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TECHNOLOGY & ANALYSIS
OF
IRAQIAN SESAME OIL

By

FADHIL A. TA'I

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PREFACE.....

This paper includes that part of the work which has been carried out on vegetable oils during the academic year 1943 - 1944 in this institution . It contains the technology and the analysis of Iraquian and Lebanese sesame oil and several experiments on the hydrogenation of these samples, with their results .

The work on oil in general and on sesame oil in particular is not the whole work which I have done during the year . I was asked by the Iraquian Government to study the commercial analysis of beverages i.e the determination of aldehydes furfural and alcohol content as well as the analysis of tobacco and other insecticides . Thus I have analysed different samples of beverages, soap, tobacco one sample of pyrethrum and two samples of sesame seed were sent by the Iraquian Government for analysis; other samples such as soap, coal and beverages were brought to me by Prof. Constan .

Since the regulation of this institution does not permit general analysis and graduating without giving a thesis on a particular subject I decided at the beginning of the year, after I had taken the advice of Prof. Constan, to study the technology and the analysis of Iraquian sesame oil and to write a thesis about this subject .

Thanks to Prof. N. D. Constan who helped a lot in my work and by whose aid I was able to visit several factories and plants and work in an oil plant to get the technique and be familiar with the machinery and the process of producing oils on a large scale . As a matter of fact I was allowed to treat a sample of 15 tons of cotton seed oil by a refinery process which is different from that used in the plant; the process was successful and more economical. At the end of May I received some samples of tobacco from the government and I have analysed them in

(b)

the tobacco laboratory as well as our laboratories . I have spent one week in the tobacco laboratory and probably I will spend more time to get the technique of the drying process of the tobacco leave, because the drying of the samples which I have received and analyzed is very bad and needs a lot of improvement .

The chemistry of tobacco is rather simple, on the other hand, the technology and the drying process of the tobacco leaves requires a good study . I was not able to study the drying process due to the two factors; firstly the date of receiving the tobacco samples, is very late and secondly the season of cultivation and drying the leaves is usually performed at the end of July .

I hope I will be able to study the drying process at its proper time in the Regie farms as well as our laboratories, so as to improve the way of drying which is used in Iraq .

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PART "I"

INTRODUCTION ON VEGETABLE OILS

Fats and oils are esters of fatty acids and glycerol . Fats are rich in saturated fatty acid; while oils are rich in unsaturated fatty acids . In each oil and fat a number of different fatty acids occur, sometimes as many as ten, while six or more as a rule; this would make the study of the composition of an oil difficult enough. The complication of mixed glycerides such as glycerol-distearate monopalmitate raises the difficulty still further ; it is therefore, not surprising that there are many oils and fats whose composition is still unsettled .

The most important vegetable oils are cotton seed, lin seed, olive, corn, peanut, rape, coconut, sesame and castor . The method of extraction is similar for all . The fruit or seed after cleaning is crushed and first cold-pressed for the highest grade, then pressed warm for technical grades ; the crushed mass may be extracted further by solvents .

Most of the important oil-bearing plants are grown in this part of the world; olive trees are grown extensively in Syria and the Lebanon . Flax, cotton and sesame are widely distributed in Iraq ; the third one is consumed in greater amount . The extraction of vegetable oils, in Iraq, is very primitive and it has no existence on industrial scale . Most of the oil-bearing seeds are shipped to Europe as such, while the vegetable oils of the same seeds are imported from outside . I obtained a paper , or a list from the Ministry of Economics in Iraq, which shows the export and import of the oil-bearing seeds and vegetable oils respectively during the pre-war years . This list is put as it is on the next page . Because of the previous mentioned condition the concerned departments in Iraq have taken part in the establishment of a new plant for the extraction of vegetable oils, using the "French Expeller" . So it was ^{deemed} worthwhile to study the technology of oils in general and that of the sesame oil in particular .

<u>IMPORTS</u>	<u>Stand. Unit.</u>	<u>1942</u>	<u>1941</u>	<u>1940</u>	<u>1939</u>
Olive oil	liter	12,755	19,734	64,074	53,571
Caster oil	liter	50,994	19,631	1,426	5,302
Sesame oil)	liter	1049745	1,355,640	1,742,420	867,192
Cotton oil)					

(Continued)

<u>IMPORTS</u>	<u>Stand. Unit</u>	<u>1938</u>	<u>1937</u>	<u>1936</u>	<u>1935</u>
Olive Oil	liter	73,107	52,523	56,479	36,587
Caster Oil)	liter	888,704	981,980	526,252	639,662
Sesame Oil)..					
Cotton oil)	liter				

EXPORTS	Stand. Unit	1942	1941	1940	1939
Cotton seed	Ton.	----	1,419	2,594	3,510
Sesame seed	Ton.	----	1,135	625	631
Flax seed	Ton.	1,542	1,135	3,405	2,841
Caster seed	Ton.	----	----	----	----
Fruit seeds	Ton.	----	----	----	----

Continued

EXPORTS	Stand. Unit	1938	1937	1936	1935
Cotton seed	Ton.	7,945	4,698	2,033	326
Sesame seed	Ton.	1,126	189	150	694
Flax seed	Ton.	3,719	2,313	1,102	744
Caster seed	Ton.	2	----	----	4
Fruit seeds	Ton.	5	4	15	5

METHODS OF EXTRACTION

The methods used in the extraction of fats and oils from the natural sources depend on the nature of raw seeds or tissues and the purpose for which the oil or fat is used . Two methods are used extensively namely expression and solvent extraction. Other methods are also used such as boiling the oleaginous products with water, and recently a third main method for the recovery of vegetable oils has been proposed by J.W. Bekman . This method taking advantage of a special kind of bacteria .

Recovery of vegetable oils by expression :

This method involves the extraction of oils from oil-bearing seeds by destroying the cell walls by applying high pressures . It is extensively used in the case of producing oils for edible purposes . The process is rather a simple one, and the percentage of oil obtained by this method is always lower than that obtained by the solvent extraction . The production of oil by this method is usually accomplished in five steps :

- 1-. The seed must be clean and free from any foreign substances . This is usually done by sifting the raw materials in an inclined revolving cylinder, or sieving machines covered with woven wires whose meshes may be varied according to the size of the seed and its nature . In some cases the seed may contain small pieces of iron or nails, so it is necessary to pass the seeds over magnetic separator which retain the iron .
- 2-. The clean seeds are crushed , if they are big, and ground ; in the case of nuts the shells are removed and the rest is converted into a pulpy mass or meal by passing through a hopper over rollers . The distance between the rollers may be varied according to the size of the seeds so as to have the seeds leaving the bottom roller have the desired fineness .

- 3-. The ground seeds are heated to a temperature which facilitates the flow of oil and coagulates the albumins, .
- 4-. The product is subjected to a low pressure to prepare it for the hydrolic press . The use of this step is to reduce the volume of the mass in order not to occupy a large space in the hydraulic press .
- 5-. After the mass has been packed in bags and reduced in volume it is subjected to the pressure of the hydraulic press . For the preparation of edible oils, the mass is expressed in hydraulic presses in the cold. Such oils are called "Salad oils, cold-pressed oils or cold-drawn oils". Under these conditions the oil contain the least amount of coloring matters . It is obvious that only part of the oil is obtained by the cold-expression method . The other part is obtained by heating the mass to an elevated temperature previous to expression . The quality of this oil suffers and it can hardly be used for edible purposes . The hot-expression method is largely used for the production of oils which are used for technical purposes such as linseed, cotton seed oils, where the quantity of the oil is more important than its quality .

It is necessary to regulate the pressure , so that the liberated oil may have time to flow out, a pressure that increases in proportion as the resistance of the mass increases , and that maintain itself as the volume of the mass decreases as a result of the escaping oil .

There are many kinds of presses, the most important are the Anglo-American the Marseille and the Cage press . In all these presses, the pressure ranges between 250 and 300 atm.

The crude oil is conducted by channel to the tank, and the cake remains in the press . The cake is either-used as a cattle food, or it is further extracted by volatile solvents, for it contains from 5 to 10 percent oil .

Extraction of oils by means of volatile solvents :-

Most of the oils used for technical purposes are obtained by this method; moreover, the cakes obtained by the expression method contain a considerable amount of oils and fats which may, more or less, completely extracted by the solvent method . This method is more efficient if we are after the quantity and not the quality of the oil .

More than 20 solvents have been prepared for the commercial extraction of fats and oils . Among these may be mentioned the specially prepared solvents such as gasoline, benzine, benzene, and various chlorinated products such as di and tri-chloroethane . Carbon disulphide was extensively used, but its use is decreasing because of its bad physiological effects on the workers, and because of some sulphur which remains in the cake if the carbon disulphide is not well-purified . For the extraction of oils intended for edible purposes in which it is essential that all traces of the solvent be removed, the gasoline (benzine) is used because of its low boiling point and practically all distills within a range of 200°C.

Here are some of the characteristics of the good solvent :

- a- Non inflammable to avoid danger during hot extraction .
- b- Low boiling point .
- c- Low latent heat of vaporization
- d- Low specific heat
- e- Low density, because the amount of the solvent used in the extraction depends upon the volume . If the solvent is inflammable, the density of which should be more than that of water, since this property offers certain advantages in the storage of volatile and inflammable solvents, because the vapor can be readily prevented from coming in contact with an open flame .
- f- Cheapness , or low price .
- g- It has no corrosive property on the metal of the containers.

- h- It should be stable and non-toxic
- i- Good extraction power for oil.
- j- Low extraction power for coloring materials .
- k- It must not have any residue on evaporation .

It is worthwhile to mention some solvents which are used for the extraction of fats and oils, and satisfy most of the above-mentioned conditions . No single solvent is known to satisfy the whole conditions .

- 1-. Carbon disulphide CS_2 :- Although it is inflammable, it may be stored safely because of its specific gravity being more than that of water . It is cheap, stable, volatile, good extraction power, low boiling point, low specific heat, and non-corrosive .
 - 2-. Petroleum ether :- It is volatile, inflammable, cheap, non-corrosive, stable It has low specific heat, good extraction power for oil, and low extraction power for coloring materials .
 - 3-. Carbon tetrachloride CCl_4 :- It is a very good solvent , it satisfies all the conditions except it is expensive and corrosive .
 - 4-. Dichloro-ethylene :- It is a good solvent, but it corrodes the iron and copper containers.
 - 5-. Benzene :- It satisfies the whole conditions except it is inflammable and not very cheap .
- $C_2H_2Cl_2$, C_2HCl_3 and C_2Cl_4 may be used inspite of their narcotics and some corrosive property . Tetrachloroethane , and pentachloroethane cannot be used, because they decompose when they are in contact with metal giving rise to HCl . On the other hand, the addition of small amount of oil of turpentine absorbs the HCl, and yet these solvents are not used now .

A list showing some oil and fat solvents :

Name	Formula	Molec.Wt.	Sp. Gra.	B.P.	Sp.Ht.
Benzene	C_6H_6	78.06	.878 at 20°C.	80.2°C.	.436 cal.
Carbon disulphide	CS_2	76.13	1.2927 at 0°C.	46 °C.	.157 "
Carbon tetrachbride	CCl_4	153.8	1.583 at 25°C.	76.7°C.	.21 "
Chloroform	$CHCl_3$	119.38	1.526 at 0°C.	61.2°C.	(.33) "
Dichloroethylene	$C_2H_2Cl_2$	98.95	1.257 at 20°C.	83.4°C.	.305 "
Petroleum ether	---		.75 at 15°C.	(110-120)	.5 "
Benzine	---		.68 - .72 at 15°C.	(70-90)	---
Acetone	C_3H_6O	58.1	.796 at 15°C.	57 °C.	.47 "

The seed for extraction by volatile solvent is prepared in a similar manner as for pressing, except that the seed is not reduced to a fine meal, which prevent the free percolation of the solvent through the whole mass . As it is mentioned before, the oil obtained by this method is not used for edible purposes, the preliminary cleaning of the seed is not carried out as carefully as is done in the case of seed destined for the production of edible oils . The preliminary warming of the seed is not necessary since the moisture does not prevent thorough extraction .

Many types of extractors have been proposed, nearly all of these designs are built upon the same principle of the soxhlet apparatus . It should be remembered that the process is not strictly continuous . In many cases agitation of the mass is not necessary and yet there are many designs which

are equipt with agitators . With any type of extractors, all connections should be kept gas tight to avoid any danger .

The removal of the last traces of the solvent from the mass is rather difficult, because the meal has a tendency to retain the solvent . The use of free steam to drive the last traces of solvent from the cake may spoil the second and make it to lose its value as a cattle food . The usual way for the removal of the solvent from the cake is carried out by spreading the mass in thin layers while it is turned over from time to time by mechanical means .

Recovery of vegetable oils by a bacterial process :

It has been found , that in some cases we need rather a very high pressure to obtain the oil from its original cells, specially when the cells are very small . In the case of coconut the cells are so small that even by passing the dried nut through a grinding mill only a limited amount of oil is freed, therefore various high-temperature treatments of the nut are necessary before the cell walls become brittle enough to crush under the high pressure .

The bacterial process provides a good mean by which the cell walls are decomposed without raising the temperature . Since the cell walls are composed of cellulose, ^{sugar and} other carbohydrates like sugar ; so they may be decomposed by inorganic chemicals as well as organic in the form of enzymes or similar substances that might attack the cell walls . It is difficult to find an inorganic substance which is able to decompose two of the constituents of the cell walls and yet keep the residue capable of being used as a cattle food . On the other hand, the organic substances in the form of bacteria has been applied successfully, and the process is rather simple .

The bacteria, extensively used in this field is "bacillus dolbruekia", which is readily obtained from brewers malt . This bacteria attack the sugar

changing them into lactic acid, and produce in so doing an enzyme which vigorously attacks proteins changing them into water-soluble amino acids .

The process may be summarized as follows :

A culture of this organism made from brewer's malt is mixed with disintegrated nuts together with a weight amount of ground limestone and sufficient water to make a mush, and the whole mixture is placed in an incubator at the proper temperature with the exclusion of air . Growth of the bacteria takes place, and CO_2 evolves as a result of the action of lactic acid produced on limestone; and the oil appears on the surface . After six days the evolution of CO_2 ceases and the oil can be recovered by filtration .

The quality of the oil obtained by this method depends , of course, on the quality of the nuts used . The percentage of the acidity is increased by a small amount after fermentation takes place .

The color of the oil produced by this process is superior to the average color of oils obtained by the usual pressure methods since the latter method involves high temperature .

