Decolorization of Tallow by Liquid-Liquid Extraction With Propane[1]

E. B. MOORE, Lever Brothers Company, Cambridge, Mass.

THE application of liquid-liquid extraction to glycerides using propane as a solvent has recently become a commercial reality. A unit for the decolorization of crude tallow is now in successful operation at the Lever Brothers Company plant in Baltimore, Md. The unit was designed and erected by the M. W. Kellogg Company of New York City and has a capacity of over 200,000 pounds a day.

The present process is the outgrowth of earlier work in the petroleum industry dealing with the removal of asphalt from heavy oils. The process proved very useful in the solution of this problem. A logical sequence of this success was to find new applications for the process. The installation of the commercial tallow decolorization unit at Baltimore is a result of this effort. Experiments conducted in the M. W. Kellogg Company laboratory at Jersey City, N. J., demonstrated that a crude tallow having a color of 37-45 F.A.C. could be processed by liquid-liquid extraction in propane solution to yield a finished product having a color of about 7-11 red on a 5¼-inch Lovibond column. In September 1946 experimental work was begun in the newly constructed pilot plant at Cambridge, Mass., under the supervision of the research department of Lever Brothers Company. Here many of the operational factors which influence the decolorization of tallow were studied.

Propane is an odorless gas at atmospheric pressure and room temperature. It is abundant in the gases liberated in the crude oil fields and in the gases produced during the process of refining petroleum. It is readily liquefied by compression. For use in the decolorization of tallow it is necessary that it be free of mercaptans and other odoriferous compounds which tend to concentrate in the decolorized tallow.

Pure propane boils at —44°F. under one atmosphere of pressure and has a critical pressure of 643 pounds absolute at 212.2°F. At 70°F. the gage pressure of saturated propane is 110 pounds while at 100°F. it is 174 pounds. The specific gravity of propane varies from 0.50 at 70°F. to 0.25 at 212°F. Surface tension and viscosity measurements decrease to nearly negligible values just below the critical temperature. As liquid propane approaches its critical temperature, it becomes highly compressible.

Gaseous propane is heavier than air. Its molecular weight of 44 corresponds to that of carbon dioxide. It is of course highly flammable and has an explosive range with air of 2.37-9.5% by volume. Because of these properties care must be exercised to prevent its accumulation in sumps, drains, and other depressions where it might collect and create a hazard. One property of liquid propane which can also be a hazard is its refrigerating ability. Care must be taken to avoid personal contact with liquid propane since its evaporation to a temperature of —44°F. can cause a "burn" similar to that caused by dry ice. Breathing propane vapors may result in dizziness if continued over a moderate length of time. Among its desirable qualities are its stability, non-corrosive nature, and low cost.

Plant

The major process equipment of the propane plant is located out-of-doors. The ground area around the tower and its accessory equipment is covered with a concrete mat. To the east of the tower is a building which houses the tallow storage tanks, the tallow and product pumps, the propane pump and propane compressor, and the control instrument room. To the west of the tower is the water cooling tower and the water circulating pump house. This latter building also houses the water chlorinator. Several hundred feet north of the tower and plant buildings is the 125-foot high blowdown stack to which propane gas may be vented in an emergency. At a nearly equally distant point in the same general direction is the unloading station for the propane and an 18,000-gallon propane storage tank. Liquid propane is normally pumped to this tank as received and is withdrawn to the working propane supply tank as required.

All equipment is grounded and sprinkler and gas detecting systems have been installed. Portable gas detectors are available for checking gas leaks or the presence of gas in supposedly gas-free vessels. Special automatic shut-off valves have been provided at the outlet of the working propane supply tank and at the top and bottom of the fractionating column. These valves will automatically shut off the flow if a major break occurs in the piping system in which they are installed. Flood and mist fire protection nozzles protect the tower and surrounding outside equipment. Grinnell "H.A.D." heads located strategically about the plant actuate a trip valve located within the tallow tank room and, in the event of fire, flood the otherwise dry fire protection lines with water. Wet sprinkler heads of the conventional type are installed in the heated buildings. An emergency steam turbine-driven electric generator is located in the water pump room. This generator automatically trips on power failure and furnishes sufficient power to light important areas of the plant and operate the control instruments on the panel board so that an orderly shutdown may be effected, if required.

