as well as from the liners of cans used by butcher shops to collect fat and meat scraps. When these polymers enter the rendering process, they disperse in the tallow and are difficult to remove. During the subsequent use of tallow in fat splitting, the polymers are reported to accumulate in the splitting towers and present a hazard there.

Finally, we should take a quick look at uses that are made of tallow. The data for 1976 are given in Table V, and domestic use trends over the past twenty years are shown in Figure 3. It is evident that the United States exports almost as much tallow as it uses at home, and, in fact, the United States product represents about three-fourths of the world trade in tallow. At home, by far the largest single use for inedible tallow is in animal feeds, especially in formulated beef and poultry feeds and in pet foods. Fatty acids and soaps consume about equal amounts. Before petroleum-based detergents became popular in the 1950s, soap constituted the largest single use for industrial tallow. With increasing prices and decreasing availability of petroleum, the day may come again when tallow will become an important raw material base for soap-derived detergents.

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New Fatty Acids from Outer Space

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ABSTRACT

A recent space exploration has revealed that in the far reaches of outer space matter attains a state of complete weightlessness. Herman Brown, reporting on his latest spaced-out venture, indicates that weightless fatty acids obtained from the Superba Galaxy are ideally suited for the manufacture of improved food additives. What a magnificent way to provide the diet-control foodstuffs of the 21st Century!

(**Course Chairman's Note:** Fully cognizant of the results of Orson Welles' famed radio broadcast, where he promoted the idea that the Martians were engaged in a real earth invasion, we find it necessary to state unequivocally: *as far as we know, there are no fatty acids in outer space.* Furthermore, if there *is* organic matter within the meteorites that enter the earth's atmosphere, it is probably *not* in the form of fatty acids. Publication of the above abstract in our preliminary program occasioned dozens of inquiries on this subject. Mr. Brown's paper at the Short Course was a hilarious spoof on this subject as well as a few others. We include the abstract here to complete the entire story of "AOCS at Tamiment.")

Fat Splitting

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ABSTRACT

Fat splitting, particularly the continuous, high pressure, countercurrent hydrolysis of fats and oils, typified by the Colgate-Emery or modified processes, represents the technological cornerstone for today's American fatty acid industry. Internationally, other methods such as Twitchell or batch autoclave "medium-pressure" catalyzed or uncatalyzed splitting are still important. All industrial fat splitting methods have as their objectives the attainment of a high rate of hydrolysis together with a high degree of completeness. This objective is achieved, more or less, by the proper optimum balance of: (a) use of excess water; (b) selection of appropriate combination of temperature and pressure to optimize the solubility of liquid water in the fat phases with or without use of suitable "water-in-oil" emulsifiers; (c) use or nonuse of acidic catalyst (rarely basic catalysts); and (d) removal of byproduct glycerol. Significant conditions and details in fat splitting by the important commercial processes are described.

Fundamentally, fat splitting is generally represented in all the textbooks as an oversimplified reversible chemical reaction consisting of adding H_2O to a glyceride to produce glycerine and three mols of fatty acids. Fat splitting, as might be expected, is far more complex than this simple reaction. Some idea of the overall complexity may be given by a consideration of the stepwise nature of fat hydrolysis from triglyceride to diglycerides to monoglycerides to fatty acids and glycerol. For practical purposes, the following facts enable us to discover the true nature of the fat splitting reaction: (a) water is increasingly soluble in di- and monoglycerides and in fatty acids than in the starting material triglycerides; (b) higher temperatures and pressures as shown in Table I increase the rate of hydrolysis as a

TABLE I

Influence of Temperatures in the Range 225–280 C on Splitting Time (2)

Temp °C	Time to reach equilibrium (min.)			Half life time (min.)		
	Beef tallow	Coconut oil	Peanut oil	Beef tallow	Coconut oil	Peanut oil
225	156	158	156	62	58	50
240	82	85	85	34	33	25
260	47	46	53	18	23	16
280	34	33	33	8	10	10
260 (catalyst 0.2% ZnO)	21	--	--	4	---	---

consequence of an increase in the solubility of water in all the fat phases (1,2); (c) di- and monoglycerides have been detected in partially split fats (3.5% of excess combined glycerol from some autoclave split fats [Fig. 1], 1–3% from Twitchell [3], 1–2% in fermentative but never in saponification reactions); (d) the reaction is reversible (unless glycerol is removed); reaction is slow to start, fast in the middle stages, and slows down as glycerol concentration increases as shown in Figures 2 and 3 (1,4).