The residue obtained after the removal of oil is composed of Ca-lactate, amino-acids and bacteria .

Ca-lactate is produced as a result of the action of lactic acid produced on limestone . The neutralization of lactic acid is necessary, since the accumulation of the free acid retards the action of the bacteria . The final feed contains in the dry condition, amino-acids, Ca-lactate the cellulose pulp and the bacteria and about 5% of oil . This residue as a cattle feed is far better than the other residue obtained by the other methods, since the former contains Ca-lactate and bacteria which are valuable food for the young cattle .

The author has recommended this process by claiming the following advantages:

- 1-. The process is simple and in many respects automatic in its control, so it does not need high technical knowledge of operations .
- 2-. A method of high promise as to yield in quantity and quality of both oil and cake .
- 3-. A method requiring low capital investment per ton of capacity, low power cost , low maintainance, and low labor charges .

Recovery of oils and fats by rendering (boiling out with water)

This method consists of boiling the nuts of the adipose tissues in closed vessels with water to cause bursting off the fat-containing cells . The oil floats on the surface and is collected in tanks for further treatment of refinery. The method is more successful in the case of animal fats; as a matter of fact, some authors recommend the method for the extraction of tallow from the "rought fat", claiming that it is the simplest and the most effective method of obtaining tallow for technical purposes .

In some cases, a solution of sodium chloride or dilute sulphuric acid is used instead of water. The percentage of the free fatty acids does not increase when the tissues of the nuts are bouild out with dil. H_2SO_4 , since the acid is diluted enough, so as to be incapable of effecting hydrolysis .

The method is employed in the extraction of bone fat as well as tallow .

Refining and Bleaching of Oils

Oils and fats obtained by the above mentioned methods contain in general some foreign materials which give rise to an undesirable color, flavour and taste. In some cases, where the seeds employed are fresh the oil is practically neutral and can be used as such .

The majority of oils and fats, especially those obtained at an elevated temperature, contain as a rule mucilaginous matters, coloring matters and other impurities ; moreover the existence ~~of free fatty~~ of free fatty acids in a considerable amount is not seldom, a matter which renders the oils unfit for edible purposes . So the refinery of oils and fats, for both edible as well as technical purposes is of great importance .

Different devices have been used for the purification and bleaching of oils and fats. The best method is selected only by experiments and technique, and the method is more or less specific, i.e. for each oil or each group of oils, there is a method which can be employed successfully in the case of that oil or that group of oils, and which is of no value when applied to other oils . The purification of linseed oil is carried out by keeping the oil for a long time in tanks at a temperature below zero ; the mucilaginous matters being insoluble and settle at the bottom of the tank .

The removal of coloring matters from edible oils is accomplished by filtering the oil or fat over charcoal or over natural absorbant earths, such as fuller's earth . It is impossible to state general rules ; for each individual fat and oil must be studied separately as to the most suitable condition of the powdered earth, as to the temperature and the length of treatment .

Chemicals have been applied in the purification of oils and fats, since the object of this process is the removal of the coloring matters and other impurities without effecting the glycerides, hence any non-poisonous chemical may be used . Thus conc. Sodium hydroxide, conc. sulfuric acid, chlorine and oxygen (the latter two are produced by the action of mineral acids on MnO_2 or $K_2Cr_2O_7$, and by bleaching powder ; the reaction takes place inside the crude oil).

It should be remembered that with the exception of alkalies or alkaline earths no other chemicals should be used for the removal of the coloring matters and the free fatty acids from the edible oils . The amount of the chemical used should be adjusted carefully by experimenting on small samples , otherwise many difficulties may arise .

The most important method in which chemicals are used is the so-called "caustic soda process". The practice in the method varies considerably in the hand of different operators and in general, a small amount of caustic soda solution enough to neutralize the free fatty acids is added to the oil ; this will combine with the fatty acids to form soap . On precipitating, the soap drags most of the coloring matters leaving the oil lighter in color and free from fatty acids . In most cases the soap drags with it some neutral oil besides the coloring matters and impurities and settle to the bottom of the refining kettle; this mass is called soap stock, and it is either used for manufacturing laundry soap or it is centrifuged to obtain the neutral oil . The refining kettle is equipped with a mechanical agitator . It is necessary to agitate the oil on adding the caustic soda solution, so as to accomplish a thorough mixing of the lye with the oil . The concentration of the caustic soda solution varies from 16° to 24° Bé; the lower the grade of oil, the stronger is the solution as a rule . An initial temperature of 20° - 25° C should be maintained during the addition of the solution . Necessary cooling is carried out by passing cold water through the steam coils of the kettle . Few minutes after the addition of the caustic soda solution the appearance of the oil changes . The oil becomes more fluid and turns to a brownish or black after 20 minutes . When a sample shows a bright appearance with black flocules it is a sign

that the oil has reached the stage of a "breaking" . At this stage no more caustic soda solution should be added . The oil is heated by passing steam through the steam coils to 50°C., and agitation should be decreased . The time required for the whole process is not more than 50 minutes . The soap and the other impurities settle to the bottom and the clean oil is transferred to the tank .

The oil, after being treated, is washed with water to remove all the traces of the caustic soda . Then a small amount of fuller's earth ranges between 2 to 4 percent and from .5 - 1 percent of the charcoal, is added to the oil and pump it through a filter press .

The above mentioned treatment of oils is only used when the crude oil contains a high percentage of free fatty acids , otherwise bleaching and deodorization are performed only . In bleaching vegetable oils from 2 to 3 percent of fuller's earth is added to the oil . Low grade oils require sometimes about 6 percent of the fuller's earth and 1 percent of decolorizing carbon . It is necessary to drive the moisture from the oil before adding the fuller's earth ; this is accomplished either by heating the oils under reduced pressure or by adding from .25 to 1 percent of plaster of Paris .

I have treated two samples of crude oils, one being castor oil and the other is sesame oil, with 2 percent of fuller's earth and .5 percent of decolorizing carbon . The direction of the process is as follows :

To the crude oil which contains a considerable amount of coloring and mucilaginous matters, 2 percent of fuller's earth and .5 percent of decolorizing carbon is added . The oil was heated to a temperature ranges between 60° - 70° C with continuous agitation for 45 minutes , then the sample was cooled rapidly by stream of water passing around the outer wall of the container . In order to

hasten settling of the foreign matters and the bleaching reagents, the sample was centrifuged for 30 minutes and decanted . The oil, after decantation, still contains small particles of decolorizing carbon . This was removed by filtering the oil . The color of the samples was very pale yellow, and the acidity was determined . The percentage acidity of sesame oil was 1.13 and that of the castor oil was 2.18 . The high acidity in the case of castor oil was not due to the treatment , but the seed which was expressed is old and not properly kept .

In some cases, oils prepared for edible purposes contain some odoriferous constituents which give rise to an undesirable odor in oils . Thus deodorizing is necessary . In order to make the oils free from the odoriferous constituents a special device should be used . This includes heating of the oil in a tank , provided with steam coils by superheated steam . The temperature to which the oil is heated varies with respect to the nature of the oil . The pressure over the oil should be reduced to few inches . It is desirable to keep air from entering the tank, to avoid rancidity of the residue oil .

Another method of deodorizing may be accomplished by passing superheated steam through perforated pipes in the bottom of the tank, which contains the oil at a temperature of 110°C. After steam is passed through the oil the temperature rises to several degrees centigrades . The oil is subjected to the current of steam for six or eight hours . The steam is turned off and water is passed through the coils to cool the oil to a temperature at which it can be stored safely .

CLASSIFICATION OF OILS & FATS

Formerly, the classification of fats and oils was built upon their physical properties . Thus all fatty liquids were called "oils" while fatty solids were called "fats" . However, an oil may be liquid in one country and solid in another according to differences in temperature . Names have been put wrongly to oils before their chemical nature was understood e.g. "sperm oil" is nothing but a liquid wax and "Japan wax" is a solid fat . Another classification of oils was based on the plant families ; this classification was also abandoned because of the existence of oils relating to the same or similar families of ^{plants} oils and yet they are different . Later on a classification based on the chemical properties of oils and fats was proposed . This classification being the most consistent one . Thus the term "oil" is applied to those whose glycerides are rich in unsaturated fatty acids and are liquid at 20°C and the term "fat" is used to designate those whose glycerides are rich in saturated fatty acids and are solid at 20°C. For this purpose, the iodine value is the most reliable factor in the classification of oils and fats, and includes the other classification as well . The iodine value is a good measure for the subdivisions of fats and oils and classification may be stated as follows :

I Liquid fats "Oils"

A - Vegetable oils

1. Drying oils
2. Semi-drying oils
3. Non-drying oils

B - Animal oils

1. Marine animal oils
2. Terrestrial animal oils.

II A - Vegetable solid fats

B - Animal fats

1. Drying fats
2. Semi drying fats
3. Non drying fats .

Sesame oil falls under class I division A subdivision 2, i.e. it is an oil of vegetable origin and of the semi drying oils since its iodine value ranges between 104 and 113 .

- Properties of oils and fats -

The most ^{important} constituents of fats and oils are the neutral glycerides, that is glycerides which are formed as a result of the combination of the three hydroxyl group of the glycerol with three molecules of mono-basic fatty acids . The three molecules of fatty acids which combine with glycerol may be the same or different . When the three molecules of fatty acids combining with the glycerol are the same, the glycerides result are called "simple glycerides" . However, if different molecules of fatty acids combine with the same molecules of glycerol, the resulting glycerides are called "mixed glycerides" . It should be remembered that one hydroxyl group of the glycerol two or the three may combine with one molecule , two molecules or three molecules of mono- basic fatty acids respectively, giving rise to mono-glyceride, diglyceride and triglyceride.

Mixed triglycerides are the most common glycerides occurring in natural oils and fats . The occurrence of simple glycerides is very rare . Natural oils and fats contain besides the glycerides many other constituents such as free fatty acids, coloring matters, cholesterol, phytosterols, chlorophyll, protein, and some cellulose . Thus natural oils must not be looked upon as chemical individuals, but rather as natural species, whose composition is subjected to limited variation .

No definite freezing point can be obtained for natural oils and fats, because on cooling, glycerides of the saturated fatty acids may crystallize out from the oils .

Fats and oils, in their liquid state penetrate into the pores of dry substances; if a drop of oil is left on a dry paper a translucent drop is formed which cannot be removed by washing with water .

Pure glycerides are colorless, odorless and tasteless ; on the other hand, natural oils have characteristics color, odor and taste arise from the existence of minute amounts of the non-glyceridic constituents .

Natural oils and fats are practically insoluble in water, although traces of oils and fats are dissolved on shaking with great amount of water . On the other hand, oils dissolve small amount of water and form a homogenous solution . Practically all traces of water can be removed on heating the oil to 100°C .

Oils and fats dissolve sparingly in cold alcohol, while hot alcohol dissolves a considerable quantity of oils . Castor oil being exceptional since it is completely soluble in cold alcohol . The solubility increases as the percentage of free fatty acids in natural oils and fats increases .

In general, oils and fats are soluble in ether and in all the previous mentioned solvents . Castor oil deviates from this rule, because it contains some glycerides which are not soluble in carbon disulphide and petroleum ether .

Oils can be heated to 250°C without any chemical change, provided contact with air is avoided . Some oils become paler on heating , due to the destruction of the coloring matters . Other oils form condensation products on being heated to a temperature ranges between 250°C and 300°C . Thus linseed oil gelatinizes on heating, and castor oil changes into a solid mass . This chemical change is suspected to be due to polimerization . If natural oils and fats are subjected to prolong heating, destruction takes place giving rise to different compounds such as volatile acids, hydrocarbon of the ethane, ethylene and aromatic series .

These hydrocarbons are closely related to the oil from which they are formed e.g. if an optically active oil is subjected to destructive distillation the hydrocarbon formed exhibits optical activity .

Effect of air, light and moisture on natural oils and fats will be discussed under the heading "Rancidity", since this effect is of great importance from the chemical and commercial points of view .

R A N C I D I T Y

Some organic compounds are subject to deterioration on exposure to air, light and moisture . The most important of the degenerative changes which oils and fats may undergo are those which lead to a condition known as rancidity . An oil or fat may be described as "rancid" when it contains enough oxidation products which give rise to a bad taste and odor . The most oxidation products found in rancid oils or fats are fatty acids of low molecular weight, hydroxy acids, lactones, ketones and aldehydes . In those natural oils or fats containing appreciable amount of lower fatty acids, hydrolysis induced by lipases derived from tissues or micro-organisms is, in itself, sufficient to produce rancidity for oxidation may accompany such hydrolysis .

It has been stated by many investigators that spontaneous atmospheric oxidation, non-enzymatic in character is the most common cause of rancidity .

The cause of rancidity was thought to be due in the first instance to hydrolysis which is accelerated in the case of unrefined oils and fats by enzymes . This explanation of rancidity rendered invalid, since the new methods of refinery operate at high temperature which destroy, practically all the enzymes.

The true cause of rancidity is not yet properly understood , but the change

is certainly accompanied by oxydation, both of the glycerol and fatty acids of the glycerides, with the production of free fatty acids of low molecular weight. However, the amount of free fatty acids bears no relation to the degree of rancidity . An oil may contain more than 10% percent free fatty acids and yet it is not rancid . As a matter of fact, I have analysed a sample of a lebanese olive oil, the percentage acidity of which was 12.4 and yet the sample shows no sign of rancidity at all .

Difficulties arise in the explanation of rancidity may be estimated by the varieties of the descriptive terms given to the odor of the rancid oil , e.i. pungent, tallowy, oily, ester-like, and perfume of ketonic rancidity.

Most of the investigators agree that the ethylenic linkages are the points of attack by oxygen . It is stated as well, that the amount of unsaturation in fatty acid of the glycerides increases the susceptibility of oxydation . Lanolic acid is oxidized more quickly than olive acid, and linolenic acid is still more rapidly . The molecular structure of the fatty acids determines the ease with which a fat or an oil is oxidized . In polyethemoid acids the relative positions of the double bonds with respect to each other in the chain are critical factors. For instance pseudo-oleostearic acid (conjugated) is more susceptible to oxidation than its isomer linoleic acid (non-conjugated); this property being against the well-known concept that compounds contain conjugated double bonds are more stable than their isomers which contain non-conjugated double bonds . Absorption spectra indicate the existence of traces of fatty acids with conjugated double bonds in natural oils and fats . These minute amounts of more reactive fatty acids may readily produce peroxides which initiate the oxidation .