The practice of color-coding lines and equipment has been followed at this plant. Propane lines are orrange; stock lines, dark green; steam, aluminum; fire protection, red; air, black; water, light green; and vacuum, white. Steam lines are banded with a stencil L.P. for low pressure and H.P. for high pressure. This coding of lines has been very helpful, particularly to new operators following the course of any particular line in the maze of piping which is encountered.

The process equipment utilizes a considerable proportion of type 316 stainless steel, either as stainless-clad for the tower, strippers, etc., or entirely stainless, such as piping for overheads. In general, all metal contacting decolorized tallow after leaving the tower is 316 stainless steel. Liquid and gaseous propane lines and vessels are carbon steel. The tal-

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low feed tanks are carbon steel while the finished product tanks and lines are aluminum. Lines used for tallow, tallow bottoms, water, etc., have been rather heavily steam-traced, using copper tubing, to prevent freezing during winter conditions. It was necessary to steam-trace liquid gage glasses on the flash drums and strippers, etc., and insulate them well since the slight internal liquid movement proved insufficient to prevent solidification of the tallow in severe weather.

Process

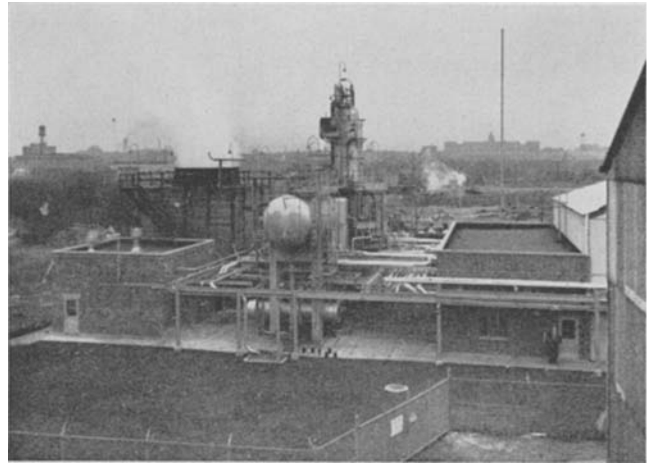
The plant was originally designed to decolorize 300,000 pounds of crude tallow per stream day at a propane ratio of 10:1. The decolorized overheads product was to amount to 97% of the tallow charged to the unit while the remaining 3% was to be withdrawn as bottoms. The bottom fraction was to be rerun at a 50:1 propane ratio and 50% of the charge was to be recovered as overheads while the residue was to be withdrawn as final bottoms. The recovered overheads were to be blended with fresh crude stock and rerun.

Under present conditions of operation the primary bottoms are not rerun since it is uneconomical to do so. A propane-to-tallow ratio of 17:1 is employed rather than the 10:1 design figure. Finished product yields are approximately 98% of the crude feed.

Basically the process is very simple. It involves the pumping of the tallow and propane to a tower in the correct proportions and the subjecting of the mixture to the proper conditions of temperature and pressure, causing the color bodies to fall to the bottom whence they are removed, while the decolorized tallow in propane solution is recovered from the top of the tower. The flash drums, strippers, compressor, and other accessory equipment serve to separate and recover the propane and tallow fractions.

The operation of the process is as follows: Crude settled tallow at a temperature of about 130°F. is pumped to one of two 120,000-pound scale tanks. One tank is being filled and settled while the second tank is discharging to the tower. Tallow from the feed tank flows by gravity to a simplex, high pressure Union steam pump, which discharges it at a pressure of about 475-480 psig to the tallow preheater and thence to the tower. There is a check valve in the tallow lines at the entrance to the tower to prevent a reversal of the flow should the tallow pump or line become defective. The flow of tallow is controlled by the combined action of a Hayes Veriflow meter and a Brown electronic flow meter, which in turn actuate an air-controlled valve in the steam supply line to the pump. The tallow preheater is automatically controlled at the desired temperature by a Foxboro temperature recorder controller connected with a thermocouple installed in the tallow feed inlet connection to the tower.

