of sieve-bottom baskets containing oilseed flakes, which are introduced into

(1) Ind. Eng. Ch., 18, 605, (1926).   (2) See appendix "B".
(3) Goss, p. 12.

the top basket on the descending side and are discharged into C by inverting each basket on the top, after it has gone through the complete circuit. The ascending baskets are washed at A with a spray of fresh solvent which trickles downward countercurrently. The "half miscella" collected from this side is then re-used to wash the descending chain of baskets at B. The resulting "full-miscella" is then pumped to evaporators, and the spent meal is conveyed through a series of driers.

Figure 3 shows a sectional view of the Kennedy continuous countercurrent extractor.[1] This extractor consists of a long horizontal chamber, the lower portion of which is made up of a number of semicircular sections or pockets. Each section contains a paddle wheel having four perforated blades, all turning simultaneously in a direction opposite to the movement of the miscella. The ground raw material, fed at one end of the extraction chamber, is moved slowly from section to section by the perforated paddles, and is finally drawn up a long incline by a drag conveyor; there it is thoroughly drained and delivered to a solvent-recovery vacuum drier, where the meal is freed from the last traces of solvent. For more detailed discussion the original article must be referred to.

B. The refining of Soybean oil.[2]

In refining soybean oil five steps are needed:[2]

a) Neutralization.

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(1) Ind. Eng. Ch. 36, 138, 1944.
(2) Ind. Eng. Ch. 28, 898, 1936.

b) Washing.

c) Bleaching.

d) Winterization.

e) Deodorization.

a) Neutralization: This is effected by alkali treatment in large open tanks equipped with a stirring device, heating coils, sprays for the alkaline solutions, and a jacketed settling cone.

Oil at a temperature of $26^0 - 27^0$C. is emulsified with sodium hydroxide (10^0-14^0 Bé).

Heating is carried on with moderate stirring until the "break" occurs, consisting of small clots of soap which, as heating continues, grow larger and become sufficiently fluid to coalesce if allowed to settle. Heat is shut off (the temperature being around 65^0C), and stirring stopped, in order to allow the settling of the "soap stock". This settling takes 18 to 24 hours, after which the clear oil is drawn off, leaving the soap stock as a by-product for the manufacture of distilled fatty acids.

b) Washing: is carried out by stirring with at least 8-10% of pure water and heating to boiling. The water must be free from calcium and magnesium, as their soaps may cause flavor difficulties later.

c) Bleaching: is accomplished by drying the oil and stirring it under vacuum with Fuller's earth or activated carbon. The temperature should not exceed 120^0C.

d) Winterization: is usually unnecessary, as the oil is a natural winter oil, with a freezing point of around -4^0C. Nevertheless,

P A R T   II

THE CHEMISTRY OF SYRIAN SOYBEAN OIL

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The main work for this thesis has been conducted on oil obtained from soybeans planted in the region of Hama, in the year 1939. The oil was obtained by grinding the beans and extracting the oil with benzine (S.B.P.B. grade.). The oil-bearing solvent was then distilled off over a water-bath; but as this treatment could not remove the last traces of the solvent the oil was boiled with water for some time. This resulted in an amber-colored crude oil with a characteristic "beany" taste and odor, and which amounted only to 11.5% of the beans. It was on this oil that experiments were conducted and determinations made, except when otherwise stated.

A. Physical Constants

1.   The **specific gravity** was determined on a sample of the refined oil with a Westphal balance. Its value was 0.925 at $20^{\circ}/4^{\circ}C$.

2.   **Viscosity:** This determination was conducted at $37.7^{\circ}C$ ($100^{\circ}F$) in a Redwood viscosimeter. The viscosity, expressed in seconds per 50 c.c., was 149.

3.   The **refractive index** was determined with a Zeiss Abbe refractometer on a sample of decolorized oil at $22^{\circ}C$. The value obtained was 1.474.

4.   **Color:** Crude soybean oil gave a reading of Y20 R2.4 in a standard Lovibond tintometer, with a 1 cm. cell.

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(1) Reference 12 in Bibliography.

(b) 3% kieslguhr and
2% carbon at
45°C. for 15 mts.   Y 3.3   R 0.5

(c) 3% kieslguhr
at 30-35°C. for
15 mts.   Y 6   R 1

A similar attempt was made to refine crude cotton seed oil, with the following results:

Crude Oil	Black	
Neutralized oil	Y 10	R 1
Oil decolorized with 3% kieslguhr at 80°C. for 45 mts.	Y 2.4	R 0.6

5.   <u>Volatile fatty acids</u>

a. The <u>Reichert-Meissl</u> value is a measure of the soluble fatty acids (butyric, caproic, and caprylic). Its value was 1.83.

b. The <u>Polenske number</u> is determined in conjunction with the above one, and is a measure of the insoluble fatty acids (capric and lauric). The value obtained was 0.58.

6.   <u>Soluble and insoluble fatty acids:</u>

This determination is carried out in conjunction with the saponification value. The soluble fatty acids, expressed as butyric acid, amounted to 1%, while the insoluble fatty acids (Hehner number) amounted to 92.83%.

7.   The <u>acetyl value</u> was determined by the method of Roberts and Schuette.[1] The reaction was carried out in a sealed tube in the presence of freshly distilled acetic anhydride. Two determinations gave an average of 15.5.

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(1) Ind. Eng. Chem. Analyt. Ed. <u>4</u>, 257, (1932)

C. The Chemical Composition of Syrian Soybean Oil.

1.   Separation of saturated from unsaturated acids.

This separation was effected by the lead salt ether method on a 200 grams sample, with the following results:

Saturated acids   = 14.28%   Iodine No. =   3.06

Unsaturated acids = 75.73%   Iodine No. - 158.8

The iodine number of the saturated acids indicates the presence of some unsaturated acids as well. Accordingly the correction was made as follows:

$$\frac{\text{Iodine No. of Saturated fraction}}{\text{Iodine No. of Unsaturated fraction}} \times 100 = A \quad \begin{pmatrix} \text{percentage of} \\ \text{unsaturated acids} \\ \text{in saturated fraction} \end{pmatrix}$$

$$\text{or} \quad \frac{3.06}{158.8} \times 100 = A = 1.92$$

but since the saturated acids amount to 14.28%, then

$$\frac{1.92 \times 14.28}{100} = 0.2752$$

The corrected values then become

14.28 - 0.2752 = 14.0048 %   saturated acids.

75.73 + 0.2752 = 76.0052 %   unsaturated acids.