All industrial fat splitting methods have as their objectives the attainment a high rate of hydrolysis together with a high degree of completion. This objective is achieved, more or less, by the proper optimum balance of (a) use of excess water, (b) selection of appropriate combination of temperature and pressure to optimize the solubility of liquid water in the fat phases with or without the use of suitable "water-in-oil" emulsifiers, (c) use or nonuse of acidic catalyst (rarely basic catalysts), and (d) removal of byproduct glycerol. In connection with the items (b) and (c), the use of zinc oxide (ZnO) as a so-called "catalyst" for medium pressure splittings is more likely the application of an in situ emulsifier generator since zinc soaps of fatty acids are oil-soluble and function as emulsifiers to give fat and water the opportunity to come into close *reactice* contact. Sulfuric acid is ordinarily considered to be a true acidic catalyst, but when it is used in combination with sulfonic acids in batch Twitchell splittings, it may be argued that its function is rather to depress the solubility of the sulfonic acid in the aqueous phase and to increase its solubility in the oil phase, where the latter functions both as an emulsifier and as an *acidic* hydrolysis catalyst. Thus, the exact line between the function of catalysts and emulsifiers in fat splittings is vague and indefinite indeed.

Significantly, the initial objective in conventional fat splitting is to obtain as fast as possible a high solubility of liquid water in the triglyceride fat phase because fat splitting occurs *homogeneously*, with very little contribution from hydrolysis at fat-water interfaces (1). As soon as water is homogeneously dissolved in the fat phase, we have essentially passed the slow initial part of hydrolysis and can enter the relatively fast part, which slows down ultimately, only because glycerol concentration buildup is permitted. If, on the other hand, glycerol is removed from the sphere of the reaction (and there are innumerable methods applied to achieve this), we can force fat splitting to the desired completion. From the practical point of view, all the existing processes achieve these objectives with varying degrees of success, but, from the theoretical point of view, there are still a number of things about fat splitting that aren't entirely clear.

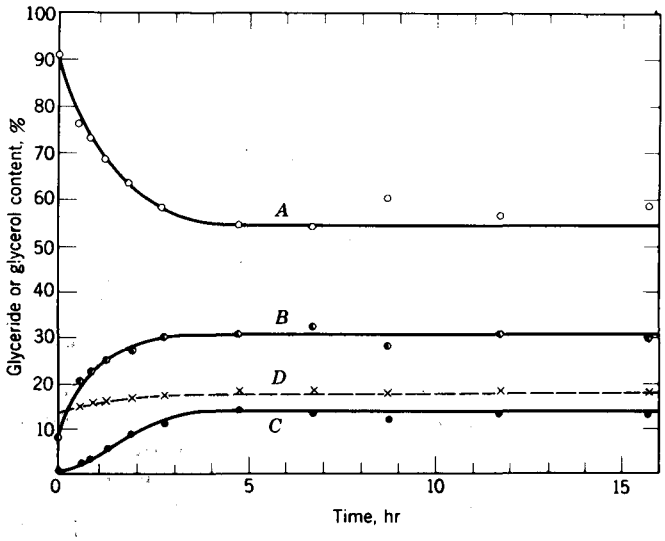
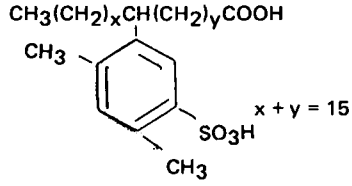


FIG. 1. Composition of unsplit fat during the first boil in the Twitchell splitting of coconut oil: (A) triglycerides, (B) diglycerides, (C) monoglycerides and (D) combined glycerol content (3).

