tallow fatty acids have been investigated on laboratory scale. The results of the pretreatment/hydrogenation trials are summarized in Table I. They indicate that pretreatment of the fatty acid with spent catalyst prior to hydrogenation with fresh catalyst has some influence on catalyst consumption. Approximately 40% Ni can be saved. The results demonstrate that, at least in the case of tallow fatty acids, distillation is by far the most effective way to remove impurities adversely affecting the hydrogenation process. Under the stated conditions a split tallow fatty acid yielded an IV of 9.6, using 0.25% Ni. After a straight distillation of the split tallow fatty acid, the corresponding hydrogenation trial ended at an IV of 5.8, although only 0.0625% Ni was applied.

There are also a few other methods of pretreating fatty acids prior to hydrogenation, e.g., use of bleaching earth. The cost of such purification steps has to be calculated and compared with catalyst savings. The most economical way will depend upon local circumstances.

TABLE I

Effect of Pretreatment of Split Tallow Fatty Acid (IV = 57.6) on Hydrogenation Rates[1]

Run	Pretreatment	Final IV
1 a	No pretreatment	47.3
1 b		9.6
2 a	H_2SO_4 wash	41.3
2 b		4.5
3 a	0.1% Ni (fresh), with filtration	40.8
3 b		4.2
4 a	0.1% Ni (spent), with filtration	37.8
4 b		3.3
5 a	0.1% Ni (spent), no filtration	39.2
5 b		4.4
6 a	0.05% Ni (spent), no filtration	41.3
6 b		4.4
7 a	Straight distillation	5.8
7 b		1.0

[1]Standard hydrogenation conditions: 300 g fatty acid; 200 C; 30 bar; 850 rpm; 150 min.

Run a with 0.0625% Ni; run b with 0.25% Ni.

ACKNOWLEDGMENT

G. Klauenberg provided technical assistance.

REFERENCES

1. Babuchowski, K., and A. Rutowski, Seifen, Oele, Fette, Wachse 95:27 (1969).
2. Ottensen, I., Presentation at the 6th Scandinavian Symposium of Fats and Oils, Grena, Denmark, 1971.
3. Mork, P.C., JAOCS 49:426 (1972).
4. Mork, P.C., and D. Norgard, JAOCS 53:506 (1976).
5. Drozdowski, B., and M. Zajac, JAOCS 54:595 (1977).
6. deMan, J.M., E. Pogorzelska and L. deMan, JAOCS 60:558 (1983).
7. Klostermann, K., and H. Hobert, J. Catal. 63:355 (1980).
8. Ottensen, I., and B. Jensen, Presentation at the ISF/AOCS Congress, New York, 1980.
9. Coenen, J.W.E., and B.G. Linsen, Physical and Chemical Aspects of Adsorbents and Catalysts, edited by B.G. Linsen, Academic Press, London, 1970, p. 496.
10. Coenen, J.W.E., Fette, Seifen, Anstrichm. 77:341 (1975).

Fatty Acid Fractionation by Column Distillation: Purity, Energy Consumption and Operating Conditions

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ABSTRACT

This paper discusses the optimal process conditions for production of individual fatty acids of any desired purity up to higher than 99% and describes especially the influences of column internals as well as exchange numbers, reflux ratios and fatty acid residence times at distillation temperatures. The new process conditions are characterized by degasification at low temperatures followed by efficient dehydration together with separation of first cuts at high reflux ratios by short-time dephlegmation. The design of columns for efficiency and low pressure drop is influenced by the thermal properties of crude acids and the quality demands on distillate fractions. Environmental requirements can be met by working without open steam. Bottom temperatures should not exceed 250 C, to prevent thermal degradation of fatty acids as well as corrosion of stainless steel.

FATTY ACID FRACTIONATION IN THE PAST

Industrial separation of individual fatty acids with high purity by column distillation from raw acids of natural origin such as from splitting different kinds of vegetable oils or animal fats is a fairly new technique (1-7). This process came into use mainly after World War II using bubble cap or packed columns (8-13) with unsaturated open steam (14) for lowering the evaporation temperatures to avoid thermal degradation of the heat-sensitive fatty acids (15-17). Early pioneers in this field were R. A. Potts and F. B. White (1,8,9,11-14). More recently, the economics and environmental regulations have changed decisively. Also the demands for purity have increased greatly. Therefore, new process principles became necessary which influenced equipment construction as well as operation conditions (18-26).

THE BASIS FOR A NEW FRACTIONATION PROCESS

The most important step in a new process was complete removal of open steam as part of developing new high effective column construction with very low pressure drop, together with new evaporation and condensation systems (18-25). Besides using special distillation columns of low pressure drop, today's process is characterized by effective film degasification at moderately low temperatures, followed by efficient dehydration together with separation of the odor cut as first cuts at high reflux ratios by short-time dephlegmation and a film-type pitch separation step. According to Figure 1, the precut step consists of a once-through falling film evaporator as stripping section and an enriching zone designed as dephlegmator column in the

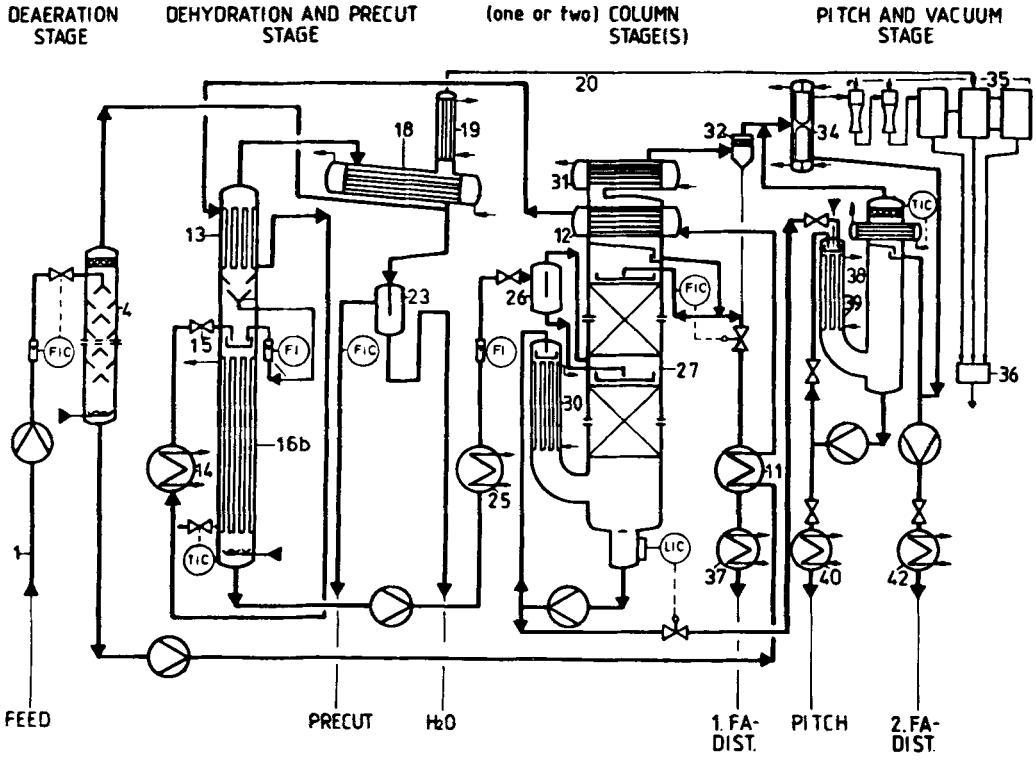

FIG. 1. Flowsheet of today's fatty acid fractionation process. (1) Feedline, (4) film deaeration stage, (11) feed preheater/distillate cooler, (12) feed preheater/column dephlegmator condenser, (13) feed preheater/precut dephlegmator condenser, (14) end-preheater, (16) precut falling film stripper, (18) precut condenser, (19) precut gas cooler, (23) precut separator, (25) column feed preheater, (26) flash pot, (27) fractionation column, (30) column film evaporator for forced circulation, (31) column end-condenser, (32) mist separator, (34) cooling trap, (35) steam ejector stages, (36) hotwell, (37) columns distillate end-cooler, (38) vapor liquid separator with condenser of pitch stage, (39) falling film evaporator of pitch stage, (40) pitch cooler, (42) distillate cooler of pitch stage.

form of a vertical film-type bundle cooler.

