

NEW DEVELOPMENTS IN SUNFLOWER OIL REFINING  
AND SOAPSTOCK SPLITTING

By

Mr. Gunnar Haraldsson  
Afla-Laval, The De Laval Separator Company  
A. B. Separator Division  
Tumba, Sweden

Though the sunflower has been known for several hundred years as an oil producing plant it has not got its important position until the last decades. However, the production of sunflower seed as a source of oil and protein is now increasing rapidly and the sunflower oil represents already about 10% of the world-production of fatty oils. This is not surprising as sunflower oil has some very attractive properties as an edible oil (e.g. fatty acid-composition) and as it can be cultivated with good yield to competitive prices in the proper climate. As all other oils sunflower oil has its own, special characteristics and the processing therefore requires special attention. In the following some special techniques, which with success has been tried on sunflower oil refining will be described. The first problem to be discussed is the dewaxing of sunflower oil and the second is the splitting of soapstock from sunflower oil.

Both expeller pressed and extracted sunflower oils contain a small percentage of waxes (normally less than 0.5%) mainly originating from the seed husk. Some properties of the sunflower oil and the waxes are shown in fig. 1. Due to the high melting point of the wax and to its low solubility in the oil, a cloudy precipitate will be found in the refined and bleached oil when stored at refrigerator temperature or even at room temperature if the waxes not are removed from the oil. Up to the present day the standard procedure for sunflower oil refining has been a conventional lye refining, continuous or batch, at 70 - 90°C, event. followed by a bleaching with Fullers earth and then a chilling of the oil to a low temperature where the waxes are precipitated. The waxes are then removed by filtration and the oil is after deodorization ready as a high quality edible oil with a good cold test. The above mentioned filtration is, however, a difficult and slow operation which requires a large filtering capacity and makes the operation quite expensive as also the labor requirements are high. The maximum filtration speed has in some cases been reported to be 1 - 2 kg oil/m<sup>2</sup> an hour (corresponding to about 2 - 4 lbs/ft<sup>2</sup> x h.)

In order to get away from this disadvantage a modified refining operation has been developed which eliminates the need for the above mentioned filtration. The principle of the new technique is based on the fact that the wax has a polar nature and shows hydrophilic properties. If an oil containing waxes, is mixed with water or an aqueous solution at a relatively low temperature, the waxes are concentrated to the surface between oil and aqueous solution and can under suitable conditions be removed from the oil by separation of the oil from the aqueous phase.

To facilitate a comparison with conventional refining this is first shortly mentioned, compare fig. 2 where a 3-stage refining plant is shown.

The crude oil enters the plant via pump P 1 and is heated to about 80 - 90°C and is then treated with a gum conditioning agent such as phosphoric acid in the reaction mixer M 1 and then continually neutralized with caustic in the special mixer M 2 before separation takes place in the first centrifuge S 1. Here the soapstock is separated from the neutralized oil which goes to the next sections. In the following refining sections another caustic wash or a water wash is carried out before the oil goes to vacuum drying and to bleaching. This refining method gives an oil which still contains the waxes, which have to be removed as described, normally by chilling the oil and filtering.

The new refining technique for simultaneous removal of waxes and gums is illustrated in fig. 3. The crude oil is chilled down in a plate heat exchanger to the desired temperature, normally about 10°C and then kept at this temperature for about 2 - 4 hours in a heat isolated tank, fitted with a slow rotating stirrer. From this tank the chilled oil is metered by a pump into the first of the two mixers, where the oil is treated with special agents. In order to get a good degumming it is necessary to treat the oil with phosphoric acid (about 0.1 - 0.2% by vol.) which is done in the first mixer. In the second mixer an aqueous solution containing a wetting agent such as sodium lauryl sulphate is added. Here occurs the transfer of the waxes and lecithins to the aqueous phase which then is removed from the oil in an hermetically closed centrifuge. The oil is then heated to normal refining temperature, about 80 - 90°C neutralized with caustic and washed with water as described above.

