Analysis of Fatty Acids by Ester Fractionation

By A. W. WEITKAMP and L. C. BRUNSTRUM
STANDARD OIL COMPANY (INDIANA), WHITING, INDIANA

Introduction

THE purpose of this paper is (a) to describe equipment which has been found suitable for fatty acid analysis by methyl ester fractionation, and (b) to point out that variations in composition which are not detectable by the specifications commonly employed are detected by this method of analysis.

The use of soap stocks in the manufacture of lubricants constitutes an important market for suppliers of these products. Statistics reported by Lincoln, Byrkit, and Nelson (1) indicate that the pretroleum industry, as a whole, annually purchases on the order of $23,000,000 worth of fats, fatty acids and derivatives, nearly all of which is used in the manufacture of lubricants.

The petroleum industry is continually faced with the problem of securing adequate supplies of soap stocks sufficiently uniform to give reproducible results when processed by closely controlled methods. That constant composition is not always assured by the common specifications regarding titre, saponifaction number and iodine value is now well known. Hilditch and his coworkers (2) have long since demonstrated the vast difference between the component acids of partially hydrogenated whale oil and ordinary beef tallow, although the ordinary tests would seem to indicate a high degree of similarity. Such differences are now so well recognized that they are no longer a problem.

However, the minor variations which frequently occur between shipments of a particular kind of fatty acid often lead to very real problems in the manufacture of the more highly specialized lubricants even though narrow ranges of saponification number, iodine value and titre are met. One illustration of this is given by the data in Table 1. The analyses (by ester distillation) of several shipments of hydrogenated sardine oil fatty acids are given. The difference between part A and B of the table is in the degree of hydrogenation of the fatty acids. We should expect this to cause little variation in the content of fatty acids of any given chain length, and indeed, analyses 1A and 1B, which are each typical of a considerable number of shipments, do show a close similarity.

TABLE 1

A. Partially hydrogenated sardine acids

No.	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	Bottoms
1.		0.3	6.7	28.2	26.4	19.1	12.6	6.7
2.	1.0	6.2	8.2	22.8	19.7	20.1	11.0	3.8
3.		Trace	6.2	27.9	24.5	14.0	8.1	19.3

B. Fully hydrogenated sardine acids

No.	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	Bottoms
1.		Trace	6.7	28.8	25.1	21.1	15.4	2.9
2.			2.0	30.8	29.0	23.2	12.1	2.9
3.			7.2	24.3	19.8	23.7	22.3	2.8

The reasons for these deviations are best known to the suppliers. We believe the following opinions to be nearly correct:

No. 1A. This analysis, as was mentioned, is typical of low titre hydrogenated sardine acids. (1939 crop.)

No. 2A. The presence of capric (C_{10}) and lauric (C_{12}) acids is indicative of admixture with some coconut or palm oil derivative.

No. 3A. The large residue and low C_{20} and C_{22} content would seem to indicate rather extensive polymerization prior to hydrogenation.

No. 1B. This is typical of high titre hydrogenated sardine oil. (1939 crop.)

No. 2B. The very low content of myristic acid (C_{14}) is notable.

No. 3B. This consignment was unusually high in C_{20} and C_{22} acids, possibly as a result of cold settling or "winterizing" the oil prior to hydrogenation. On the other hand, it may represent a normal variation in the composition of the sardine oil due either to seasonal or geographical factors.

Fractionating Equipment

Fractionating columns are of two general types, the bubble tower and the packed column. The packed column is usually preferred for laboratory stills because of its smaller liquid holdup.

A modern laboratory still consists essentially of three parts; the column packing, the insulation, and the still head. The column packing must have good height efficiency or low H.E.T.P. value, good throughput rate, low liquid holdup and freedom from channeling. The insulation and auxiliary heating equipment must maintain a close approach to adiabatic conditions at all times. The still head should be designed to provide variable or total reflux, easy control of the reflux ratio, accurate observation of the boiling point, and negligible liquid holdup, and should permit the taking of cuts without disturbing the vacuum of the system.