This new process for fatty acid distillation is based on our observation that fatty acids are extremely sensitive to heat, oxidation and corrosion effects (18-37). All are caused by the chemical constitution of fatty acid molecules with their reactive acid group at the end of a long carbon chain, mainly interrupted by one or more double bonds. As all effects are influenced by temperature and time, both have to be kept as low as possible, taking into consideration the special constitution of the fatty acids handled. We found that all three sensitivities require nearly the same limiting values for temperature and residence time.

According to the results of our long-time laboratory tests, open steam cannot be used. Under its influence, low boiling degradation products formed are carried to the vacuum system and today, all over the world, this is not allowed because they cause extra water pollution problems. Since highest temperatures and residence times in column distillation equipment always occur in the bottom sections of the evaporator, all product degradations such as oxidation and polymerization begin here. Therefore, its construction and mode of operation are of special importance.

Not only from the viewpoint of fatty acid thermal and oxidation behavior, but also in relation to environmental effects, the most serious point in each fatty acid distillation plant is strict control in the installation to avoid fatty acid oxidation causing product degradation and corrosion as well as water and air pollution (18-44). In our opinion, the best and only effective method to limit air leakages, especially at high fatty acid temperatures, consists in drastically reducing the seal area to the minimum possible, mainly by using welded connections for pipes and valves. In addition, at least all those flanges which are subjected to thermal stress should be designed in such a manner that the two parts can be additionally sealed by welding both together with a thin metal band (18-25,38-44). Figure 2 shows such a design with clamp screws. When necessary, this connection can be easily separated with a cutting disc and can be reapplied later. For the same reason, in the high vacuum

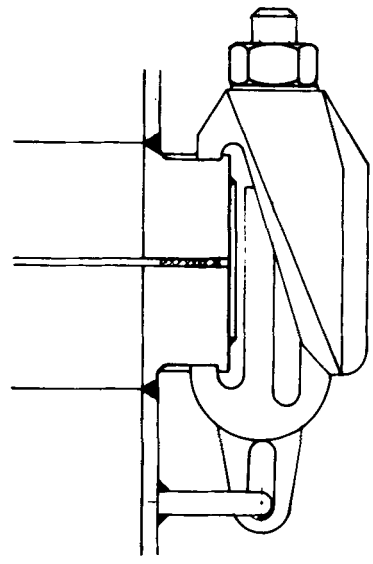

FIG. 2. Seal-welded flange joint with clamp-screws using a sheet strap.

area, one should use as fittings only valves with bellows or a special type of temperature-resistant ball valve. Further on, for movement of hot fatty acid products, exclusively canned motor pumps or those with magnetic coupling are preferable (18-25,38,39,45,46). With respect to the melting points of the higher saturated fatty acids, they must have separate provisions for electrical or steam heating.

The resulting environmental loads depend on the composition and the physical properties of the components of the vapors (26,47-53) which are finally exhausted by the vacuum system. In this context, the content of inert gas and water vapor together with their condensation behavior are particularly important. Because of the water solubility of fatty acids and byproducts as well as fatty acid vapor pressures at low temperatures shown in Figures 3-6, their content, together with that of other organics present, will be determined by waste gas temperature as well as by waste water quantity, especially in relation to dissolved lower fatty acids with less than 12 carbon atoms. To meet the environmental requirements of less than 50 ppm organics/m^3 water effluent, waste gas loads of vacuum system must be less than 0.1 m^3 of fatty acid vapor/m^3 total vapor flowing to the condenser and no open steam can be used in high vacuum fatty acid evaporation below 20 torr. Also under these conditions in the distillation of coco and palm kernel fatty acids, the content of organics in the small precut water fraction will be higher by reason of solubility. Therefore, this fraction has to be cleaned in another way or burned, if it cannot be returned to a splitting installation.

According to our experience (18-25), the limiting factor for corrosion in fatty acid distillation (34-37) is, besides the temperature, the molybdenum content of the stainless steel used. For fatty acids with 12 and more carbon atoms, it should be at least 2.2% as long as the allowable limiting temperature values are not exceeded. In accordance with thermal stability and oxidation effects for saturated higher

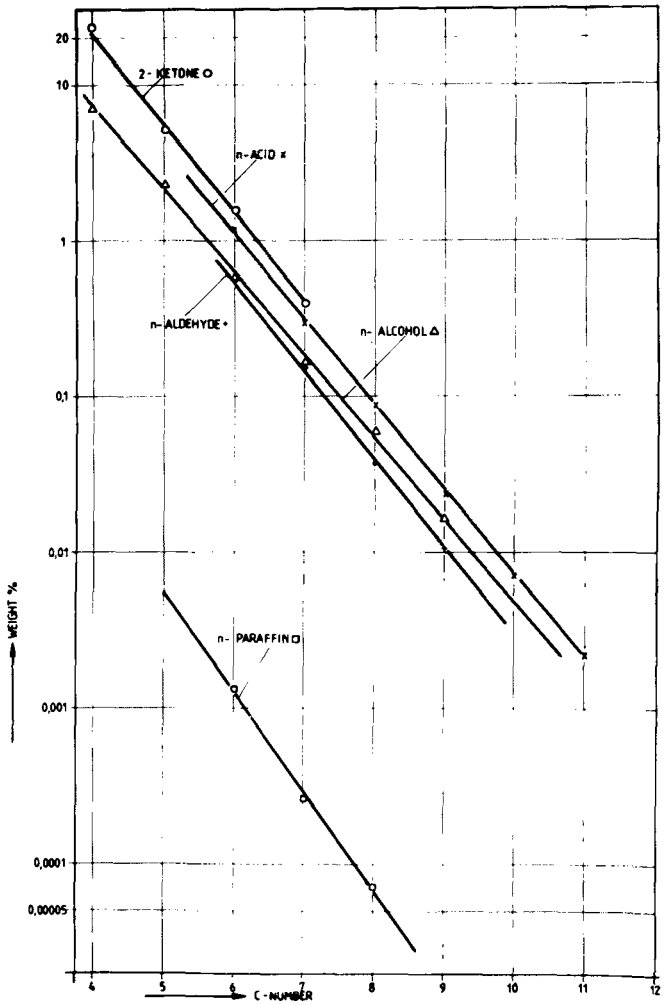

FIG. 4. Relationship between water solubility of different straight-chain organic compounds (fatty acids, aldehydes, 2-ketones, 1-alcohols and *n*-paraffins) at 30 C in weight % and their carbon number.

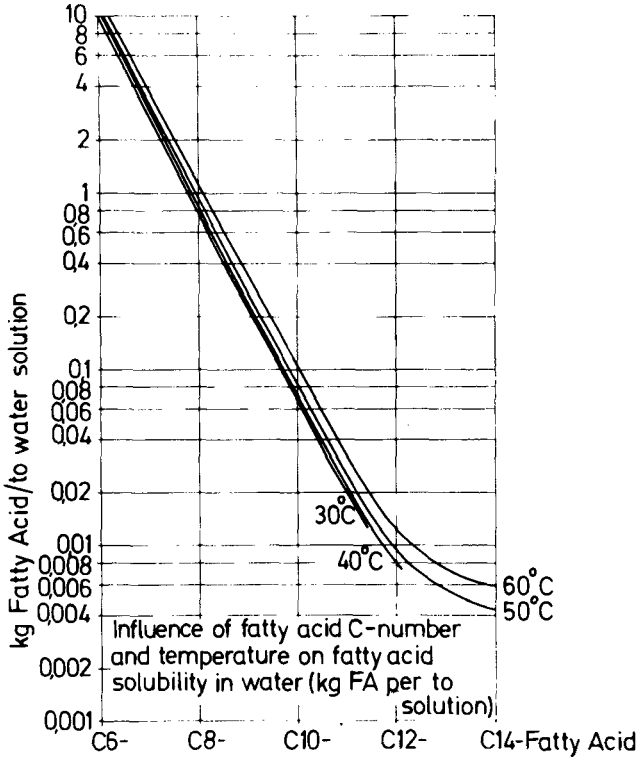

FIG. 3. Relationship between water solubility of fatty acids and their carbon number, with temperature as the parameter.

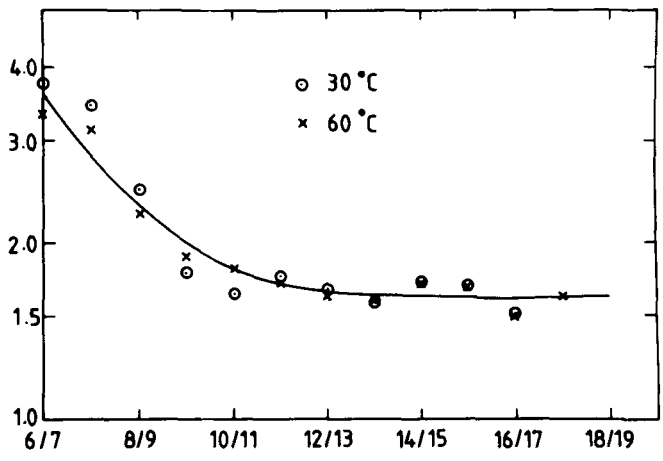

FIG. 5. Quotient of solubility (ordinate) decreasing with increasing carbon number of fatty acids (abscissa).