2.   Composition of the unsaturated fraction.

This determination is possible through the simultaneous use of the iodine and thiocyanogen-iodine numbers of the oil, together with the knowledge of the percentage of unsaturated fatty acids. Since the oil is known to contain ^(at least) three unsaturated fatty acids, the percentages of which will be expressed as X for oleic acid, Y for linoleic acid, and Z for linolenic acid, the formula used for the computation of their respective amounts must have three simultaneous equations, each of which expresses, in terms of

X, Y, and Z, one of the properties of the oil. Two properties have so far been determined, namely, the iodine value and the percentage of unsaturated fatty acids. The third property is the thiocyanogen -iodine number, which expresses, in terms of iodine, the percentage of thiocyanogen absorbed by one gram of the oil. This constant is of value due to the fact that thiocyanogen adds to the double bonds of oleic acid, to one of the two double bonds of linoleic acid, and to two of the three double bonds of linolenic acid. Its value was found to be 72.1. The equation is derived as follows:

Acid	Per cent in oil	Theoretical Iodine No.	Theoretical Thiocyanogen- Iodine No.
Oleic	X	89.9	89.9
Linoleic	Y	181.1	90.5
Linolenic	Z	273.7	182.5

Therefore

$89.9X + 181.1Y + 273.7Z = 100$ (Iodine No.) $= 12950$

$89.9X + 90.5Y + 182.5Z = 100$ (Thiocyanogen-iodine No.) $= 7210$

$X + Y + Z = 76 =$ Percentage of unsaturated acids in oil.

By solving these equations the following values are obtained.

		% in oil		% in Unsaturated fraction
X	=	12.85	Oleic acid	16.96
Y	=	57.71	Linoleic acid	76.17
Z	=	5.2	Linolenic acid	6.863
		75.76		99.993

3. Composition of the saturated fraction

The composition of this fraction was determined by fractional distillation under a high vacuum of the methyl esters of the saturated acids. The saponification value of each fraction was then determined, from which its mean molecular weight, and

hence its composition, could be calculated respectively.

The methyl esters were prepared according to Baughman and Jamieson.[1] The results of the fractional distillation are as follows:

Preliminary distillation

Sample = 27.64 grs. of methyl esters of saturated acids.

Fraction	Temperature	Pressure	Weight
A	173-175°C.	Less than 0.5mm	6.2532 grs.
B	175-177	" "	3.536
C	177-180	" "	4.499
D	180-181	" "	6.947
Residue	-------	----------	4.66
			25.8751

Final Distillation

	Fraction	Temperature	Pressure	Weight
A and B	(1)	170-174	Less than 0.5mm	4.2248
C added	(2)	170-174	" "	4.7868
D added	(3)	170-174	" "	4.268
	(4)	174-179	" "	6.836
Residue added	(5)	179-189	" "	2.9986
Final residue	(6)	-------	--------	1.768
				24.8822

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(1) Jour. Am. Chem. Soc., 42, 1200, (1920).

ESTER-FRACTIONATION DATA

Fraction	Iodine No.	Saponification % value	Mean Mol.weight	Esters of Unsat.acids	Saponification value,sat.esters	Mean mol.weight Saturated esters
1	1.51	201.2	278.8	0.99%	201.4	278.6
2	1.58	208.1	270.3	1.04%	208.3	269.5
3	2.24	225.9	246.5	1.48%	226.5	247.9
4	3.00	193.5	289.9	1.59%	193.6	289.6
5	4.50	175.1	320.6	2.97%	174.8	321.3
6	4.55	159.1	352.8	2.99%	158.0	355.1

MOLECULAR WEIGHT

ESTER	
Methyl myristate	242.4
Methyl palmitate	270.45
Methyl stearate	298.5
Methyl arachidate	326.55
Methyl lignocerate	382.66

% ACID

85.9% myristic
94.82% palmitic
95.28% stearic
95.72% arachidic
96.1% lignoceric

The method of calculation is as follows:[1]

280.6 = mean molecular weight of unsaturated acids.

280.6 + 14.03 = 294.63 = mean molecular weight of the methyl esters of unsaturated acids.

56.1 = molecular weight of KOH

(56.1 ÷ 294.63) x 1000 = 190.4 saponification value of the methyl esters of unsaturated acids.

158.8 = iodine number of unsaturated acids

$$\frac{280.6}{294.63} = \frac{X}{158.8}$$

X = 151.3 = iodine number of the methyl esters of unsaturated acids.

Sample calculation for fraction (1)

1.51 = iodine number of fraction (1)

$$\frac{1.51 \times 100}{151.3} = 0.9995 = \text{percentage of unsaturated esters in fraction(1)}$$

100 - 0.99 = 99.01 = percentage of saturated esters.

0.0099 x 190.4 = 1.9 mgs. KOH required to saponify the unsaturated esters in 1 gram of fraction (1).

201.2 = Saponification value of fraction (1).

201.2 - 1.9 = 199.3 mgs. KOH required to saponify the saturated esters in 1 gram of fraction (1).

199.3 ÷ 0.9901 = 201.4 = saponification value of the saturated esters in fraction (1)

56.1 ÷ 0.2014 = 278.6 = mean molecular weight of the saturated esters.

From the mean molecular weight fraction (1) appears to contain methyl-palmitate and methyl-stearate.

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(1) Jour. Am. Chem. Soc. 42, 156, (1920).

Let A represent the molecular weight of methyl-palmitate and X, its proportion in fraction 1; and let B represent the molecular weight of methyl stearate,

Then AX + B (1-X) = mean molecular weight of the fraction,

or 270.45X + 298.5 (1-X) = 278.6

from which X = 0.7094 and 1-X = 0.2906.

Therefore, 70.94 = percentage of methyl palmitate

and 29.06 = percentage of methyl stearate.

Now 4.2248 grs = weight of fraction (1)

94.82 = percentage of palmitic acid in methyl palmitate.

95.28 = percentage of stearic acid in methyl stearate.

Therefore fraction (1) contains

4.2248 X 0.7094 = 2.99 grs. of methyl palmitate

and 1.23 grs. of methyl stearate.

corresponding to 2.84 grs. of palmitic acid

and 1.17 grs. of stearic acid.

Similar calculations were done for the other fractions with the following result:

fraction (2) ~~2.89~~ 4.466 grs. palmitic and ~~0.54~~ 0.14 grs. ~~stearic~~ myristic.

" (3) 2.97 grs. myristic and 0.7666 grs. palmitic.

" (4) 2.09 grs. palmitic and 4.42 grs. stearic.

" (5) 0.535 grs. stearic and 2.33 grs. arachidic.

" (6) 0.83 grs. arachidic and 0.868 grs. lignoceric.

Total Acids

Myristic	=	3.11	grs.
Palmitic	=	10.162	"
Stearic	=	6.125	"
Arachidic	=	3.16	"
Lignoceric	=	0.868	"

23.425 grs.

