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Fractional Distillation of Fatty Acids[1]

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WHAT appears simple today was a vexing problem in an earlier day. Back in the early 1930's when continuous processes in the fat and oil industry were not as generally available as they are now, the separation of many crude fatty acid mixtures into relatively pure chemical components had been considered. Yet these separations had not been successfully accomplished in the broad industrial sense because batch operation had been a primary limiting factor for most feed stocks. Application of heat to a batch of crude fatty acids at high temperatures over long periods of time, measured in hours, caused coking, polymerization, and breakdown of the fatty acids. Because of these difficulties some separation of fatty acids was accomplished by crystallization followed by hydraulic pressing.

By continuously introducing fresh feed and simultaneously removing the products from the fractionation, they reasoned it should be possible to cut down the time the fatty acids would be held at high temperature. Continuous operation on an industrial scale justified this idea.

By applying heat to a continuous feed stock and by cooling the products as soon as possible after separation, the heating and cooling times were greatly reduced compared to batch distillation. In addition, the period of stock retention at elevated temperatures after heating and before cooling in a commercial continuous fractional distillation system could be made far less than in a batch still of comparable size.

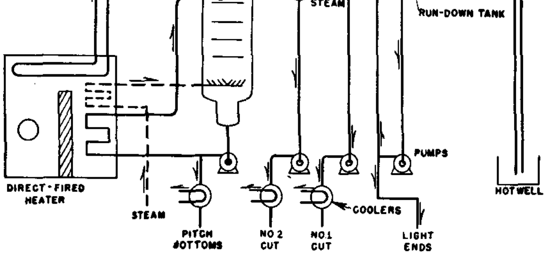

FIG. 1

The foregoing statements are only a brief glimpse of the core of the problems relating to fatty acid distillation. Many other factors, with only indirect or even no effect upon operating temperatures, are directly involved in assuring product quality.

The first continuous fractional distillation unit for separation of fatty acid mixtures was installed by Armour and Company in 1933. Reference to a previous article (1) on this subject shows that the first fractional still consisted of a main tower, two smaller side stripping towers, conventional air ejectors and boosters, condensers, coolers, and a direct-fired fatty acid heater. The flow sheet of this unit is shown in Figure 1. Though commercially successful, considerable operating difficulty was experienced, particularly in coking of the heater and by corrosive attack on the equipment by the fatty acids themselves.

The next step was the elimination of the direct-fired fatty acid heater with an indirect heating system, using condensing Dowtherm vapor. This means of heating had not been available when the distillation system was originally designed. Its use made possible the installation of stand-by shell and tube heaters, which eliminated fouling or coking as a reason for plant shutdown. In addition, the relatively gentle indirect Dowtherm heat resulted in considerably lower fatty acid film temperatures with a consequent reduction in corrosion and in the amount of coke formed. The general arrangement of this modified distillation system is shown in Figure 2.

When a completely new, second, fatty acid fractional distillation system was installed in 1941, it included many features of design found lacking in the original unit. It consisted of a three-tower system,

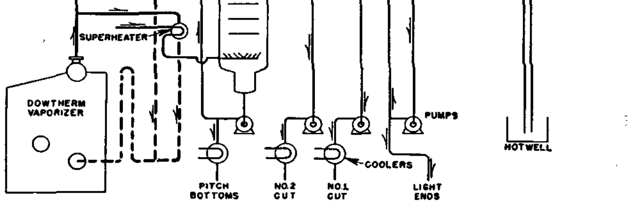

FIG. 2

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[1] Presented at the spring meeting, American Oil Chemists' Society, Houston, Tex., April 26-28, 1952.

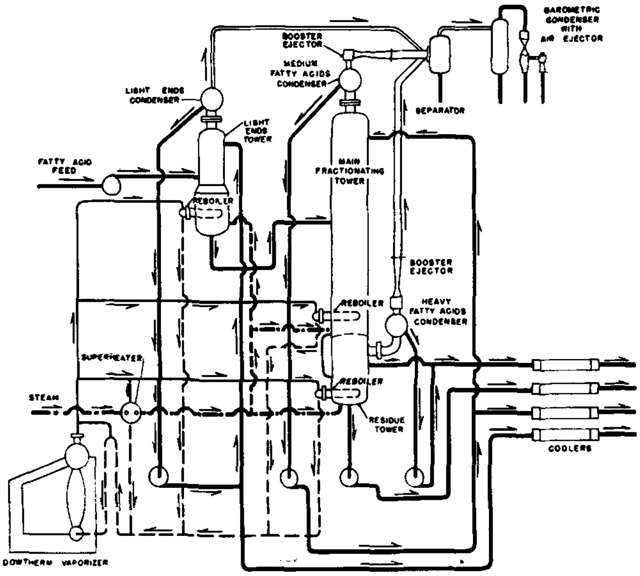


FIG. 3

similar in principle, but quite different in detail from the first unit in its modified form. Quite logically, the identical comments can be made about subsequent more modern distillation units built since 1941 in comparing them with the second unit.