A principal drawing of the centrifugal separator used is shown in fig. 4. The process can be further simplified by adding the caustic to the cold oil (10°C) in which case the soap formed act as a detergent and remove the gums and waxes together with the soapstock. As a matter of fact this is not quite a new idea and some older patents have described similar processes as a combination of the refining and the winterization process but the idea seems not to have been used industrially. A matter of great importance is the refining losses which can be expected to become higher as the neutralization and separation is made at a low temperature. Laboratory tests on a pilot plant scale have, however, shown that this operation works quite satisfactory. The dewaxing and the refining equipment can thus consist of the apparatuses as shown in fig. 5 and in this case only two refining sections are required, i.e. the first for the removal of gums, waxes and the soapstock and the second for the water washing. If the crude sunflower oil is high in free fatty acids, say over 2%, it may be preferable to use the 3-stage operation (a cold degumming and dewaxing stage, followed by a hot neutralization stage and washing stage) in order to minimize the total refining losses. In fig. 6 is shown results obtained in pilot plant tests, comparing the different methods. The crude oil with a FFA of 1.5% and a lecithin content of 0.6% is a mixture of pressed and extracted oil. The wax content is difficult to analyse but it is estimated to about 0.4%.

If this oil is refined in the conventional manner at high temperature the refined oil develops a heavy cloudiness at room temperature consisting of very small wax crystals. After cooling this oil to 8°C storing for 4 hours and filtering an oil which a cold test of about 3 days at 0°C was obtained. In another test the oil was degummed and dewaxed at 8°C and after that refined at 85°C, washed and bleached. This oil had a cold test of 5 days at 0°C. Finally the results from a test where the oil has been neutralized at 8°C without any prior separate degumming and dewaxing are

shown. This gave an oil with a cold test more than 5 days at 0°C. If we look at the losses we can see that the conventional refining gave a refining loss of 2.5% and a dewaxing loss of 1% or in total 3.5%. This is about the same loss that has been obtained also in the other tests, described in fig. 5. The economical advantage with this modified refining method lies thus not in a better total yield of oil but in a simplified technique which reduces the capital costs as well as the operating costs.

The splitting of the soapstock from sunflower oil can in some cases be done without difficulties and be carried out in a normal batch splitting equipment. In many cases, however, one is met with a special phenomenon when splitting soapstock from a sunflower oil which can make the splitting very troublesome. In these cases a milky oil-water emulsion is formed which is very difficult to break. Boiling the acidified soapstock with large excesses of sulphuric acid for several hours has only small effect. This emulsion has also such properties that it can not be satisfactorily separated in a centrifugal separator bowl as the surface active forces between the particles in the emulsion are much larger than the centrifugal force created in an industrial separator. The formation of these difficult emulsions can probably be attributed to the properties of the non glycerid constituents present in the oil. To solve the problem with the above mentioned difficulties a special technique has been developed in combination with Alfa-Lavals continuous soapstock splitting plant. First a conventional splitting plant will be described and then the modifications made in order to handle the special soapstocks from sunflower oil. Fig. 7 shows a simplified flow-sheet of a continuous soapstock splitting plant. The soapstock, heated to about 90°C is fed by a pump into a mixer MT, where it is mixed with diluted sulphuric acid. If the soapstock has a high total fatty matter content the splitting is facilitated if it is diluted by water. For this dilution acid water coming from the settling tank RT via pump P 2 can be used in order to save fresh water consumption. The acidified soapstock goes from the mixer into a reaction and settling tank where agglomeration of the fatty (phase) and separation of the aqueous phases occur. The fatty acid phase on the top of RT flows by gravity into a centrifugal separator together with some hot washing water. In this separator the fatty acids are separated from any mechanical impurities and traces of mineral acid, while heavy mechanical sludge automatically is shot out from the separator bowl without interruption of the separation.