Propane is supplied from a 14,000-gallon capacity working supply tank at a pressure of about 270 psig and a temperature of approximately 120°F. From this tank the liquid propane flows to a steam turbine-driven, 3-stage, centrifugal Pacific pump, where at a pressure of about 570 psig it discharges to the propane preheater and into the tower at a point about 3 feet from the bottom. The preheater temperature is controlled by a Foxboro temperature recorder controller, mounted on the panel board and actuated by



Lever Brothers Pilot Plant.

a thermocouple installed in the inlet line to the tower. A check valve located at the line entrance to the tower functions in a similar manner to the one in the tallow line. The flow of propane is controlled by means of an orifice in the line. The pressure differential across the orifice is transmitted to a Taylor flow recorder controller which, by means of controlled air pressure, operates a Hammel-Dahl control valve in the propane line.

The fractionating tower has a height of 39 feet, 6 inches and an internal diameter of 5 feet, 6 inches. The internal heating coils, baffles, supports, etc., are fabricated from type 316 stainless steel. The internal surface of the tower shell is 316 stainless steel-clad. There are 16 slot-type baffles in the column as well as a group of three temperature control steam coils in the upper section. Fairly equally spaced between the top and bottom of the tower are eight thermocouples for measuring the temperature of the solution within the tower. These thermocouples connect to a multipoint Brown electronic temperature indicator, mounted on the panel board in the control room.

As the tallow enters the tower, it has a tendency to settle. However the stream of propane rising through the tower mixes with it almost immediately, and the propane solution of tallow then begins to rise. A temperature differential is maintained within the tower in such a manner as to fix the lowest temperature in the lower portion of the tower and a somewhat higher temperature at the top of the tower. If this temperature differential, or gradient as it is usually termed, is correctly chosen, there will be a precipitation of the color bodies, or bottoms, as the tallow-propane solution rises in the tower. The bottoms phase consisting of color bodies, water, dirt, and some glycerides is heavy and is withdrawn from the column in combination with approximately one volume of propane. The continuous phase, which is withdrawn from the top of the column, contains the bulk of the propane charged to the system and the decolorized overheads. The pressure in the tower is normally held at 465 psig. It is controlled by a Brown pressure recorder controller, which maintains the required air pressure on a control valve in the overheads line.