In 1948 General Mills started operation of its Chemoil plant in Kankakee, Illinois, a complete fat and oil processing plant. As raw material, it used low grade fats, oils, acid oils, and tall oil to produce finished fractionated fatty acids, fatty acid esters, and their derivatives (2). The fractional distillation section is representative of modern practice and is shown schematically in Figure 3.

Note that, at first glance, the distillation system has only two towers. Closer inspection shows three towers are actually present, with the second superimposed upon the third to conserve space and construction costs.

In this plant, as in all subsequent ones, the fatty acid preheater was eliminated. This piece of equipment proved to be a source of maintenance expense, due to periodic blockages inside its heated tubes. Inorganic material in water solution, carried along by the fatty acid feed stock, deposited inside the tubes as soon as the water vaporized. Complete dehydration of the feed stock before distillation would eliminate this difficulty but was not adopted due to its added complexity.

The problem was solved by introducing fatty acid feed directly into the first distillation tower. Sensible heat to preheat the feed stock, as well as latent heat, was provided by fatty acid vapors rising from the reboiler in the base of the tower. Thus, dissolved solids are dispersed harmlessly in the tower and may be easily carried along with the bottoms stream. This makes it possible to operate satisfactorily with a wet feed stock, a difficult problem at best when using a preheater.

Since the sensible preheat represents a significant part of the load, the base of the first tower must be made larger in diameter than the upper section above the feed plate.

To review the schematic flow diagram, reference is made to Figure 3. Feed stock fatty acids containing a small amount of moisture are fed directly to the light ends tower in which a low boiling distillate is removed. This may consist of a concentrated odor and dark color-bearing fraction, whose removal upgrades the remaining fatty acids. Bottoms from this tower are transferred to the main fractionating tower by gravity and vacuum.

In the main tower, if feed stock is similar to tallow or cottonseed oil fatty acids, a fraction high in palmitic acid is removed from the overhead condenser.

From the base of the main tower the bottoms stream flows by gravity to the third tower directly below. In this tower higher boiling fatty acids, such as oleic acid, are recovered from the condenser. Residue from the base of the third tower may be converted into pitch.

Continuous fractional distillation systems of the type illustrated in Figure 3 were subsequently installed in three other locations.

Armour and Company at McCook, Illinois, put in a plant to be used in conjunction with their production of long chain fatty nitriles, amines, and amides. Another article (3) describes this plant in detail. Particular emphasis was placed upon convenient operability and labor-saving automatic control. To this end all regulators and controls were installed in a single control room adjacent to the tower structure.

Other plants of this type are in operation at Hess Products Ltd. in England and at Sandar Fabrikker in Norway (4). While these plants are designed to handle fish and whale oils as a principal feed stock, palm kernel, tallow, cottonseed, and other stocks will be processed.

Materials of Construction

Materials of construction for these plants originally represented a major obstacle to successful operation. As a matter of fact, this problem has not been completely solved since reboiler bundles require periodic replacement.

At one time ordinary type number 304 stainless steel, containing about 18-20% chromium, 8-11% nickel, a small percentage of carbon, and the balance mainly iron, was thought to be adequate. This belief was abruptly changed by commercial operation. Type number 316 stainless steel, containing approximately the same constituents, but with the addition of molybdenum, was substituted. Certain steel mills have sold type number 316 stainless steel with 1.75-2.5% molybdenum content, while others included 2-3%. Experience indicates that a high molybdenum content is desirable and that a minimum value of 2.5% looks right. Lower molybdenum contents do not necessarily imply the stainless steel will have a short life since operating conditions vary, but the higher content is generally preferable. Low carbon content is also helpful to minimize precipitation in the metal of chromium carbide concentrations. These points of carbide precipitation are more susceptible to fatty acid corrosion than other portions of the metal.

Inconel has also been used with success in place of stainless steel in these distillation systems, but at the moment a considerably larger amount of type number 316 is in use.