The aqueous phase from the separator is (by the pump P 2 together with a desired amount of acid water from the RT-tank) mixed with the incoming soapstock as mentioned before. The acid water with a pH of about 3 formed in the settling of the acidified soapstock in the settling tank RT flows from the bottom via a monkeys tail continuously out to drain, eventually after neutralization to neutral pH or after further purification. In many cases an intermediate "emulsion layer" (consisting of lecithin, protein etc.) is formed in the RT-tank between the fatty acid layer on the top and the acid water at the bottom. This layer can be taken out from the RT-tank intermittent or continuously.

The soapstock splitting just described works satisfactorily with a number of different soapstocks as those from tallow, lard, fish oil, palm oil, coconut oil etc. and also in some cases with a soapstock from sunflower oil. If, however, the special phenomenon described above with the formation of a fairly stable oil in water-emulsion occurs, the settling of the acidified mixture does not take place in the RT-tank. It was also mentioned

before, that if all the acidified soapstock is sent to a centrifugal separator it is not possible to get a water phase out of the separator with an acceptably low fatty matter content.

To solve this problem it was necessary to change the surface chemical conditions between the phases in the emulsion. A lot of different agents were tested as additives to break the emulsion but only one had a sufficient effect to be interesting in practice. This product is a watersoluble ethylhydroxyethyl cellulose and its structure is shown in fig. 8. This product is manufactured commercially and sold under the trade name "Modocoll".

The use of this additive in splitting of sunflower oil soapstock is described in connection with fig. 9, where is shown also the additional equipment compared to the standard plant.

Modocoll is dissolved in cold water to a solution (about 1 - 5% concentration) and entered into the soapstock in an amount corresponding to about 50 ppm Modocoll of the total soapstock volume. The soapstock with Modocoll is then mixed with the sulphuric acid and the acidified mixture is transferred to a reaction tank. Due to the addition of Modocoll the oil-in-water emulsion has got other properties and it will separate into an acid oil layer and a clear acid water layer after a certain time. This separation is, however, not as fast as normally is the case with other kinds of soapstock and therefore it is necessary to have a longer retention time in the reaction tank. In order to make possible a continuous operation of the whole plant, it is therefore suitable to work with two reaction and settling tanks as shown in fig. 9. That means, that while one of the tanks is in operation, e.g. receiving acidified soapstock and giving away acid oil and acid water, the other tank is full of acidified soapstock which gets some time to "ripen" and settle in its phases. Simply by switching the feed of acidified soapstock from one tank to the other, the plant can be kept in continuous operation. The suitable size of the reaction tanks are depending on several factors as the total capacity of the plant.