The effect of unsaturated fatty acids on the susceptibility of fats and

oils to rancidity may be studied through synthetic glycerides . This may be accomplished by keeping a saturated glyceride in contact with air, moisture and light for a long time . A test for rancidity in these glycerides is performed, if they get rancid the whole explanation given for rancidity and which depends on the unsaturated fatty acids is invalid; on the other hand, if these glycerides do not get rancid the explanation of rancidity from this point of view is valid . I had no time to carry out these experiments since the development of rancidity may take several years .

The problem of rancidity has been studied by great number of chemists yet none of them could provide a definite mechanism for that phenomenon . The statement of Lewkowitzsch shows the stage at which the explanation of rancidity has reached . "In the present state of our knowledge we are still unable to discuss rancid oils and fats by chemical means, and we must rely on the taste and smell as being the best means of ascertaining whether a fat is rancid or not". This statement seems very strange for the first time, but the number of experiments which have been carried out by different chemists justifies it .

The influence of light, moisture and air on natural oils and fats has been studied both separately and conjointly . The action of light alone, air and moisture being excluded, has not been studied thoroughly due to some experimental errors . However, it is well known that oils and fats acquire a paler color under the influence of insolation, some oils even become colorless . As a matter of fact, the application of insolation on oils has been applied on an industrial scale in many cases, as the light destroys the minute chromogenetic substances which give rise to the color of the oil . On the other hand, all the experiments which have been carried out on oils proved that light alone is incapable of producing a change which would lead ultimately to rancidity .

Moreover, air alone, moisture and light being excluded, has no action on oils and fats, which therefore will remain unchanged for practically an indefinite length of time . However, some fatty acids were produced due to the presence of small amount of moisture which is very difficult to be excluded completely, and yet the existence of these fatty acids did not lead to rancidity .

The above mentioned experiments were carried out by Lewkowitseh on samples of linseed oil kept for thirteen years in bulk and another sample of cocoa butter kept in a sealed bottle for ten years .

The action of moisture alone on fats and oils is a remarkable one since water is necessary for hydrolysis, i.e. one molecule of water is required to hydrolyse one esteric linkage. Water does not attack glycerides at ordinary temperature nor even at 150°C, but at 200°C it does leading to the formation of the corresponding fatty acids and glycerol . If some catalyst is present, water attacks the glycerides at a very low temperature. The catalyst may be strong acid or base , and in the presence of enzymes or ferments which are usually found in the oil-bearing seeds, water attacks the glycerides and causes hydrolysis at room temperature . As a matter of fact, the enzymes found in castor seed are able to hydrolyse the oil, more or less, completely in a short time .

The remarkable effect of enzymes and ferments on oils and fats in the presence of water had lead many authors to consider the enzymes and ferments have far-reaching effect on the production of rancidity in oils and fats, and all of them have agreed that the first stage in rancidity is due to the accelerating power of the enzymes on the hydrolysis of oils and fats in the presence of water.

The experiments which have been performed by Lewkowitseh and his co-workers concerning rancidity are inefficient . As I have mentioned before, Lewkowitseh tried to study the phenomenon of rancidity by taking each factor separately, i.e.

..air, light and moisture . (It is obvious that light alone could not oxidize the ethylenic linkages of the fatty acids in oils hence it could not lead to rancidity. The effect of moisture alone may hydrolyze oils slowly if it is kept in contact with them for a long time and it is incapable of producing rancidity . However, oxygen alone may oxidize natural oils and produces some oxidation products, but this process of oxidation is very slow but it may be catalyzed by other factors. Hence the study of rancidity in natural oils and fats may be accomplished more satisfactorily than that of Lewkowitseh, by taking each two factors separately Since there are these factors which cause rancidity we have only these experiments to be done if we are to take each two factors separately namely :

- 1-. Effect of Moisture and light , air being excluded.
- 2-. Effect of Moisture and air, light being excluded.
- 3-. Effect of Light, and air, moisture being excluded .

The procedure of each of the three above mentioned experiments was carried out on the sesame oil as follows :

- 1-. Take a 250 cc.flask with a long narrow neck, (see figure 1), connect it to a vacuum pump by means of a thick rubber tubing .

Reduce the pressure inside the flask so as to be able to fill it with convenient amount of oil. Add few drops of water to the oil and connect it again to an efficient vacuum pump. Evacuate the flask from air as much as possible , this may be done easier by heating the flask to about 40°C by means of a water bath to expell any dissolved air . Close the flask tightly by means of a screw clamp and seal it at the thinned point A. Hence the oil inside the flask is subjected to moisture and light only, and it is practically free from air .

- 2-. Fill an ordinary brown bottle incompletely with oil, close the mouth of which

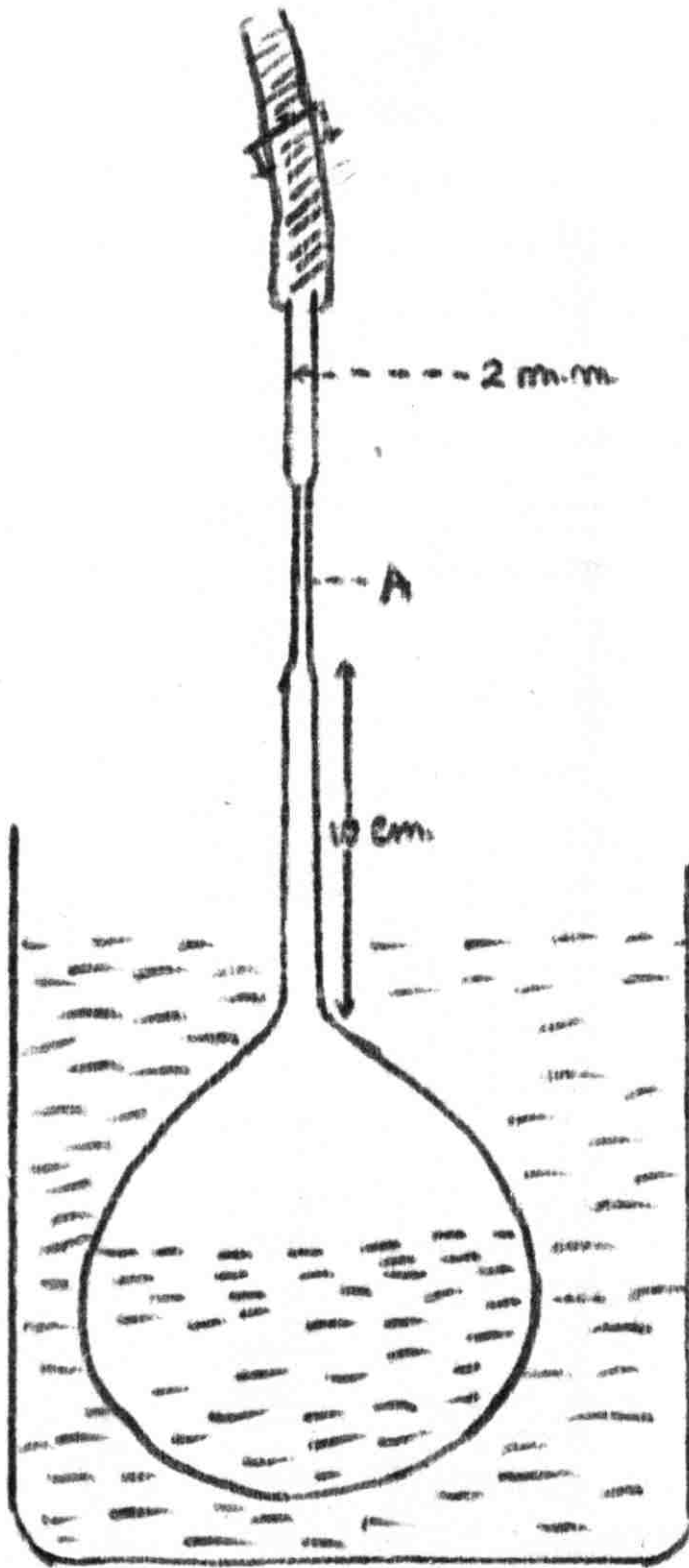


Figure No. 1

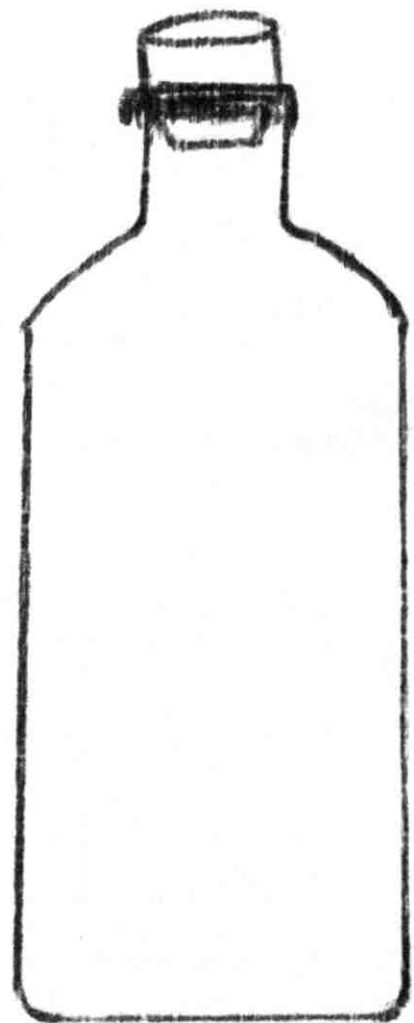


Figure No.2

by means of a Gooch crucible to keep the oil in contact with air . Paint the flask with black paint as well as the crucible . Fill the latter with black cloths and keep it in a dark place . The oil is exposed to air and moisture alone, while light is practically excluded . (See figure 2).

3-. Heat a sample of oil in a flask to 110°C under reduced pressure to expell any traces of moisture . Fill the flask with a series of U - tubes filled with CaCl, BaO or NaOH, and keep it in a dry place . An alternative procedure may be accomplished by keeping the flask containing the oil which is free from moisture in a dessicator .

Those samples should be kept under the above mentioned conditions at least two years . The result of the analysis of the experimented sesame oil is listed below .

a. Acidity	1.23	e. Acetyl value	11.42
b. Sap. equiv	188.37	f. Ref. Index	1.4749 at 27°C.
c. I-value	106.71	g. Unsap. matters	1.14
d. R. M. value	1.12		

Analysis for each sample is necessary . In experiment No.1, some of the oil should be exposed to air for few days and again to test whether the presence of free fatty acids makes the oil more susceptible to rancidity or not .

An explanation for rancidity :

Since rancid oils and fats contain different oxidation products such as fatty acids of low molecular weight, oxy and hydroxy acids, aldehydes, ketones and lactones, which give rise to the undesirable odors and tastes, hence oxygen is a necessary factor in the development of rancidity . Atmospheric oxygen effects the oxidation of the ethylemic linkage but very slowly . On the other hand, this

process may be accelerated by light, especially the green and orange light . Moreover oxidation of the free unsaturated fatty acids takes place more rapidly than it is the case with glycerides.

The study of antioxidants in oils and fats has shown that when a sample of oil is kept from light and subject to oxygen remain free from rancidity even though it may have a peroxide value equal or even higher than that of oil which has not been protected from light and become rancid . If a protected sample has a high peroxide value and is exposed to light it gets rancid within a short time . Hence we may conclude that the oxygen forms the peroxide at the ethylenic linkages this process may be accelerated by light of different waves without breaking the double bond . On the other hand light is necessary for the breakage of the peroxides, thus the formation of different oxidation products is accomplished . The effect of water being the production of free fatty acids, which are more liable to oxidation than the glycerides especially if the free fatty acids contain ethylenic linkages .

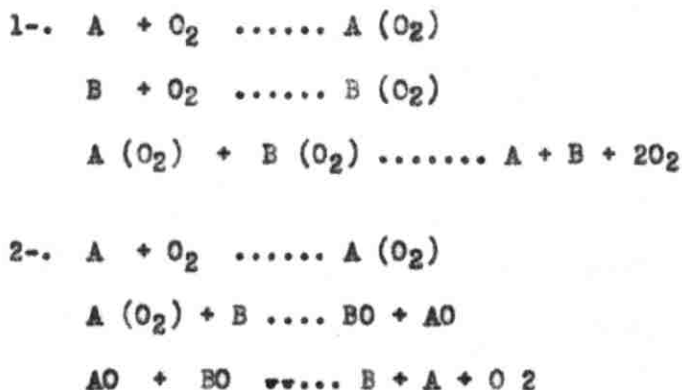
Antioxidants for fats and oils :

It has been observed that some natural oils and fats resist rancidity more than other oils or fats having similar or higher number of double bonds. Later on it has been explained by a number of investigators that these oils and fats contain compounds, non-glyceridic in nature, which make the oil more resistant to oxidation and rancidity . These antioxidant compounds are called "Inhibitors". Tocopherol, sesamol, gasypoly-gallic acid act as stabilizers in oils and fats against rancidity .

The real work on antioxidants began with the study by Mouré and Dufraisse of the inhibiting effect of hydroquinone upon the oxidation of a crolein and of

benzoldhyde . It was previously known that substances having a phenolic group ^{against the action of oxygen} protected a number of autooxidizable compounds, not necessarily phenolic in ^{character} compounds character, which under suitable conditions are easily oxidizable, act as anti-oxidants .

The authors explained the mechanism of the antioxidants as follows :



where A and B represent an activated molecule and antioxidant molecule respectively .

It is obvious that the explanation of this mechanism is built upon the assumption of the antioxidant molecules being capable of combining with and releasing the oxygen atoms or molecules easily .

The authors offered a good method for the determination of the anti-oxidant power in different antioxidant compounds, and since the method is not mentioned in available books it is worthwhile to put it here .

Untreated samples and samples to which 0.1 percent of the antioxidant has been added were stored at a temperature of 42°C for ten days and the peroxide content was then determined as follows :

50 c.cs of a solution consisting of two parts of acetic acid and one part of chloroform by volume was added to a weight sample of fat or oil . To this mixture 1 c.c. of conc. KI solution was added . The mixture was kept in the dark for ten minutes, and 50 c.cs of distilled water were added . The liberated

iodine was titrated against .002 N sod. thiosulphate . The number of c.cs of .002 N Sod. thiosulphate per gram of fat is equivalent to the number of millimoles of peroxide per Kg of fat . The weight of the sample of fat used must be adjusted by the peroxide content . In no case should the iodine liberated be equivalent to more than 15 c.cs of .002 N $\text{Na}_2\text{S}_2\text{O}_3$ from .25 to .75 grams of sample is usually a convenient and satisfactory quantity to use .