If full details of operation are known, the less expensive type number 304 stainless steel may sometimes be used. However under no conditions should the metal temperature exceed 350-400°F.

Important Design Factors

As stated above, the need for minimum temperatures and minimum holding periods while the fatty stock is hot govern the design of fatty acid distillation systems. It is necessary to:

a) Provide good vacuum equipment for the system to permit operation at low absolute pressures.
b) Minimize the pressure in the tower and tower reboiler by careful design and generous proportioning of vapor passages.
c) Reduce liquid hold-up to a minimum.
d) Make use of stripping steam as an inert medium to reduce the fatty acid partial pressure needed for boiling.

The first point a) can be covered by specifying use of the most reliable type of vacuum equipment for this service; namely, steam jet air ejectors. For handling large volumes of vapor at low absolute pressure no device has been developed to challenge this type of vacuum equipment.

It is worthwhile to note that an ejector, which has no moving mechanical parts, cannot be installed haphazardly if maximum efficiency is to be obtained. At the high vacuums used in continuous fractional distillation, care must be taken to provide completely dry steam. In outdoor installations in the northern part of this country particular attention must be given to this point.

It is also necessary to steam-trace part of the diffuser and throat of the first stage ejector, which is alternatively named the booster ejector or thermocompressor. If this precaution is not taken, both congealed fatty acids and ice could partially block the vapor passageway through the booster ejector and thus adversely affect its efficiency.

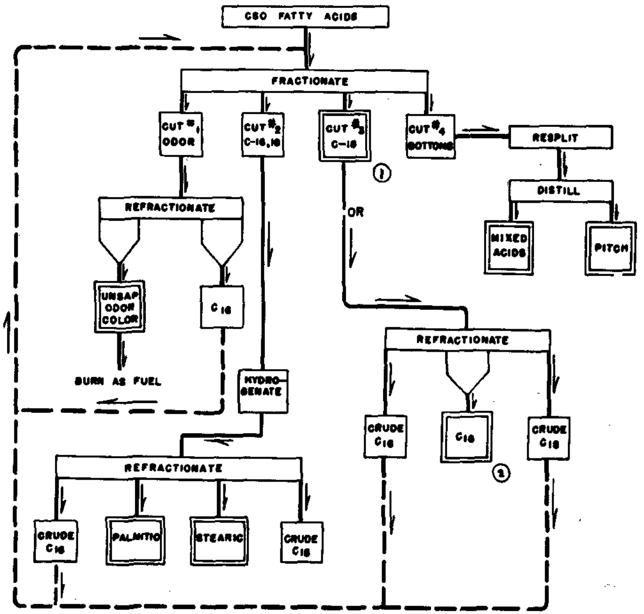
The second design factor mentioned calls for minimizing pressure drop in the tower and reboiler. Such a requirement is basically apparent since lower pressure drops will result in lower absolute pressures and lower fatty acid boiling temperatures. This end may be accomplished by careful attention to detail in the design of reboiler, trays, vapor lines, and condenser.

As an example, you will recall from Figure 3 that the fatty acid condensers are mounted directly on the towers (or adjacent to them). Since the volume of vapor leaving the condensers is so much lower than the amount entering, it is highly desirable to condense the distillate as soon as it leaves the tower. External condensers are so arranged that pressure drop through any one of them is only a fraction of a millimeter of mercury, limiting any reduction in pressure drop to a negligible factor.

Bubble trays and reboilers should be proportioned to minimize the liquid head resistance to vapor flow. Bubble caps with their vapor risers must have interrelated proportions, which are far more important at low absolute pressures than at higher pressures. This attention to detail makes possible an average pressure drop of approximately one millimeter of mercury per tray. Entrainment eliminators must be of low pressure drop types if located between a condenser and its booster ejector. In short, all items of equipment in the vapor path must be tailored for high vacuum service.

Previously the need to handle heat sensitive materials for only short times at high temperature was stated. Naturally the higher the temperature, the greater will be the degradation of the feed stocks per unit of time, and conversely higher temperatures are feasible if the time at high temperature is limited. To give some order of magnitude to this idea, a fatty acid feed stock based upon cottonseed oil foots can be maintained at 450-500°F. for 30 to 60 minutes without danger of excessive degradation due to cracking or polymerization.