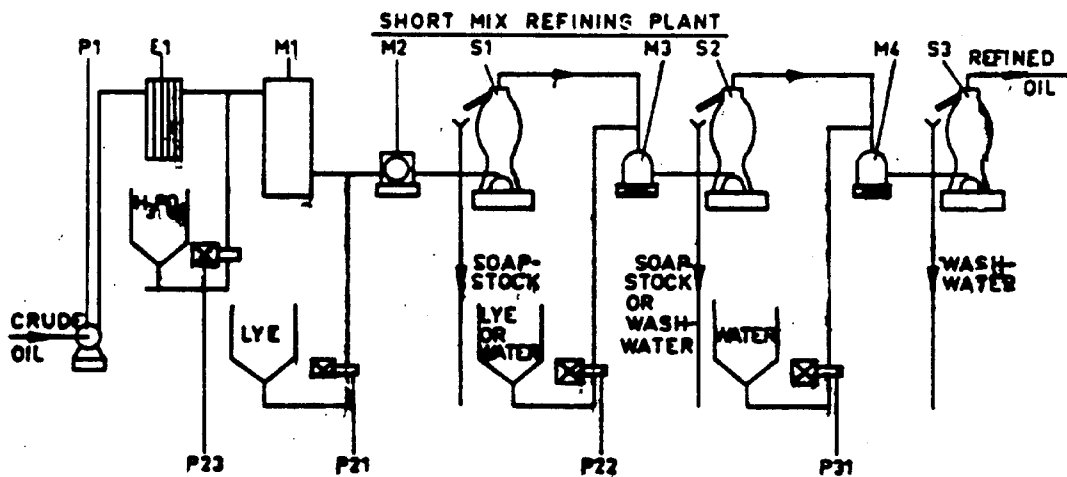
The soapstock from a well degummed sunflower oil is normally easy to split while a soapstock, which also contains a higher content of gums makes difficulties as described above. By the addition of Modocoll to the soapstock this problem can be solved, but still the gums can make trouble by forming the earlier mentioned intermediate layer in the reaction tanks. This is also the case for other soapstocks derived from lecithin containing oils as soybean oil, peanut oil etc. In order to overcome these inconveniences it is possible to introduce extra equipment for a more or less complete saponification in a soapstock splitting plant. In fig. 10 is shown how such a saponification section can be constructed. As it sometimes may be necessary to saponify the soapstock in a fairly diluted solution it is not possible to make the saponification with a high concentration of sodium hydroxide. Therefore it is of advantage to work at an elevated temperature, say 150 - 160°C in order to reduce the reaction time to get the desired degree of saponification. A FFA content in the acid oil of over 95% can normally be obtained with a saponification time of about one hour. A full saponification of a sunflower oil soapstock will also normally facilitate the separation of the phases after acidification. Thus, a combination of saponification of the soapstock with the use of Modocoll additive makes it possible to get a good result with splitting of sunflower soapstock which otherwise may create difficulties.

Fig. 1.

SUNFLOWERSEED OIL (TYPICAL DATA)

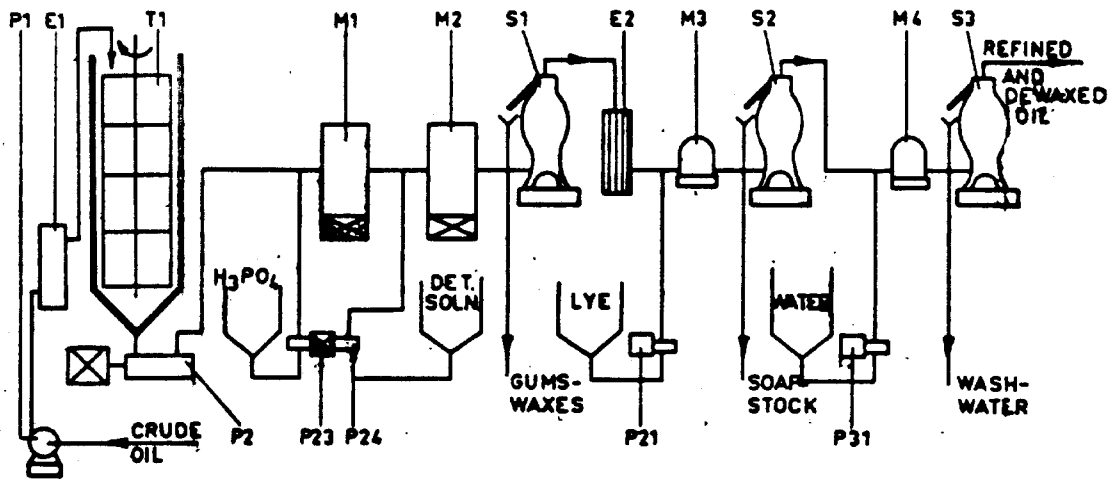
FATTY ACID COMPOSITION		GLYCERIDE COMPOSITION		WAX PROPERTIES
	%		%	
MYRISTIC ACID	0.1	MONO-UNSATURATED	1	FATTY ACIDS ..... C <sub>16</sub> -C <sub>20</sub> MAINLY SATURATED
PALMITIC - " -	7.0	DI - " -	41	ALCOHOLS ..... C <sub>14</sub> -C <sub>32</sub> MAINLY SATURATED
STEARIC - " -	3.0	TRI - " -	58	SAPONIFICATION VALUE 85-90
ARACHIDIC - " -	2.0		100	JODINE VALUE 8-12
OLEIC - " -	13.1			MELTING POINT, °C...70-80
LINOLEIC - " -	72.4			
	100.0			

