Part IV. Advantages of the Fermentation Process.

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The "autoclave" process for the manufacture of glycerine has the advantage that it yields a high grade crude glycerine which is readily purified by distillation; it has, however, various drawbacks the more important of which are:—

(a) The relatively high cost of the plant; it is stated that the cost of an autoclave is about 10 times that of a "Twitchell splitting" vat of the same capacity.

(b) The autoclave process produces a 90 per cent. saponification under normal conditions as compared with 94—95 per cent. decomposition by the Twitchell process.

(c) The fatty acids formed are partly in the form of calcium or zinc salts and a treatment with sulphuric acid is essential before good quality fatty acids can be obtained.

A comparison of the Twitchell and Lipase Fermentation processes indicates that there are no outstanding differences: in fact the two methods are very similar. In order to arrive at any conclusion as to their relative merits with reference to both initial and working expenses, it is necessary to enter rather more fully into details. For this purpose a brief account of the Twitchell process is given and is followed by a short comparative statement of the two processes.

Splitting process with ordinary Twitchell reagent.

1. *Preliminary refining of the oil.* This is essential for most vegetable oils and consists in heating the oil with sulphuric acid (60°B=78 per cent) for one hour. The oil is first raised to a temperature of 30—50° by means of direct steam and whilst stirred by means of an air blast about 1·25 to 2·0 per cent of sulphuric acid (60°B) is added in a slow stream. At the end of one hour the mixture is allowed to settle. If possible it is kept for 36 hours when the dilute acid (15—20° B.) is run off from the bottom and the clear oil is ready for the first splitting.

2. *First Splitting.* For every 100 part of oil to be hydrolysed 20 parts of glycerine water from the 2nd splitting of a previous run are put into a tank and brought to the boil by means of an open steam coil, 0·1 per cent of sulphuric acid and 0·5 per cent of Twitchell reagent previously diluted with soft water, are run in and the whole thoroughly mixed. Whilst still agitated

by means of the live steam the 100 parts of purified oil are added and the man-hole closed. The mixture is kept agitated and emulsified by means of the steam and after about 5 hours 0·2 per cent. of sulphuric acid and after a further 5 hours another 0·2 per cent. of the acid is run in. At the end of 32 hours the first splitting is complete and the ratio fatty acids: glycerine water should be 100: 65. Steam is then shut off and the glycerine liquor allowed to settle; whilst this takes place steam is passed into the upper part of the vessel in order to prevent entrance of air and discoloration of the fatty acids. After about one hour the glycerine liquor may be drawn off.

3. *Second splitting.* Ten per cent of water is added to the oil left in the splitting vessel and the whole kept in motion for a further period of 12 hours by means of live steam. At the end of this time when the splitting is complete, about 0·05 to 0·06 per cent of barium carbonate, ground with water to form a cream is added and the whole stirred for about 15 minutes and then allowed to settle. After one hour the 2nd glycerine liquor is run off and is used for the next batch of oil to be treated.

4. *Treatment of the glycerine water from the first splitting.* This is generally neutralised with lime (about 2·4 parts for every 100 parts of of liquid) until the addition of a few drops of phenolphthalein produces a pink coloration. The calcium sulphate which remains dissolved in the dilute glycerine liquor (6—7°B) is apt to cause trouble during the subsequent evaporation and the addition of small amounts of barium carbonate and finally barium hydroxide is sometimes employed.

5. The length of time required for the complete splitting (40—48 hours) can be reduced by using a larger proportion of the reagent; this, however, increases the cost and at the same time is apt to produce darker coloured fatty acids and a lower quality glycerine

II. *Splitting by more efficient Twitchell Reagents.*

1. A reagent under the name of "double strength Saponifier" was introduced by the Twitchell Company several years ago. It has the advantage that only 0·25 per cent. is required to produce the same effects as 0·5 per cent. of the original reagent. The time required is practically the same and steam is necessary during the whole period of the splitting operation. The percentage of oil hydrolysed is much the same as in the originally process and approximates to 95.

2. "Kontakt" Reagent.

In 1916 the same company introduced a solid reagent termed " Kontakt ". This has about three times the efficiency of the original " Twitchell " reagent: 0·5 per cent. gives much the same results in 15—20 hours as 1·5 per cent of the original Twitchell reagent.

This reagent has the advantages that larger quantities affect neither the colour of the fatty acids nor the quality of the glycerine water. As the cost of the reagent is relatively high, e. g. one shilling per pound in 1916, the use of the higher proportions is prohibitive. The reagent has practically replaced the older Twitchell reagents. It is claimed that the colour of the fatty acids obtained is equal to that of the original oil and that the glycerine water is of good colour and quality.

The general method of procedure is practically the same as with the older reagent.

When vegetable oils are used these are subjected to a preliminary process of refining and are then run into the splitting vat which already contains water (25-33 per cent by weight of the oil), sulphuric acid of 66° B (0·1 to 0·3 per cent.) and saponifying reagent (1 per cent). The whole is emulsified by means of steam and after 6—9 hours the first splitting is complete. The first glycerine water is then removed and the 2nd glycerine water from a previous run is added to the oil together with 0·1 to 0·2 per cent. of sulphuric acid and the boiling continued for another 2-3 hours.