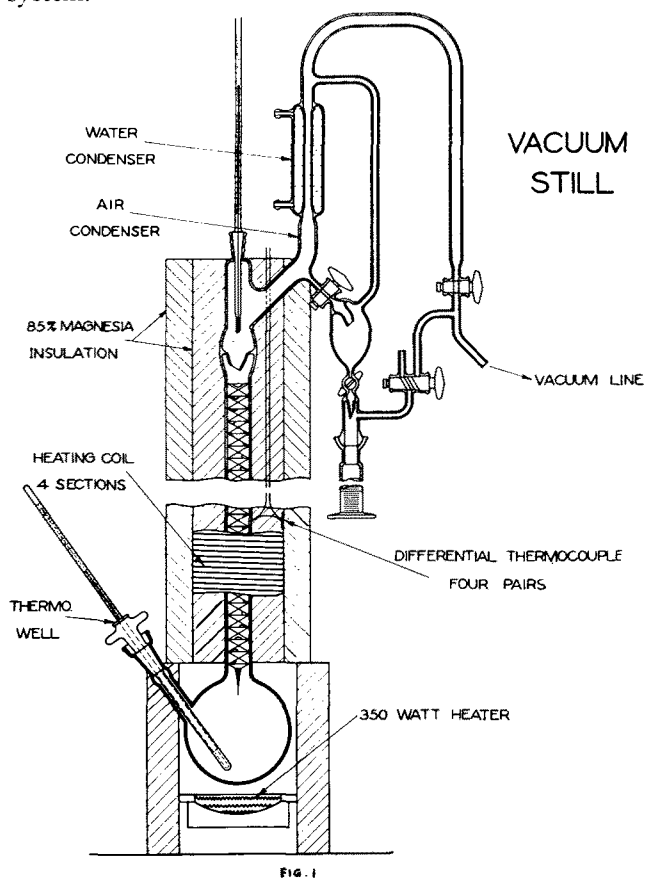
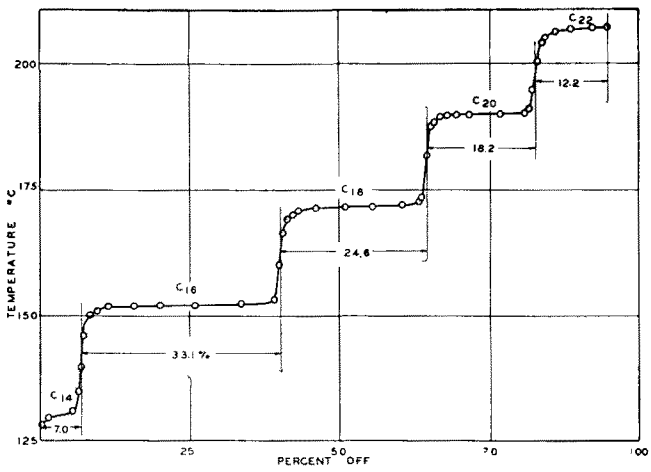


FIG. 1



FRACTIONATION OF METHYL ESTERS FROM HYDROGENATED SARDINE OIL
FIG 1

Numerous packing materials have been proposed. All but the most recent consist of small objects packed at random. Such packings rely on "the uniformity of complete disorder" to obtain maximum contact between liquid and vapor. Fenske, et al (3, 4), have collected a mass of data covering many sizes and shapes of objects made of various materials. Of all the packing materials tested, single and double turn helices of 3/32" inside diameter were best for small columns. Thus, single turn helices packed in a 0.79" (20 mm.) column gave a minimum H.E.T.P. value of one inch. The liquid holdup was not excessive and reasonable throughput was obtained. Berl saddles and jack chain gave approximately one-fourth the height effectiveness and other types were still less satisfactory.

The most recent advances in column packings utilize an orderly arrangement to obtain even distribution of the liquid over the packing material and procure maximum contact between the liquid and vapor phases. These include multiple concentric tubes (5), spiral gauze packing (6), and the various modifications of Stedman wire gauze packing (7, 8). The multiple concentric tube arrangement at very low distillation rates is nearly comparable to Stedman packing in height effectiveness, and due to its very low back pressure and extremely small holdup is adaptable to the fractionation of quite small samples. However, the throughput rate is very low. Little is known about the spiral gauze packing, except that it has excellent height effectiveness and is difficult to fabricate.

The Stedman wire gauze packing is available in the conical pattern for laboratory columns. Tests conducted by L. B. Bragg (9) on ⅜, ¾ and 1" columns yield minimum H.E.T.P. values of 0.42, 0.48, and 0.50", respectively, and throughout the operating range, that is, from incomplete wetting to incipient flooding, is equal or superior to the best of the randomly packed columns. Furthermore, the throughput capacity is comparable and the liquid holdup appreciably lower. At present, no other metallic packing is as attractive.