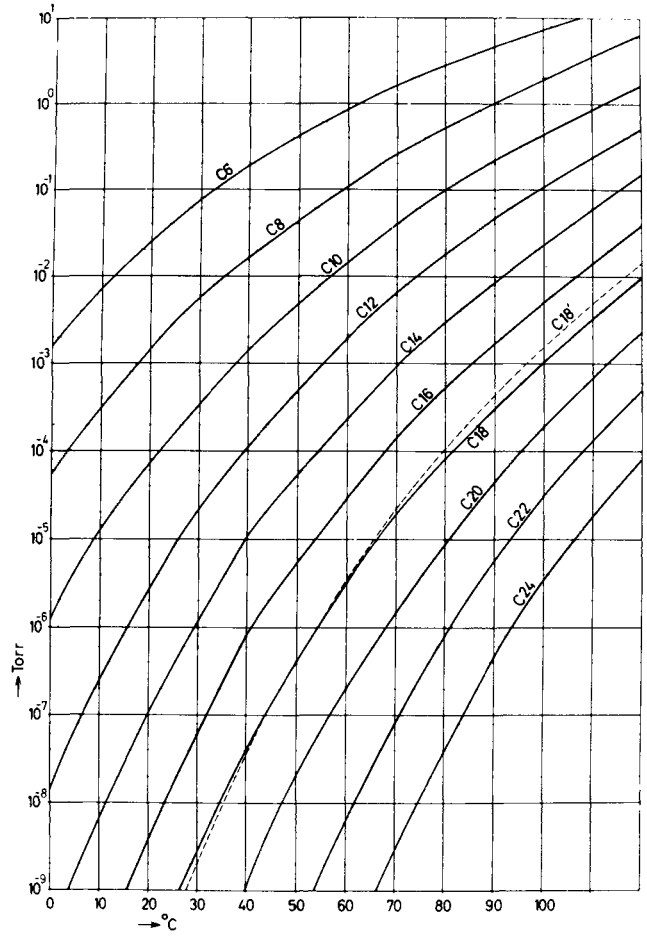

FIG. 6. Relationship between vapor pressure of fatty acids and the temperature, with their carbon number as parameter.

fatty acids and even for reasons of corrosion, temperatures above 260 C have to be avoided. For lower fatty acids with less than 12 carbon atoms, molybdenum contents higher than 2.2% are needed. Even though 3-4% molybdenum is desirable, it should not fall below 2.5%. Because of the possibility of forming further acid groups by oxidation, the corrosivity of such mixtures increases with iodine value or the degree of unsaturation. In our observations this is especially true for the most important C_{18} range which is for all technically important raw fatty acids of natural sources.

RAW MATERIALS FOR FATTY ACID FRACTIONATION (53)

The main raw materials for pure saturated fatty acids up to myristic acid are unhydrogenated or hydrogenated coconut and palm kernel acids. Since these contain virtually no unsaturated acids with 16 carbon atoms, they are, with their average of 42% palmitic acid, the most popular sources for pure palmitic acid. Yet, most individual fatty acids used for technical applications are distilled from raw acids of tallow, cottonseed, soybean, groundnut, rapeseed, castor or linseed oils. These raw acids consist mainly of mono- and polyunsaturated fatty acids, each with an even number of carbon atoms of 18 or more.

SEPARATION CONDITIONS FOR DIFFERENT RAW ACIDS IN RELATION TO TEMPERATURE, RESIDENCE TIME AND FATTY ACID CONSTITUTION

Up to and including myristic acid, all types of natural fatty acids are only saturated, straight-chain *n*-fatty acids with an even C number (18-25,54,55). For separating them, relative volatilities (α) of between 2.75 and 2.0 (with 2.2 as mean value) are to be expected in temperature ranges of 180-250 C which are allowable in large-scale plants (27,28).

The separating conditions for mainly unsaturated mixtures with compositions of C_{18} and higher will be completely different, as their relative volatilities α are much lower. The relative volatilities α for such mixtures of neighboring saturated and monoenic fatty acids of the same C number and a C number two higher are shown in Figure 7 (18-25). From this diagram it can be seen that, for mixtures with different C numbers, the relative volatility α of both types of mixtures vary within the allowable temperature range of large-scale plants from ca. 1.9-1.6 at the top to ca. 1.3-1.2 for mixtures with the same C number at the bottom. The mean values for both types of mixtures are ca. 1.8 and 1.25, compared to 2.2 for mixtures of successive even-numbered saturated fatty acids (18-25).

Figure 8 shows the vapor load/100 kg of feed versus the number of theoretical separation stages, with the distillate concentration and the reflux ratio R used as parameter. It can be seen that for these mixtures with $\alpha = 2.2$ the separation stages have to be in the range between 10 and 20 if distillate purities up to 99% are to be realized.

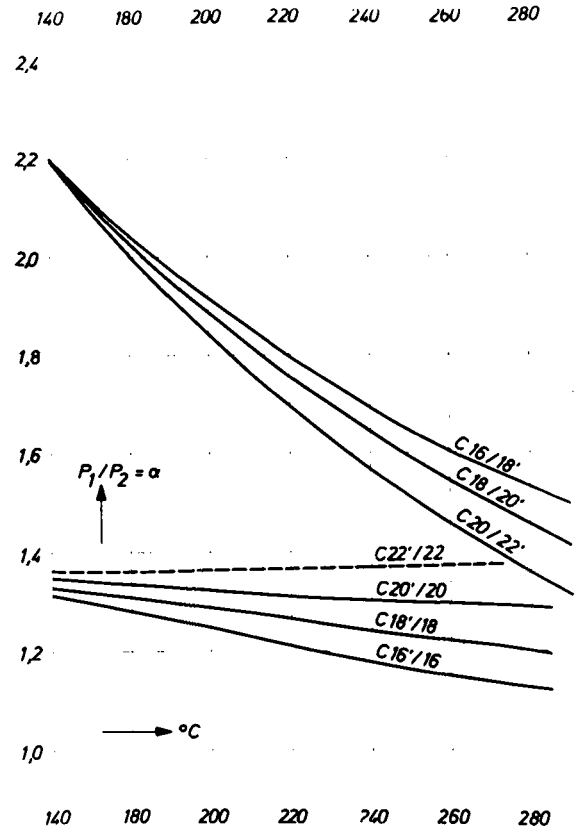

FIG. 7. Relationship between temperature and relative volatility α for mixtures of saturated and unsaturated monoenic, even-numbered fatty acids differing by two carbon atoms, such as palmitic acid-oleic acid (higher lines), or with the same carbon number, such as oleic acid-stearic acid (lower lines).

From Figure 9 it can be seen that the minimum number of theoretical plates should be in the range of at least 25. For the separation of mixtures like oleic and stearic acids with α values in the range of 1.25, the number of enriching and stripping separation stages together for similar distillate concentrations, according to Table I and Figure 10, increases to 60 with much higher reflux ratios and energy consumption.

These separation efficiencies in the range of 20, 30 or 60 theoretical stages for the three types of mixtures have to be accomplished in technical installations as plate, packed or film-type columns. The upper limit for the number of practical exchange units is determined by their particular pressure drops and the resulting bottom temperature for a given top pressure. According to our observations, temperature and residence time as well as mode, arrangement and quantity of double bonds in the fatty acid molecules, together with the heating process used, are all responsible for quality, yield of fatty acid distillate and the production of undesired byproducts.

Therefore, the most important influencing variables in fatty acid distillation fractionation are: temperature and working pressure in the bottom evaporator; residence time, especially in column sections with temperatures above 240 C; and degree of unsaturation (IV) of fatty acids in column parts at temperatures above 240 C.