COTTONSEED FATTY ACIDS FRACTIONATION



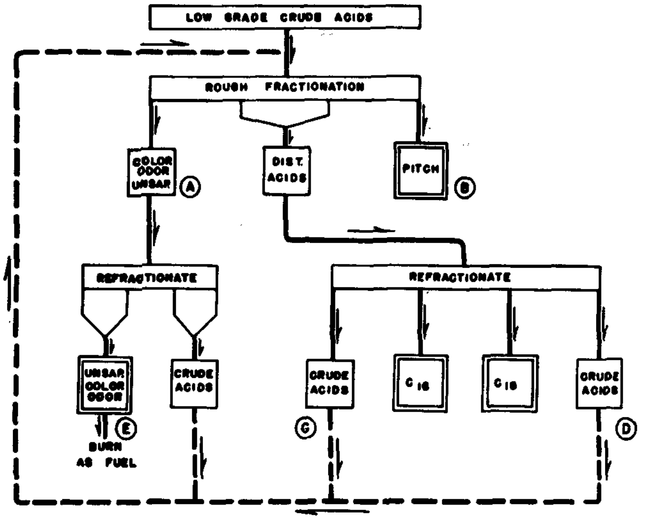
THIS EXAMPLE SHOWS WAY TO OBTAIN FRACTIONS OF INCREASED (AND DECREASED) UNSATURATION.

THE RECYCLED MATERIAL IS SMALL IN QUANTITY AND MUST BE ACCUMULATED OVER LONG PERIODS BEFORE REPROCESSING.

FIG. 4

Bubble trays or other fractionating devices must be designed for small holdup, and this indirectly helps reduce tower pressure drop as well.

FOOTS, ACID OIL– FATTY ACIDS FRACTIONATION



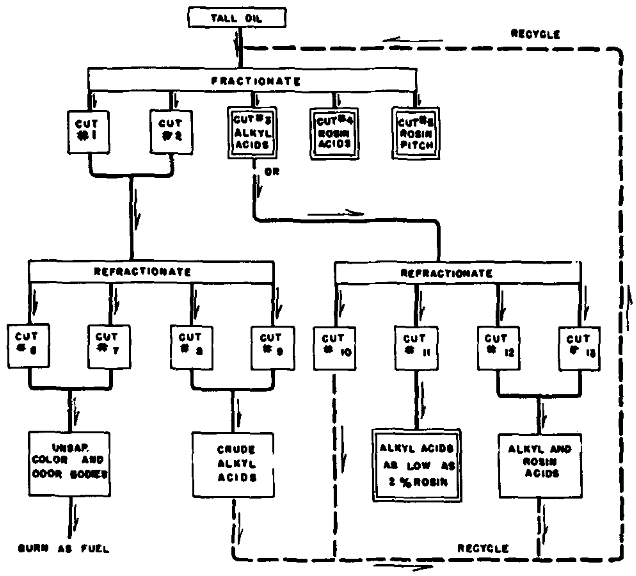
THIS EXAMPLE SHOWS WAY TO OBTAIN HIGHLY PURIFIED N-ALKYL ACID FRACTIONS FROM LOW GRADE FOOTS, ACID OIL, ETC.

AT A,B,C,D, THE IMPURITIES ARE REMOVED, I.E. COLOR BODIES, ODOR, UNSAPONIFIABLES, OXYACIDS, POLYMERS, ETC.

AT E,B, THEY ARE ISOLATED FROM THE SYSTEM.

FIG. 5

EXAMPLES OF TALL OIL FRACTIONATION



NOTE: RECYCLE STREAMS ARE SMALL AND MUST BE ACCUMULATED BEFORE REFRACTIONATION.

FIG. 6

The last factor is one which again relates to the designer's attempt to cause boiling at the lowest possible temperature consistent with equipment size and vapor losses. The use of stripping steam to promote boiling has a good analogy in the deodorization of vegetable oil, in which steam is used to help remove volatile undesirables in the oil, such as fatty acids. There is naturally a proper balance between the degree of vacuum maintained in the fractional distillation system and the quantity of stripping steam used.

The "Why" of Fractional Distillation

Coming from naturally occurring sources, fats or oils used for the production of fatty acids are complex compounds. Their glycerides include over a dozen types of fatty acid chains of various carbon molecule lengths and degrees of unsaturation. Even the same type of fat or oil will vary markedly in its composition from one season to the next or from one geographical area to the next. Generally speaking, the farther north the source of the sample, the greater its degree of unsaturation. Changes of this sort are providential from the standpoint of the farmer and the fish that swim in the sea, but inconvenient to users of naturally mixed fatty acids who are seeking raw materials of consistent composition.

