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A Commercial Process for the Recovery of Deodorizer Distillates[1,2]

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A BASIC PROBLEM facing the fat and oil industry is the recovery of the organic distillates from the deodorization process. Currently these distillates are drawn from the deodorizer into the vacuum system where they are condensed with water. This method of operation dilutes the distillates to a point where conventional recovery techniques are neither economical nor efficient. This problem is two-fold since the organic distillates which are lost represent commercially valuable materials and stream contaminants which complicate disposal techniques. Because of increasing community pressures and advancing costs, much concern over the recovery of these materials has been shown.

To correct this situation the Croll-Reynolds Company has developed a novel vapor-scrubbing unit. This unit, the Convactor, effects the removal of essentially all of the organic distillates from the deodorizer effluent vapors, thereby reducing stream pollution. Furthermore the organic distillates are concentrated by the Convactor in a closed-circuit, condensing-water system, making economic recovery of the distillates possible.

At Staley process water from the deodorizer barometric condensers is discharged to a hotwell. Here 50–75% of the organic material is recovered. The process water from the hotwell is then discharged to city sewers. The city Sanitary District treats this water on a toll basis, depending on its BOD content, dissolved solids, and volume. In order to reduce the organic load to the sewer system a method for recovering all of the deodorizer distillates was desired. To do this a Croll-Reynolds Convactor was installed in August, 1957, in the Staley oil refinery in conjunction with a conventional Girdler Semi-Continuous Deodorizer. This paper therefore explains a system for recovering the organic distillates, which were formerly lost in the deodorization process. This system may be divided into two separate operations: the vapor-scrubbing operation, which utilizes a Croll-Reynolds Convactor to remove the organic distillates from the deodorizer vapors, and the recovery operation, which utilizes a unique process developed by Staley for separating the organic materials from the Convactor condensing-water. For the purpose of simplicity these two operations will be considered separately.

The Vapor-Scrubbing Operation

The vapor scrubbing operation is performed in a Croll-Reynolds Convactor (Figure 1). This consists of a black iron tower, which is divided into four specific sections: a barometric-condenser section, a scrubber-condenser section, a flash chamber, and a water reservoir. The barometric condenser and the flash chamber are joined by a vapor-balance line. This allows flashed vapors to rise from the flash chamber to the barometric condenser for condensation and to discharge from the system *via* the barometric downleg.

The auxiliary equipment required to complete the vapor-scrubber system are a scrubber-condensing-water recirculation pump and a scrubber-condensing-water-level controller. The deodorizer effluent vapors

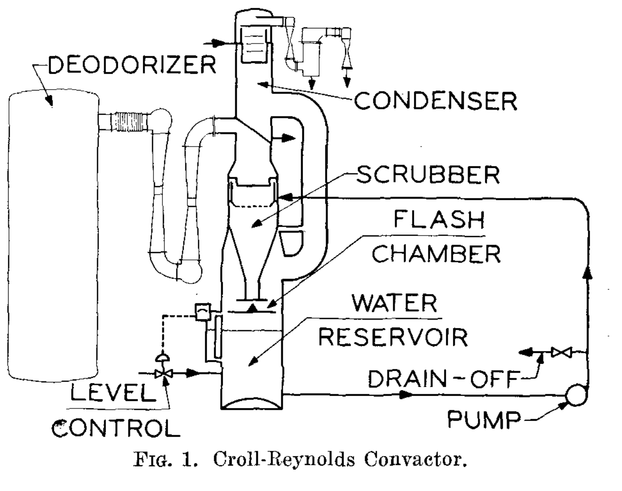

FIG. 1. Croll-Reynolds Convactor.

enter the upper portion of the scrubber-condenser section of the tower and are deflected downward through a curtain of "cool" (100°F.) scrubber-condensing water. The scrubber-condensing water, which will be referred to as scrubber water, is contained in a closed-circuit system and is continuously recirculated through the scrubber condenser, flash chamber, and water reservoir at a nominal rate of 1100 gpm. In the scrubber-condenser section of the tower the entire stream of vapors leaving the deodorizer, organics plus steam, are condensed. The temperature of the "cool" scrubber water is raised slightly on account of the release of heat by these condensed vapors. This "warm" (105°F.) scrubber water then falls through a water-collecting cone (parallel flow condenser), where intimate contact between any remaining uncondensed vapors and the scrubber water occurs, then into the flash chamber.