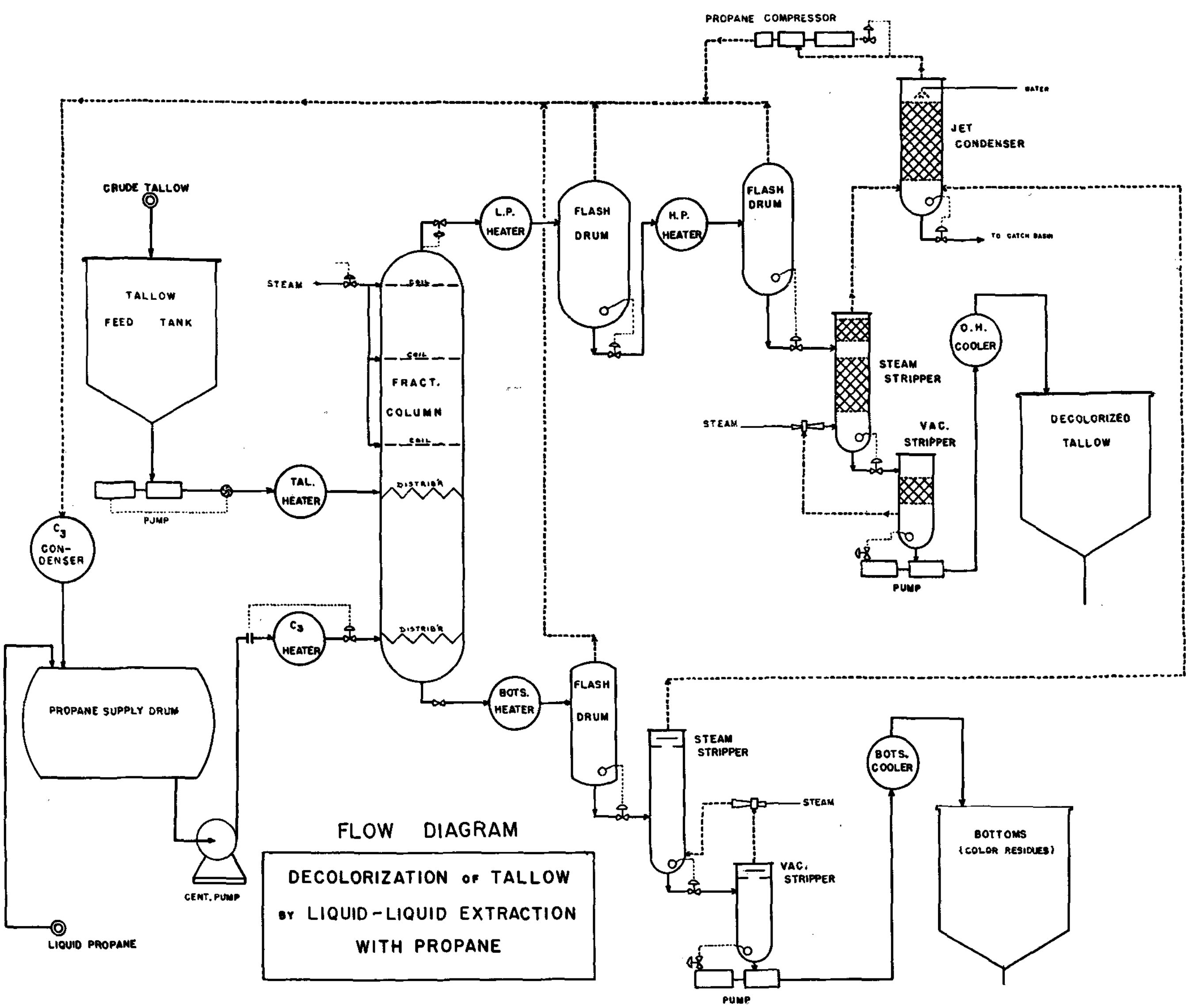
If for any reason the tower pressure becomes excessive, a high pressure alarm will sound a howler.

If corrective measures do not reduce the pressure immediately, an emergency push button has been provided, which cuts off the steam to the tower coils and shuts down the tallow feed pump and the propane supply pump. This action will shut off all sources of pressure increase and prevent popping of the tower relief valves.

After leaving the tower, the overheads solution enters a low pressure steam heater where the temperature is controlled at approximately 167°F. Leaving this heater, the solution enters the first overheads flash drum where about 95% of the propane flashes off. The pressure in this drum is about 275 psig and is controlled by the pressure within the propane supply tank, to which it is connected through the propane condenser. The oil-rich solution collecting in the bottom of this vessel passes under liquid level float control to a high pressure steam heater, where the temperature is increased to about 260°F. The heated solution then flows to a second flash drum, where substantially all of the remaining propane is removed. The pressure in this flash drum is also about 275 psig since it too connects back to the propane condenser and supply tank. The slight amount of propane then remaining in the oil is recovered by withdrawing the oil through a liquid level controller at the bottom of the flash drum into the overheads stripper, where the residual propane flashes off at a pressure of about 5 psig.

The overheads stripper is 21 feet high and 2 feet in diameter. It contains a 10-foot bed of 1-inch Raschig ring packing over which the tallow flows, and an 18-inch bed of dry packing at the top of the tower to prevent entrainment of tallow in the exhaust vapors. This stripper is functionally connected with a final vacuum stripper, which removes any traces of propane from the overheads product. Steam from the ejector used to maintain a vacuum on this final stripper is blown into the low pressure stripper where, with a small quantity of additional steam, it is utilized in stripping the propane from the oil as it falls through the 10-foot packed section of Raschig rings.