Examples of means of separating typical fatty acid feed stocks are shown in Figures 4, 5, and 6 for vegetable acid oil and tall oil. These were obtained from Douglas Malcolm of Hess Products Ltd. Table I shows possible products from the fractionation of cottonseed fatty acids suggested in Figure 4, while Table II covers tall oil products made as shown in Figure 6.

Users of fatty acids generally do not feel the need for a 100% pure raw material but prefer a relatively pure fatty acid or mixture of fatty acids of consistent and known properties. Frequently the preferred properties can only be obtained by tailoring the fatty acid mixture to a definite composition, one differing from the naturally occurring composition in triglycerides. A good example of this would be the mixing of oleic and lauric acid derivatives to produce good emulsification properties for use in DDT sprays. By correctly proportioning the two acids, compatibility with both oil and water is possible.

Large numbers of uses for pure fatty acids have been developed, and mixed acids are regularly being replaced by purer products of regulated properties. An example of this sort is in the detergent field, which is best served by lauric acid. Chain lengths shorter than the 12-carbon atoms in lauric acid would irritate human skin while longer length molecules would decrease the wetting ability of the detergent.

Vinyl resin plasticizers make use of caprylic acid to best advantage. A number of fatty acids are used in producing alkyd resins while melamine and urea resins may be modified with lauric acid alkyds. Lauric acid is again best in producing germicidal properties in quaternary ammonium salts. Metal stearates are used for waterproofing clothing. Oleic acid and coconut oil fatty acids are the major constituents of Napalm, the devastating contents of an incendiary bomb. Whale and fish oil fatty acids may be fractionated to produce both high and low iodine value products which have no resemblance to fish oil. There are scores of examples in which fractionated fatty acids serve a particular need.

TABLE I

Properties of Fractionated Cottonseed Fatty Acids

	A.V.	I.V.	Titre	Palmitic	Stearic	Oleic	Linoleic
			°C.				
Cottonseed acids	200	106/113	32/36	21	2	33.0	44
Fraction C_{18} (1)	198	120	23	← 10 →		40.0	50
Fraction C_{18} (2)	198	138	19	← 4.0 →		38.0	58
Palmitic acid	216	2 max.	56 min.	90	8	2.0	....
Stearic acid	198	3 max.	67	8	90	3.0	....

Fraction C_{18} (2) is obtained by redistillation of Fraction C_{18} (1).
Palmitic and stearic acids are obtained from the distillation of hydrogenated cottonseed fatty acids.

TABLE II

Properties of Fractionated Tall Oil Products

Fraction	A.V.	I.V.	Titre	Mean mol. weight	Oleic	Linoleic	Linolenic	Rosin acids
			°C.					
Alkyl acids (Cut No. 3)	190	130	20.0	295.5	46	39	3	12
Alkyl acids (Cut No. 11)	197	130	15.0	284.0	50	42	4	4
Rosin acids	175	......	(a)	298.0	← 30 →			70

Rosin pitch variable—as required. Normal 45°C. drop point.
(a) 250°F. M.P. to liquefy completely.

An excerpt from Chemical Week magazine, February 2, 1952 issue, reads as follows:

"As Bristol-Myers' Louis B. Dobie put it: 'One man's stearic should be the same as another's. A difference in iodine value or in the stearic-palmitic ratio is critical for some products.'

"Speaking only for use in toiletries, Dobie pointed out that while manufacturers don't expect it, the producer of a new fatty acid mixture or derivative who has conducted clinical test on it 'has his foot inside the sales door'."

If any conclusion is to be drawn from all of these facts, one must consider them in the light of the length of time fractionally fatty acids have been on the market in appreciable quantities. From 1935 to 1951 the market for fractionally distilled fatty acids has increased from nothing to about one hundred million pounds per year. This represents about 15% of the domestic production, and this percentage is increasing rapidly when considering new European plants of U.S.A. design. Therefore a fractional distillation plant may be considered a form of insurance of future markets as users of fatty acids set more and more rigid specifications.