Twitchell Process

Twitchell in 1898 (5,6) patented reagents made from oleic and stearic acids and sulfuric acid with the capability of hydrolyzing fats and oils to fatty acids at atmospheric pressure by boiling with steam and water in open kettles. Quickly, Twitchell reagents, made from aromatic hydrocarbons and oleic acid, such as that from *m*-xylene, were applied for this purpose.



Later, alkylbenzene sulfonic acids and other petroleum sulfonic acids (third phase Twitchell Reagents, in Europe "Kontackt" reagents) came to be used. The process is still used in Europe (7); in the U.S. there is little economic utilization of this method. Essentially, the process consists of three or four successive reboilings with fresh water containing reagent (occasionally spent waters containing glycerol are used in place of the fresh water). Thus, a four-step Twitchell method on tallow would correspond to the following time and yield requirements: 1st boil 18 hr, 60% complete; 2nd boil 12 hr, 25% complete; 3rd boil, 6 hr, 10% complete; and 4th boil, 4 hr, 5% complete. For a three step process the sequence would likely be: 1st boil 20–24 hr, 75%; 2nd boil 12 hr, 15% complete; and 3rd boil 4 hr, 5% complete. Unless very long times are involved (or larger number of reboils with consequent more dilute glycerol concentrations more costly to evaporate), the splitting efficiency is no better than 95%, steam consumption is high, but equipment is cheap, although it must be corrosion resistant. A final water wash removes sulfuric and sulfonic acids or else distillation of the split acids would cause corrosion in the distillation equipment.

Abroad, the possibility of using a continuous Twitchell process has been considered (7), also with Kontackt catalysts the possibility for using pressure and a temperature of

150 C where the relative reaction velocity is 1 (150 C): 0.03, (100 C) (8), but neither possibility has been developed, mainly because of the unavailability of suitable materials of construction able to withstand the highly acidic conditions prevailing. When castor oil is split by the Twitchell process, apparently the esterlide formation which occurs simultaneously renders the catalyst less soluble than usual in the fat phase; under these conditions 45% of the catalyst was detected in the aqueous phase (9).

Medium Pressure Autoclave Splitting with Catalyst

Previously, this was called high pressure splitting, but with the advent of continuous high pressure splitting methods operating at 500–725 PSIG, the term "medium pressure" (150–500 PSIG) is better applied to it. It is the oldest method of fat splitting; patents were issued dating as far back as 1854 (10) on this process. By using medium pressures, the need to remove liberated glycerol as in the case of the Twitchell process is eliminated; one batch operation generally brings the efficiency to ca. 95 to 96% total split with the use of high water concentrations (generally, ca. 30% of the weight of the fat employed). Zinc oxide is the preferred catalyst; occasionally calcium or magnesium oxides are used, but these are less effective. Usually, 2–4% of ZnO based on the weight of fat is used, the exact amount depending upon the maximum pressure employed and varying inversely with it.

The autoclaves are built from corrosion-resistant metal in the form of tall cylindrical vessels which may be 4 to 6 feet in diameter and 20 to 40 feet in height. The autoclaves are well insulated and are equipped with lines for the injection of steam, but have no agitators. Generally, dependent upon the stock charged, 6 to 10 hours is required for each batch split. Examples of fat split by modifications of the autoclave batch process are coconut oil, babassu, and palm kernel oil.

Low Pressure Splitting with Catalyst

The existing conventional fat splitting processes depend upon the establishment of optimum concentrations of liquid water in the fat phase in order that hydrolysis may be initiated. It is possible to avoid the use of expensive pressure equipment and split fats and oils with superheated (gaseous) steam at relatively low pressures in the presence of a catalyst. A patent issued in 1966 to Carad Corporation (11) claims that tallow at 200–280 C is 16% hydrolyzed in 10–30 seconds in a specially designed pipe reactor with zinc oxide catalyst. A second passage of the oil phase through the reactor affords 70% complete hydrolysis. One wonders had this process been developed in the early 1940s whether the basic fat splitting technology would have been based upon the use of superheated steam rather than the application of medium or high pressure steam. Certainly, the time of reaction and the cost of the equipment required are advantageous for superheated steam splitting, while the apparent necessity for the use of catalyst might be overcome. However, this process has not yet achieved commercial use.