The vacuum stripper is a vertical vessel 6 feet, 6 inches high with a diameter of 2 feet. Upon leaving the steam stripper under liquid level control, the overheads enter the top of the vacuum stripper. A two-foot bed of one-half-inch Raschig rings distributes the oil so as to produce a film flow from which traces of propane are readily released. The vapor outlet is located below the packing so as to minimize any



FLOW DIAGRAM

DECOLORIZATION OF TALLOW BY LIQUID-LIQUID EXTRACTION WITH PROPANE tendency to foam. The level of depropanized tallow overheads in the vacuum stripper is regulated by a liquid level controller connected with the overheads product pump. Increasing the level opens the steam supply to the pump and speeds up the pump, while lowering the level gradually closes the steam supply and reduces or stops the pump action. Before passing to the 120,000-pound aluminum finished product tanks, the overheads are cooled to about 120°F. in tubular coolers.

The precipitated bottoms, or color bodies, collect at the bottom of the tower and are withdrawn under manual control, using a Willis valve. Since for purposes of calculating yields it is desirable to maintain a uniform bottoms level, a recorder is mounted on the panel board to indicate the interfacial level between bottoms and overheads solution. To remove the propane the tower bottoms are passed through a tubular heater, where the temperature is raised to about 260°F. Partial vaporization occurs in this heater, and this vapor together with the residual liquid flashes into the bottoms flash drum, where the major portion of the propane is separated.

The liquid bottoms collecting in the flash drum flow under level control to a steam and vacuum stripper system very similar to that used in overheads recovery, except that no packing is used in the bottoms system. The recovered bottoms are rather viscous, and it was considered inadvisable to risk clogging a packed column. Instead the feed is introduced tangentially into the strippers, where it contacts the walls and falls as a thin film. A disc and doughnut baffle arrangement in the top of the strippers minimizes possible entrainment.

To reduce the water content of the bottoms it was found expedient to install a high temperature heater in the bottoms line between the flash drum and the low pressure stripper. The water thus evaporated leaves the stripper along with the propane and stripping steam vapors. Bottoms from the vacuum stripper are pumped, using the liquid level control system described for overheads recovery, to a tubular cooler, where the temperature is reduced to about 150°F., and thence to a steel scale tank of approximately 100,000 pounds capacity.

Propane Recovery System

The high pressure propane vapors from the overheads flash drums flow directly to the propane condenser. The condensed propane at a temperature of 118-120°F. is then returned to the 14,000-gallon working supply tank. The high pressure propane vapors from the bottoms flash drum are led directly into the propane supply drum after passing through an entrainment separator. The quantity of propane gas recovered from the bottoms is relatively low and the exposed interior surface of the propane drum serves to condense these vapors. The low pressure propane and steam vapors from both the overheads and bottoms stripper systems are conducted to an inlet near the bottom of a jet condenser. This condenser is a vertical tower 20 feet high and 2 feet, 2 inches in diameter. It contains 5 feet of 1-inch Raschig ring packing. Water is pumped over the packing at a rate of about 24 gallons per minute. The mixed vapors passing up through the packing are cooled to about 80°F. while the steam is condensed and flows to the bottom of the condenser, where it is released to a sump together with the scrub water under liquid level control. Any traces of propane gas which might possibly be dissolved in the discharged water have ample time to escape before the water is discharged beneath the surface to the sewer lines. Any entrained fat which might find its way to the jet condenser will collect on the surface of the water in the sump and may be reclaimed by skimming.

The propane vapor leaving the jet condenser flows to a Worthington steam-driven, tandem, two-stage compressor. A pressure differential controller mounted on the control board fixes the pressure maintained in the jet condenser by controlling the speed of the compressor. The normal pressure in the jet condenser is about three pounds.