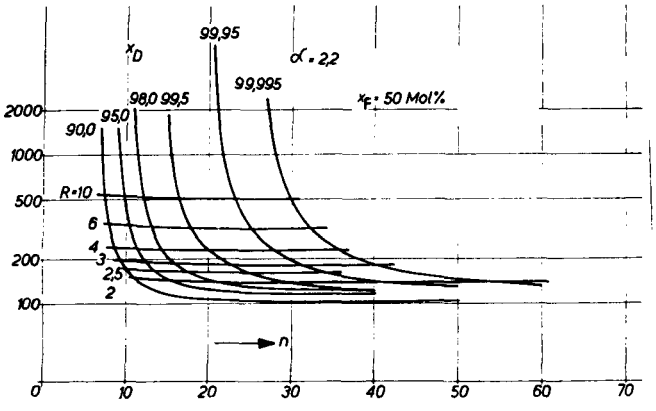

FIG. 8. Relationship between vapor quantity/100 kg of feed (ordinate) and the necessary number of theoretical plates (abscissa) with distillate concentration in connection with reflux ratio as parameter for saturated fatty acid mixtures with α = 2.2 and a feed concentration of 50 mol %.

CONDITIONS AND INSTALLATIONS FOR EFFECTIVE AS WELL AS SENSITIVE EVAPORATION AND CONDENSATION

Iodine values as shown in Table II for the most important raw acids to be fractionated can be separated into three groups with IV less than 60, 60-140, and more than 140. The maximum allowable bottom temperatures for each group for residence times of 40, 20 or 10 min are shown in Table III. This is only true so far as sensitive film-type heating arrangements are used without causing any thermal stress on fatty acids in the vapor or liquid state. According to our observations, the temperature of the heating medium should be kept no higher than 20 C above the bottom temperatures mentioned. Therefore, this value depends on the prevailing residence time of the special technical installation used.

For a fatty acid falling film evaporator, the circulation quantity has to be chosen so that, per meter inside circumference of the evaporator pipes, the downflow is ca. 2 m^3/hr. Under the then-prevailing temperature conditions, this will give film thicknesses of ca. 0.3-0.6 mm (18-25). To achieve really careful film evaporation, we calculate the

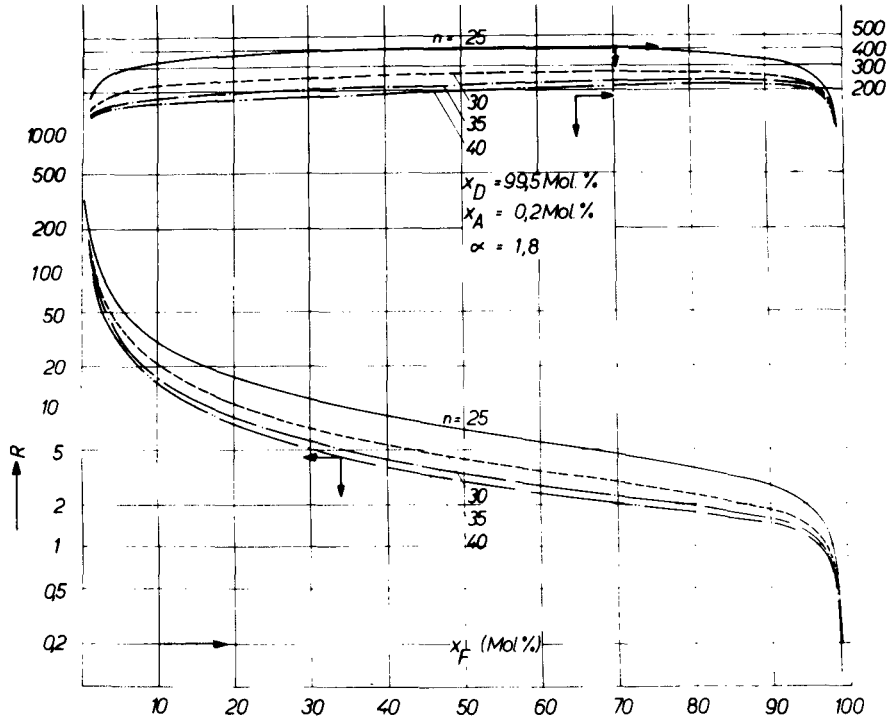

FIG. 9. Relationship between feed concentration X_F (abscissa) and reflux ratio R (left-hand ordinate) or the amount of vapors at top of column (kg vapor/100 kg feed) (right-hand ordinate) and the number of theoretical plates as parameter for mixtures like palmitic acid-oleic acid with α = 1.8.

TABLE I

Influence of Reflux Ratio R on Enriching (n_E) and Stripping (n_S) Numbers in the Separation of Oleic Acid-Stearic Acid Mixtures with a Feed Concentration of 66 mol % Oleic Acid and a Separation Factor α = 1.25

Oleic acid (mol %) Top/bottom	90/19		94/06		96/04		98/02		99/01		99.5/0.005	
R	n_E	n_S	n_E	n_S	n_E	n_S	n_E	n_S	n_E	n_S	n_E	n_S
5	14.4	26.1	34.5	40.4								
5.5	12.8	23.9	24.0	32.2	38.8	41.1						
6	11.7	22.5	20.2	28.9	28.3	34.3	47.4	44.2	70.3	54.8	99.3	67.6
8	9.8	19.4	15.1	23.5	19.5	26.7	27.2	31.9	34.8	36.7	42.1	41.2
10	9.0	18.0	13.3	21.4	16.8	24.1	22.8	25.5	28.6	32.7	34.4	36.8
12	8.5	17.1	12.4	20.2	15.4	27.7	20.7	26.7	25.8	30.7	30.8	34.6
15	8.1	16.3	11.6	19.2	14.3	21.4	19.0	25.2	23.5	29.0	28.1	37.6
20	7.8	15.6	10.9	18.2	13.4	20.3	17.6	23.9	21.6	27.4	25.7	30.9
30	7.4	15.0	10.3	17.4	12.6	19.7	16.4	22.7	20.1	26.0	23.8	29.4
50	7.2	14.5	9.9	16.7	12.0	18.6	15.6	21.8	19.0	25.0	22.5	28.3
100	7.0	14.1	9.6	16.3	11.6	18.1	15.0	21.2	18.3	24.3	21.6	27.5

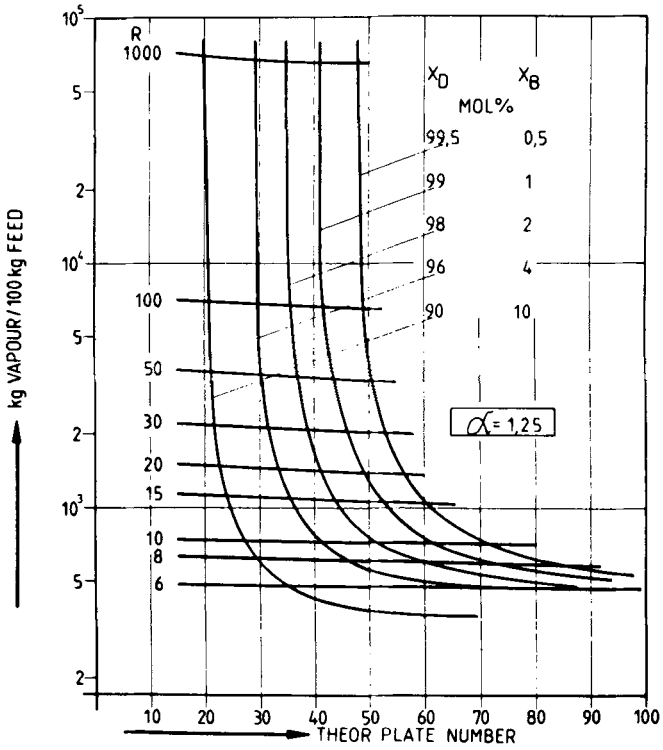

FIG. 10. Relationship between vapor quantity/100 kg of feed (ordinate) and the necessary number of theoretical plates (abscissa) with distillate concentration in connection with reflux ratio as parameter for mixtures like oleic acid-stearic acid with α = 1.25 and a feed concentration of 66 mol % oleic acid.

TABLE II

Iodine Values for the Most Important Raw Acids in Technical-Scale Fractionation

Raw acid origin	Iodine value (medium)
Coco oil	9
Palm kernel oil	16
Tallow	50
Palm oil	55
Lard	60
Peanut oil	99
Cottonseed oil	111
Rapeseed oil	123
Sunflower oil	137
Soybean oil	138
Linseed oil	193

TABLE III

Maximum Allowable Boiling Temperatures at Different Residence Times

Residence time (min)	40	20	10
Iodine value range	Maximum allowable boiling temperatures (C)		
<60	245	250	260
60-140	235	240	245
>140	225	230	235

dimensions of the tubes in such a way that the flow pressure drop caused by the vapors formed is always below 5% of the particular operating pressure prevailing there. To obtain really careful evaporation with no signs of thermal decomposition, especially in evaporation mixtures containing unsaturated fatty acids, it is not sufficient to use normal falling film evaporators with forced circulation. In all these cases it is necessary to lower the residence time of the heat-sensitive material in the heating zone, including circulating line and liquid level regulation device. For this purpose, models have been developed with vapor bypass lines (38-44), as shown in Figure 11. By using this principle, the number of pipes with the same diameter and shorter length can be reduced considerably, which will give lower pressure drop as well as much smaller circulation quantities with shorter residence times.