Fig. 2



- S1, S2, S3 CENTRIFUGAL SEPARATORS
- P1, P21, P22, P31, P23, DOSING PUMPS
- E1 HEAT EXCHANGER
- M1, M2, M3, M4 MIXERS

Fig. 3



S1 S2 S3 CENTRIFUGAL SEPARATORS  
 P1 P21 P23 P24 P31 DOSING PUMPS  
 M1 M2 M3 M4 MIXERS  
 E1 OIL COOLER  
 E2 OIL HEATER  
 T1---RETAINING TANK

Figure 4

ALFA-LAVAL

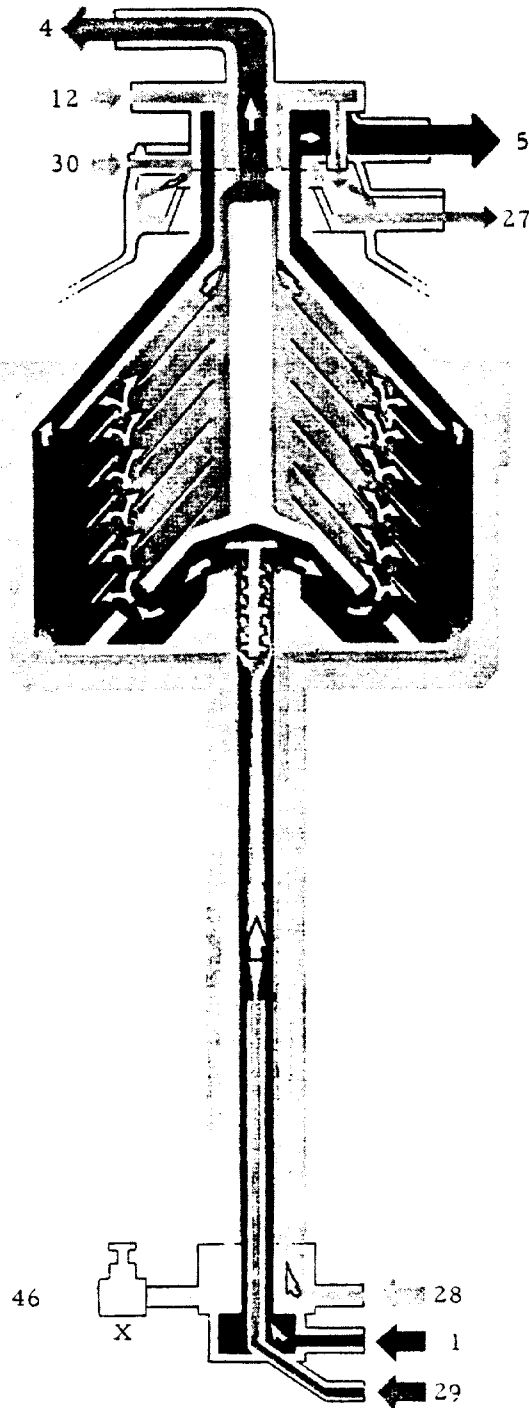
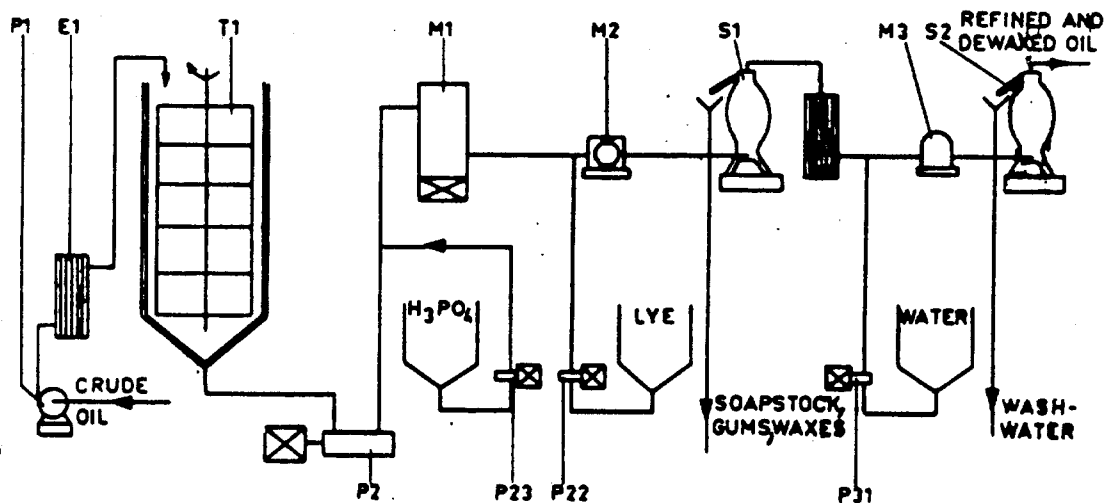