Continuous, High Pressure Uncatalyzed Countercurrent Splitting

High temperatures and high pressures and continuous removal of the liberated glycerol with a water stream are the features of the countercurrent, continuous high pressure (500–725 PSIG) fat splitting process, steadily developed since the original work of Ittner (12) and Mills (13) in the period 1939–1942. This process, essentially the Colgate-Emery process, or modifications of it, is the most efficient and inexpensive method for large scale production of saturated fatty acids from fats and oils, and for the production of unsaturated fatty acids generally below IV

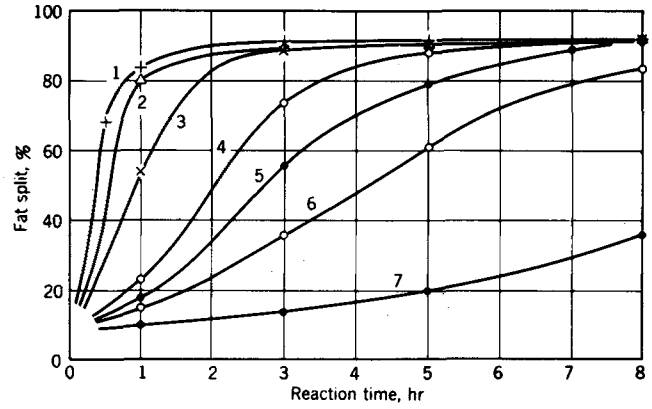


FIG. 2. Autoclave splitting of tallow with 60% water: 1. 220 C (322 PSIG) with 0.5% NaOH as a catalyst; 2. 185 C (148 PSIG), 0.5% ZnO; 3. 200 C (210 PSIG) 0.5% NaOH; 4. 185 C (148 PSIG), 0.5% NaOH; 5. 185 C (148 PSIG), no catalyst; 6. 170 C (100 PSIG), 0.5% NaOH; and 7. 140 C (38 PSIG) 0.5% NaOH; (1).

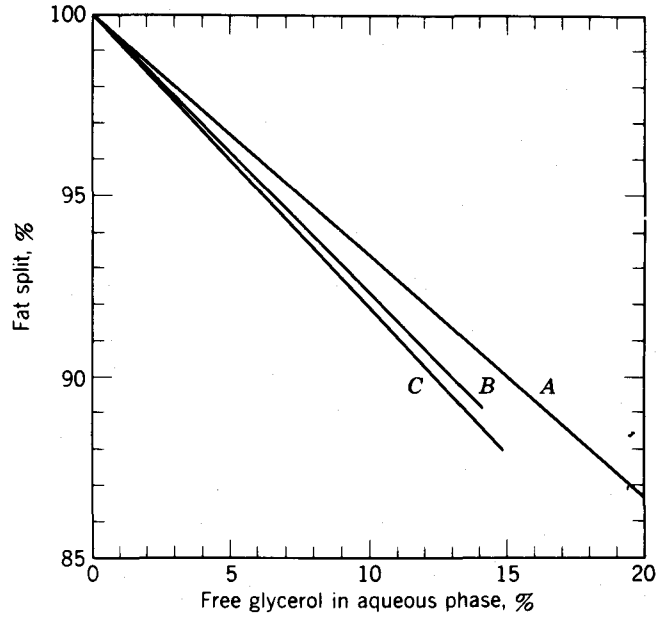


FIG. 3. Maximum hydrolysis in fat splitting as a function of the glycerol content of the aqueous phase: (A) Twitchell splitting of palm kernel oil (1); (B) autoclave splitting of tallow (4); and (C) autoclave splitting of coconut oil (1).