For sensitive distillation conditions, not only must the column and evaporator be constructed for very low pressure drop, but also the condenser together with the vacuum line. Therefore we use a special condenser type (18-25, 38-44), as shown in Figure 12, directly mounted on the top of the column. In the outer parts, where the main condensation takes place, vapor and liquid condensate are flowing cocurrent. Only in the middle region which acts as gas cooler with low vapor velocities is there counterflow between the upflowing gas and a small quantity of condensate formed in the gas cooling section.

For separating fatty acid droplets which have been

mechanically entrained as mist or fog by the waste gas coming from the column condenser, as shown in Figure 13, a high performance demister directly mounted above our special top condenser is used (40-44). The vertical long cooling trap of low pressure drop (shown under no. 2) is provided with fintubes and serves for the reduction of the additional fatty acids in the exhaust gas leaving the condenser due to partial pressure. From here the gases reach the multiple-step steam ejector with jet condensers which are working with circulating water, which will be cooled indirectly via plate heat exchangers.

Direct condensation cooling in the ejector stages is effected by means of a closed water-circuit via two exchangeable plate heat exchangers. Therefore, besides the water phase of the precut stage, only the small amount of the ejector vapor condensate would count as waste water, which has to fulfill regulatory requirements. Employing such processes in fatty acid fractionation plants with closed cooling water circulation in the vacuum system similar to that of Figure 13, the organic content of the ejector waste water can, at 25-50 C circulation temperature, easily be kept below 50 ppm, even for the lower fatty acids of coconut and palm kernel acids.

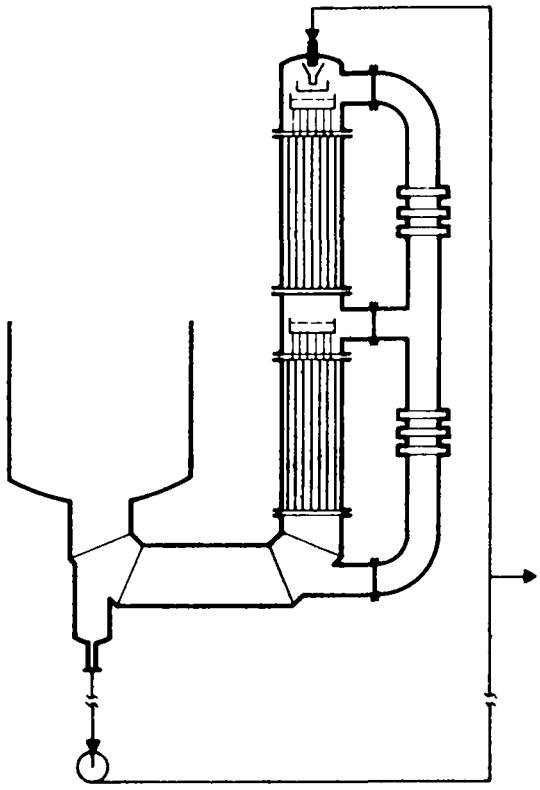

FIG. 11. Falling film evaporator for forced circulation with vapor bypass for reducing vapor pressure drop and liquid residence time.

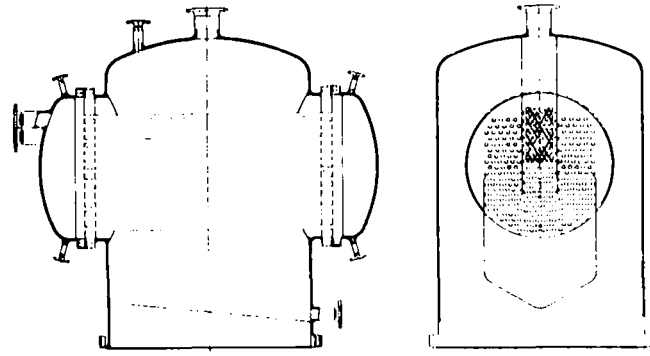

FIG. 12. Top condenser with cocurrent vapor and liquid flow in condensation area and countercurrent flow for gas cooling area.

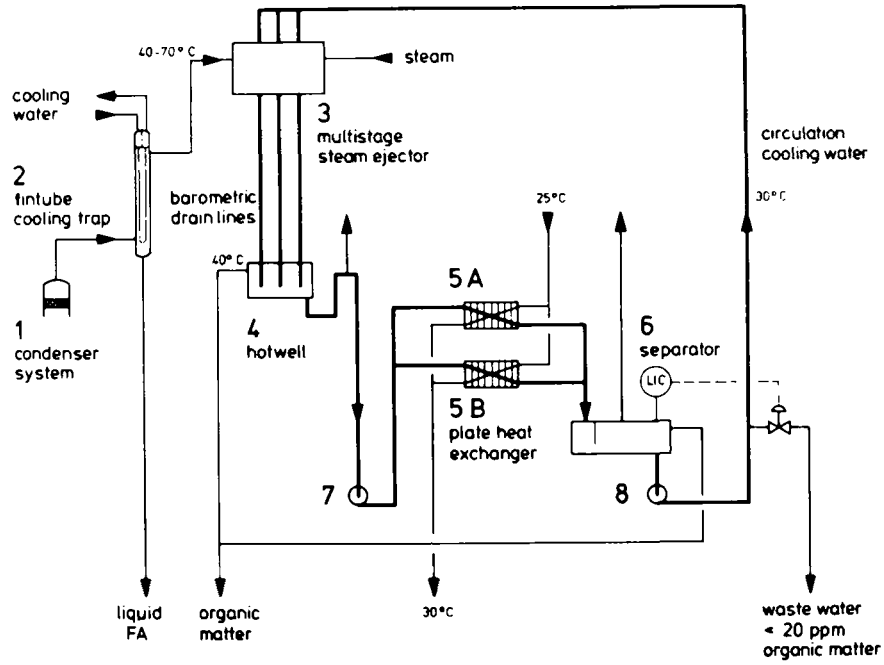

FIG. 13. Vacuum system for fatty acid fractionation process. (1) Mist separator, (2) fintube cooling trap, (3) multistage steam ejector, (4) hotwell, (5) exchangeable plate heat exchangers, (6) liquid separator for fatty acids and water, (7), (8) circulating pumps for cooling water circulation.

NEW COLUMN CONSTRUCTIONS OF LOW PRESSURE DROP ACHIEVING HIGH EFFICIENCIES

So far as only the continuous separation of coconut fatty acids up to myristic acid is concerned, bubble cap columns of low pressure drop can be used. Calculating for 20 or 30 theoretical plates with efficiencies of 80%, this will give 25 or 38 actual plates. Umbrella-type bubble trays (54-56), shown in Figure 14, not only have lower pressure drops but also greater flexibility than normal plate columns with virtually constant efficiency. Such a two-column installation shown in Figure 15 with 44 and 32 practical plates of 2.100 mm diameter has been working very successfully for several years.

These columns are designed in such a manner that, at the low liquid loads normally encountered, the pressure drop averaged over the length of the column can be kept at 1.2 torr per actual plate. To aim at distillate concentrations in the range of 99% for capric, lauric, myristic and palmitic acids out of coco or palm kernel raw acids at 5 torr top pressure, the bottom pressure of such plate columns will be in the range of 35-50 torr. As can be seen by the vapor pressure/temperature curves of Figure 16 for the different bottom products of a coco fatty acid fractionation, with these bottom pressures, the limiting allowable temperature values for palmitic acid have been exceeded. According to this, the fractionation of higher fatty acids with 18 or more carbon atoms is only possible if the pressure drop of the columns can be reduced markedly.