Since the flash chamber is in balance with the barometric condenser, it operates at a lower pressure than the scrubber condenser. Therefore the heat which was picked up by the scrubber water in the scrubber condenser is immediately dissipated in the flash chamber by rapid evaporation or "flashing" of steam from the warm scrubber water. This evaporation process is facilitated by the tremendous surface-area of the warm scrubber water, which is exposed by splashing on a cone-shaped baffle as the scrubber water falls into the flash chamber. This flash-cooling process returns the scrubber water to the equilibrium temperature of the water reservoir (100°F.).

Since a fairly high degree of superheat is present in the vapors entering the Convactor, the total weight of saturated steam flashed from the warm scrubber water is greater than the weight of the incoming vapors. This "excess" flash, caused by the superheat of the vapors, is continuously made up by adding water to the Convactor water reservoir *via* the liquid level controller. The flashed vapors, which are relatively free of organic contaminants, rise through the vapor-balance line and are condensed in the barometric condenser. The condensed distillates, being relatively nonvolatile in the conditions existing in the flash chamber, do not flash but accumulate in the scrubber water.

The net result of this operation is the removal of the organic distillates from the deodorizer vapors and the concentration of these distillates in the scrubber water.

Physical Properties of the Scrubber Water. The condensed organic distillates continuously accumulate in the scrubber water. These distillates, including the physically entrained solids, consist of varying amounts of fatty acids, glycerides, sterols, and tocopherols. These materials are relatively immiscible with the water in which they are condensed. This accumulation of organic distillates in the scrubber water takes the form of an oil-in-water emulsion. The unusual physical behavior associated with this emulsion is of great significance both in the operating characteristics of the Convactor and in the design, operation, and economics of the distillate recovery system.

From a qualitative stand-point four distinct phases occur as the concentration of the organic distillates in the scrubber water increases from 0 through 1.5%. The limits described for each phase are not rigid entities and are representative only of distillates received from the deodorization of Staley's 50 Oil. 50 Oil is an acetic anhydride degummed soybean oil, which is break-free but contains 0.2–0.3% FFA (1, 2). Since the characteristics of the scrubber-water emulsion are dependent upon the composition as well as the concentration of the distillates, different feedstocks may behave in slightly different manners.

Phase I occurs betweeen 0 and 0.15% organic distillates in the scrubber water. The scrubber water becomes a turbid white, resembling milk. The fluidity characteristics are not greatly different from water during this phase.

Phase II occurs over the range 0.15–1.0% organic distillates in the scrubber water. Over this range increasing portions of the organic materials begin to associate, forming solid aggregates or flocs which float in the scrubber water. This phase is characterized by a gradually increasing scrubber-water viscosity. However this "thickening" does not materially affect the flow properties of the scrubber water.

Phase III covers the concentration range from 1.0–1.5% organic distillates in the scrubber water. The flocculent organic solids which float in the scrubber water become very dense, causing the scrubber-water viscosity to increase more than a hundred-fold. In this phase the fluidity characteristics of the scrubber water are greatly reduced.

Finally phase IV occurs when the concentration of organic distillates in the scrubber water rises above 1.5%. This is not illustrated on the graph. This phase is characterized by "gelling" of the entire scrubber-water stream. Any force which is applied to this mayonnaise-like gel merely deforms it, extruding some of the entrapped water and further tightening the emulsion. At this point, because of the plastic character of the gel, no scrubber-water can be recirculated, and the Convactor is, in effect, inoperative.