The first stage discharge pressure of the compressor generally runs about 70 pounds while the discharge pressure is about 280 pounds. The maximum compressor speed is 300 R.P.M. and the minimum 85 R.P.M. A mechanical flyball governor will prevent operation above 300 R.P.M., and a spring loaded plunger in the rim of the flywheel which will trip a valve in the steam supply line is provided as a second safety against excessive speed. The discharge of the compressor, which ties in with the high pressure overheads propane recovery system, is condensed and returned to the propane supply drum.

In operating the jet condenser, it would be most hazardous to have water overflow into the propane compressor due to clogging of the packing. As safety measures a warning signal light and howler have been installed in the control room. If the water level rises above the packing, a signal light and howler are activated. If the rise in level is not corrected, a second light is flashed on and the compressor is automatically shut down.

One other interesting item is the method preventing tallow and propane from blowing through the overheads or bottoms product pumps in the event of pressure build-up in the vacuum strippers. Cut-off valves have been located in the discharge lines of the steam-driven product pumps and are connected to the steam supply line to each pump downstream of the control valve operated by the liquid level in the vacuum strippers. Should the level in a stripper drop, the steam control valve will close, dropping the pressure in the line to the cut-off valve, which then shuts off, effectively blocking the line to the tank room. As the level in the stripper rises, this cut-off valve will again open.

As non-condensable gases and small amounts of ethane and other light hydrocarbon gases accumulate and cause increased pressure in the propane supply tank, it becomes necessary to purge them from the system. To do this without losing considerable quantities of propane, a purge gas cooler has been provided at the top of the propane supply tank. Liquid propane is expanded through the tubes of this condenser, creating temperatures as low as −40°F. This expanded gas is recycled through the jet condenser to the compressor, propane condenser, and back to the propane supply tank. Propane vapor, along with the undesirable gases, is discharged under manual control through the shell side of the purge cooler, where most of the propane will recondense and flow back to storage, while the non-condensable gases are vented to the blow-down stack.

Operation

In discussing the quantities of tallow and propane being used, there is frequent reference to a certain number of barrels per day or per stream day. This is a carry-over from the petroleum refining industry and is new to soap terminology. In this particular instance a "barrel" is 52 gallons. With tallow the 52-gallon barrel has a weight equivalent of 395 pounds. "Per stream day" or "day" refers to a 24-hour period.

The term "propane ratio" refers to the volume of propane used per volume of tallow. "Gradient," or "temperature gradient," is the term used to denote the differential in °F. between the temperature at top of the column and the established temperature in the lower section of the column.

The useful temperature range for the decolorization of tallow lies between 150° and 170°F. A set of tower operating conditions might be as follows:

Propane ratio	15:1
Tower pressure	465 psig
Tower temperatures, °F.	
Top	162.0
Baffle 2	161.5
Baffle 4	161.0
Baffle 6	160.3
Baffle 8	159.5
Baffle 10	158.5
Baffle 12	158.0
Baffle 15	158.0
Propane feed	7,500 bbl./day
Tallow feed	500 bbl./day (8,229 lb./hr.)
Tallow inlet temp. °F.	159.0°F.
Propane inlet temp. °F.	158.0°F.

In setting the operating conditions, the highest temperature which may be encountered in the tower must be carefully considered since this temperature determines the pressure which must be maintained within the tower. Using the conditions just outlined, the highest tower temperature is 162°F. At this temperature reference to a chart of propane temperatures vs. vapor pressures indicates that the vapor pressure of propane is 380 psig. It is recommended that an additional pressure of at least 30 pounds be superimposed to avoid gasification in the tower. This would then give an operating pressure of 410 psig. The chosen pressure of 465 psig is entirely arbitrary. It covers the range of operating temperatures which are likely to be encountered; and rather than change the tower pressure to correspond with the temperature in use, it is preferred to keep the pressure constant.