The cone type Stedman packing is made of 40 x 60, or 50 x 50 mesh wire cloth which has been formed into truncated conical disks. A semi-circular section is cut from one side of the cone and extends about two-thirds of the distance from the edge of the cone to the flat in the center. The disks are packed in the column alternately back to back and edge to edge with the cutout sections located alternately at opposite sides of the column.

In operation, the reflux liquid flows along the gauze and seals the openings of the mesh. The cones which are concave downward distribute the liquid toward the sides of the column and those which are concave upward concentrate the liquid toward the points of juncture between adjacent cones at the center of the column. In this way, there is continual redistribution of the liquid across the column. The vapors enter the space between two adjacent cones, concave toward each other, through the open section of the lower cone, passing across the column and out through the opening in the upper cone of the pair. The vapor stream then divides and flows back across the column around the point of junction between two cones. This process is repeated until the vapor leaves the packing at the top of the column. In this manner intimate contact between liquid and vapor and turbulence in the vapor phase is realized to a very high degree.

For best results a fractionating column should be operated as nearly adiabatically as possible, that is, the reflux should originate at the top of the column rather than along the wall. Numerous devices have been proposed for reducing or preventing heat loss by radiation. Perhaps the best known is the ordinary silvered vacuum jacket. H. M. Evans (10) has shown that ordinary steam pipe covering is even more effective in reducing radiation in high temperature ranges, such as are encountered in ester fractionation. Fenske and coworkers (11) placed a heating coil around a two-inch layer of magnesia pipe covering and used thermocouples placed under the heating coil and near the column to measure deviations from adiabatic conditions. Sectional heating was introduced to maintain adiabaticity throughout the whole length of the column. This is a very effective arrangement.

Still head designs are nearly as numerous as investigators in the field. They may be conveniently classified as liquid or vapor splitting and fixed or variable reflux ratio.

Vapor splitting heads have the advantage of no liquid holdup, but mostly are of the orifice or fixed ratio type (12). One designed by Brunn and Shicktanz (13) employs an external cock to provide a variable orifice. Others utilize partial condensation as a means of providing variable reflux or variable overhead rate.

Liquid splitting heads have the common advantage of total condensation in a single condenser. Fixed reflux ratios are usually provided by partitioning the condensate with capillary tubes or by use of a cup extending partly around the circumference of the column beneath a vertical condenser (11). Several such cups may be used in various combinations to give a choice of ratios. Variable ratio heads normally use either an internal or external cock to control the overhead stream. One such designed by M. J. Marshall (14) fulfills most of the requirements. A thermometer well is placed directly above the column, a total condenser is displaced to one side, permitting the stream of condensate to flow over a stopcock so that any desired proportion may be drawn off. A head of this type adapted to vacuum has been used satisfactorily.

Description of the Still

Figure 1 shows the general setup of the column as finally adapted to ester distillation.

It consists of a four-foot length of 25 mm. glass tubing packed with Stedman wire gauze cones and

sealed directly to a one-liter pot and to the still head. The cones are pressed ¼" deep from 50 x 50 mesh stainless steel screen. The cutout section is circular, 7/16" diameter by 11/32" deep. Smaller sizes were avoided since, with an abundance of raw material, it seemed unnecessary to introduce the complications of microtechnique. Glass seals were used in preference to standard taper joints because of lubrication difficulties at high temperatures. The pot is provided with a standard taper side tube which serves both to receive a thermometer well and as a cleanout. Cleaning is accomplished by drawing a suitable solvent down through the column and out through the side tube by means of an auxiliary tube fitted with a standard taper joint and reaching just to the bottom of the pot. The pot is heated in an air bath with a 350-watt heater, controlled by a type 200 C Variac. Heat input is determined by observation of the reflux rate.

The column is imbedded in magnesia pipe insulation 1½" thick and heated in four sections with Nichrome wire of suitable size and spacing to permit a maximum current of about 1.5 amperes to flow in each section. These four heating elements, joined in parallel, are controlled by a Variac and are individually compensated by small 50 ohm dial-type rheostats. Equilibrium between the column and heaters is maintained with the aid of four differential thermocouple pairs, one junction of which is located near the column and the other near the heater. The four thermocouple pairs are connected through a selector switch to a sensitive galvanometer.