Fig. 5



S1, S2 CENTRIFUGAL SEPARATORS  
 P1, P2, P22, P23, P31 DOSING PUMPS  
 M1, M2, M3 MIXERS  
 E1 OIL COOLER  
 E2 OIL HEATER  
 T1 RETAINING TANK

Fig 6.

COMPARISON BETWEEN DIFFERENT DEWAXING AND REFINING METHODS

CRUDE OIL : FFA = 1.5 %

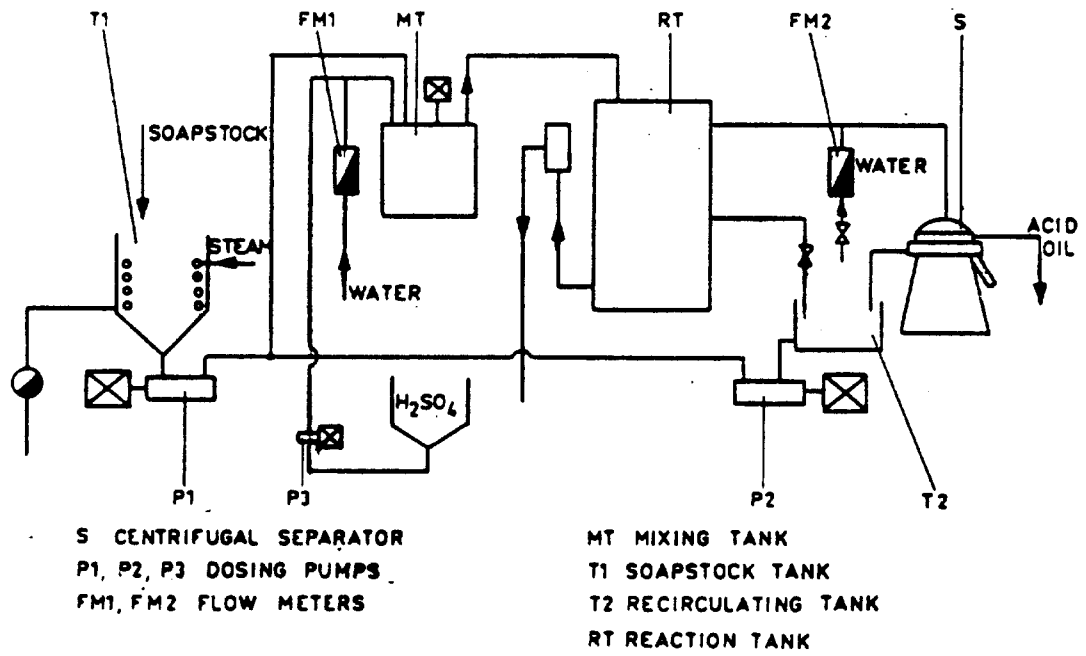
LECITHIN = 0.8 %

WAXES = 0.4 % (ESTIMATION)