The tower temperatures are extremely important, particularly the top tower temperature. Variations of a few tenths of one degree will often be sufficient to change the color of the overheads product substantially. The top temperature also exerts a strong effect on the amount and composition of the bottoms product. The bottom tower temperature is also important although moderate changes in it do not cause the marked variations noticeable with changes in top temperature.

Contrary to most solubility effects, it is found that the solubillity of tallow in propane decreases as tower temperatures are increased. At low temperatures, i.e. 120°F., the oil is completely soluble while at temperatures of 180°F. the oil is almost completely insoluble. In pilot plant work it was found that

a) High operating temperatures produce more bottoms while low operating temperatures produce less bottoms and these low temperature bottoms contain a more concentrated proportion of the undesirable constituents.

b) The top tower temperature is directly related to the per cent bottoms produced and inversely related to the color of the overheads product.

c) Long temperature gradients produce better overheads colors than short gradients. However oxerextending the temperature gradient may result in flooding the column with oil.

Better overheads colors are obtainable with high solvent ratios than with low solvent ratios. When solvent ratios are changed, there must be an adjustment in temperature conditions to produce the desired effect. The temperature adjustment increases with increasing ratios and in the range between 10:1 and 30:1 is of the order of 3°F. change for every five-unit volume change in the propane ratio.

Changing the pressure maintained in the column also exerts a change in the decolorization process. Increased pressure results in increased solubility of the oil, and higher temperatures are required to precipitate the color bodies. It is therefore extremely important that the pressure maintained on the tower be held at a uniform and fixed value since variations in this pressure would result in erratic operation. This is not a difficult control problem, and no difficulty has been experienced in the pilot plant or the commercial unit in holding the pressure rigidly at a fixed value.

The use of overheads reflux was also investigated because it was thought that the increase of oil concentration in the top of the tower would change the equilibrium conditions between overheads and bottoms, thereby eliminating the last traces of bottoms from the overheads solution. "Reflux" refers to the volume of oil-propane solution from the first overheads stripper which is pumped back to a point near the top of the column. The composition of the reflux may be varied by imposing different conditions of pressure and temperature on the overheads in the stripper. If the pressure within the stripper is held close to that of the column, the propane content of the overheads will be high while if the pressure is held at a lower value, the propane content will decrease correspondingly. No appreciable benefit however has been found as a result of operations with external reflux.

The composition of the oil being decolorized also has an effect upon the temperature conditions required. Generally speaking, it can be expected that as the F.F.A. content of the oil increases, an increase in the tower temperatures will be required since fatty acids are appreciably more soluble in propane than are the corresponding glycerides. This change in temperature is in the order of .4°F. per every 1% increase in F.F.A.

Man-Power

It is considered that this type of operation is most economical when run on a continuous basis. A complete plant shutdown will require a minimum of about 8 hours. In starting up, the plant requires nearly 24 hours before entirely stable operating conditions are attained. In order to operate continuously, four operating crews are required. Each crew consists of a Number 1 operator, a Number 2 operator, and a pump man. The Number 1 operator is in charge of all plant operations and is assisted by the Number 2 operator, whose major function is to keep a strict watch over the instrument control operation and to keep the operating records. The pumper's responsibility is to see that the feed tanks are filled with crude stock and to make stock transfers as required. He is also responsible for the hourly weight checks which are used to estimate operating efficiency. In addition to these men, there are one plant supervisor and one man assigned to general housekeeping and utility work.

Conclusion

The decolorization of tallow by liquid-liquid extraction in propane is a significant advance in the treatment of tallows. It greatly surpasses the effectiveness of bleaching earths and chemical bleaches such as have been in use for many years.