The still head is an adaptation of M. J. Marshall's design. A thermometer is placed vertically above the column so that temperature readings may be made with minimum eyestrain and error due to parallax. A reflux drip tip is placed on the same level as the overhead drip tip so that both may be observed simultaneously for estimating the reflux ratio. The reflux drip tip is observed through a small window in the insulation. Regulation of the overhead rate is by means of a capillary stopcock. Liquid holdup is less than 0.1 ml. Condensation is mainly by air cooling although a water cooled condenser is provided for the more volatile materials. A small receiving bulb and suitable arrangement of stopcocks permits the taking of cuts without disturbing the vacuum or interrupting the distillation. Fractions are received in tared graduated cylinders equipped with standard spherical joints.

Vacuum is supplied with a Cenco Megavac pump and regulated by means of a capillary leak. Distillations are normally conducted at 2 mm. pressure. Except for occasional leakage at the stopcocks, pressure variations seldom exceed —0.05 mm. A miniature McLeod gauge is used to check the pressure.

Operation

The sample for fractionation, usually 200 grams, although larger or smaller amounts may be handled satisfactorily, is charged to the still through the top of the column. This insures complete wetting of the packing which is necessary for efficient operation. The time required for the column to reach equilibrium varies from about one to two hours, depending on the initial distillation temperature. Satisfactory separation of homologous esters is readily obtained at distillation rates of 25-40 grams per hour with reflux ratios of three or four to one, provided care is taken to decrease the overhead rate and increase the reflux ratio as the transition points are approached. The total time required to fractionate a 200-gram sample ordinarily does not exceed 7-8 hours.

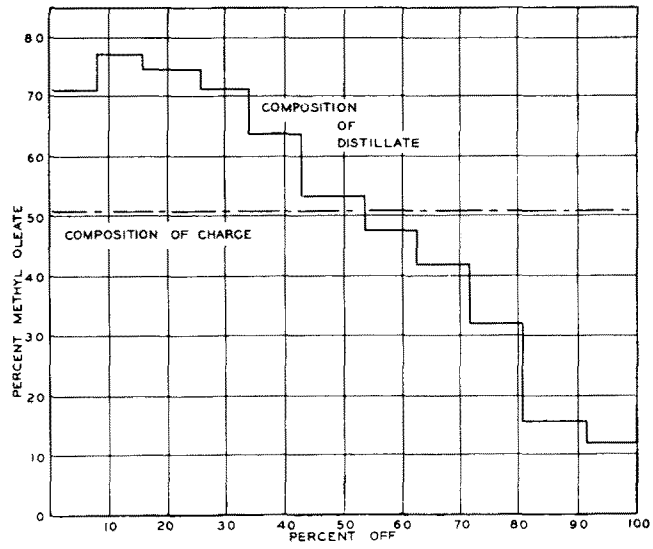


FIG. 3
FRACTIONATION OF METHYL OLEATE-STEARATE MIXTURE

Results

The theoretical efficiency of a column, expressed in any of the common units, is useful for comparing it with other columns. However, the usefulness of a column for any particular job is best illustrated by typical data. For this purpose several distillation curves are presented.

(1) The ester distillation curve, Fig. 2, of a typical sample of hydrogenated sardine fatty acids shows the sharp separation obtainable between adjacent homologous fatty acid esters. The plateaus are flat and the transitions are abrupt. In determining molecular composition, especially of completely hydrogenated fatty acids, it is customary to take cuts at the mid point of the transition between two plateaus. The ratio of the weight of the cut to the total charge to the still is the fraction of that component in the mixture. This method is not quite exact, but it eliminates the need for determining saponification numbers and consistently yields results which are believed to be accurate to within a few tenths of one per cent.

In case unsaturated components are present it is convenient to take the cuts at the beginning of the transition rather than the mid point. In this way the unsaturated esters of the transition mixture are included with the succeeding plateau to which they rightfully belong. Alternatively, the transition mixture may be isolated and analyzed separately by saponification number and iodine value, assuming that only two saturated and one unsaturated component are present. If two unsaturated components are known to be present, e. g., oleic and linoleic acids along with palmitic and stearic, then a lead soap-alcohol separation prior to ester fractionation will yield the necessary additional data for complete analysis.