14.0048 = percentage of saturated acids in the oil.

The composition of the saturated fraction is:

Acid	Percent in oil	Percent in saturated fraction
Myristic	1.86	13.3
Palmitic	6.09	43.55
Stearic	3.64	26.03
Arachidic	1.88	13.45
Lignoceric	0.51	3.648
	13.98	99.978

To confirm the above findings the saponification value of the saturated fraction was determined, and the mean molecular weight calculated therefrom:

205.0 = saponification value of the saturated fraction.

3.06 = iodine number.

205.2 = corrected value for the saponification value.

$56.1 \div 0.2052 = 273.4$ = mean molecular weight of the saturated acids.

The mean molecular weight was also calculated from the above percentage composition. The two values were found to agree very well:

273.4 = mean molecular weight, as calculated from the saponification value.

274.4 = mean molecular weight, as calculated from the percentage composition.

0.7 = percentage error.

D. Analyses of the Extracted Beans.

The analyses hereby undertaken are not complete, but serve to give a general idea about the soybean meal. All the analyses were conducted on a meal with a moisture content of 9%.

1.   Protein Content.

The Kjeldahl method for nitrogen determination was used.[1]

Nitrogen content = 6.00 %

Protein content = 6.00 x 6.25 = 37.5 %

No further analysis of the protein was made, but it is reported to consist largely of the globulin glycinin, together with smaller quantities of albumin-like legumelin.[2]

2.   Ash Content.

The ash content amounted to 4.96 %, and was analyzed for calcium and iron. The calcium was determined by the oxalate method and the iron by Farrer's colorimetric method,[3] except that 1 % potassium permanganate was used instead of nitric acid to oxidize the iron to the ferric state.[4] The ferric thio-cyanate was then extracted with iso-amyl alcohol, and compared in a colorimeter with a standard. The results are:

Ash content   =   4.96 %

Calcium in Ash =   6.077 %

Iron in Ash   =   0.22 %

(1) A.O.A.C., p. 25   (2) Reference 14, p. 3.
(3) J. Biol. Chem. 110, 685, (1925)   (4) Reference 18, p. 441.

P A R T   III

CATALYTIC HYDROLYSIS WITH SULFONIC ACIDS

CATALYTIC HYDROLYSIS WITH SULFONIC ACIDS

Hydrolysis, as its name implies, has for end the breakdown of glycerides into their component acids and glycerin. In all such cases, water is the hydrolysing agent; without it no hydrolysis can take place, as it is necessary for the reaction.

$$(RCOO)_3 C_3 H_5 + 3H_2 O = C_3 H_5 (OH)_3 + 3 RCOOH$$

Although glycerides are hydrolysed with water alone, in the form of superheated stem, or when fats are digested with it under considerable pressure, yet the reaction can be considerably speeded up by the use of catalysts, which, in addition, allow for a great reduction in temperature. These catalysts include concentrated sulphuric and hydrochloric acids, alkalis, aromatic and aliphatic sulfonic acids, and hydrolytic enzymes.

For the following experiments it was decided to work with sulfonic acids, both aliphatic and aromatic, in order to determine their relative suitability as hydrolytic catalysts.

Twitchell's catalytic process has been known for a long time, and is based on Twitchell's discovery that a certain class of sulphonated aromatic fatty acid compounds has the property of accelerating the hydrolytic decomposition of fats.[1] Their action is due to the fact that they are soluble in water and oil, acting thereby very much like soap. At the same time they are acids which are electrolytically dissociated to a high degree, and the hydrogen ions set free cause the hydrolysis of the portion of the

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(1) Wright, p. 736.

fat dissolved.[1] It appears therefore that the bulk of the molecule acts as an emulsifying agent, while the hydrogen ions accelerate the hydrolysis.

All that is mentioned about the preparation of these acids in the available literature does not go beyond the statement that they are prepared by adding concentrated sulphuric acid to a mixture of oleic acid and an aromatic hydrocarbon, such as benzene or naphthalene.[2]

$$C_{10} H_8 + C_{18} H_{34} O_2 + H_2 SO_4 = C_{10} H_7 (SO_3) C_{18} H_{35} O_2 + H_2 O$$
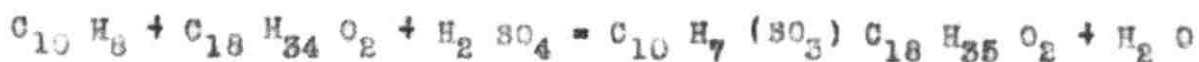
Now since the resulting compound is made up of naphthalene on the one hand and oleic acid on the other, it was planned to conduct experiments in the following manner:

a. Hydrolysis with aromatic hydrocarbons alone.

b. Hydrolysis with Twitchell's reagent.

c. Hydrolysis with the sulfonation product of oleic acid.

All these experiments were conducted on olive oil with an original acidity of 1.5 % (oleic).

a. <u>Hydrolysis with aromatic sulfonic acids.</u>

For this experiment five aromatic sulfonic acids were tried, of which four were derivatives of naphthalene, and one of benzene. To each of five 100 grs. sample was added 2 % of the sulfonic acid and 1 gram of stearic acid. About 30 c.c. of water were then added and the mixture steamed in 500 c.c. round bottom flasks, each of which had steam generated from a liter distilling flask. Steaming was carried out for 10 hours; none of the five samples showed any considerable increase in acidity, proving

(1) Jour. Am. Chem. Soc., 28, 197, (1906).
(2) Wright, p. 736.

thereby that aromatic sulfonic acids alone are not efficient under the conditions of the experiment.

b. Hydrolysis with Twitchell's reagent

The reagent was prepared by adding 6 c.c. (1/10 mole) of concentrated sulphuric acids to a mixture of 14 grs. (1/20 mole) of oleic acid and 6.5 grs. (1/20 mole) of naphthalene. The whole was then heated for about four hours on a water bath. This treatment resulted in a viscous black liquid, which was used as such for the subsequent hydrolysis.

To test the effectiveness of this preparation 2 grams of it were added to 100 grams of olive oil. To this mixture 4 grams of oleic acid were added to act as a "starter" for the hydrolysis.[1] Steaming was carried on for 34 hours:

Time	% Acidity (oleic)
3.5 hours	32.6
28 "	57.2
34 "	76.09

The next step was to determine the relative effectiveness of different percentages of this reagent. Five 100 grs. samples of oil, to each of which 4 grams of oleic acid had been previously added, were treated with different concentrations of Twitchell's reagent. The results are shown in the following table; the acidity is expressed in terms of oleic acid.