Therefore, in this range, for several years we have been using very successfully, instead of plates with umbrella caps, regular film-type packings (18-25,56) like that shown in Figure 17. By its use, it was possible to lower not only the pressure drop down to less than 10 torr but also the hold up and thus the residence time for fatty acids in the column at boiling temperatures above 240 C. In the meantime, better efficiencies and especially much higher theoretical plate numbers per meter of column length with similar pressure drops per theoretical exchange unit can be realized in this field (56-62) of highly corrosive mixtures. An example that works very well is the so-called Sulzer

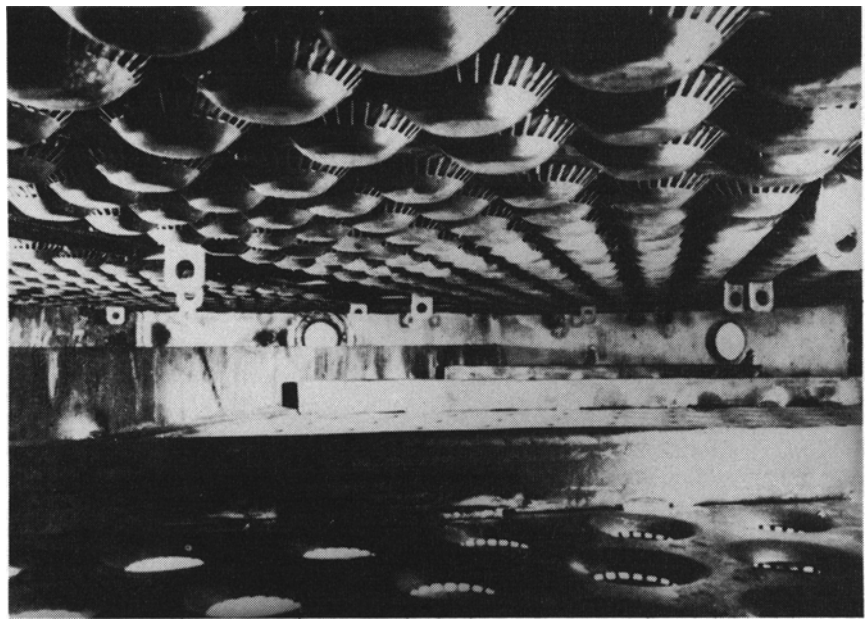

FIG. 14. Plate with umbrella bubble caps for low pressure drop.

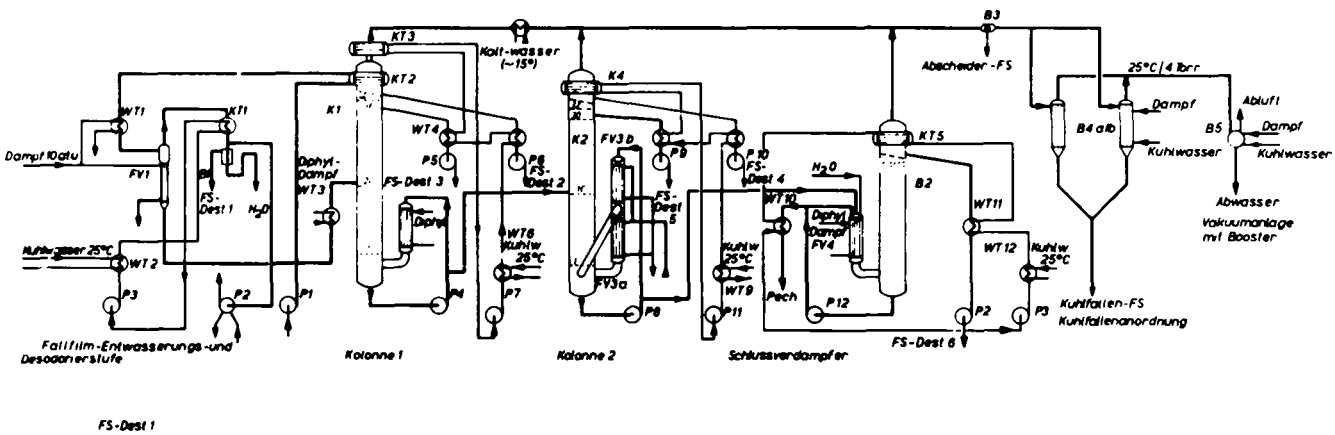

FIG. 15. Flowsheet of a coco fatty acid fractionation plant with two umbrella bubble cap columns of low pressure drop together with degasification and precut stage as well as falling film stage for pitch separation.

film-type packing Mellapak® 250.y (59-62). As shown in Figure 18, this is also a regular column packing which has excellent wetting properties at very low liquid loads down to less than 1 m^3/m^2 hr. Therefore, it allows, even at the low liquid loads of fatty acid fractionation, reduction in each case of the reflux ratio to the value required according to the vapor liquid phase equilibrium for the special separation itself. With the pressure drop and efficiency data shown in Figure 19 for this packing it is possible to realize, in the C_{18} region at 3 torr top and 17 torr bottom pressure with an evaporation temperature of only 243 C, theoretical plate numbers of up to 60 or more. Such efficiencies are even sufficient for the separation of oleic and stearic acid both in purities of 98% at reflux ratios in the range of only 8-10.

For normal fatty acid separation problems for which 20-25 theoretical separation units are needed, with this kind of film-type column the bottom pressure can easily be reduced to less than 10 torr with highest bottom tempera-

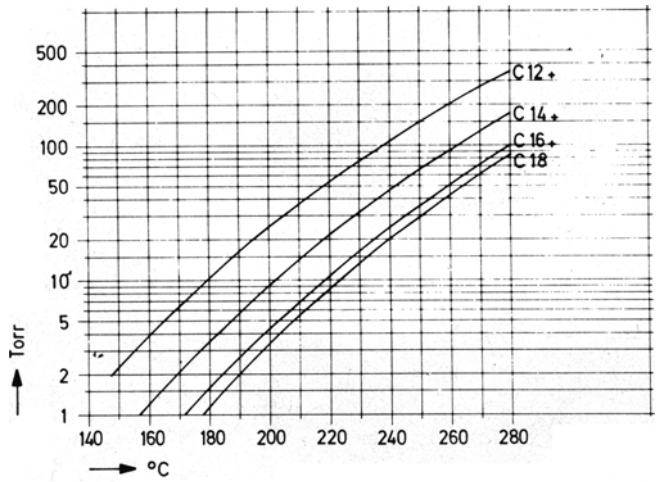

FIG. 16. Relationship between vapor pressures (ordinate) of following bottom products in coco raw acid fractionation and their boiling temperatures (abscissa).

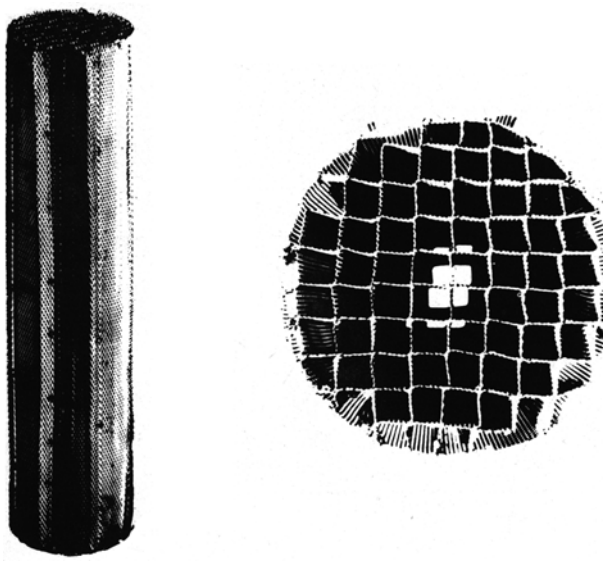

FIG. 17. Elements in cross-section and length of a film-type packing made out of expanded metal sheets (54-56) successfully used for fatty acid fractionation in C_{16} and higher range.

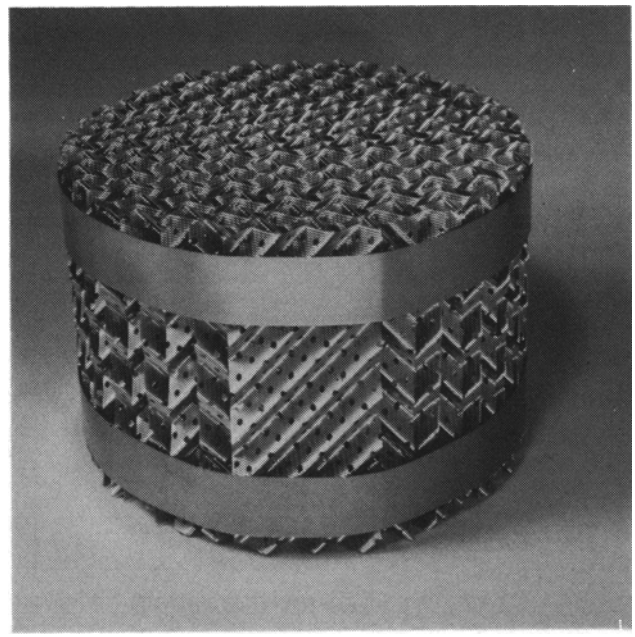

FIG. 18. Regular Sulzer film-type column packing MELLAPACK® 250.