The results obtained have been expressed in terms of the relative amounts of peroxide formed in a sample of fat or oil and in another sample of the same fat or oil to which an antioxidant had been added . This ratio has been designated by the author as the protective factor and is obtained as follows :

$$\text{P.F.} = \frac{\text{millimoles of peroxide per Kg. of untreated sample}}{\text{millimoles of peroxide per Kg. of treated sample.}}$$

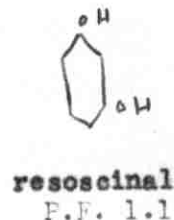
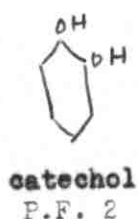
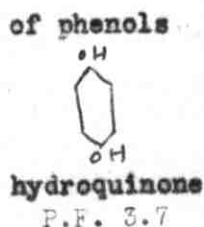
It is obvious that the protective factor of one indicates no protective action, and a factor of more than one indicates a protective power, this power increases as the protective factor increases . A factor of less than one indicates that the compound is an accelerator for oxidation .

The protective factors of some compounds :

I-. Natural pigments .

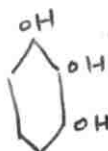
Name	Millimoles of peroxide per Kg. of untreated sample	Millimoles of peroxide per Kg. of treated sample	P.F.
Carotien	25	27.1	less than one
Hycopene	25	24.9	1
Quercetin	25	13.2	1.9

II. P.F. of phenols

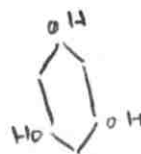




hydroxyhydroquinone
P.F. = 3.6

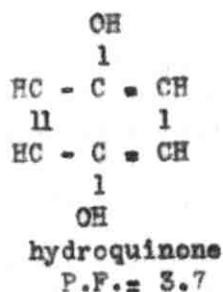
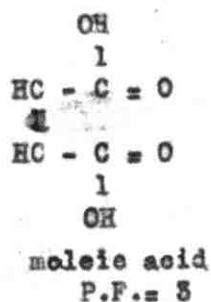


Pyrogallol
P.F. = 3.6



Phloroglucinol
P.F. = 1

It has been found that some of the unsaturated acids, which have a similar structure to hydroquinone act as antioxidants. The similarity between the structure of maleic acid, which is proved to be a good antioxidant, and that of the hydroquinone is illustrated by the following structural formulas :



It has been proved that the oil may have a high peroxide value and yet does not show any sign of rancidity. Oils which have been protected from light by an opaque black paper, or with green paper transmitting of wave-length ranges between 4900 to 5000 A°, remain unrancid even if their peroxide value is equal or higher than that of unprotected oil which has become rancid. If a protected sample of oil, still free from rancidity but having a peroxide value higher than that of an unprotected rancid oil is exposed to light it will acquire a rancid taste and odor after 52 days. On the other hand, if the original sample is not exposed to light it will remain unrancid though it has a high peroxide value.

Examination of oils by physical means :

The physical properties of oils differ from each other and in many cases this difference offers a valuable information in the identification of samples of oils and in the detection of some adulterants.

The most important constants used in the identification of oils, are specific gravity, refractive index, viscosity, melting and solidifying points, rotatory power, solubility, microscopic examination, calorimetric examination and specific heat .

The selection of the physical constant for the identification of oils and the detection of adulterants depends largely on the oil itself as well as its market .

Different devices are used for this purpose, the kind of equipment is dependent on the physical properties of the oils and fats to be examined .

Examination of oils and fats by chemical means :-

The examination of oils and fats by strictly chemical means is not available in our present state of knowledge since it involves the separation of the glyceride and the fatty acids . The separation of the different glycerides present in one individual oil or fat is the most difficult subject in oils . As a matter of fact, the inability in the determination of the constituents of an oil or fat is due to our lack of knowledge in the separation of the glycerides and not in the separation of fatty acids . If we are able to separate the glycerides efficiently a qualitative test or a semi-quantitative test for fatty acids is sufficient to determine the constituents of an oil or fat .

The introduction of different "values" or numbers in the technical analysis of oils and fats satisfies, more or less, completely our need . These "values" were classified by Lewkowitzsch into two classes :

A-. Characteristics

B-. Variables .

"Characteristics" comprise those "values" which depend entirely on the specific nature of an oil or fat .

"Variables" comprise those "values" which are dependent on the quality of an oil or fat hence it varies with the state of purity, rancidity, age etc. of the sample .

The "characteristics" are :

- 1-. Saponification value.
- 2-. Iodine value
- 3-. Riechert-Meissel value .

The "variables" are :

- 1-. Acid value
- 2-. Amount of glycerol, expressed in per cent.
- 3-. Diglycerides and Monoglycerides.
- 4-. Amount of unsaponifiable matters expressed in percent .

The acetyl value stands midway between the "characteristics" and "variables" and in some cases must be considered with the first, while in other cases it is with the second .

A-. Characteristics

- 1-. Saponification value (or Kottstorfer value)

The saponification value indicates the number of milligrams of potassium hydroxide required for complete saponification of one gram of an oil or a fat ; or it represents the amount of potassium hydroxide expressed in tenths percent to neutralize the total fatty acids in one gram of a fat or an oil .

Since the glycerides of each are different from that of others, although some oils contain glycerides in common yet their composition is different, hence the saponification value is constant to some extent for each individual oil .

The presence of monoglycerides, diglycerides and free fatty acids in small amounts does not seriously effect the value . It is obvious that this value increases as the molecular weight of the fatty acids of the glycerides decreases . The saponification value of an oil changes seriously when the oil becomes rancid, since rancid oil contains fatty acids of low molecular weight.

Different methods have been proposed for the determination of this value in a sample of oils and fats . The most general method is that which involves a reflexing of a known amount of oil or fat with standard alcoholic potash for one hour and titrating the excess alkali with standard hydrochloric acid . The use of alcohol as a solvent for the potassium hydroxide used is necessary ,since aqueous solution leads to hydrolysis of the soap formed during saponification.

2-. Iodine value (Bromine value)

This value indicates the percentage of iodine chloride or (bromine) absorbed by a fat or oil, expressed in terms of iodine or (Bromine).

This value is used for the measurement of the proportion of unsaturated fatty acids whether in their combining state in the glyceride or in their free state . The amount of the halogen absorbed is dependent on the number of unsaturated linkages in the oil . Evidently, each ethylenic linkage requires one halogen molecule or two halogen atoms . The absorption of chlorine by unsaturated glycerides is very slow because of its gaseous state it cannot be used for this purpose . Bromine and iodochloride being the most extensively used solutions for the the determination of bromine and iodine value respectively . Bromine in its pure dry state cannot be used since the reaction is very violent and evolution of hydrobromic acid results . Different proposals were offered to fulfil the condition . Thus the bromine value of an oil or fat can be obtained by dissolving a convenient amount of that oil or fat in carbon tetrachloride, then a

known volume of the standard bromine solution is added . When the reaction is complete, the excess bromine is titrated against B-Naphthol ,(a standard solution of B-Naphthol in carbon tetrachloride) . Instead of B-Naphthol potassium iodide may be added and the liberated iodine is titrated against a standard solution of sodium thiosulphate .

Some substitution reaction may take place to a small extent, which changes the bromine value . Hence it is necessary in some cases to determine the substituted bromine and subtract it from the total bromine absorbed .

For the determination of iodine ^{value} two solutions are generally used namely, Hubl's solution and Wijn's solution . The first solution consists of an alcoholic solution of iodine and mercuric chloride, while the second is simply a solution of iodochloride in glacial acetic acid .

The determination of the iodine value by the iodine as well as the iodochloride is accomplished by dissolving a convenient amount of the oil in Carbon tetrachloride or chloroform, a known volume of the solution is added, the whole mixture is kept in the dark (In case of Wijn's solution, one hour is sufficient for a complete reaction, while from eight to ten hours are necessary in the case of Hubl's solution .). To take the excess iodine or iodochloride a solution of potassium iodide is added and the liberated iodine is titrated against standard sodium thiosulphate solution .

The iodine value provides one of the most valuable characteristics in the technology of oil analysis . Moreover, it is the best method for the determination of the class of an oil since the drying property of oils or fats is related closely to their unsaturation.

3-- Reichert (Reichert-Meissl, Reichert-Wollny). value

The Reichert (or Reichert Meissl) value indicates the number of cubic centi-

meters of decinormal potash requisite for the neutralization of that portion of the soluble volatile fatty acids which is obtained from 2.5 (or 5) grams of a fat or an oil by the Reichert distillation process .

This value is a measure for the soluble volatile fatty acids occurring in natural fats and oils . The estimation of the total volatile acids in a sample of oil or fat is rather difficult, since on distillation decomposition may take place . Thus an arbitrary procedure is proposed to measure the volatile fatty acids in oils or fats without decomposing other constituents . The direction of this procedure should be followed literally otherwise the determination may lead to ~~an~~ erroneous results. This value is of great help to the analyst in the identification of butter from butter substituents .

Acetyl value :

The acetyl value indicates the number of milligrams of caustic potash required for the neutralization of the acetic acid obtained on saponifying one gram of an acetylated oil or fat .

This value is a measure of the hydroxy acids or ^{mono- and di-}glycerides . When hydroxy acids, glycerols or any alcohol are heated with acetic anhydride, an acetylated compound will result . The number of hydroxyl groups present in that oil or fat.

The acetyl/^{value}of pure triglycerides containing no hydroxy acids is zero, while that of pure glycerides containing hydroxy acids is proportional to the amount of the hydroxy acids present . The acetyl value in this case is considered as a characteristic . On the other hand, the presence of mono and diglycerides as well as free fatty acids leads to a variable acetyl value, since their proportion in an oil or fat is dependent on the quality and the age of the oil .

The acetyl value in combination with the acid value may give a good information about rancidity in oils and fats .

1-. Acid value :

The acid value indicates the number of milligrammes of potassium hydroxide required to neutralize the free fatty acids in one gram of a fat or an oil .

This value is a measure of the quality of an oil or fat, i.e. it measures the extent to which an oil or fat has undergone hydrolysis . In some cases the acid value is expressed as percentage of olive acid . It is evident that this value is variable depending on the state of purity, age, and the amount of oxidation which an oil or fat has undergone .

The determination of this value is accomplished by dissolving a convenient amount of oil or fat in alcohol and titrate the free fatty acids against standard alkali . The titration should be carried out as quick as possible, since the presence of alkali in slight excess may lead to hydrolysis of the neutral glycerides .

2-. Glycerol :

The amount of glycerol present in pure triglycerides may be considered as characteristics since 3 molecules of KOH liberates one molecule of glycerol . Thus the quantity of glycerol in this case may be calculated from the amount of KOH used for complete hydrolysis . However, natural oils and fats contain mixed glycerides as well as free fatty acids, mono and diglycerides in variable proportion, thus the proportion of glycerol in this case cannot be calculated from the saponification equivalent. It is evident that the higher the proportion of free fatty acids in an oil or fat the smaller is the amount of glycerol . Moreover, the proportion of glycerol in an oil or fat increases as the amount of mono and diglycerides increases .

It is mentioned before, that when the molecular weights of the fatty acids

attached to glycerol in the glycerides are small the saponification ^{value} ~~equivalent~~ will be high, hence the amount of glycerol will be more than that of glyceride whose saponification ^{value} ~~equivalent~~ is small .

Different methods have been used for the determination of glycerol in oils and fats . The general method used is the quantitative oxidation of glycerol with alkalic potassium permanganate into oxalic acid, this acid is precipitated as Ca-oxalate and the latter is titrated in the presence of sulphuric acid with standard potassium permanganate.

3-. Mono and di-glycerides :

The occurrence of diglycerides and monoglycerides is not unusual in natural oils and fats, especially if the oil has undergone some hydrolysis during the lapse of time . These incomplete glycerides are found in great proportion in rancid oils and fats . The detection of these glycerides has been carried out by Lewkowitzch . The process involves the acetylation of the free hydroxy groups of the glycerol; it is obvious that the weight of mono and diglycerides increases on acetylation, namely each free hydroxy group takes one acetyl radical, thus if the weight of the mono glyceride is known, the weight of the acetylated product of this glyceride will be that of the original glycerides plus 2×42 . Thus we get the following relationship .

$$\frac{d}{d + 1} = \frac{M}{M + 84}$$

where d is the weight of the monoglycerides used

$(d + 1)$ is the weight of the acetylated monoglycerides used.

M is the molecular weight of the monoglycerides

$(M + 84)$ is the molecular weight of the acetylated monoglycerides

a similar relation holds true in the case of dyglycerides namely :

$$\frac{d}{d + i} = \frac{M}{M + 42}$$

This determination is rarely used since the method is liable to great variation; as a matter of fact the whole determination will be invalid in the presence of free fatty acids and hydroxy-acids .

4-. Unsaponifiable matters :

Substances which are insoluble in water^{and}/do not combine with alkali are called "unsaponifiable matters". Natural oils and fats contain small amounts of these substances e.g. vegetable oils and fats contain phytosterol, while animal oils and fats contain cholesterols . Moreover, other unsaponifiable matters may occur besides phytosterol and cholesterols, the nature of which are not fully ascertained yet . The existence of resinous, coloring matters, and hydrocarbon in some oils, has been observed .

The quantitative determination of unsaponifiable matters occurring in oils and fats is accomplished by saponifying a convenient amount of oil or fat as complete as possible with alcoholic potash . The soap obtained is dried from alcohol and extracted several times with ether . The ether extract is washed with water to remove any traces of soap which might be dissolved in ether . The washed ether extract is evaporated on a water bath, then in a dry oven at a temperature not more than 100°C. The substance which remains after the evaporation of ether is the unsaponifiable matters .

PART "II"

" SESAME OIL "

Sesame oil, also known as beniseed oil, gingelli oil, and teel oil is obtained from the seed of a herbaceous plant, *SESAMUN INDICUM*, of which several species are known. Sesame belongs to the small family of Pedaliaceae, which is sometimes related to the Bignoniaceae.

The full-grown plant is usually from two to four feet high; its lower leaves are usually broad, coarsely toothed or lobed, and its upper leaves are lanceolate. The flowers of this plant are tubular two lipped and 1.8 cm long. They vary in color; some are yellow and others are pinkish. They have four stamens of unequal length. The seed pod is two-valved and contains numerous small seeds. When the plant is matured, the pods open and often scatter much of the seed.