	A C I D I T Y				
Time	1 %	2 %	3 %	4 %	5 %
6 hrs.	11.4	21.8	29.4	36.6	52.8
14 "	12.0	30.0	42.0	45.0	66.0
25 "	13.28	40.45	52.2	54.05	72.2

Hydrolysis with Twitchell's reagent.

(1) Lewkowitsch, Vol. I, p. 66.

c. Hydrolysis with sulfo-stearic acid.

The following experiments were conducted to test the ali-phatic part of Twitchell's reagent, after it was shown that the aromatic part alone had no value as a hydrolysing agent.

The reagent was prepared by adding 6 c.c. of concentrated sulphuric acid to 14 grs. of oleic acid, and heating on a water bath. This time also a viscous black liquid resulted, very much like the Twitchell's reagent mentioned above.

A preliminary test was made, using 3 % of this reagent with olive oil to which 4 grams of oleic acid had been added. Steaming for 10 hours gave an oil with an acidity of 39 %.

Again a series of experiments were conducted with different concentrations of the reagent, as shown in the following table:

| | A C I D I T Y | | | | |
Time	1%	2 %	3 %	4 %	5 %
5 hrs.	8.1	12.18	23.46	23.78	41.18
14 "	10.44	21.0	-----	39.44	75.4
25 "	12.785	32.485	43.91	48.18	83.75

Hydrolysis with Sulpho-Stearic acid.

From this table it is seen that sulfo-stearic acid compares favorably with Twitchell's reagent, and can therefore replace it in case it is not available.

Industrially, 24 hours of steaming with 0.5 % to 1.5 % of Twitchell's reagent are usually enough to obtain an almost complete conversion of the glycerid to free fatty acids, but the steam used is under, while in the above experiments steaming was done under atmospheric pressure. This probably accounts for the imcomplete hydrolysis of the oil in the time used for steaming.

Figure 4. Hydrolysis curves

Red= Twitchell's reagent   Green= Sulfo-stearic acid
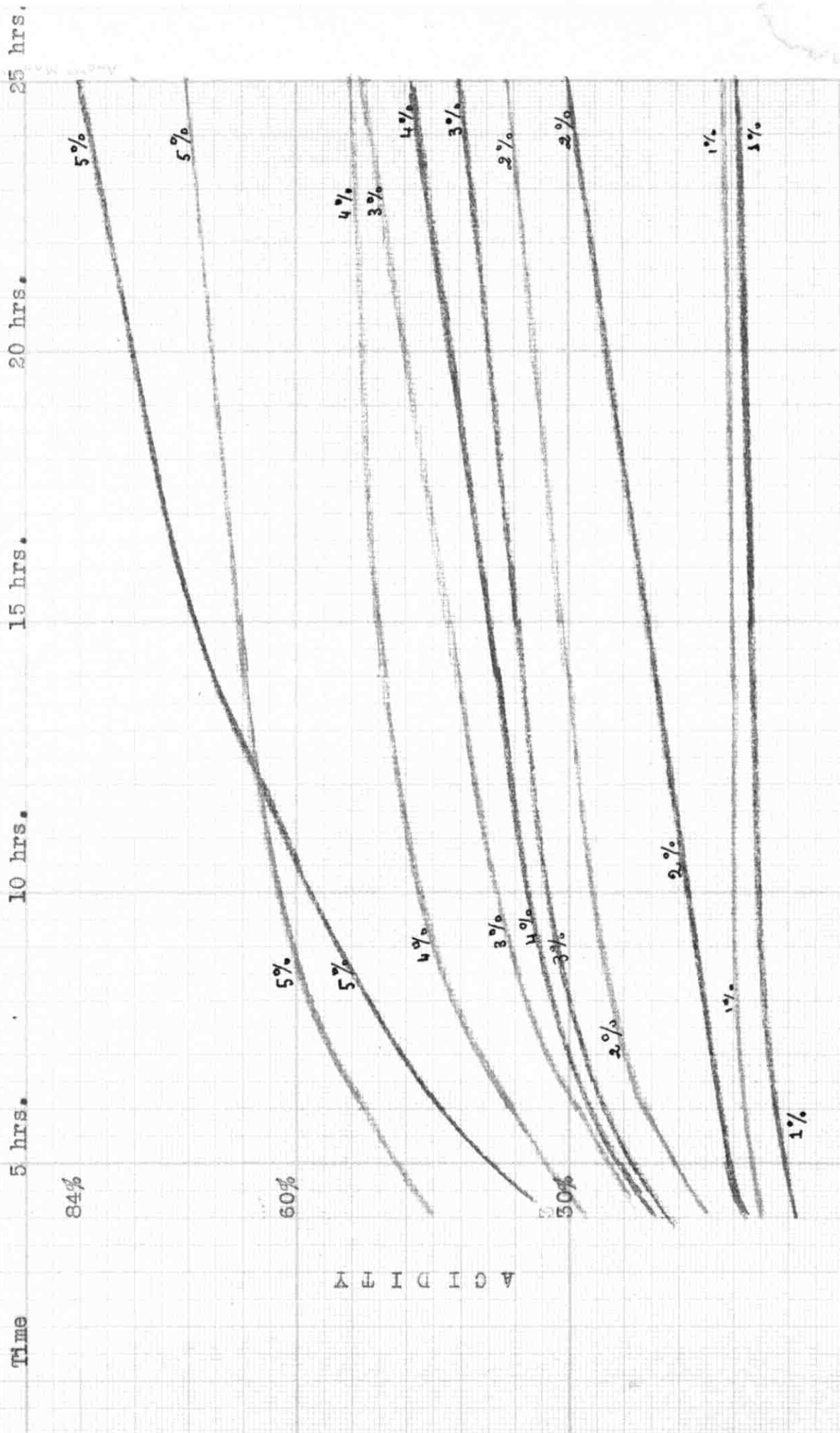
APPENDIX "A"

A COMPARATIVE TABLE OF RESULTS

COMPARATIVE TABLE OF RESULTS

Specific Gravity

0.924 (15°C.)	Shukoff
0.9242 (15°C.)	De Negri and Fabris
0.9270 (15°C.)	Morawski and Stingle
0.925 (20°C.)	Syrian oil

Refractive index

1.472-1.475 (25°C.)	Fellers
1.4745-1.4755 (40°C.)	Oettinger and Buchta
1.474 (22°C.)	Syrian oil

Saponification Value

189-194	Jamieson
190.2-195.8	Fellers
190.6	Shukoff
190.6-192.5	Lewkowisch
192.5	De Negri and Fabris
192.9	Morawski and Stingle
193.4	Syrian Oil