TEST NO.	TREATMENT OF THE OIL	COLD TEST OF OIL (AFTER BLEACHING)	LOSSES % (EXCL. BLEACH. LOSS)
1A	H <sub>3</sub> PO <sub>4</sub> -PRETREATED, LYENEUTR. AT 85°C, WASHED	CLOUDY AT ROOM TEMPERATURE	2.5 (LECITHIN, FFA, ETC)
1B	REFINED OIL FROM TEST NO 1A COOLED TO 8°C AND FILTERED	MORE THAN 3 DAYS AT 0°C.	1.8 (WAX, OIL)
2A	H <sub>3</sub> PO <sub>4</sub> -PRETREATED AND DEGUMMED/DEWAXED AT 8°C	—	1.4 (LECITHIN WAX ETC)
2B	DEGUMMED OIL FROM TEST NO 2A NEUTRALIZED AT 85°C, WASHED	MORE THAN 5 DAYS AT 0°C	2.2 (FFA, OIL, ETC)
3	H <sub>3</sub> PO <sub>4</sub> -PRETREATED NEUTRALIZED AT 8°C, WASHED	—	3.7 (LECITHIN, FFA, WAX, OIL, ETC)



**Fig. 7**  
**SOAPSTOCK SPLITTING PLANT**



**Fig. 8**

**STRUCTURAL FORMULAS (SCHEMATIC) FOR CELLULOSE AND ETHYL-HYDROXYETHYL CELLULOSE**

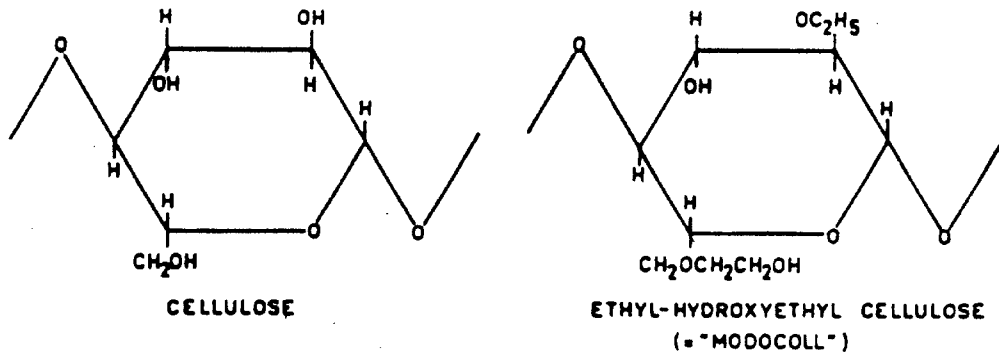
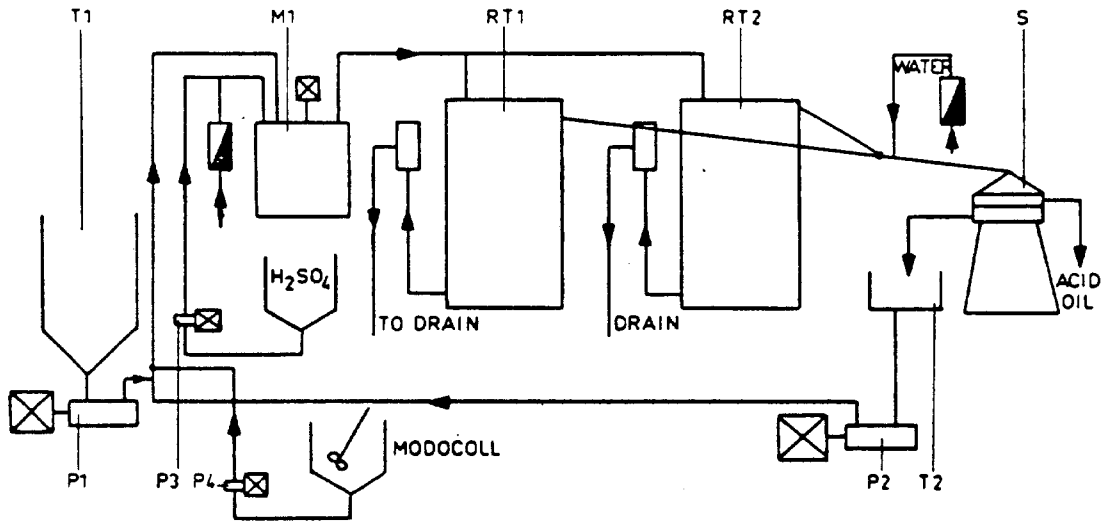