The color of this seed varies from white, pale yellow, dark red, brown and black. Commercially, the seed is known as white or black. "White Sesame" must not contain more than fifteen percent of other seeds, when the percentage of the dark seed is more than 15% the seed is no more called as "white sesame". Different names are used when the percentage of white seed is less than 85%; these names, used when the percentage of white seed is less than 85% depend on the composition. The white sesame yields the best sesame oil, while the Indian black sesame yields the greatest amount of oil.

Sesame plant is widely distributed on the globe; it is produced in India, China, North East and West Africa, Japan, Java, Siam, the Levant, Egypt and elsewhere. The original home of the plant is unknown, but it is suspected to be Sunda Islands, then the seed is migrated from its original home to India, and then through the Euphrate basin to Egypt.

Sesame plant is grown extensively in Iraq, especially in the middle part of the country . Baghdad and the adjacent Lewa's produce the greatest amount of sesame seed in the country . All the kinds of sesame seed have been grown there except the black one . The quality of the seeds produced due to the old fashioned plantation used by the farmers, is not superior . On the other hand, the experimental farm of the government which was established fifteen years ago at Zu'fariana produces superior quality of sesame seeds .

Sesame seed is not expressed in Iraq , but it is mostly used as such in making various kinds of confectionary, the remaining seed is shipped to Europe or America . The oil of this seed is imported from Europe and used as table oil, for cooking, burning and for soap manufacturing .

Industry of Sesame oil ;

The sesame oil industry is not of great importance in Europe, and there is no special design for the expression of oil from sesame seed . The production of sesame oil is accompanied with that of cotton seed oil . However, Lewkewitseh mentions that ; Bang and Sanguinetti of Marseilles devised a special apparatus for the extraction of sesame seed with petroleum ether . This devise is patented in Austria ; I could not find any other reference which mentions the smallest detail about this devise .

Since sesame seed belongs to that class which is rich in oil, it is necessary to use successive expressions to obtain most of the oil content of the seeds. The usual method used for the expression of this seed is accomplished by the French Expeller . The Iraqi Government has recently established a plant for the production of sesame and cotton seed oil in which the French Expeller is used , but it has not been operated yet . I have visited a similar plant using the

French Expeller for the expression of the seeds . The detail of the process is as follows :

Since sesame seed is not hard, therefore crushing of the seed is of no use. Thus the seed is cleaned and made free from any foreign matters . The expeller is fed with clean seed . The rate of feeding should be adjusted otherwise incomplete expression may result . The oil obtained passes through the small wholes to the basin of the machine . The oil may contain small amount of un-expressed seed so the crude oil is conducted through channels into a big tank, then it is pumped through a filter press to remove the foreign matters . The color of the oil at this stage varies from brown to dark orange depending upon the quality of the seed used . Analysis for the free fatty acids is done in order to calculate the amount of caustic soda which will be used during the refinery .

Refinery :

There are two kinds of refining kettles, both of them are provided with steam coils, but one of them is provided with a mechanical agitator ; while agitation of the oil in the other kind is performed by passing air through a perforated plate at the bottom of the refinery kettle . The size of the kettle depends upon the amount of oil produced . The handling of the refinery kettles varies in the hand of different operators . The way of refinery used in the factory which I visited in contrast to the one mentioned at the beginning of the paper, is accomplished by passing steam through the coils and pumping air through the perforated plate until the oil reaches about 40° to 50°C. Then the required amount of caustic soda as a solution of 17.5 Bé is added while continuing the

agitation . After eight to ten minutes the oil becomes yellow in color and carrying small black particles . At this stage air and steam are turned off, and the oil is allowed to stand for ten hours in order to give chance for the soap formed to settle carrying with it most of the foreign matters . The soap and the coloring matters usually settle at the bottom of the refining kettle, and it is removed through a tap . Sometimes the soap and the coloring matters float on the surface of the oil ; in this case it must be scum off .

The oil, after the removal of the soap and other matters, is washed with water to remove any traces of caustic soda and soap . The color of the oil is yellow, but it is rather a dark yellow . In order to make the color of the oil bright or pale yellow it is necessary to bleach it with fuller's earth alone or together with decolorizing carbon . It is worthwhile to mention that washing of the oil with water is carried out in the same kettle used before .

Bleaching :

The oil is free from any traces of soap or caustic soda is transferred directly without filtration to the bleaching kettle, which is provided with heating coils and a mechanical agitator . The agitator is turned on and the oil is heated by the steam coils to a temperature ranges between 100° to 110°C and held at this temperature until the moisture is removed . Five per cent of fuller's earth is sucked into the bleaching tank . Due to the high prices of the decolorizing carbon, it is not used during these war days in the factory ; but as I have said before .5 to 1 percent of decolorizing carbon is used usually . After agitating the oil with the bleaching reagents for 15 minutes or somewhat longer, it is filtered through filter presses, and the oil is sent to the deodorizing tank, either directly or it is left for few days in the storage tank .

The odor of the oil is not desirable, so it is necessary to odorize the oil if it is to be used for edible purposes .

Deodorization :

Deodorization takes place in a vertical vessel provided with a suitable sized closed heating coils, a perforated plate at the bottom, and connected to an efficient vacuum pump. The object of this device is to heat the oil to a high temperature and under reduced pressure to provide a good way for the volatile matter to escape .

There is a special furnace heated by crude kerosene (mazoute), and through which several turns of steam coils are heated . The desired temperature of steam is between 230° and 250°C . This steam is sent while agitating the oil to the coils of the deodorizing vessel in order to heat the oil . The desired temperature of the heated oil is not more than 200°C , this temperature is obtained after passing the steam for one hour and a half . Under this condition of heating, and under this reduced pressure, the oil loses most of the volatile matters which give rise to the undesirable odor . The removal of the remaining odoreferous matters is done by turning on the superheated steam through the perforated plate located at the bottom of the vessel or the tank . The process continues from 3 to 6 hours depending upon the quality of the oil used . When the process is completed, the vacuum is maintained until the oil is cooled, otherwise the oil may be oxidized to some extent at this high temperature . Cooling of the oil to the ordinary temperature is achieved by turning off the steam and passing cold water through the coils . The oil is pumped for the third and the last time through filter presses, then it is conducted to the storage tanks . During the third filtration by means of filter presses, filter paper is used instead of cloths, and the pressure is not

as high as that used during the first and the second filtration, since the oil contains very small amounts of foreign matters .

Destiny of the bye-products :

During the production of oils from the seed, two main bye-products result, namely the cake which is obtained after expression and the soap stock obtained after refinery . The cake of sesame seed is rich in oil, it contains about 10% oil . So the destiny of the cake as well as that of the soap stock depends largely on the price of the oil . If the price is high the cake is extracted with volatile solvents and the exhausted cake which remains after the extraction is sold as fertilizer . The oil may also be obtained from the soap stock by dissolving the latter in water and the mixture is centrifuged . This process is rather a difficult one and the yeild of 65 percent of the oil present in the soap is considered high . The oil obtained by this process is sent with the crude oil to the refinery kettle . The remaining of the soap stock is used for soap manufacturing. However, if the price of the oil is not high, the cake of the sesame seed is mixed with other cakes of other seeds to bring about the percentage of oil to the allowable amount and sold as cattle food . The soap stock is made directly into soap. In this part of the world the cake is sold as cattle food and soap stock is mixed with neutral oils and made into soap .

Analysis of the Iraquian sesame oil :

Sesame oil has been examined by a great number of chemists . However, the composition of vegetable oils and fats derived from one and the same species of plant will fluctuate somewhat with the variety of the plant, the climate, and the soil . Thus , the Iraquian sesame oil, examined in the A.U.B. laboratories shows slight diviation from other sesame oils examined in Europe or America .

Two different samples of the iraquian sesame seeds as well as one sample of the Lebanese sesame seed were extracted, and the characteristics as well as other properties were determined .

a-. Determination of oil content in the above-mentioned samples :

The determination of oil content in these samples (1) were carried out by means of the Soxhlet's apparatus using that part of the aviation benzine which distills below 68°C. The result was as follows :

White Iraquian Sesame	49.73 %
Brown Iraquian Sesame	51.22 %
Lebanese mixed sesame	49.36 %

b-. Specific Gravity :

The specific gravity of these samples was determined by means of the Westphal balance and the result was as follows :

White Iraquian Sesame	0.922	(at 18°C)
Brown Iraquian Sesame	0.9223	(at 18°C)
Lebanese Sesame	0.922	(at 18°C)

c-. Refractive index :

The results of the three samples determined by the refractometer and the butyro-refractometer were as follows :

<u>Refractometer</u>		
White Iraquian Sesame	1.4752	at 20°C.
Brown Sesame	1.4749	at 25°C.
Lebanese Sesame	1.4753	at 20°C.

(1)-. The Iraquian samples are of the best kind grown in the experimental farm of Zufurania .

Butyrorefractometer

White Iraquian Sesame	67.34	at 27°C
Brown Iraquian Sesame	67.3	at 27°C
Lebanese mixed sesame	67.35	at 27°C

d-. Rotatory power :

Iraquian White sesame	1.1 °	(at 17°C.)
Iraquian Brown Sesame	1.13°	(at 17°C.)
Lebanese mixed sesame	1.1 °	(at 17°C.)

Examination of ^{H.c} three above mentioned samples by chemical means :

a-. Free Fatty acids :

<u>Sample</u>	<u>Percentage of fatty acid</u>	<u>Acid number</u>
White Iraquian Sesame	1.13	2.25
Brown Iraquian Sesame	1.15	2.29
Lebanese mixed Sesame	1.02	2.014

b-. Saponification value :

This value for the three samples was obtained by saponifying about 5 grs. of oil by 50 c.cs. of .5N alcoholic KOH . The mixture was reflexed for one hour and the excess of alcoholic KOH was neutralized with .5N HCL

The result obtained for the samples was as follows :

White Iraquian Sesame	189.62
Brown Iraquian Sesame	189.87
Lebanese mixed sesame	188.91

c-. Reichert Meisl value :

The result obtained in the determination of this value was as follows :

White Iraquian sesame 1.11
 Brown Iraquian sesame 1.08
 Lebanese mixed sesame 1.20

d-. Iodine value :

This value was determined by the Wij's method, using Carbon tetrachloride as a solvent . The result was as follows :

White Iraquian sesame 106.8
 Brown Iraquian sesame 107.2
 Lebanese mixed sesame 106.6

The iodine value of the sesame oil varies slightly with temperature and time. No factor of proportionality was obtained because of the uneven variation which resulted on changing the temperature or the time of contact between Wij's solution and the oil . These results were as follows :

Wt. of the sample	Iodine value	Temperature	Time	.1N F = 1.07 cc. of Wij's solu.
0.3484 g.	108.6	5°C.	50 min.	25 c.cs.
0.3037 g.	106.2	5°C.	45 min.	25 c.cs.
0.4380	108.1	5°C.	45 min.	25 c.cs.
0.4382	108.4	5°C.	310 min.	25 c.cs.
0.3136	100.2	5°C.	20 min.	25 c.cs.
0.2750	112	5°C.	65 min.	25 c.cs.
0.2468	110.5	5°C.	30 min.	25 c.cs.
0.2377	101.3	5°C.	20 min.	25 c.cs.
0.2164	112.5	5°C.	120 min.	25 c.cs.
0.3923	105.5	18°C.	60 min.	25 c.cs.
0.3760	105	18°C.	60 min.	50 c.cs.

Wt. of sample	Iodine value	Temperature	Time	.1N F = 1.07 c.c. of Wij's sol.
0.3552	107.5	50°C.	60 min.	50 c.cs.
0.2900	107.2	50°C.	195 min.	50 c.cs.
0.2983	107.01	21°C.	60 min.	50 c.cs.

It seems that the effect of the ratio of Wij's solution to the oil is more remarkable than that of time or temperature .

By the above mentioned experiments an attempt was made to find a cause for the variation of the iodine value for the same oil, and to avoid this variation by giving a definite direction and definite condition for the determination of this value . However practically nothing ^{can} be added to the condition which is mentioned in many books namely : that the Wij's solution should be added in great excess to the amount absorbed by the oil, and the time should not be less than 60 minutes . But according to these experiments 30 minutes will be enough instead of 60 minutes .

e-. Acetyl value :

This value was determined for the three samples and the results were as follows :

White Iraquian sesame	10.83
Brown Iraquian sesame	11.21
Lebanese mixed sesame	11.42

f-. Unsaponifiable matters :

The result obtained in the determination of this value for the three samples was as follows :

White Iraquian sesame	1.28
Brown Iraquian sesame	1.34
Lebanese mixed sesame	1.31

The unsaponifiable matters consist of phytosterols, sesamin, and a thick brown oil of unknown composition.

g-. Separation of saturated and unsaturated fatty acids :

This separation was carried out according to the "Lead-Salt Ether Method", i.e. taking advantage of the solubility and insolubility in ether of the lead soap of unsaturated and saturated fatty acids respectively. The preliminary percentage of each was as follows :

White Iraquian sesame : (12.9% saturated fatty acids
(76.6% unsaturated fatty acids

A correction should be made by determining the iodine value of the saturated and the unsaturated acids. It is obvious that the iodine value of the pure saturated acids should be zero. On the other hand, the separation of saturated and unsaturated acids by this method is not complete, since some of the lead soap of the unsaturated acids may precipitate with that of the saturated acids. Moreover the lead soap of the saturated fatty acids, specially if they are of relatively low molecular weight, may dissolve in ether and pass with that of the unsaturated acids.

The correction was made as follows :

Iodine value of unsaturated fatty acids obtained : 123.5

Iodine value of saturated fatty acids obtained ... : 12.55

$$\frac{12.55 \times 100}{123.5} = 10.05 \text{ percentage of unsaturated fatty acids in saturated acids}$$

$$\frac{10.05 \times 12.9}{100} = 1.29 \text{ percentage of unsaturated fatty acids which was considered with the saturated fatty acids.}$$

Hence the correct percentage of the saturated and unsaturated fatty acids in the above mentioned sample is :

Saturated fatty acids ... $12.9 - 1.29 = 11.61 \%$

Unsaturated fatty acids ... $76.6 + 1.29 = 77.89 \%$

The percentage of saturated and unsaturated fatty acids in the Lebanese sesame oil was determined by the above mentioned method and the same correction was made . The result is :

Saturated fatty acids ... 12.22 %

Unsaturated fatty acids ... 78.03 %

No attempt was made to separate the individual fatty acids^{due} to lack of references as well as proper equipments . .