Iodine Value

121.3	De Negri and Fabris
122.2	Morawski and Stingle
123-132.3	Fellers
124	Shukoff
124-148	Jamieson
133.2-135.5	Bailey and Baldseifer
134	Smith
136.39	Jamieson
137.4-138.4	Low
129.5	Syrian Oil

Thiocyanogen value

79.21 (Iodine No. 136.39)	Jamieson
72.1 (Iodine No. 129.5)	Syrian Oil

Hehner Value

93.0-94.3	Fellers
95.8-96	Oettinger and Buchta
96.1	Low
92.83	Syrian Oil

Reichert-Meissl Number

4.3-5.2	Fellers
0.45-0.56	Oettinger and Buchta
1.83	Syrian Oil

Unsaponifiable matter

0.39-0.59	Oettinger and Buchta
0.3-1.2	Jamieson
1.16	Low
1.29	Syrian Oil

COMPOSITION

Myristic	Palmitic	Stearic	Arachidic	Lignoceric	Oleic	Linoleic	Linolenic	Observer
	6.5	4.4	0.7	0.1	33.7	52.0	2.3	1
	11.5				35.9	55.8	3.8	2
	14.5				35.9	56.9	2.9	3
	7.0	5.5	0.3		26.1	54.7	5.8	4
	9.0	3.9	0.6		30.6	55.8	2.1	5
	9.5	2.4	0.9		28.9	50.7	6.5	6
0.5		0.3			26.5	56.6	2.4	7
	14.1				35.9	35.9	3.5	8
	6.6	4.4	0.7		33.6	51.3	2.5	9
1.7	5.8	3.2	1.8	0.5	12.6	57.7	5.2	10

Observers:

1. Bangham and Jemieson
2. Kimura
3. Heiduschka and Eger
4. Griffiths
5. Grun and West
6. Jamieson
7. Smith
8. Hilditch
9. Wellis and Burroughs
10. Syrian oil

A P P E N D I X "B"
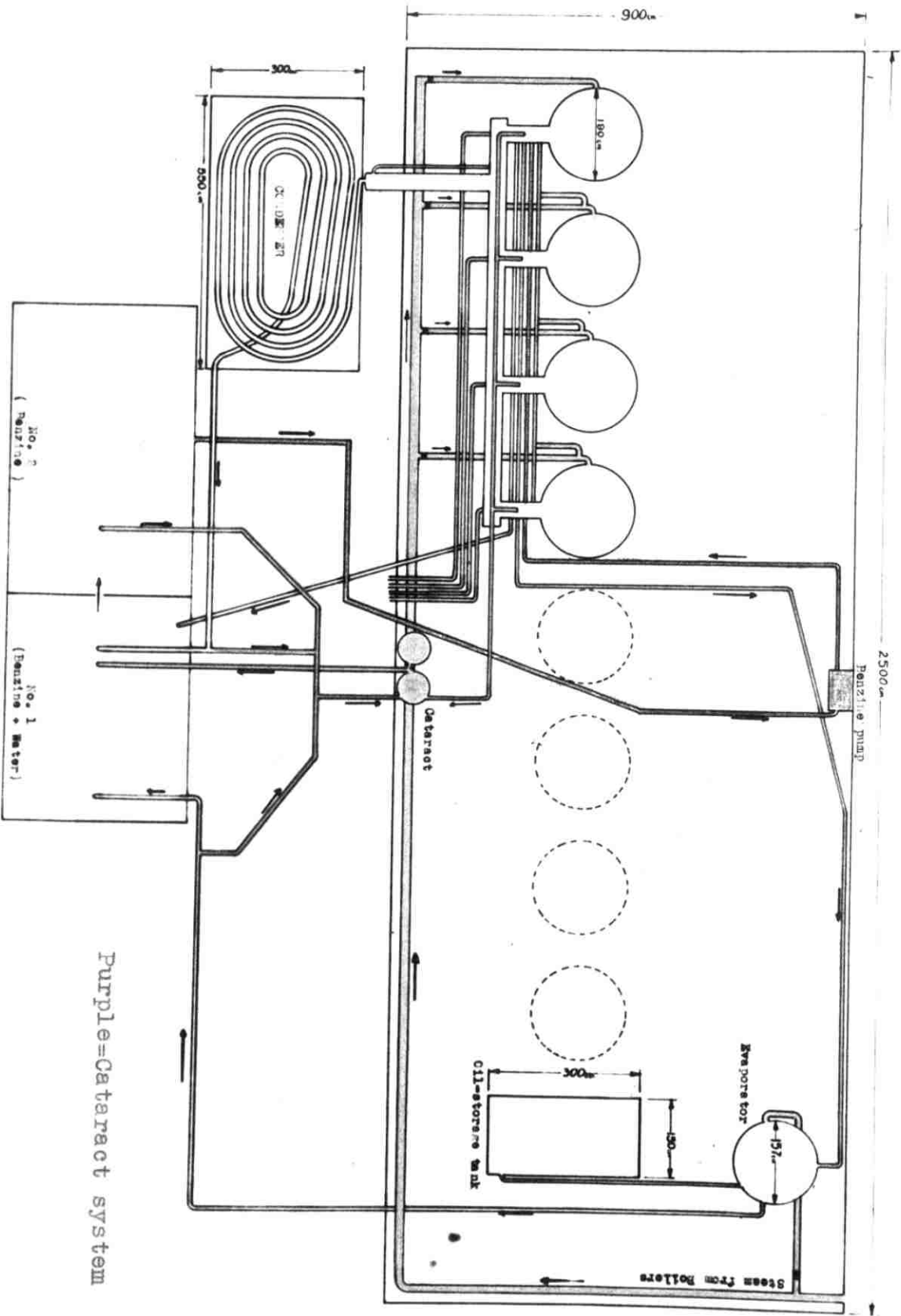
A CRITICAL STUDY OF A SOLVENT EXTRACTION PLANT
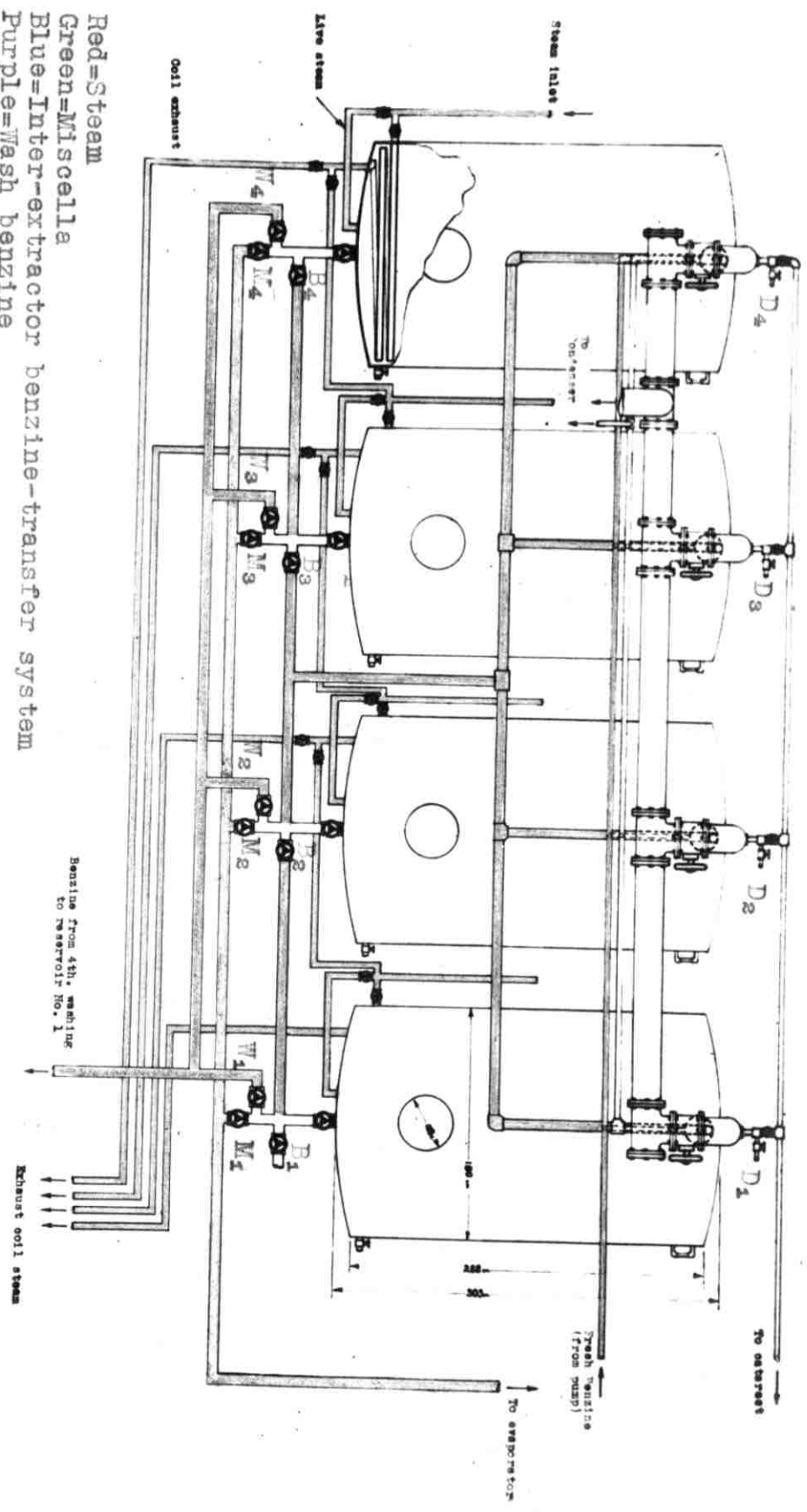
Figure 5