Fig 9

SOAPSTOCK SPLITTING PLANT, ADAPTED FOR SOAPSTOCK FROM SUNFLOWEROIL

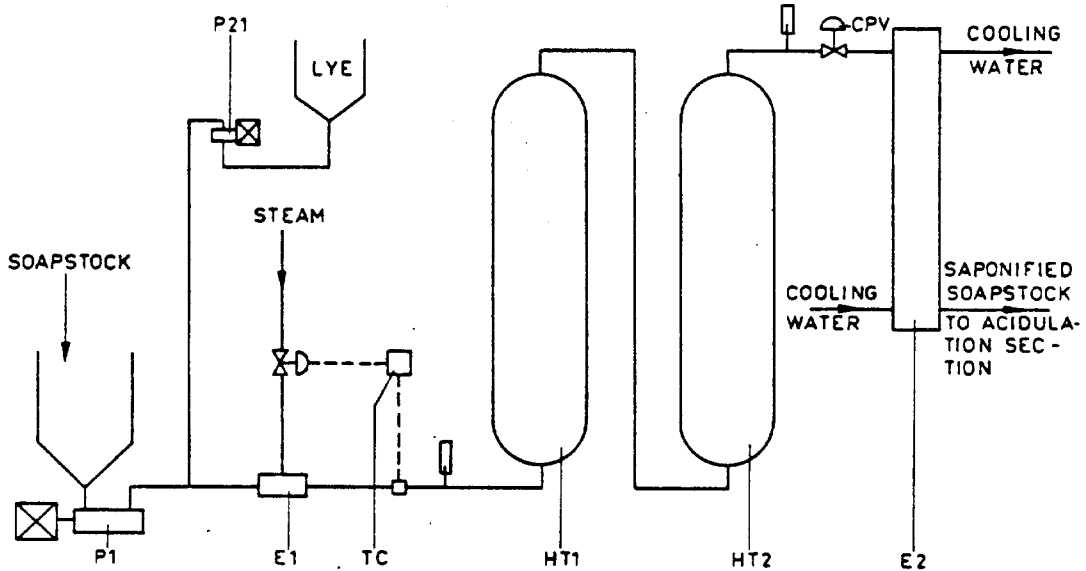


S CENTRIFUGAL SEPARATOR  
 P1, P2, P3, P4, DOSING PUMPS  
 FM1, FM2 FLOW METERS

MT MIXING TANK  
 RT1, RT2, REACTION TANKS  
 T1 SOAPSTOCK TANK  
 T2 RECIRCULATING TANK

Fig 10

SAPONIFICATION SECTION OF SOAPSTOCK SPLITTING PLANT.



P1, P21 DOSING PUMPS  
 E1 SOAPSTOCK HEATER  
 E2 SOAPSTOCK COOLER  
 TC TEMPERATURE CONTROLLER

HT1, HT2 HOLDING TANK  
 CPV CONSTANT PRESSURE VALVE