Physical and Chemical Characteristics of Sesame Oil
and the oil content of the different seeds.

SPECIFIC GRAVITY

<u>At °C.</u>		<u>Observer</u>	<u>Name of the country</u>
15	0.923 - .9237	De Negri and Fabris	African oil
15	0.924 - .926	Shukoff	Russian oil
15.5	0.9203	Boley	Jaffa oil
20	0.917 - .921	Wijs	Curacao
23	0.919	Dieterich	-----
35	0.9078 - 0.9098	Long	-----
18	0.922	---	Lebanon oil
18	0.922 - .09223	---	Iraqian oil

ROTATORY POWER

<u>At °C.</u>	<u>Degrees</u>	<u>Country</u>
17	1.1 - 1.3	Iraqian oil
17	1.1	Lebanese oil

OIL CONTENT

<u>Percentage</u>	<u>The solvent used</u>	<u>Name of the Country</u>
49.76	Ether	Indian seed
47.57	Ether	Indian seed
50.14	Ether	Levant seed
54.14	Ether	African seed
52.54	Petroleum ether	African seed
49.36	volatile gasoline	Lebanese seed
49.73	volatile gasoline	White sesame 'Iraq'
51.22	volatile gasoline	Brown sesame 'Iraq'

REFRACTIVE INDEX

<u>At °C.</u>		<u>Observer</u>
15	1.478 - 1.4762	Strohmer
20	1.4728	Harry
60	1.4561	Thoerner
20	1.4752	Iraqian sesame oil
25	1.4744	Iraqian Sesame oil
20	1.4753	Lebanese sesame oil

SAPONIFICATION EQUIVALENT

<u>M grams of KOH</u>	<u>Observer</u>	<u>Name of the country</u>
194.6	Longs and Lione	-----
187.6 - 191.6	Filinger	-----
188 - 190	Shukoff	Russian oil
188.9	-----	Lebanese oil
189.6 - 189.9	-----	Iraqian oil

IODINE VALUE

<u>Per cent</u>	<u>Observer</u>	<u>Name of the country</u>
106	Hubl	-----
106.9 - 107.8	De Negri and Fabris	African oil
114 - 115	Shukoff	Russian oil
106.6	-----	Lebanese oil
106.8 - 107.2	-----	Iraqian oil

REICHERT MEISSL VALUE

<u>C.c. of .1N KOH or NAOH</u>	<u>Name of the country</u>
1.2	-----
1.11	White sesame "Iraq"
1.08	Brown sesame "Iraq"
1.2	Lebanese oil .

Qualitative Test for Sesame oil :

a-. Bandouin test :

Different color reactions have been proposed for the detection of sesame oil in other oils or fats . The most important one is the Boudouin test . This test is performed by dissolving 0.1 gram. of sugar in 10 c.cs. of hydrochloric acid of specific gravity 1.19 in a test tube . 20 c.cs. of the oil to be tested is added and the mixture is shaken thoroughly for one minute . The aqueous layer separates almost immediately . In the presence of small amount of sesame oil a crimson color will develop in the aqueous layer after 15 minutes . This color is due to the condensation reaction which takes place between the furfural obtained from the sugar and the thick brown oil which is found in small amount in sesame oil and whose composition is not determined yet .

The test is very simple and very sensitive . As a matter of fact, the simplicity with which sesame oil is detected leads many states to oblige the manufacturers of margarine to use small amounts of sesame oil in their products.

Dilute alcoholic solution of furfural may be used instead of sugar . Thus 0.1 c.c. of the 2% furfural solution may be used instead of the 0.1 gr. of sugar which is used in the above mentioned test .

b-. Soltsien's test for sesame oil :

This test is particularly useful for detecting sesame oil in margarines. It is carried out as follows :

5 c.cs. of the sample to be tested (melted margarine) are dissolved in 10 c.cs of petroleum ether in a test tube . 2.5 c.cs. of stannous chloride solution (a mixture of 5 parts of crystallized stannous chloride and one part by weight of hydrochloric acid is completely saturated with HCl gas. and filtered

through asbestos if necessary), is added . The mixture is shaken thoroughly until homogenous and is placed in a water bath heated to 40° C. After the acid solution has separated, ^{the} test tube transferred into another water bath whose temperature is 60° C. In the presence of sesame oil, a distinct red coloration will result after washing for three minutes .

Lewkowitsch states that the test is not given by rancid sesame oil . He does not recommend its use, because fat extracted from cakes or pastry prepared from pure butter always give a red coloration .

It should be noted that the milk of animal fed with sesame oil cake gives a test for sesame oil . The adulteration of sesame oil with other oils, due to its low price is very rare . However, sometimes it is adulterated with cotton seed oil, and can be detected by the Halphen test. In Lebanon sesame oil is sometimes, adulterated with peanut oil, this may be detected by the separation of arachidic acid .

Composition of sesame oil :

An attempt was made by Jemieson and Banghman for the determination of the composition of sesame oil . The following was the result obtained :

Sat. Acids12.2%
Unsat. Acids81.2%
Unsat. Acids ..1.73%

The following individual fatty acids were separated and their percentage was determined :

Linolic acid 35.2%
Oleic acid 46.0%
Palmitic acid 7.3%

Stearic acid 4.4%

Arachidic acid .. 0.4%

Legnoceris acid ..0.04%

Sesame oil contains (according to Villavecchia and Fabris) the followings, besides the glycerides of the above mentioned fatty acids :

a). Alcohol which melted at 139°C and gave a specific rotation at 20° to 30°23' which was undoubtedly a mixture of sterols .

b). Sesamin was also separated and found to give a specific rotation at 20°C of + 68.36° .

c). Viscous non-crystallizable thick oil . This substituent of the unsaponifiable matter which contain the substance which gives the Boudouin color test .

d). Sesamol : This substance was detected by Kreis, it is considered to be a phenol as it combines with diazo compounds . According to the discoverer sesamol does not occur in the free state in sesame oil, but as a complex body from which sesamol is set free on adding a mineral acid .

Uses of sesame oil :

The cold-pressed sesame oil is used as an edible oil either as such or in the manufacture of margarine . Sesame oil is used in Iraq by a great number of people for edible purpose. It is used in Iraq as extensively as olive oil used in Syria and the Lebanon . The use of "Tahyna or Rashi" for edible purpose is very large in this part of the world .

The best sesame oil is also used in the production of perfumes by the "enfleurage" method .

The lower qualities of sesame oil are used for soap making, burning and lubricating .

Stability of sesame oil :

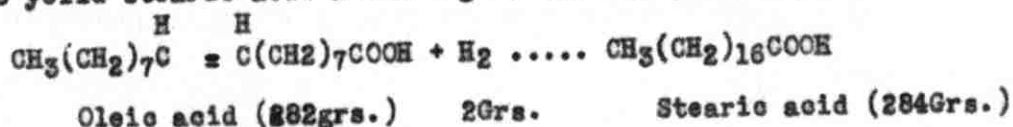
Although sesame oil is mostly composed of unsaturated glyceride which are known very liable to rancidity , yet the oil is very stable . The stability of the oil against rancidity is due to the natural antioxidants occurring in the natural oil such as sesamol and phytosterols . As a matter of fact , the stability of sesame oil and almond oil has led the investigators to the discovery of the antioxidants .

P A R T I I I

HYDROGENATION OF OILS .

Liquid oils whose glycerides are rich in unsaturated fatty acids can be "hardened" by the catalytic action of hydrogen . The principle of this process is the addition of hydrogen to the double bonds of the unsaturated glycerides to yield saturated glycerides . Olein, linolein and other unsaturated glycerides may be converted into stearin under the catalytic addition of hydrogen .

The addition of hydrogen without using a catalyst is extremely slow and of no practical use . However, hydrogen in the presence of catalyst such as nickel palladium, platinum etc., adds to the double bonds of the unsaturated glyceride. The weight of hydrogen, added to the double bonds of the unsaturated glycerides is comparatively low, for instance oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the following equation .



Thus the percentage of hydrogen will be about 0.7

A great number of unsaturated compounds may be hydrogenated by this method to yield products of great uses. On the other hand, this process is largely practiced in the hardening of vegetable oils such as cotton seed, sesame, soya bean and peanut oils as well as some marine oils. The analytical constants of oils change on hydrogenation; the melting point will increase as well as the specific gravity while the iodine value and the index of refraction gradually decreases as the process of hydrogenation is going on.

Several devices for the hydrogenation of oil on an industrial scale are in use, the principle of all is the same i.e. to bring about intimate contact of hydrogen gas with the oil and catalyser.

The essential of all catalysers used in the hydrogenation of oils at the present time is nickel, although platinum, palladium and certain other metals which in their finely divided state act as carriers for hydrogen may be used for the same object. Sometimes nickel is used in conjunction with other metals such as copper which act as an auxiliary.

The preparation of catalyzers differs in the hand of different operators. The way of preparation is divided into two kinds, one is known as the dry process which involves the reduction of nickel compounds in the dry state, and the other is known as the wet process which involves the reduction of nickel compounds inside an oil or any other suitable vehicle.

The dry process of reduction has been used extensively in the past, but it is almost displaced now by the wet process. The reduction by the dry process is accomplished by precipitating an insoluble nickel compound on a carrier of finely divided character. The carriers used are inert mineral powders such as fuller's earth, clay or infusorial earth. The support or the carrier is added

a solution of nickel salt such as nickel sulphate or nickel nitrate, and sodium carbonate is added to precipitate nickel carbonate upon the carrier. The whole mass is washed thoroughly by decantation, dried and reduced in a current of hydrogen gas. The precipitated nickel carbonate is placed in a closed receptacle which is heated to a temperature range between 250°C and 500°C, and hydrogen gas is passed through the mass until water is no more evolved. The reduction of the mass may be carried out rapidly by agitation during the reduction period, or by placing the mass in a rotatable drum.

The temperature at which the reduction of the raw materials takes place has a great influence on the quality of the catalyser. The most sensitive catalyser is obtained by reduction at lowest temperature. Although nickel begins to reduce at 220°C, yet at 270°C the reduction is not complete even if the mass is exposed to hydrogen for a long time. A temperature of 300° to 325°C gives rather a complete reduction and is a satisfactory working temperature. Hence the reduction of nickel should be carried out carefully and at a temperature which gives a sensitive catalyser. Nickel is readily poisoned by chlorine or sulphur in the sulphide form.

After the reduction of nickel is complete, the product should be kept out of contact with air, because the catalyser loses its activity on being exposed to air. Hence, it is necessary to displace air by hydrogen in the hydrogenation kettle before the addition of the catalyser.

The wet process of reduction, i.e., the reduction of nickel compounds inside the oil to be hydrogenated has proved superior to the other method, since the latter is cleaner. This process is carried out by adding finely ground nickel compound to the oil, heating and passing hydrogen until complete reduction is secured.

The most popular compound of nickel used in wet reduction is nickel formate. This compound when heated in an oil to about 240°C it decomposes to yield

finely divided nickel. The introduction of hydrogen is not necessary for the decomposition. On the other hand, it is customary to pass a slow current of hydrogen into the oil containing the nickel formate. The formate may be admixed with oil in a large proportion so as to produce a concentrated catalyzer. In this case the oil which contains this great amount of finely divided nickel may be used as a catalyzer in the hydrogenation of other oils. The oil containing the nickel and which is intended to be used as a catalyzer for the hardening of other oils, is washed with the oil to be hydrogenated to remove the old oil. The percentage of the catalyzer used in the hydrogenation of oils varies between .2 to 1 and that the temperature ranges between 140°C to 190°C depending upon the method which is used for the hydrogenation.

Hydrogenation practice :

Many attempts to hydrogenate oleic acid and other unsaturated fatty acids have been made. Lawkowitzsch refers to the ease with which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenation", further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results".

Goldschmidt, however, had reduced oleic acid by means of hydroiodic acid and amorphous phosphorous at 200 - 210°C. The yield was low, and the method is rather expensive and cannot be put into commercial practice.

Tissier, in 1897, lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein introduced and treated under pressure.

Under these circumstances the glyceride is hydrolyzed to fatty acids and

and according to Tissier nascent hydrogen is evolved by virtue of the finely divided metal and reduces the oleic to stearic acid . However, other investigators claim the Tissier process is inoperative .

Hydrogenation processes involving application of electricity :

In 1886, Weineck called attention to the possibility of electrolytic addition of hydrogen to oleic acid . Kuess later attempted to apply the electric current in the steam distillation of fatty acids .

In patents taken out by Magnier, Bragnier and Tissier, the fatty material is acidified with sulphuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atm. is subjected to the action of an electric current, which generates hydrogen in a nascent state .

An interesting method of converting oleic into stearic acid is that comprised in the Hemptinne electric discharge process . The method is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil. The figure No.3 shows the arrangement of apparatus for this purpose . The conversion is effected in a chamber having an inlet pipe H, furnishing hydrogen under constant pressure . Oleic acid is supplied by a pipe O, to sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass plates G and alternately the metal plates M,N. The metal plates M are connected to one pole, the others N, are connected to the other pole of a source of electricity . As the oil passes over the plates, the electrical discharge causes conversion of some oleic acid into stearic acid .

The proposer of this method prefers to work at a pressure less than atmospheric. He claims that the yield is greater under reduced pressure . By treatment in this manner it is not difficult to obtain 20% of stearic acid . Repeated treatment permits even up to 40% of stearic acid . Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of

reaction greatly decreases . Much better results are obtained by saturating to the extent of about 20 percent, removing the stearic acid by pressing, when the oil of reduced stearic content is again subjected to the electric discharge, and a further 20 percent yeild obtained .

Other investigators mention different devices by the electric discharge, but the above mentioned method is superior to the rest of the methods . The work of Sabatier and Senderens laid the foundation for the present processes of hydrogenation of oil. Their work is based upon the catalytic hydrogenation of bodies capable of vaporization by means of purified hydrogen gas in the presence of finely divided nickel as catalyst.

Since the time of Sabatier and Senderens, different devices have been proposed for the hydrogenation of oils using the same catalyst namely, finely divided nickel. Some of these devices are very simple and cannot be put in practice, others are complicated and involves heavy prices . Due to the repeated caution given by Sabatier to bring in contact with the catalyzer only the vapors of the material to be hydrogenated most of these devices are not broadly applicable to the treatment of oils as the glycerides cannot be vaporized without undue decomposition .