(2) The distillation of a mixture of quite pure methyl oleate and methyl stearate (Fig. 3) at a rate of 8.5 grams per hour, with a reflux ratio of ten to one, shows the degree of separation obtainable between a saturated ester and its unsaturated analogue. The dif-

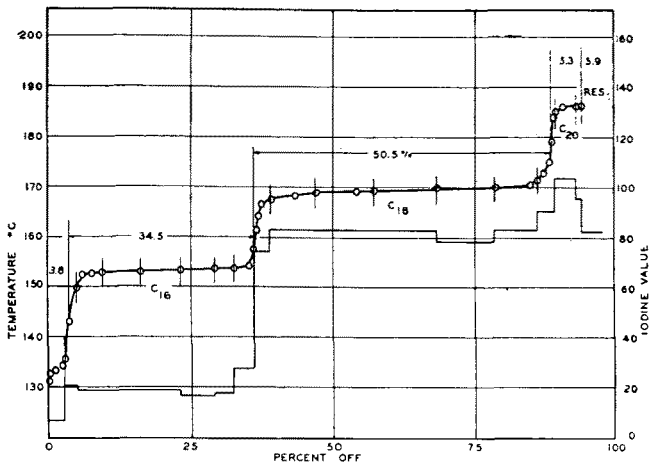


FIG
FRACTIONATION OF ALCOHOLS FROM SPERM OIL

ference in boiling points is not accurately known, but probably does not exceed 2-3° C. A plot of per cent methyl oleate in the distillate against per cent off shows appreciable concentration of the methyl oleate. A complete separation at reasonable distillation rates would require a much longer column.

(3) Fig. 4 illustrates the possibility of separation of the homologous fatty alcohols from sperm oil. Although numerous constituents have been identified, the literature contains little, if any, quantitative data on such mixtures. On the basis of the distillation and iodine value curves, the following approximate composition has been calculated:

Name of Alcohol	Carbon Atoms	Double Bonds	% Present
Myristyl	14	0	2.1
Physeteryl	14	1	Trace
Cetyl	16	0	21.1
Zoömaryl	16	1	7.4
Stearyl	18	0	5.0
Oleyl	18	1	49.7
Eicosenol	20	1	6.1
Eicosdienol (?)	20	2	2.1
Residue	—	—	6.5

Many more curves and tables of data could be shown, but we think the utility and efficiency of Stedman wire guaze packing for ester fractionation has been adequately demonstrated. Very little novelty can be claimed for the distillation equipment which has been described. It consists mainly of a combination of the best contributions of the pioneers in this field. The future will undoubtedly bring forth apparatus of even better design.

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The Role of Oxidation in Drying Oils

By J. D. VON MIKUSCH and G. W. PRIEST
WOBURN DEGREASING COMPANY OF NEW JERSEY, HARRISON, N. J.

IN THE conventional classification of the fatty oils into non-drying and drying oils, the latter are characterized by their power to absorb oxygen from the air and to form "dry" or coherent films when exposed in thin layers. It is this ability to dry which makes these oils useful as the principal ingredients in paints, varnishes and numerous other commercial products. The role played by oxidation in this drying process has long been a subject of primary interest in the chemistry of drying oils.

Since oxidation plays a vital part in the process of film formation, it has a decidedly constructive role, which is, perhaps, a somewhat unusual aspect with fats and oils in general. At the same time, oxidation has its destructive aspects and the coatings formed by drying oils are themselves subject to further oxidation, leading to their deterioration and destruction.

Another important aspect of oxidation in drying oils is connected with color changes, i.e., the yellowing of oil films under certain conditions on one hand, and the bleaching which may occur in the oils as well as the films, on the other.

Finally, oxidation has an informative role and is employed in the laboratory for the identification of fatty acid components and for the characterization of the oils.

In order to limit the scope of this discussion, the main section will be devoted to the role of oxidation in film formation, while the other aspects will be briefly reviewed.

I
COMPOSITION AND CLASSIFICATION

Most of the natural oils are complicated systems of mixed glycerides which frequently contain half a dozen or more fatty acid components. Since both drying and non-drying fatty acids are found together not only in the same oils but in the same triglyceride molecule as well, their analysis and identification are both difficult and important. Although numerous contributions have been made to this branch of chemistry in the last few years, our knowledge on this subject is still in its infancy. It is only necessary to remember that even with the best methods now available it is still not possible to give the exact percentages of the various fatty acids and triglycerides in an oil such as linseed oil, without provoking discussion as to the validity of the methods employed.

However, the constitution of the various fatty acids occurring in the drying oils has, in general, been established beyond doubt. As a result, the drying oils may be subdivided according to the fatty acids occurring in them. Most classifications (11, 96, 99) recognize the differences in behavior of the fatty acids containing isolated double bonds and those containing conjugated double bonds or "dienes." Since the presence of the latter in any substantial proportion causes the oil to