Figure 2 illustrates the Scrubber-Water Viscosity and the Scrubber-Water Recirculation Rate as a function of the concentration of the organic materials in the scrubber water. The viscosity illustrated in Figure 2 is more correctly referred to as an "apparent viscosity" since physical measurements on heterogenous solutions cannot be considered as absolute. The reported viscosity values were measured on a standard Brookfield Viscosimeter, using vertical agitation uniformly to disperse the flocced organics throughout the solution. This mode of agitation was reported on water-control samples with no adverse effects. It was then assumed that the vertical agitation, being at right angles to the plane in which the viscosity measurements were made, did not significantly affect the final results. The recirculation rate illustrated in Figure 2 represents the volume of scrubber water

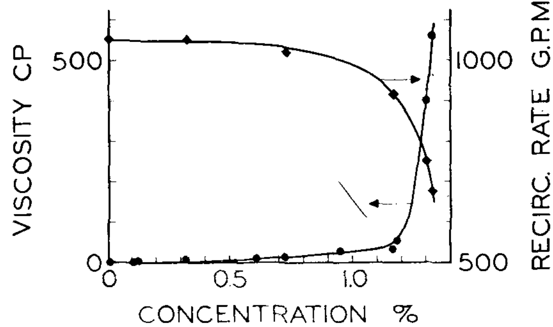

FIG. 2. Viscosity and recirculation rate *vs.* organic concentration in scrubber water.

recirculated through the system at normal pump loads.

Figure 3 is an actual photograph of scrubber water as it appears in the first three previously described phases. This gives some idea of the nature of the material being handled.

Operating Characteristics of the Croll-Reynolds Convactor. It may be seen from the preceding description that for the Convactor to operate satisfactorily the concentration of the organic material in the scrubber water must be maintained somewhere below 1.5% and preferentially below 1.0%.

The concentration of organic material can be maintained at any pre-determined level of continuously removing a portion of scrubber water from the system. The actual drain-off rate required is primarily a function of the rate and chemical composition of the oil to and from the deodorizer and of the concentration of the organic distillates in the scrubber water.

Study of the Convactor reveals that its efficiency is affected by either one, or a combination, of three mechanisms:

a) organic vapor losses because of the partial pressure exerted by the organic material in the scrubber water;
b) organic vapor losses because of a loss or impairment of the water seal in the scrubber-condenser section of the Convactor. A loss of seal would, in effect, allow the deodorizer effluent vapors to by-pass the scrubber and go directly to the barometric condenser;
c) organic losses because of the physical entrainment of droplets of scrubber water containing condensed organic materials in the vapors flashed to the barometric condenser.

Studies were made to determine the magnitude of the organic losses which could be attributed to each of these preceding mechanisms.

The organic vapor losses caused by the partial pressure exerted by the organic material present in the scrubber water may be shown to be negligible. This results from the extremely low vapor pressures exerted by these substances at the temperature of the Convactor flash chamber.

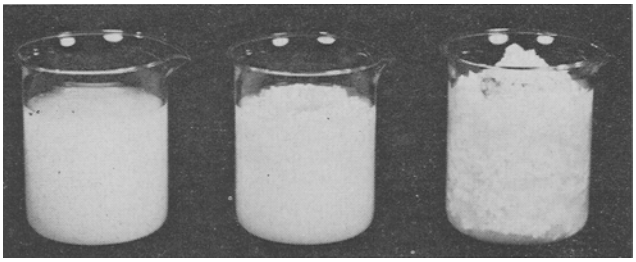

Fig. 3. Convactor scrubber water.

Likewise the organic vapor losses resulting from a loss or impairment of the water seal in the scrubber-condenser section of the Convactor may be neglected. Proper care must be taken to maintain the organic concentration of the scrubber water at a sufficiently low level so that normal scrubber-water recirculation rates are maintained. Normal recirculation rates will insure a condensing water seal on the Convactor at all times.

It can be seen therefore that the main source of organic losses may be traced to a physical entrainment of droplets of scrubber water in the vapors which flash to the barometric condenser. The method employed to determine the magnitude of entrainment was one in which the chloride content in samples of water to and from the barometric condenser were compared after 300 lbs. of sodium chloride were added to the scrubber water. Since sodium chloride is a nonvolatile salt, it was assumed that any increases in the chloride content of the water passing through the condenser would, of necessity, be caused by a physical entrainment of the scrubber water containing the chlorides in the flashed vapors.