levels of 120 (fish-derived) or 140 (soya, etc). The heart of the splitting system is a tower 20 to 48 inches in diameter, 60 to 80 feet high of solid type 316 stainless steel or Inconel to withstand the operating pressures, generally over 700 PSIG and well insulated. The fat is introduced by a sparge ring about 3 feet from the bottom with a high pressure feed pump. Water is introduced near the top of the column at a ratio of 40–50% of the weight of the fat. The fat rises through the hot glycerol-water collecting section at the bottom of the column and passes through the oil-water interface into the continuous phase, the oil layer in which hydrolysis takes place. Direct injection of high pressure steam quickly raises the temperature to 260 C. Pressure is maintained at 700–725 PSIG. The continuous, countercurrent high pressure process splits fats in 98–99% efficiency in only 2–3 hr with little or no discoloration of the fatty acids and an efficient use of steam. It is NOT applicable in its high temperature, high pressure modification to splitting of heat sensitive triglycerides such as those containing conjugated double bonds, unconjugated systems capable of thermal conjugation, hydroxy-containing fats and oils like castor oil or hydrogenated castor oil, fish oils

containing polyunsaturated acids with 4 or more double bonds, and, in fact, soybean oil of IV greater than about 140 (and containing 7–9% linolenic acid). For these oils, hydrolytic methods at lower temperatures are required.

Enzymatic Fat Splitting

Lipolytic enzymes such as those obtained from castor beans have been used in the past to split fats (14), but this technique is inefficient (best conversions approximate only 90%), sluggish and not especially easy to handle as a unit operation. In process, the method was a batch operation suited only for fats limited to a melting point of 40 C, and consumed from 24–48 hr for completion. However, this technique, in the case of very sensitive fats and oils such as conjugated components or those containing up to four or five double bonds (from fish oil) may be the only one of all the methods capable of generating fatty acids from triglycerides with minimal structural changes (see M.E. Stansby's paper). Although castor oil has been split in the past by this method, it is no longer split this way today, recourse being made to other less drastic hydrolyses than medium or high pressure splitting techniques.

Although enzymatic splitting has had little value in the past as an industrial method of fat splitting, its use in the laboratory for the determination of fat and oil structure has been very important. Pancreatic lipase has been discovered to preferentially hydrolyze the 1- (or 3-) positions of glycerides (15). Under controlled conditions the specificity may be made absolute (16,17). Already, hundreds of fats and oils have been investigated with this technique; much triglyceride structure definition has accrued. More recently, the discovery that the lipase from the seed of *Vernonia anthelmintica* is capable of preferentially hydrolyzing the 2-position of fats and oils, first established with trivernolin oil itself (18), appears to be a useful discovery. Immediately it was established that the unique keto structure of this oil was not responsible for the specific positional hydrolysis, for pancreatic lipase hydrolyzed it to the expected 1,2-diglycerides (19) indicating that the normal 1- or 3-hydrolysis had indeed occurred. It remains to determine if the 2-position specificity for this lipase is characteristic of other fats and oils.

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Hydrogenation of Fatty Acids

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ABSTRACT

Catalytic hydrogenation is a vital process for both the edible fats and oil and the industrial fatty chemical industries. The similarities and differences between the fat and oil and fatty acid hydrogenations in equipment, processing conditions, and catalysts employed are of some importance since both are used in the various operations. Generally, the catalytic hydrogenation of fatty acids is carried out in corrosion-resistant equipment (316SS), whereas for fats and oils while 316SS is desirable, 304SS or even black iron suffice. The speed of hydrogenation varies radically with the content of impurities in both fat and oil and fatty acid feedstocks. Especially detrimental for both hydrogenations are soap and sulfur contaminants. proteinaceous materials left in the oils from poor refining, etc. Fatty acids from vegetable oil soapstocks are especially difficult to hydrogenate. Soybean-acidulated soapstock must usually be double-distilled for good results; cottonseed soapstocks frequently triple-distilled in order that they can be hydrogenated below iodine values of 1. Fatty acid hydrogenation effectiveness is measured by achieving a low iodine value as fast and as economically as possible. Variables that influence hydrogenation effectiveness are reactor design, hydrogen purity, feedstock quality, catalyst activity and operating conditions.

INTRODUCTION

History and Background

The origin of vapor phase hydrogenation is usually traced to Sabatier and his associates (1). In 1897 they were trying to make nickel carbonyl by the addition of ethylene to nickel. The experiment was "unsuccessful." Analysis of the gaseous residue revealed ethane rather than nickel carbonyl. The nickel had served as two catalysts. It first decomposed some of the ethylene to form carbon and hydrogen and then hydrogenated the remaining ethylene to ethane.

Hydrogenation in the liquid phase is generally credited