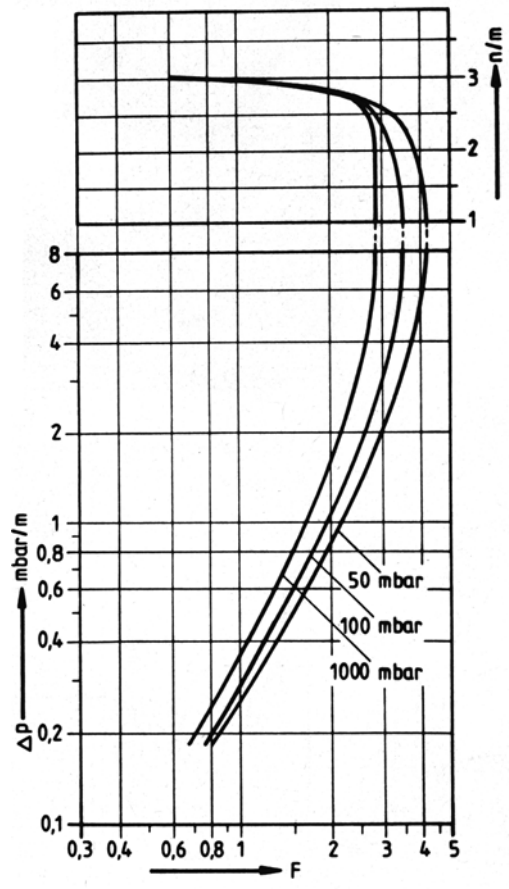

FIG. 19. Relationship between loading factor F [m/sec. $\sqrt{(kg/m^3)}$] (abscissa) and pressure drop as mbar/m packing height or number of separation stages/m packing height for Sulzer film-type column packing MELLAPACK®.

tures of less than 230 C. Under these conditions it is also possible to work in the fatty acid fractionation field batchwise. This is of particular interest for cases where only smaller throughputs of strongly changing demands have to be processed. The flowsheet of such an installation is shown in Figure 20.

TODAY'S PROCESS POSSIBILITIES

For large-scale fractionation of natural fatty acids, the most successful as far as economics is concerned use deaeration and precut stages both working at the same medium pressure together with one or two columns combined with a final stage for pitch separation—the latter working all at the same low pressure and equipped with falling film evaporators. The plate columns with umbrella-type bubble trays or film-type columns with regular low pressure packings like MELLAPAK® have proved excellent on account of their large operating ranges and low pressure drops. For evaporation in the bottom, no carrier such as open steam is needed if the necessary falling film evaporators are working with forced circulation of correct design in relation to pressure drop and residence time.

Under these conditions with normal cooling water temperatures of 20-25 C, the environmental load for water and air are within the legal limits. In each case the effluent water output together with process and ejector open steam consumption is less than 200 kg/kg fatty acid fractionated, which can be used as reaction water for high pressure splitting.

The energy consumption relative to fatty acid distillate depends not only on the special fractionation problem for separating lower and higher boiling fatty acids in the desired purity and yield, but also in each case on the necessary removal of precut together with dearation and dehydration as well as pitch under sensitive distillation conditions.

The dream of yesterday for distillation separation of monoenic and saturated fatty acids with the same carbon number, as, e.g., oleic-stearic acid mixtures, has now become reality with today's knowledge about their phase equilibria relationships as well as their thermal and oxidative behavior, and with much better separation processes with very low pressure drops and sensitive film heating arrangements. As this really is possible after four decades of hard work, one can now have another dream: the distillation separation of mono-, di- and trienic fatty acids with the same carbon number, e.g., mixtures of oleic, linoleic and linolenic acids under economical industrial conditions. The relative volatilities of these mixtures shown in Figure 21 are 1.156 for linoleic acid-oleic acid and 1.140 for linolenic acid-linoleic acid at 2 torr top and 15 torr bottom pressure with temperatures between 185 and 230 C. For separating linoleic acid from cottonseed raw acids or linolenic acid from linseed raw acids under these conditions at reflux ratios of 15, columns are needed with efficiencies of 80-90 theoretical plates. We hope and believe that this dream may be realizable after several more decades of hard work.

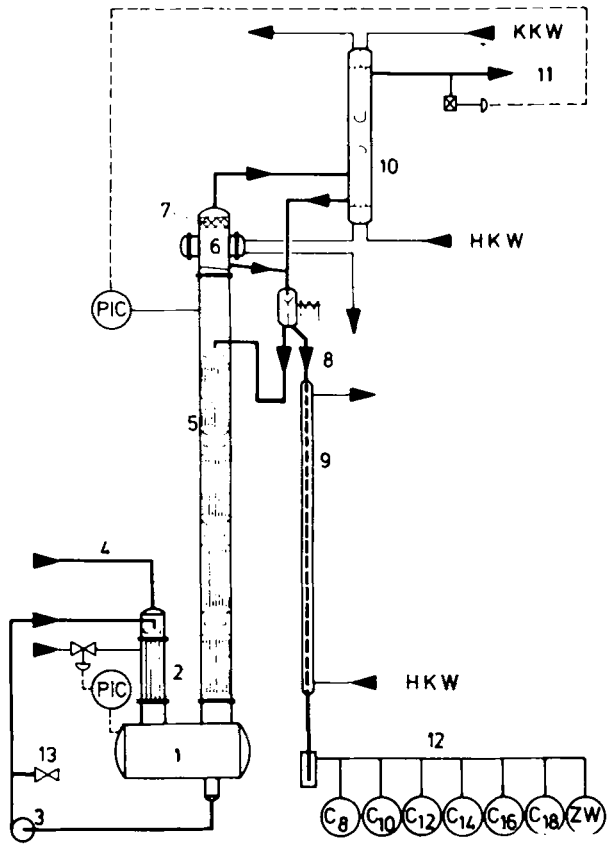

FIG. 20. Flowsheet of a discontinuous running fatty acid fractionation plant with regular film-type packing. (1) Still for batches of 4,000 kg, (2) falling film evaporator for forced circulation, (3) canned motorpump for forced circulation and still emptying, (4) feed line for open stripping steam, (5) column with regular film-type packing of low pressure drop, (6) top condenser, (7) demister, (8) reflux divider, (9) distillate cooler, (10) cooling trap with fin-tubes for hot (HKW) and cold (KKW) cooling water, (11) vacuum line, (12) distillate receivers, (13) line for still emptying.

REFERENCES

1. Potts, R.H., and V.J. Muckerheide, in Fatty Acids and Their Industrial Applications, edited by E.S. Pattison, Marcel Dek-

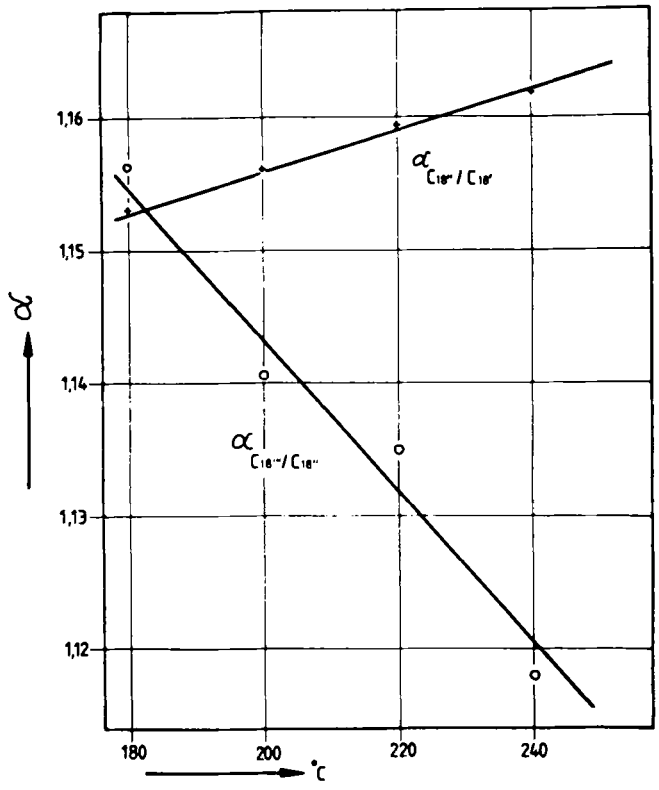

FIG. 21. Relationship between temperature (abscissa) and relative volatility α for mixtures of linoleic acid-oleic acid and linolenic acid-linoleic acid.