Analyses of these samples indicated that no statistically significant entrainment of chlorides, or scrubber water, occurred. It was decided to operate the Convactor at a scrubber-water concentration of 1% organic material. At this operational range it may be stated that the over-all efficiency of the Convactor is above 99%.

The Recovery Operation

It has been seen that a continuous drain-off of scrubber water is required to keep the Convactor operative. It can also be seen that, if this drain-off is put directly to the hotwell or to the sewer, neither loss reduction nor material savings are realized. Likewise the added expense to over-all refining operations prohibits discharging the drain-off to either the soapstock-acidulation system or the waste-water-treating system. Without a suitable system for recovering the organic distillates from the scrubber water, operation of the Croll-Reynolds Convactor held no particular advantage for Staley.

It was found that a number of unit operations are applicable to the problem of separating the orpanic materials from the scrubber water. The process chosen as most suitable to our needs was one which utilized heat to "break" the scrubber-water emulsion into two liquid phases and centrifugation to separate the organic and aqueous phases.

Preliminary testing indicated that, depending on the concentration of organic materials in the scrubber water, the temperature required instantly to break the scrubber-water emulsion into two liquid phases varied from 212–240°F. Lower temperatures could be employed if long contact periods between the scrubber water and heat were utilized. The temperature at which the scrubber-water emulsion "breaks" to two liquid phases, referred to as the "Heat Break Temperature," is illustrated in Figure 4 as a function of the Concentration of Organic Material in the Scrubber Water.

It was further found that by recycling as little as 5% of the hot liquid distillates from the centrifuge back to the scrubber-water drain-off, the temperature required to "instantly break" the scrubber-water

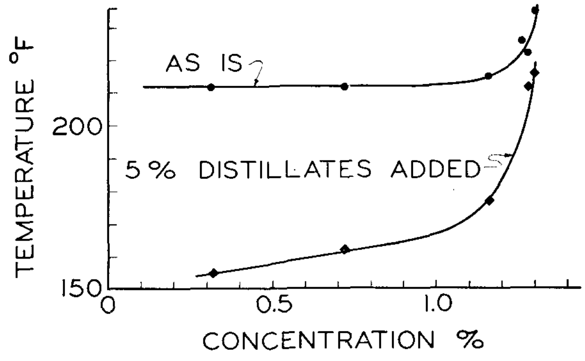

Fig. 4. Heat-break temperature *vs.* organic concentration in scrubber water.

emulsion was lowered to 155–165°F. over the normal range of scrubber-water concentrations. This finding considerably improved the economics of this mode of recovery.

The efficiency of the centrifugal step, defined as the percentage of organic material removed from the scrubber-water emulsion, was determined to be between 75–85% for the normal range of organic concentrations in the scrubber water. Since this efficiency was not significantly greater than the hotwell separation, it was decided to return the processed scrubber water from the centrifuge to the Convactor tower. In this way all of the distillates were recovered. This had one further advantage in that an economy of water was realized. Economic considerations indicated that heat economy was also necessary for economic operation. The hot, processed scrubber water from the centrifuge therefore was returned to the Convactor *via* a heat economizer.

Based on laboratory and pilot-plant experimental work, a temporary distillate recovery system was installed in the Staley oil refinery. This system was operated for a test period of two months, from October 31 to December 31, 1957. Two methods of operation, with and without recirculation of the processed scrubber water, were studied. This experimental system gave the data subsequently used in the economic justification and the design of the recovery system.

The process being considered for use in the Staley oil refinery is indicated in Figure 5. Scrubber-water will be drawn from the Convactor by a centrifugal pump. Roughly 5% of the liquid distillates will be recirculated to the drain-off stream at the suction side of this pump. The scrubber water will pass through a heat exchanger, where heat will be picked up from the hot processed scrubber water returning to the Convactor. Next it will be heated to a prescribed point by the injection of steam into the line. This steam will supply heat and will serve as a portion of the scrubber make-up water.