Comparative Determination of the Consistency of Fats

ERNEST SCHLENKER and MARYSE FIDALEO, Research Laboratory, Fournier-Ferrier, Marseilles

IF one has to compare the consistency of a standard fat with the consistency of fat mixtures prepared in the laboratory, a penetrometer of the type described by Freyer (2) and by Feuge and Bailey (1) is of great help. The depth of penetration of a needle entering with a known force into the fat is a measure of the consistency, and identity of consistency may be assumed if the penetration has the same value for the standard and for the examined sample. Naturally, where the goal is to meet the consistency of a given standard, a certain (and sometimes a very great) number of mixtures has to be prepared before the desired identity will be reached. In each mixture it is necessary to know how much the experimental preparation differs from the standard if one is to give proper direction to the further investigation. The answer given by the penetrometer is, in this special case, unsatisfactory for penetration measurements determine only how much two samples are different at a given temperature. As a matter of fact, it is not certain that the same difference will be observed or maintained at another temperature as penetration is by no means a linear function of temperature. To make sure of an increasing resemblance of sample to standard, it would be more advantageous to know for a given sample how many degrees above or beneath a given temperature it assumes the consistency of the standard. This knowledge requires at least three determinations with the penetrometer at different temperatures and the construction of a curve, which is too long a procedure for a routine test.

Gradual approach to the standard is more easily observed with the apparatus described here, in which a metallic weight falls through a sample of the fat at the moment when its consistency, under the influence of heating, has attained a definite value. The observed consistency is defined by the range of temperature in which the falling weight covers a predetermined distance. Thus one is informed at which temperature a given sample has the same consistency as the standard. The difference between the new apparatus and the penetrometer is that the penetrometer gives the consistency at a well-defined temperature whereas the new apparatus indicates the temperature at which a sample has a well-defined consistency. One consistency only, that which corresponds to the weight of the metallic cylinder, serves to establish the degree of resemblance between sample and standard. Theoretically, any consistency of an infinite number may be chosen; it is necessary only to increase or to diminish the weight of the metallic cylinder. Practically, the choice is made in such a manner that the cylinder begins its course at a temperature easy to observe. It has to be sufficiently light that it cannot fall until the temperature is about 30°C., and it should be sufficiently heavy

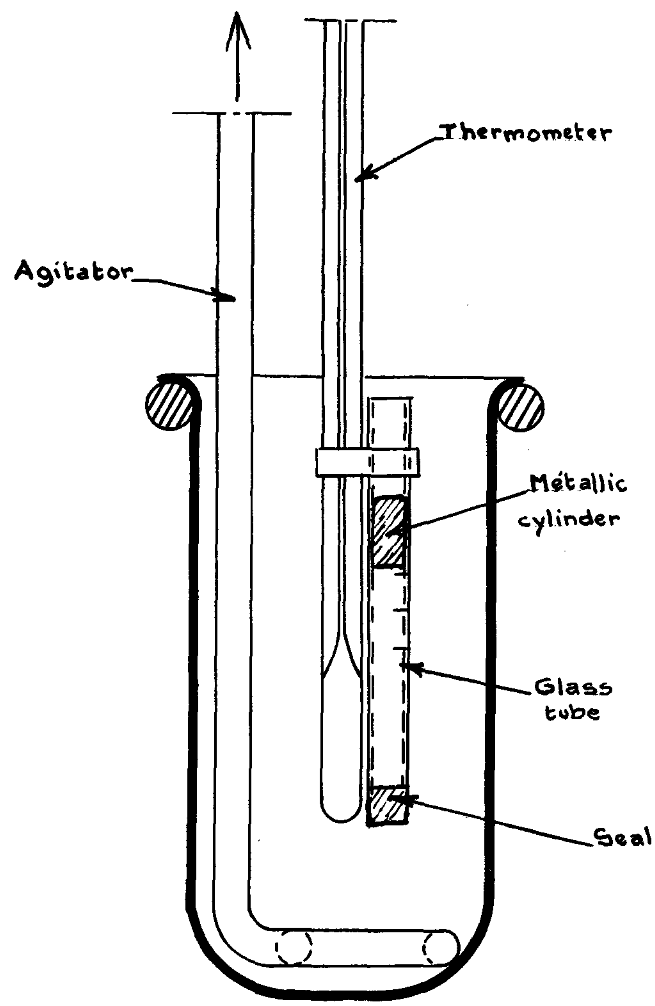


FIG. 1.