Erdmann, however, has abandoned the idea of Sabatier and taken out a German patent involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like . The detail of the device is shown in figure 4, which probably indicates one form suggested by Erdmann, who , by the way, does not show any drawing in the patent . The chamber A has a rotatable cylinder, B, which is coated with nickel catalyzer . In the bottom of the receptacle is a quantity of nickelized pumice . Oil enters at O and is atomized by entering at H. The atomized mixture impinges upon the rotating cylinder B, then passes through the pumice bed C, the oil being drawn off at D. The excess of hydrogen is presumably vented in the upper part of the apparatus .

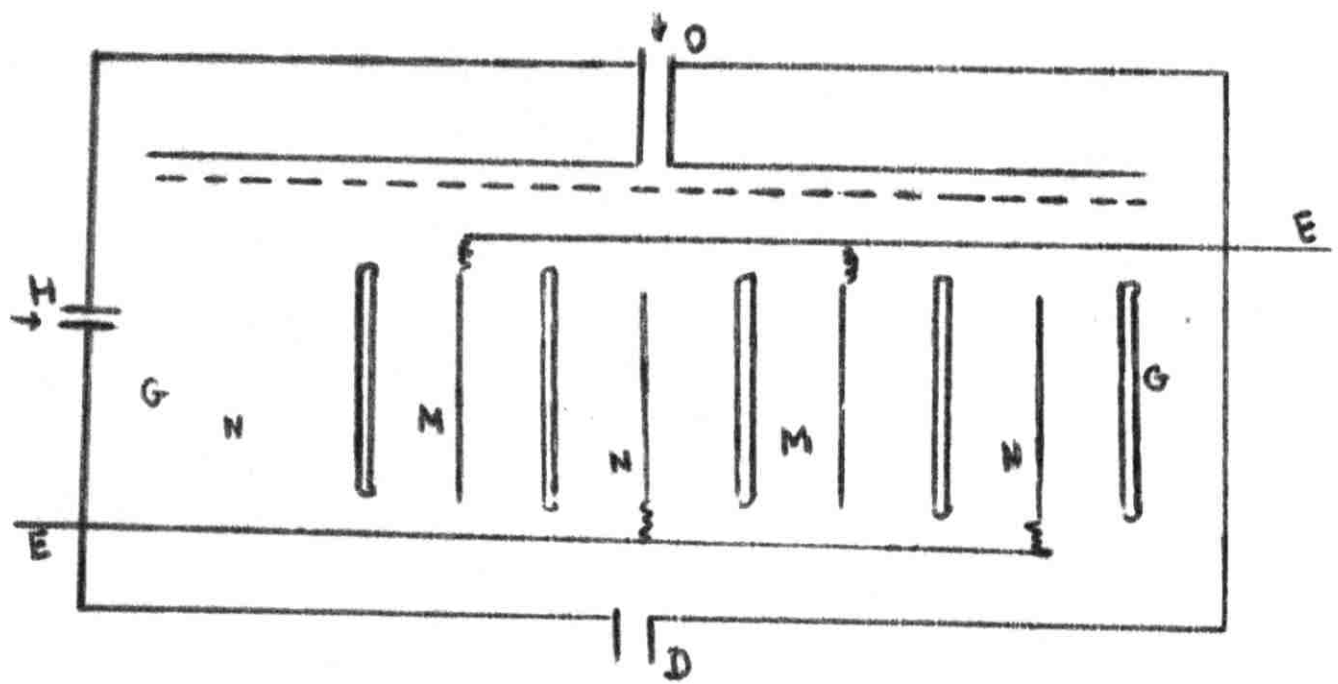


Figure No. 3

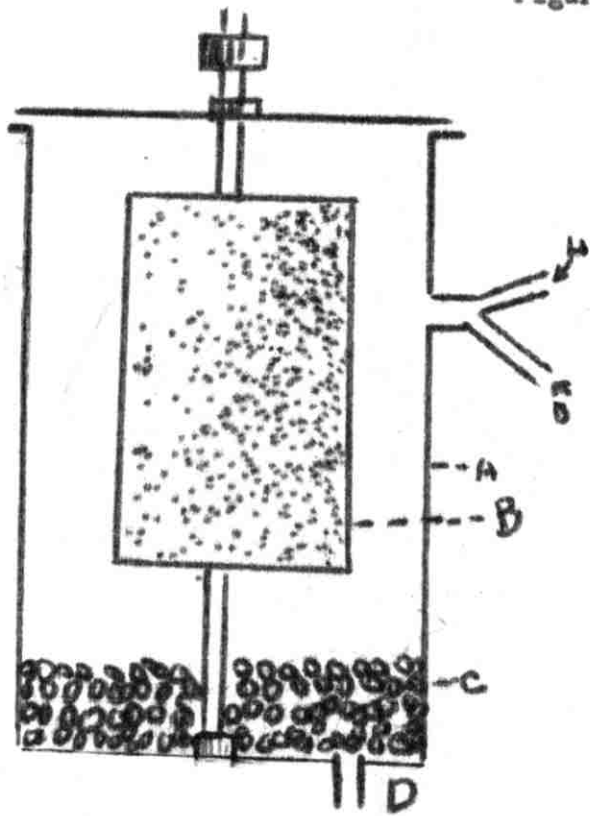


Figure No. 4

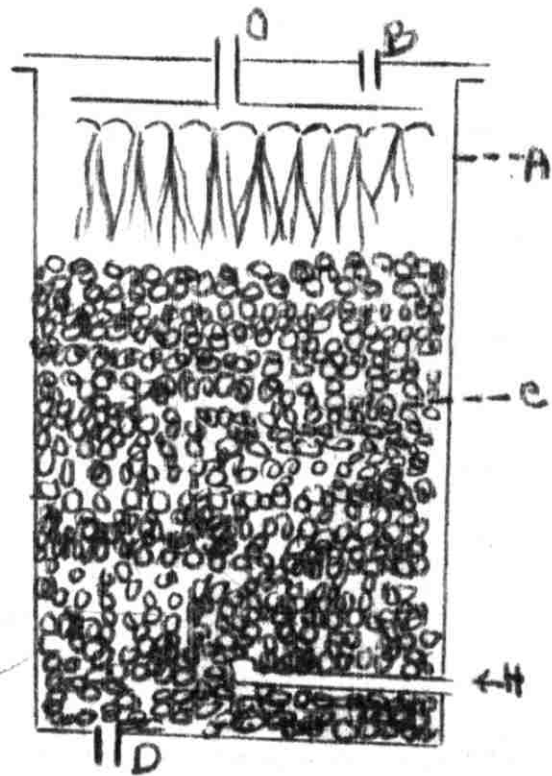


Figure No. 5

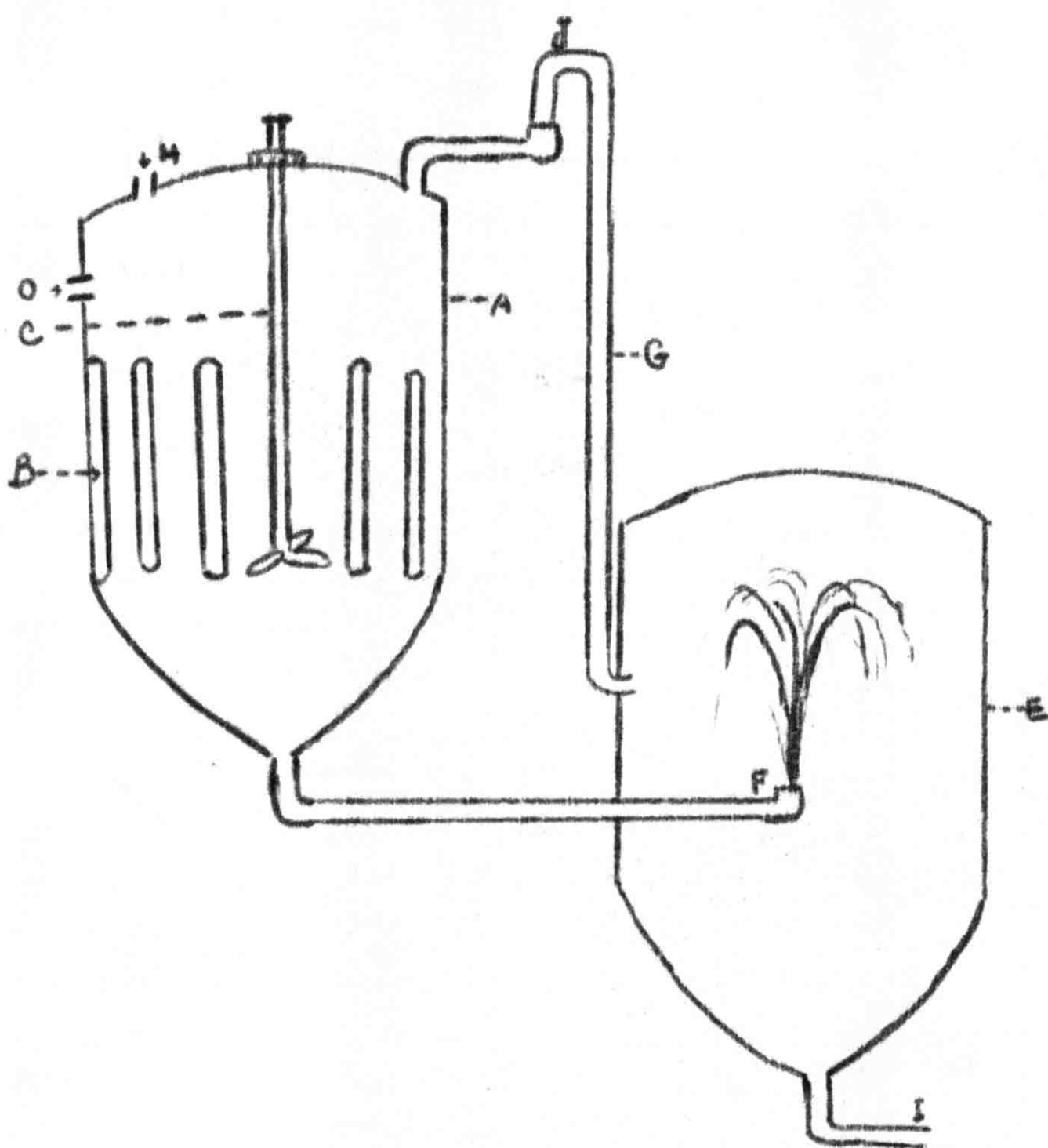


Figure No. 6

A second modification (fig. No.5) involves a tower A, filled with catalyzer C, which may be in the form of nickel supported on coarse fragments of pumice . By the pipe O , oil is admitted to the chamber in an atomized or finely divided state. Hydrogen gas enters the pipe H. Erdmann states that the temperature of treatment should be from 170 to 180°C. The treated oil is drawn off at D₂ while the excess of hydrogen passes away at B.

Another two patents relating to the spraying of oil in a chamber containing compressed hydrogen have attracted attention . In both patents the catalyst is not precipitated on pumice, but it is pumped with the oil . The principle of both devices may be made clear by fig No.6 .

Oil and catalyzer are pumped through the pipe O, into the tank A, and hydrogen is admitted by the pipe H, to furnish a gas pressure of 15 atmospheres . The tubes B are heated by steam and the stirrer C circulates the oil and catalyzer in the tank A until the oil has become heated and presumably somewhat hydrogenated . The oil is allowed to pass into the adjacent tank E, entering this tank by the spray nozzle F. Hydrogen gas is admitted to the tank E. A series of tanks may be arranged with a constantly decreasing pressure so that the differential pressure enables the spraying of the oil from tank to tank . The proposer of this method states that spraying the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50 .

As catalyzer, the proposer, recommends finely divided palladium or preferably nickel the latter being two to three percent by weight of the oil . As a treating temperature 160 to 170°C is mentioned .

Ellis uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction . The tubes are heated by jackets, The arrangement permits of dif-

ferential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydrogenation at any given point .

Catalyzers :

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent .
oxide has been employed by some investigator . Wimmer recommends organic salts of nickel
Nickel^{oxide} such as the formate . The preparation of an effective nickel catalyzer requires considerable care, since with a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure, almost it (seems) seems, independent of the nature of the hydrogenating apparatus . In the case of nickel catalyzer, the ^{oxide} acid or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from say a nickel sulphate solution by the addition of an alkali. The next step is the reduction to metallic nickel . For this purpose the nickel oxide is placed in a receptacle which may be heated controllably and hydrogen gas is passed over the mass at a temperature ranging between 250 to 500°C., or so until water is no longer evolved .

Catalyzers made from the oxide without supporting material are hardly as efficient as when the active surface is increased by the use of a carrier . Hence we find many proposals for the production of catalyzers with a great variety of carriers .

Wibbuschwitch proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotatory drum . The temperature during the treatment is stated to be 500°C. The same investigator has patented a process of regenerating spent catalyzers of the nickel type . The process involves the extraction of the spent catalyst with benzine, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing .

Seeking to overcome the disadvantage of ready oxidation in the air possessed

by normal catalytic nickel . Kayser, reduces the nickel oxide or equivalent material at a temperature of 500°C. and then passes through the reduced material a brisk current of Carbon dioxide until the escaping gas proves no longer inflammable . By this method it is claimed that a catalyzer is obtained which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy .

Other catalyzers, besides nickel were also proposed ; palladium being the most attractive catalyst as to its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperature . As a matter of fact, some investigators on catalyzers consider palladium as the most powerful of all catalyzers; reduction with this catalyst takes place readily at 80 to 90°C. while with nickel a temperature of 180 to 200°C is necessary for practical hydrogenation .

Paal worked with colloidal palladium preparation and hydrogenated a number of liquid oils. He found that sesame oil, when hydrogenated showed the Boudoin reaction but very faintly, while cotton-seed oil, after hydrogenation is no more detected by Halphen reaction.

Karl has studied, with considerable care and in a quantitative way, the action of palladium supported on various bodies . He found that palladium precipitated on finely divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminium, iron or zinc, little or no hydrogenation was effected owing to the anti-catalytic action of these metals .

Catalyzer poisons :

The main difficulty in using nickel as a catalyzer is the hydrogenation of a low-grade oil being the life of the catalyst is relatively short . On the other hand, when hardening a good grade of oil, such as, refined edible cottonseed oil,

the life of the catalyst is very long and it may be used for months in the constant operation of a hardening plant .

The short life of the catalyst used in the hydrogenation of unrefined oils is undoubtedly due to the presence of some materials which hinder the activity or poison the catalyst . Chlorine, bromine, sulphure in the form of sulphide, arsenic and other substances have been recognized as poisons .