Red=Steam
Green=Miscella
Blue=Inter-extractor benzine-transfer system
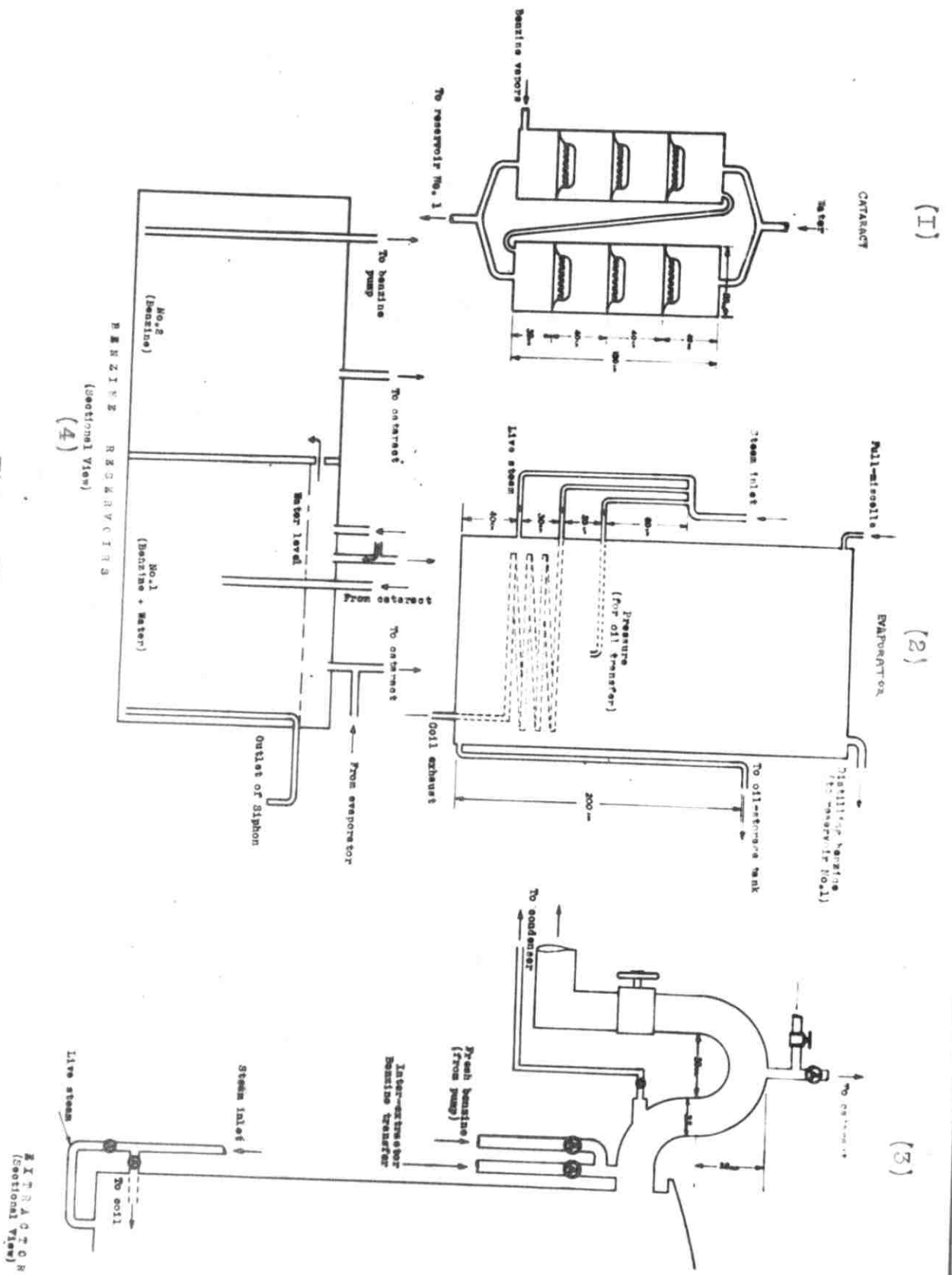Purple=Wash benzine

Figure 6

Purple=Cataract system

Figure 7(Details)

(1) CATARACT

(2) EVAPORATOR

(3) EXTRACTOR (Sectional View)

(4) BENZINE RESERVOIRS (Sectional View)

A CRITICAL STUDY OF A SOLVENT-EXTRACTION PLANT

The present study is undertaken as a practical problem in oil technology, and is the result of a study made on an actual plant for solvent-extraction of olive-kernel oil.