III. *The Plant required in a "Twitchell" Factory.*

The plant consists of wooden or iron vats in either case lined with lead. A usual capacity for a unit plant is 5 tons and and each comprises :—

a) Vat for preliminary refining of the oil. This is provided with an air blast and an open steam coil of lead

b) The splitting vat which is closed with a tightly fitting cover provided with manholes and leaden open steam coils.

c) The neutralising vat for the 1st glycerine liquor, provided with both open and closed steam coils of lead.

d) The vat for final treatment of the fatty acids with a little carbonate of soda solution in order to remove traces of sulphuric acid. This is of iron and need not be lead lined and is provided with a closed steam worm of iron and an iron cross piece for blowing air through the mass.

e) Several pumps are usually employed for transferring the liquids from one tank to another and in addition a filter press or filtering column is required for the glycerine liquor.

f) Concentrating and distilling plant similar to that used in any other type of factory for the production of dynamite glycerine is also necessary, but as this is essentially the same whichever of the three methods is employed—the autoclave the Kontakt or the Fermentation—the cost is the same in each case.

IV. *Plant Necessary for a Fermentation Factory.*

The vats for the preliminary treatment of the oil and for the neutralising of the glycerine water would be exactly the same as in the "Kontakt" process, with the exception that there would be only one glycerine liquor in each run and the volume of this would be less than in the "Twitchell" process, as the Fermentation process yields a glycerine water of higher concentration.

The main vats for the actual splitting would be simpler as they could be made of wood: the lead lining and lead steam coil would not be necessary.

The vats would be furnished with some method of agitating the mixture undergoing hydrolysis; as the mass is somewhat too viscous for air agitation, mechanical stirrers would be essential. The stirring would only be necessary during the first 4 hours in each run.

The simplest plan would be to transfer the emulsion from the splitting vat to a special vat for the purpose of breaking the emulsion and separating the glycerine water. This vat should be provided with a conical bottom, should be lined with lead and provided with a closed steam coil also of lead.

As the splitting takes about 28 hours and the breaking of the ferment and the separation of the glycerine water only 2—3, one such vat could be used in conjunction with at least 4 splitting vats.

Most of the other plant such as pumps, filter presses and evaporators would be the same as in the "Kontakt" process.

V. *Relative costs of the "Kontakt" and Fermentation Processes.*

1. The following savings would be effected in the Fermentation as compared with the Kontact process.

(*a*) *Capital Costs.* The absence of lead linings and leaden heating coils in the splitting vats would mean an appreciable saving in both the original cost of the plant and in upkeep. Against this has to be set off the cost of paddles or stirrers in the splitting vats for the fermentation process and the greater vat-capacity required for the latter process, as with the "Kontakt" process using one per cent of reagent each run takes 12 hours and in the fermentation process a run takes from 24 to 28 hours.

Extra capital costs in the fermentation process would be entailed in the provision of a small decorticator, edge runner mill and basket centrifuge for the production of the lipase preparation.

(*b*) *Working Costs.* 1. *Steam.* As the fermentation proceeds readily at the ordinary temperature in India, namely 25—32°C., there is no necessity for steam heating during the splitting process. Steam would only be required for the breaking of the emulsion at the end of the hydrolysis. Against this saving has to be set the extra power required for working the stirrers during the first four hours of the splitting process.

2. *The Splitting reagent.* In the "Kontakt" process each ton of oil requires 22·5 lbs. of reagent at one shilling per pound*

In the fermentation process each ton of oil requires about 1 cwt ** of decorticated castor seeds and either 2 lbs. of glacial acetic acid or 4 lbs. of crystallised manganous sulphate. The 1919 London prices for these chemicals are both about 9d. † per pound wholesale.

The cost of decorticating the castor seeds, grinding to a pulp and centrifuging the pulped mass and depreciation on the plant necessary should be far less than the difference between the cost of Kontakt reagent and of the castor seeds plus activator (acetic acid or manganous sulphate).

3. *Sulphuric acid and its neutralisation.* For the Kontakt process 7 lbs. of sulphuric acid per ton of oil are used and in the fermentation process under 4 lbs.‡ This also means the use of

*. This is the London price in 1916, the price in India would be more.

** The whole cost of this seed must not be regarded as the cost of the ferment comparable with 22·5 lbs. of 'Kontakt' reagent, as the oil present in the seed augments the amount of fatty acids produced, or alternately the seed can be cold pressed, the oil sold as high grade castor oil and the cake used for making the ferment.

† The pre-war price of manganous sulphate was only 1·5 pence per pound, wholesale.

‡ In comparing the fermentation process worked in India with the "Kontakt" process worked in Europe the extra price of the acid in India would quite compensate this difference in the quantities used.

less lime or barium carbonate in the subsequent neutralisation. The same process of neutralisation could be used in the two cases.

4. *Evaporation costs.* As the glycerine water from the fermentation process is more concentrated than that from the "Kontakt", the evaporating charges would be correspondingly reduced.

This brief summary indicates that the fermentation should cost on the whole rather less than the "Kontakt" process and as the latter is stated to be the most economical method of working up oils and fats for glycerine and fatty acids, the fermentation process appears to be the cheapest for India.

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