After heating, the scrubber water will be fed to a centrifuge where the separation of the organic distillates will be completed. The centrifuged distillates, containing up to 10% water, will be separated into recycle and product streams in a surge tank. The distillates will then be dried and stored. As explained, the processed scrubber water will be returned to the Convactor *via* the heat economizer.

Operational Results. The following operational results shown in Table I represent 52 operating days during the trial period. The shell drain material was weighed each day. This weight was corrected to an organic dry-substance basis, and the average was reported.

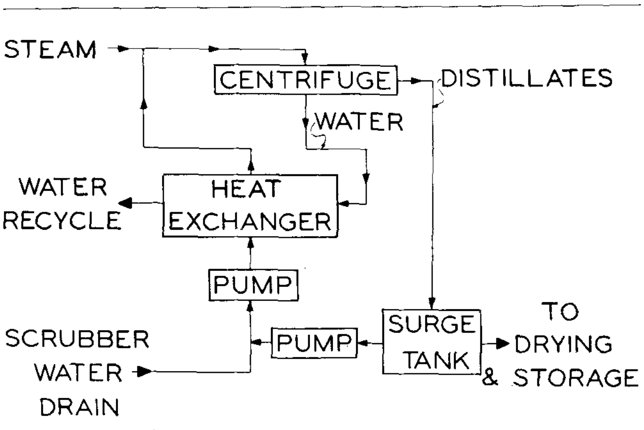

FIG. 5. Distillate recovery system.

The material recovered from the Convactor was determined by two methods. In the first method the recovered distillates were weighed each day and corrected to an organic dry-substance basis. In the second method the drain-off stream was sampled to and from the centrifuge. The change in the organic content (method described below) was multiplied by the known drain-off rate to give the weight of distillates recovered each day. The average of these two results was reported.

TABLE I
Operational Results

	November 1957	December 1957
Bleached 50 Oil to Deodorization		
TC/day	4.0	3.8
% FFA	0.18	0.22
Deodorization losses, lbs./day		
Recovered shell drain	88	93
Recovered distillates (Convactor)	825	1260
Lost in downleg	48	33
Measured deodorizer loss	0.40	0.61

The amount of organic distillates lost in the downleg of the primary barometric condenser was determined by sampling the water to and from the condenser and multiplying the average change in the organic content of these samples (method described below) by the water flow-rate in the downleg. The flow rate was determined by both heat-balance calculations and the pressure drop across an orifice meter.

The amount of organic material in the water to and from the barometric condenser and in the scrubber water to and from the centrifuge was determined as follows. Measured volumes of sample, 1 quart for the barometric water and 1 pint for the scrubber water, were acidified with 1% by volume of concentrated HCl. The fatty material was then extracted with 10% CCl_4 by beating in a Waring Blendor. The CCl_4 layer, containing the fat, was separated in a separatory funnel and filtered through filter paper into a tared evaporation dish. The CCl_4 was removed by evaporation. Corrections were made for the residue in the CCl_4 by evaporating a control CCl_4 sample.

It is most interesting to note that the deodorization of Staley's 50 Oil does not significantly increase the deodorization losses above what would normally be expected for a caustic refined oil.

The typical ranges for various analytical characteristics of the distillate material recovered from 50 Oil deodorization are shown in Table II. These analytical data were determined according to the Methods of the American Oil Chemists' Society.

TABLE II
Analytical Characteristics—Soybean Oil Distillates

T.F.A. %	97–99
F.F.A. %	55–65
Neutral oil %	10–15
Sterols %	12–16
Tocopherols %	2–5

Summary

A continuous system for recovering the organic distillates from the deodorization process has been briefly described. The operation of this system essentially eliminates barometric condenser-water disposal problems since this water is relatively free of organic contaminants.

At a nominal cost, which can be economically justified, all deodorizers could be put on a closed-circuit water system. The cooling towers in this system would remain clean and would require little maintenance. The organic materials, which were formerly lost as stream contaminants, would be recovered in a dry form which holds a premium over acidulated soapstock.