Before any comments can be made it is necessary first to give an account of the way the factory is actually being operated.

A. Operation of the Plant.

The factory works on the semicontinuous principle of solvent-extraction. It consists of a battery of four extractors with a common condenser and a common evaporator, each extractor having a capacity of four tons. Figure 5 shows the elevation of the factory, with the lower piping system shown diagramatically.

The factory starts by filling extractor No. 1 with olive kernels, and fresh benzine is pumped into it (fig. 7, detail 3) from reservoir No. 2 (fig. 6, and fig. 7, detail 4) until the extractor is filled with benzine. Coil steam is admitted 10 minutes after pumping starts. Distillation begins after 5 hours, and is continued for 30 minutes, after which coil steam is shut off, and the oil-laden benzine left to drain for about half an hour. This oil-laden benzine is then transferred into extractor No. 2, which was being filled meanwhile, through the inter-extractor benzine-transfer system. This is accomplished by pumping fresh benzine into No. 1 over the drained miscella, while valve B_2 (fig.5) is left open. The pressure of the oncoming fresh benzine forces the miscella through the pipe that delivers it to No. 2 (fig.7, detail 3). It is clear that this treatment not only results in the transfer of benzine from one extractor to another, but also

serves as a second washing to the contents of No. 1. The same
operation is conducted in extractor No. 2, and when the time comes
for its contents to be washed, fresh benzine is admitted to No. 1,
and then transferred to No. 2 through valve B_2 and thence to No. 3
through valve B_3. This treatment gives No.1 its third washing and
No. 2 its second. When No. 3 is finished its miscella is trans-
ferred into No. 4 by the same procedure, which gives No. 1 its
fourth washing, No. 2, its third, and No. 3, its second. The
excess benzine in No. 1 is then drawn into reservoir No. 1 through
valve W_1. Live steam is then admitted into No. 1 in order to free
the extracted kernels from the last traces of solvent. When this
is accomplished, it can be judged from the absence of benzine
vapors (fig. 5, valve D_1). Extractor No. 1 is now finished; it
is emptied through the manhole at its lower end, and then imme-
diately recharged.

When No. 4 has been washed once the miscella is transferred
into the evaporator through valve M_4. This is accomplished, again,
by pumping fresh benzine into No. 2, thence/ washing it a third
into No. 3,
thereby washing it a fourth time,
time, and thence into No. 4,/from which the miscella goes to the
evaporator, since the level of solvent in the extractor is higher
than the delivery pipe to the evaporator.

The factory now has started, and the operation is accord-
ingly modified. Into No. 1, which is now filled with a fresh
charge, fresh benzine is pumped only for 30 to 45 minutes, coil
steam being admitted 10 minutes after the pumping is started.
The quantity of benzine thus admitted is only enough to cover
the coils and touch the lowermost part of the kernels. It there-
fore takes only about 2 hours for distillation to begin. At this
moment the extractor is filled with hot benzine from the fourth

washing of No. 2. The excess benzine in No. 2 is then drained
to reservoir No. 1 through valve W_2, and is then steamed, emptied
and recharged.

In No. 1 distillation is allowed to continue for 30 to 45
minutes, after which the miscella is left to settle for about half
an hour. Cold benzine is then pumped over this in order to force
the miscella into the evaporator through valve M_1. The first three
washings now all go to the evaporator, while the fourth goes to
the extractor next in the sequence of operation.

No. 2 is filled the same way as No. 1 and receives its
full of benzine largely from the fourth washing of No. 3, which
is then drained, steamed, emptied, and recharged. It is then
filled with benzine from the fourth washing of No. 4. When the
time comes for No. 4 to be filled, it receives the bulk of its
benzine from No. 1, which by now has reached its fourth washing
and is ready to be emptied.

The cataract is a pair of scrubbing towers for the benzine
vapors. Pipes coming from the condenser, evaporator, extractors,
and the two benzine reservoirs all ramify at the bottom of the
first tower (fig. 6, and fig. 7, detail 1). These towers consist
each of a set of three curved plates hollowed in the middle and
surmounted by indented caps. The water trickles from above and
meets the ascending benzine vapors, which it scrubbs down. If
any vapors escape such treatment in the first tower, they will
get it in the second. The scrubbing water then goes into reser-
voir No. 1, where the water sinks to the bottom and is emptied by
siphon action (fig. 7, detail 4), while the benzine passes into
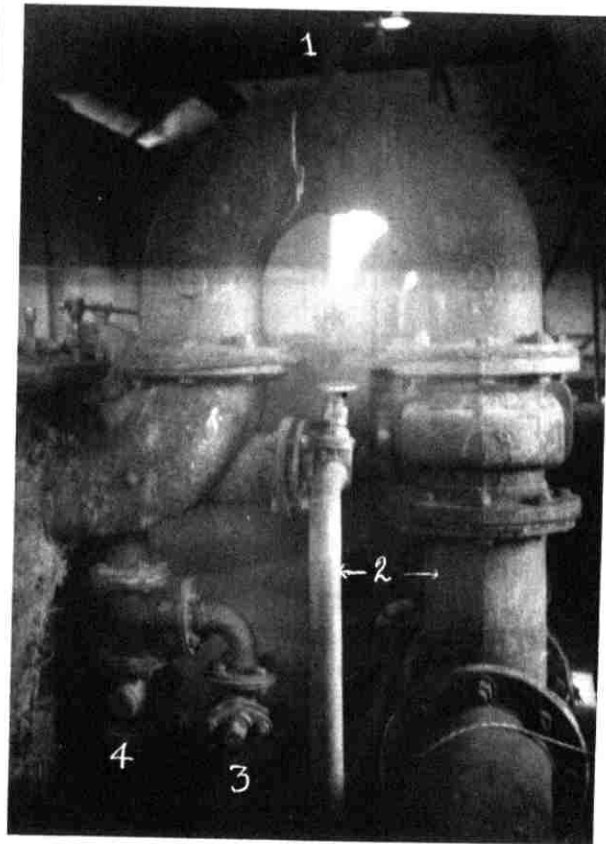the second reservoir, from which it becomes available to the
extractors.