Ellis and A.A. Wells have made an extensive investigation on catalyzers poisons with reference to the hydrogenation of fatty acids . They have determined the effect of halogen, halogen compounds, sulphure, etc., on hydrogenation of cottonseed oil (For further detail refer to Ind. Engin. Chem., vol.8, 1916).

Hydrogen :

One of the problems in the hydrogenation of oils is that a cheap supply of pure hydrogen being necessary .

The two methods now most used in the hydrogenation practice are the iron sponge steam process and the electrolytic method . The first method is demanded in large plants, and it is scarcely asked for by the small plants .

Very promising methods for the production of hydrogen are :

- 1-. The removal of carbon monoxide and hydrocarbon from water gas by liquification.
- 2-. The decomposition of petroleum at high temperatures .
- 3-. The passage of water gas and steam at a temperature of 500°C. over lime containing an iron catalyst .

Hydrogen at high temperature and pressure has an extra-ordinary penetrating power, this property must be taken in consideration in the designing of a hydrogenation kettle . A testing tank having an oil capacity of about one ton was tested to 150 pounds air pressure and found to be tight, but when hydrogen was

introduced at 60 pounds pressure, the leakage was tremendous .

Autoclaves with welded seams are desirable for high pressure and high temperature work . Moving parts should be avoided as far as possible .

Uses of hydrogenated oil :

The preparation of fatty oils of almost any desired degree of consistency renders hydrogenation especially attractive in the production of edible fats and soap-making materials . Moreover hydrogenated oils may be used in the manufacture of lubricants .

By hydrogenation, oils which formerly made soaps only of soft consistency now yield the most valuable hard soaps . This has led to a very rapid development of the process of hydrogenation . Fish and whale oils may be completely deodorized by the addition of hydrogen, and can be used in soap-making .

The odor of fish oil is due entirely to a fatty constituent and not to so-called impurities (1). This fatty constituent is cupanodonic acid having the formula $C_{17}H_{33}COOH$, which therefore, by the addition of 8 hydrogen atoms, becomes stearic acid . When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent . Even the fishy taste is scarcely recognized .

Some people claim the hardened or hydrogenated fats have the advantage that a weaker brine suffices to separate the soap from glycerol, further, that the soap produced from such hydrogenated fats is exceedingly hard. This of course, enables the admixture of a larger proportion of rosin, which naturally would be looked upon as a decided advantage . In contrast to this a German writer states that soap produced by the hydrogenated oils is too hard to give a good lathering

(1). According to a Japanese Chemist, Tsajimoto .

properties .

Since soaps are made almost invariably of mixture of fats, it is under the control of soap-makers to use such an amount of hydrogenated fat as would give the requisite degree of hardness without sensible diminution in lathering power; hence the foregoing criticism seems to be invalid .

Edibility of hydrogenated oils :

It is generally accepted by those who have investigated the matter properly that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived . It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature , hydrogenation renders the oil better adapted for human consumption .

A question of serious import has, however, arisen in the use of nickel catalyzer. Aside from the fact that by careless filtration, traces of the suspended nickel may be present in the product, there is the most serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed .

Nickel is dissolved in oils during the hydrogenation process only when the latter contains free fatty acids in considerable amounts . A sample of hydrogenated sesame oil containing 2.5 percent of fatty acid was found to contain 0.01 percent ash with 0.006 per cent, nickel oxide .

Nickel in its metallic form cannot combine with a fatty acid to produce a soap except with the elimination of hydrogen gas, and in an atmosphere wholly of hydrogen; because of the mass action such reaction is not likely to take place . On the other hand, nickel in the form of oxide would yield water on combining with fatty acids where the pressure of water upon is very small . Hence it seems that in the manufacture of products intended for edible purposes care must be taken to keep

the nickel in the metallic state . Also it is desirable not to force the reaction too rapidly with the consequent danger of breaking down the carboxyl group and setting water which would react to produce fatty acids .

Experiments on the hydrogenation of sesame oil :

An attempt was made to hydrogenate sesame oil and convert it into a solid fat but the lack of equipments has put many obstacles in the way of this attempt . Several experiments were performed using the catalyzer in different forms, yet none of these has led to success . The iodine value of the hydrogenated oil has decreased in some cases considerably but in non of them the iodine value became less than 60, so as to make a solid fat at room temperature . Few experiments are mentioned below in accordance with the iodine value of the product .

Experiment No .1

Preparation of the catalyzer :

The finely divided nickel which was used as a catalyst in this experiment was obtained by the reduction of nickel oxide as follows :

Nickel^{oxide} was spread in a thin layer over the surface of a composition tube, which was heated by twenty buhsen burners . Hydrogen prepared by the interaction of zinc and hydrochloric acid in Kip's generator was passed into the tube . The purification of hydrogen gas was accomplished by means of three U-tubes one contains calcium chloride to remove the moisture, and the rest contain peices of sodium hydroxide to remove the halogen acid which may pass with the hydrogen gas . No thermocouple was available to measure the reduction of temperature . When the reduction was complete a convenient amount of the catalyzer was added to the sample of the sesame oil which is ^{contained in} a 500 c.cs. round-bottomed flask .

The flask containing the oil and the catalyst was heated in an oil bath at

a temperature ranges between 135 and 150°C. Hydrogen gas prepared and purified by the above mentioned way was passed through a tube reached almost the bottom of the flask, so as to agitate the catalyst and provide a thorough mixing of the catalyst with the oil. The hydrogen which evolved after it had passed through the oil was conducted through a long rubber tubing and carried far from the flame. Hydrogen gas was passed by this way through the oil which contains the catalyst for six hours.

The oil undergone this process of hydrogenation practically did not change in consistency or in the degree of unsaturation. The iodine value was only reduced from 108.3 to 102.7.

The failure of this method is probably due to incomplete agitation of the catalyst in the oil, the passage of hydrogen in this way does not permit good contact with the surface of the catalyzer. The nickel oxide used as a raw material for the production of the catalyst is not chemically pure, and lastly no pressure was employed.

Experiment No. 2

The preparation of the catalyser for this experiment is similar to that used by Kelber. The procedure is as follows:

Dissolve 40 grs. of nickel nitrate or sulphate in enough water to cover 20 grams of lump pumice, and evaporate the solution to dryness on the steam bath. Put the prepared pumice in a solution of sodium carbonate and heat on a steam bath under reduced pressure to drive the air from the minute holes of the lump pumice until all of the nickel is in the form of the carbonate. Pour off the water layer and wash the pumice from the excess of carbonate. Decompose the nickel carbonate by adding it to an aqueous solution of formic acid and once more

evaporate the solution to dryness on the steam bath . Put the dry lump pumice in the combustion tube and heat in order to decompose the formate , a slow current of hydrogen gas is passed through the tube during the decomposition period to keep the finely divided nickel, which is formed as a thin layer over the lump pumice, out of contact with air; otherwise it may lose some of its activity .

The catalyzer is dumped into the oil which is placed in 500c.cs. round-bottomed flask, and heated by an oil bath to a temperature ranges between 160 and 180°C. Purified hydrogen gas is passed into the flask, by the same way which is used in the previous experiment, for ten hours .

The hydrogenated oil is thicker than that of the first experiment and the result is better, yet the process is still unefficient. The iodine value of the hydrogenated oil is 91.3

It should be noticed that this process is liable to the same errors committed during the first experiment, except the purity of the catalyst used in the experiment is guaranteed and the contact surface is more .

Experiment No. 3

In contrast to the first and the second experiments, the catalyzer in this experiment was prepared by the wet method . It involved the same steps used during the preparation of nickel formate in the previous experiments. However, the nickel formate after drying was put in the oil which was intended to be hydrogenated . The oil containing the nickel formate was heated by means of an oil^{bath} to a temperature of 240°C in order to decompose the nickel formate, where a slow current of purified hydrogen gas was passing during the decomposition of the formate; The hydrogen gas was allowed to pass through the oil for eight hours . The temperature of the oil ranges between 160 and 180°C .

The hydrogenated oil was filtered and the iodine value of which was determined; this value being 68. The oil obtained is thicker than that obtained by the first and the second experiments, but the process is still unefficient and of no practical use .

Another experiment involving the same steps and under the same condition of the third experiment was carried out, except the temperature at which the hydrogenation took place was 130°C. The iodine value of the hydrogenated oil is 87.8 . Thus the temperature of the oil during hydrogenation by this method should be kept at 160 - 180°C.

Experiment No. 4

The method used for the hydrogenation of sesame oil in this experiment is different from those of the other experiments . The catalyst is platinum instead of nickel and the flow of oil and hydrogen gas being according to the counter current principle . The detail of the process is as follows :

Preparation of the catalyzer : Finely divided platinum was precipitated on a platinum thimble by the electrical decomposition of platinic chloride .

The whole apparatus was made of pyrex glass (See fig. 7), the oil in the flask O, was heated by means of an oil bath H, to a temperature of 140°C. The rate of the flow of oil was adjusted at M; and the oil was passed through the tube D, to the platinum thimble . Purified hydrogen gas was allowed to pass through the tube A to the platinum thimble where it met the oil and it leaves through B. Hydrogenation of the oil was taking place at the surface of the platinum thimble. The hydrogenated oil flow through the tube E to the reservoir C which is contained in a water bath to prevent the solidification of the hydrogenated oil . When the level of the oil reaches L. it will be transferred into the container T, by means

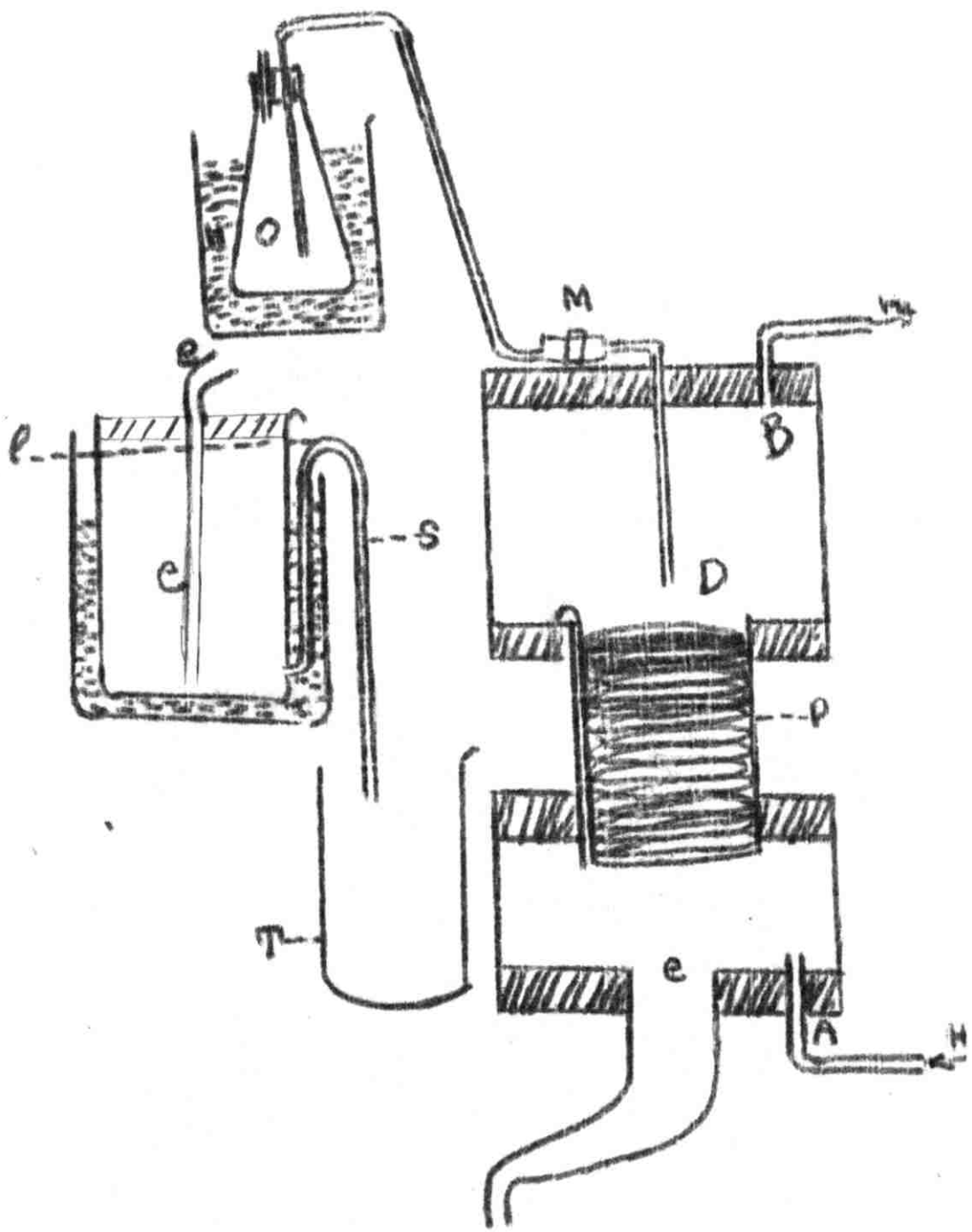


Figure No. 7

of the syphon tube S. The oil, in the container T, is carried again to the flask O and the process was repeated several times .

The process was not successful and the oil obtained was still liquid, the iodine value of which is 94.1 . The failure of this experiment is due to incomplete heating of the oil and the thimble . The oil at O is hot, but when it passes through the tube D it gets cold; because the flow of the oil should be slow enough to admit good contact with hydrogen gas on the platinum surface . Otherwise, if the oil is allowed to pass rapidly there will be no time for hydrogenation to take place at the surface of the platinum .

The fault may be mended and the process may be rendered promising by heating the platinum thimble by means of a resistance wire, but this was not available in our laboratories .

The failure of the second and the third experiments is due, undoubtedly, to the following factors :

- 1-. There is only one stream of hydrogen passes through the oil which is mixed with the catalyzer . Hydrogen gas should be passed through a perforated plate, or similar equipments such as coils with many fine holes in order to provide numerous streams of hydrogen gas to pass through the oil and the catalyst . Thus a good contact of hydrogen with the catalyst is obtained .
- 2-. The temperature at which the reduction of the catalyst takes place is not adjusted properly which is a matter of great importance in the practice of hydrogenation .
- 3-. The application of pressure is necessary in many cases, since the pressure favors the reaction to pass through the desired direction .

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