This system would prove advantageous to the many processors of fatty products who are currently having waste-water disposal problems or who are operating on closed-circuit water systems, where periodic shutdown, cleaning, and maintenance of the cooling tower are required. The system is a major step toward solving the problems which have been so important in the past few years.

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Long-Chain Unsaturated Alcohols from Jojoba Oil by Sodium Reduction[1]

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JOJOBA OIL is unique in that it is a liquid wax rather than a glyceride oil usually found in oil-bearing vegetable materials; also it is unique in that it is an excellent source of unsaturated C_{20} and C_{22} straight-chain acids and alcohols. These long-chain, monoethylenic components are present as esters and comprise 93% of the jojoba oil, of which 45% are C_{20} acids and alcohols (eicosenoic and eicosenol) and 48% C_{22} acids and alcohols (docosenoic and docosenol).

Jojoba oil is present in the seed of the jojoba plant, which is known botanically as *Simmondsia chinensis* and *Simmondsia californica,* the description of which has been reported in several publications (3, 13). The seeds contain approximately 50% oil, which can be extracted in a remarkably pure state by conventional pressing and solvent-extraction methods commonly used for glyceride vegetable oils. The chemical composition of jojoba oil as reported by McKinney and Jamieson (9) is shown in Table I. Review articles on the composition, properties, and potential uses of jojoba oil have appeared recently (6, 8).

TABLE I
Chemical Composition of Jojoba Oil (9)

Compound	%
Eicosenoic acid	30.30
Docosenoic acid	14.20
Eicosenol	14.60
Docosenol	33.70
Saturated acids	1.64
Palmitoleic acid	0.24
Oleic acid	0.66
Glycerin	0.0
Hexacosenol	2.0

The sodium reduction method has been used commercially to produce alcohols from glyceride esters. Kastens and Peddicord (7) in a staff-industry report show that the best results from the commercial scale reduction of coconut fatty esters were obtained by using molten metallic sodium dispersed in toluene, and a secondary alcohol such as methyl isobutyl carbinol as the reducing alcohol.

Application of the sodium reduction method to jojoba oil was investigated because high yields of alcohol obtained from glyceride esters were reported (4, 7) and because the ethylenic unsaturation was not affected. This paper presents the results of a study of the preparation of long-chain unsaturated alcohols by sodium reduction of the wax fatty esters of jojoba oil on both a laboratory and pilot-plant scale.

Experimental

Equipment. The laboratory reduction and hydrolysis apparatus used in this work is similar to that described and used by Hansley (4). The pilot-plant reduction and hydrolysis units shown in Figure 1 are constructed of stainless steel. The dish-bottomed, jacketed, reduction vessel has an operating capacity of 15 gal. and is equipped with an auxiliary stainless steel stopper which fits flush to the bottom outlet to prevent unreacted metallic sodium from settling in the drain line. The 20-gal. hydrolysis unit is equipped with a condenser and a steam-sparging tube for heating the water for the hydrolysis step.

Materials. The jojoba oil used in this work was prepared by flaking and cold-hydraulic-pressing raw jojoba beans supplied by Boyce Thompson, Southwestern Arboretum, Superior, Ariz. The oil was dried at 220°F. for 30 min. under a vacuum of 27 in. of mercury to remove any traces of moisture present. The oil analyzed as follows: 49.44% unsaponifiables, 0.39% F.F.A., 0.08% hydroxyl, saponification value of 88.7, and iodine value of 83.1. American Oil Chemists' Society methods were used for analyses (1). Commercial grades of methyl isobutyl carbinol, toluene, and metallic sodium were used.

Procedure. The procedures for both the laboratory scale and pilot-plant scale experiments were similar, with the exception of the amounts of materials used. Theoretical proportions of materials required for the sodium reduction reaction are four atoms of sodium

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[1] Presented at the fall meeting, American Oil Chemists' Society, Cincinnati, O., September 29–October 2, 1957.

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