Fig.8. Upper pipes and valves
1. To cataract; 2.to condenser; 3.fresh solvent; 4.inter-extractor benzine pipe
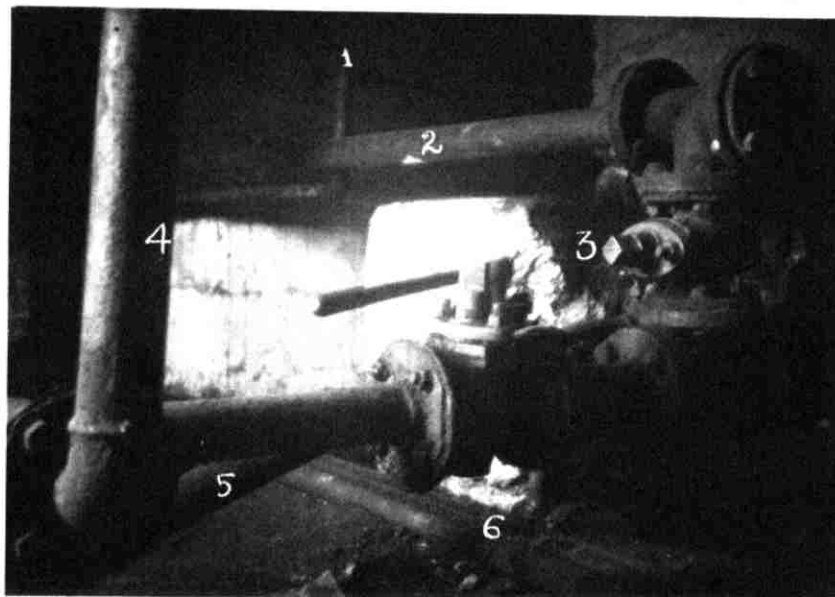(see fig.7,detail 3)

Fig.9. Lower pipes and valves

1.inter-extractor steam pipe
2.inter-extractor benzine-transfer pipe
3.inter-extractor benzine-transfer valve

4.miscella transfer to evaporator
5.wash benzine,to reservoir 1
6.coil-steam exhaust

B. **Comments.**

1.   The operation of each extractor takes more time than it should. From three to four hours are allowed for each washing, either because the extractor is waiting to wash another extractor or because the evaporator is working on the miscella from another extractor. The total time for each extractor lies between 14 to 16 hours, a considerable part of which is spent in waiting, as mentioned above. During these "waiting hours" the extractor is, for all practical purposes, out of operation. The amount of time thus lost impairs considerably the efficiency of the plant.

2.   The inter-extractor benzine-transfer system dilutes unnecessarily the solution of oil in benzine. True, this operation delivers moderately hot solvent to the next extractor, thereby reducing the amount of steam necessary for heating, but this saving is counterbalanced by the greater amount of steam necessary to evaporate all this quantity of solvent when it reaches the evaporator.

3.   The hot benzine that distills from the evaporator is conducted directly to the reservoirs. Instead, it could be used in one of the extractors, since it is moderately hot, thereby effecting a real saving in steam.

4.   One evaporator is not sufficient. This does not mean that a larger one should be used, but that three or four should be present. A large evaporator would reduce labor and cost of installation, but the oil will be exposed to heat for a longer period. In addition, intensive steaming and heating will be necessary when it comes to removing the last traces of solvent. This would certainly result in an inferior grade of oil.[1]

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(1) Ind. Eng. Ch. 18, 605, (1926).

C. Suggestions for Improvement.

1.   It was pointed out above that a lot of time is lost in
waiting, partly due to the presence of one evaporator. To remedy
this would necessitate the installation of an evaporator for each
extractor, which is certainly a costly operation. This difficulty
can be overcome, however, in a much more efficient and economical
way.

         The filter at the bottom of each extractor, just below the
manhole, serves to prevent contact between the steam coils and the
olive-kernels. But it is too low. By raising it to about 1/4 or
1/3 of the extractor will automatically provide the extractor with
a still, making it utterly unnecessary to use a separate evaporator.
In addition, this new still needs much less attention than the
more complicated evaporator, and the operations necessary for the
transfer of the miscella can therefore be advantageously dispensed
with. Of course, this suggestion means that the capacity of the
extractor is reduced from 4 to about 3 tons, but the time saved
will more than make up for it.

2.   The inter-extractor benzine-transfer system could be consider-
ably improved if the condenser and solvent-storage tanks were
higher than the extractors. But as this would mean costly repairs,
and since the benzine reservoirs and cataract system are working
very efficiently, the next best thing would be to establish connec-
tions between the upper parts of the extractors, or to connect
between the condenser and the benzine pump, so that hot benzine
could be supplied to another extractor, without the necessity of
introducing cold benzine on top of the first extractor.

3.   As can be seen from figure 6, the plant has more than four

extractors. Operating these would result in a greater yield of
oil without any great additional expense.

The diagrams accompanying this discussion show that the
plant has a lot of complications. Contrary to many types of
machinery, solvent-extraction resolves itself almost to the crude
formula - the fewer the refinements the better the extractor. In
other words, the laboratory Soxhlet on a commercial scale is
almost the ideal.[1]

It was in accordance with this practical formula that the
comments and suggestions for improvement were made, wherever their
mention or application was thought to bring about a nearer approach
to a more efficient procedure of extraction.
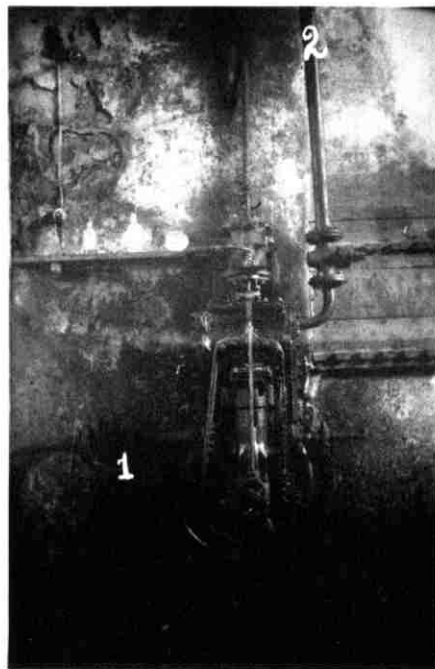
Fig.10 The benzine
pump
1. Solvent intake from reservoir No.2
2. Solvent delivery to extractors

(1) Ind. Eng. Ch. 18, 605, 1926.

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