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The Chemistry of Polymerized Oils. II.[1] Dehydro-Polymers of Methyl Linoleate and Methyl Stearate

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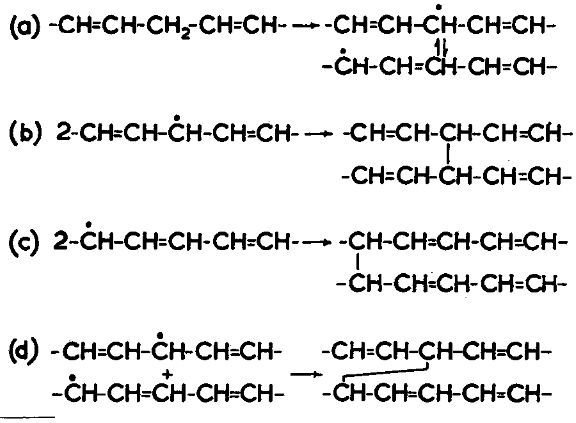
FARMER and Moore (6) investigated the reaction between a variety of olefinic and saturated hydrocarbons and various peroxides [*cf.* also Raley, Rust, Vaughan, and Seubold (15, 16)]. For example, cyclohexene was converted to a mixture of dehydropolymers when heated with di-tert.-butyl peroxide, the tert.-butoxy radicals formed by symmetrical fission of the peroxide being converted into tert.-butyl alcohol by abstracting hydrogen atoms from cyclohexene and cyclohexene dehydro-polymer molecules. We decided to study the methyl linoleate/di-tert.-butyl peroxide reaction since this seemed likely to be relevant to the researches being carried out in this laboratory (8, 11, 19) into the chemistry of both heat-polymerized and peroxidized oils. Thus the present study may have relevance to the secondary reactions of autoxidation which occur when the initially formed peroxides react with olefinic centres. Also it is relevant to the chemistry of stand oils since Sunderland has proposed (18) that the inter-chain linkages in these are single carbon-carbon bonds giving structures analogous to those outlined in schemes (b), (c), and (d) below. During this work it became necessary to study briefly methyl stearate also. We hope to report further on the structural chemistry and technical application (17) of the reaction at a later date.

From the mechanism elucidated by Farmer and Moore (6) and by analogy with the free-radical double bond rearrangement which occurs during autoxidation (1, 5), it was anticipated that the reaction product from di-tert.-butyl peroxide and methyl linoleate would consist of dehydro-polymers, some of which would contain conjugated diene unsaturation. For example, free radical attack on the central methylene group of the pentadiene system could result in the formation of dehydro-dimers as follows:



(a) $-CH{=}CH{-}CH_2{-}CH{=}CH- \longrightarrow -CH{=}CH{-}\dot{C}H{-}CH{=}CH- \rightleftharpoons -\dot{C}H{-}CH{=}CH{-}CH{=}CH-$

(b) $2\,-CH{=}CH{-}\dot{C}H{-}CH{=}CH- \longrightarrow \begin{array}{l} -CH{=}CH{-}CH{-}CH{=}CH- \\ \qquad\qquad\;\; | \\ -CH{=}CH{-}CH{-}CH{=}CH- \end{array}$

(c) $2\,-\dot{C}H{-}CH{=}CH{-}CH{=}CH- \longrightarrow \begin{array}{l} -CH{-}CH{=}CH{-}CH{=}CH- \\ \;\;\; | \\ -CH{-}CH{=}CH{-}CH{=}CH- \end{array}$

(d) $\begin{array}{l} -CH{=}CH{-}\dot{C}H{-}CH{=}CH- \\ \qquad\qquad + \\ -\dot{C}H{-}CH{=}CH{-}CH{=}CH- \end{array} \longrightarrow \begin{array}{l} -CH{=}CH{-}CH{-}CH{=}CH- \\ -CH{-}CH{=}CH{-}CH{=}CH- \end{array}$

· Denotes free radical.

In addition to (b), (c), and (d), it is possible that other less activated methylene groups in the linoleate molecule may be attacked. For example, attack could occur on the methylene group situated next to the ester group since Kharasch and his co-workers have shown (9, 10) that the free radical reaction of diacetyl peroxide with acetic, iso-butyric, and monochloroacetic acids results in attack at the α-position. However (10) dilauryl peroxide and dibenzoyl peroxide did not yield succinic acid when thermally decomposed in the presence of acetic acid, whereas Farmer and Moore found that cyclohexane was attacked at 140°C. by tert.-butoxy radicals to give di-cyclohexyl and higher hydrocarbons. The total reaction product is also likely to contain dehydro-trimers and higher species and these could partly result from purely thermal further intramolecular and intermolecular reaction.

To eliminate as many confusing possibilities as feasible it was decided to study first the dehydro-dimer fraction of a peroxide/linoleate total reaction product

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[1] Part I. Joubert and Sutton, this journal, *29*, 287 (1952).