ker, Inc., New York, 1968, pp. 21-45.
2. Osteroth, D., Natürliche Fettsäuren als Rohstoffe für die chemische Industrie, Ferdinand Enke, Stuttgart, 1966, pp. 44-49.
3. Kenyon, R.L., D.V. Stingley and H.P. Young, Ind. Eng. Chem. 42:202 (1950).
4. Stirton, in Bailey's Industrial Oil and Fat Products, edited by D. Swern, 3rd edn., Interscience Publishers, New York, 1964, pp. 1005-29.
5. Gloyer, S.W., JAOCS 27:462 (1950).
6. Muckerheide, V.J., JAOCS 29:490 (1952).
7. Lee, C.A., Chem. Eng. 63:189 (1956).
8. Potts, R.H., and E.H. Chapin, Heat Engineering, Foster Wheeler Corp., 21: 50 (1946).
9. Holt, A.B., and F.B. White, Ibid. 21:110 (1946).
10. Williams, R., Chem. Eng. 56:92,128 (1949).
11. Potts, R.H., and C.W. McBride, Ibid. 59:124,172 (1950).
12. Potts, R.H., and F.B. White, JAOCS 30:49 (1953).
13. Potts, R.H., JAOCS 33:545 (1956).
14. Potts, R.H., and coworker (to Armour & Co.), U.S. Patents 2,054,096; 2,212,127; 2,224,925; 2,224,984; 2,251,602; 2,322,056; 2,450,611; 2,450,612; 2,627,500; 2,674,570.
15. Stage, H., R. Bünger and A. Jonas, Fette Seifen Anstrichm. 55:513,580 (1953).
16. Schlenker, E., Seifen Oele Fette Wachse 81:285 (1955).
17. Broniarz, J., and J. Szymanowski, Zesz. Nauk. Pchternik Poznankiej 55:133 (1969).
18. Stage, H., Fette Seifen Anstrichm. 55:217,284,375 (1953).
19. Stage, H., Ibid. 64:93,218 (1962).
20. Stage, H., Ibid. 72:229,353,439 (1970).
21. Stage, H., Ibid. 73:10,76 (1971).
22. Stage, H., Ibid. 75:160,298 (1973).
23. Stage, H., Ibid. 77:174,383 (1975).
24. Stage, H., Ibid. 79:345 (1977).
25. Stage, H., Ibid. 80:257,377 (1978).
26. Fainberg, E.E., Rectification of Natural Fatty Acids and Higher Fatty Alcohols, Food Industry, Moskau, 1970.
27. Müller, E., and H. Stage, Experimentelle Vermessung von Dampf-Flüssigkeits-Phasengleichgewichten dargestellt am Beispiel des Siedeverhaltens von Fettsäuren, Springer Verlag, Berlin, 1961.
28. Stage, H., E. Müller and L. Gemmeker, Fette Seifen Anstrichm. 64:27 (1962).
29. Yamane, I., J. Oil Chem. Soc. Jpn. 7:298 (1958).
30. Uzzan, A., and Y. Lauchard, Rev. Fr. Corps Gras 7:267 (1960).
31. Cheng, H., and S.S. Chang, JAOCS 51:189 (1974).
32. Noworyta, A., and T. Zaleski, Inz. Chem. 6:815 (1976).
33. Noworyta, A., and T. Zaleski, Ibid. 7:143 (1977).
34. Baerlecken, E., Fette Seifen 44:228 (1937).
35. Poe, C.F., and E.M. van Fleet, Ind. Eng. Chem. 41:208 (1949).
36. Friend, W.Z., and I.F. Mason, Jr., Corrosion 5:355 (1949).
37. Kartasova, K.M., and A.M. Bodrova, Tr. Gos. Inst. Prikl. Khim. 67:159 (1971).
38. Stage, H., Seifen Oele Fette Wachse 104:445 (1978).
39. Stage, H., Fette Seifen Anstrichm. 82:337 (1980).
40. Stage, H., Riv. Ital. Sostanze Grasse 52:291 (1975).
41. Stage, H., ISF/AOCS Congress, New York, 1980, Paper 299.
42. Stage, H., Seifen Oele Fette Wachse 103:151,207,269 (1977).
43. Stage, H., Fette Seifen Anstrichm. 76:197,244 (1974).
44. Stage, H., Ibid. 84:333 (1982).
45. Kather, H., Ibid. 85:510 (1983).
46. Knorr, M., Ibid. 85:522 (1983).
47. Singleton, W.S., in Fatty Acids, Their Chemistry, Properties, Production and Uses, edited by K.S. Markley, 2nd edn., Interscience Publishers, New York, Vol. 1, 1960, chaps. 6 and 7.
48. Formo, M.W., in Bailey's Industrial Oil and Fat Products, edited by D. Swern, 3rd edn., Interscience Publishers, New York, 1964, chap. 3.
49. Taylor, M.A., and L.H. Princen, in Fatty Acids, edited by E.H. Pride, American Oil Chemists' Society, Champaign, IL, 1979, chap. 10.
50. Eggenberger, D.N., F.K. Brown, A.W. Ralston and H.J. Harwood, I. Org. Chem. 14:1108 (1949).
51. Barton, J.R., and C.C. Hsu, Chem. Eng. Sci. 27:1315 (1972).
52. Stage, H., CZ Chem. Tech. 1:311 (1972).
53. Doss, M.P., in Properties of the Principal Fats, Fatty Oils, Waxes, Fatty Acids and Their Salts, edited by The Texas Company, New York, 1952.
54. Stage, H., Chem. Ing. Tech. 42:669 (1970).
55. Stage, H., Ibid., 45:58 (1973).
56. Stage, H., CAV no. 2, 57 (1972).
57. Klamroth, K., Fette Seifen Anstrichm. 80:244 (1978).
58. Bauermann, H.-D., Ibid. 85:497 (1983).
59. Meier, W., Tech. Rundsch. Sulzer 3 (1970).
60. Kuratle, R., and W.D. Stoecker, Fette Seifen Anstrichm. 79:450 (1977).
61. Gebrüder Sulzer AG, Winterthur/Swiss, Paper: Sulzer Trenntechnik mit Füllkörperkolonnen, 1906, v. 82-45.
62. Widmer, M., Fette Seifen Anstrichm. 85:503 (1983).

The Use of Bleaching Earth in Fatty Acid Production

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ABSTRACT

Pretreatment of crude tallow or fish oil fatty acids with bleaching clays considerably improves the rate of hydrogenation with several different catalysts. Several series of tests were run to demonstrate these effects, and the data are presented.

To produce triglyceride-based fatty acids with a low iodine value (IV), a number of considerations have to be made. There exist, for instance, two principal routes: (a) hydrogenation of the neutral or slightly acidic oil followed by splitting and distillation; and (b) splitting of the triglyceride, followed by hydrogenation of the fatty acid and final distillation. The route chosen depends on the crude material available and on the facilities in the plant. Further aspects to be considered deal with some necessary purification steps.

For the splitting, followed by hydrogenation, one has also to consider whether the fatty acid should be distilled prior to the hydrogenation to remove impurities and poisons, as otherwise the hydrogenation would stop at rather high IV or the catalyst consumption would be too high. However, that means that the fatty acids are distilled twice, once before and once after the hydrogenation, which is costly. The decision for either route (a) or route (b) and for all the necessary purification steps also depends largely on the cost comparison for the possible variations. Especially for today's market, the end-product must be as cheap as possible in order to be competitive.

This paper deals with a type of purification step which we regard as interesting, as one can start from crude oils or crude fatty acids. The only necessary pretreatment is a clay treatment. For our tests, we used a crude tallow and a crude fish fatty acid.

HYDROGENATION OF CRUDE TALLOW

The crude tallow used is described in Table I. The hydrogenation of the crude untreated tallow was performed at 120-190 C under a pressure of 20 bar with 0.05% as Ni catalyst, and 1,000 rpm agitation.

Pretreatment of the crude tallow was done in the same autoclave as the hydrogenation, to simulate the cheapest way for this treatment. The conditions were with 1% Tonsil Optimum FF, at 110 C, for 30 min, at 50 mm Hg pressure.