The Acetolysis of Glycerides. II. The Production of Fatty Acids and Triacetin

EDWIN M. MEADE, Department of Food Chemistry, University of Toronto, DILYS M. WALDER, Canada Packers Ltd., Toronto, Canada

Triacetin can be made by the acetolysis of hardened tallow in consistent yields of 70% of theory (18% w/w on fat) accompanied by an 80% yield of good purity saturated fatty acids, and some 10% of a fraction of high diacetoglyceride content. The yields of both triacetin and fatty acids can be materially increased by recycling of the diacetoglycerides and the still bottoms. Tallow gives similar yields of triacetin and fatty acids, but the acetoxystearic acid by-product interferes with the separation of the diacetoglyceride fraction.

IT WAS SHOWN in Part I of this series (1) that triacetin can be produced directly from fats by an acid catalyzed reaction with acetic acid, but that water is an essential reactant, the observed overall reaction being the result of a series of successive hydrolyses followed by acetylations.

As a process, the reaction requires the conjunction of fat, acetic acid of controlled water content, and catalyst, for a relatively long residence time under highly corrosive conditions but with little heat flow. Finally the reaction products are separated by successive distillations of acetic acid, triacetin, and fatty acids. The catalyst is removed at some time prior to the vacuum distillation of the triacetin, and the excess acetic acid and still bottoms are recycled. The initial partial immiscibility of the fat with hot, slightly aqueous, acetic acid can be overcome by operating at some 20–30°C. above the atmospheric boiling point under slight pressure, or by the use of a major heel of product as a mutual solvent.

Catalyst Handling

Since water is a reaction component its presence in commercial 60% perchloric acid, and in most crystallized sulphonic acids, creates no nuisance. The risk of using perchloric acid has been overemphasized, due to its detonant properties in mixtures with acetic anhydride; the 60% acid is safe in all proportions when mixed with acetic acid. It was found to be nonvolatile in acetic acid vapor and so cannot accumulate in the recycle acid, but remains at a safe dilution in the residual oil.

The ideal catalyst would be one capable of recycle by physical phase separation. Theoretically, insoluble polystyrene sulphonic acids and the volatile lower perfluoracids and hydrochloric acid are in this class; but Amberlite 120 and perfluorpropionic acid were both found to have low catalytic activity. Hydrochloric acid proved to be excessively volatile in acetic acid which breaks up its maximum boiling point binary mixture with water, and it also leads to organically combined chlorine. Thus with a 60:1 molar ratio of acetic to hydrochloric acids in the charge stock, a 6:1 ratio of acetyl to organic chlorine was found in the acetins, which analyzed 0.2 OH, 0.4 Cl, and 2.4 acetyl groups per glycerol residue.

Effective catalysts thus require chemical inactivation, and any recycle must be by way of a chemical regeneration. Perchloric acid was inactivated by barium carbonate and the barium perchlorate was washed out by a small water wash after the completion of acetic acid recovery. It was shown that barium perchlorate reacted quantitatively with sulphuric acid in an acetic acid medium, and so perchloric acid can be recycled. Sulphuric and toluenesulponic acids were inactivated by barium or calcium compounds, calcium toluenesulphonate crystallizing especially well and giving easy and almost quantitative recovery from the reaction medium. Sodium toluenesulphonate was too soluble, enough remaining to give high viscosity difficulties in the eventual still bottoms. Since there were indications that toluenesulphonic acid gave a cleaner reaction and easier distillation than did sulphuric acid, a recycle via the calcium salt could be of value.

The Acetic Acid Recycle

The water added to the acetic acid leads to partly hydrolyzed acetins, each 1% of water causing an approximately 3% drop in their degree of acetylation. Full reacetylation of these partial acetins occurs if the acetic acid recovery is performed prior to the inactivation of the catalyst, and at the same time the increasing dehydration of the undistilled part inhibits the reversion of the main acetolysis reactions. It was shown that about 60% of the water present came over in the first third, and about 80% in the first half, of the acetic acid recovered, and that a technically complete reacetylation could be achieved either by a relatively slow (one hour) distillation of the first half of the acetic acid, or else by a flash distillation of this amount, followed by a one-hour holding time, before catalyst inactivation or final flash stripping.

The removal of the inactivated sulphate or sulphonate catalyst, by centrifugation or filtration, may precede or follow the acetic acid recovery, the later removal avoiding a potentially unpleasant handling operation. Washing out of a barium inactivated perchlorate catalyst is only feasible under conditions of low residual acetic acid content.

The control of the water content of the recycle acetic acid is important. Owing to volume contraction on mixing, neither density nor refractive index is an adequate criterion in the 95% to 100% range, and melting point is too sensitive to impurities. The dielectric constant may be best for instrumental monitoring, while chemical analysis by the Karl Fischer method involved no difficulties.

Triacetin Isolation

The three acetins have very similar boiling points around 130°C./3 mm. and they are easily separated from tallow and grease fatty acids, though they codistil with the C_8 and C_{10} acids of coconut oil. Triacetin has only a low solubility for water or higher fatty acids, but is miscible with acetic acid. Cooling to 0°C. reduces the solubility of tallow fatty acids to below 0.1% but redistillation remains the best way of obtaining high purity. Pure triacetin melts at 4.1°C. (2) but its great tendency to supercool makes crystallization exceedingly difficult.

Triacetin distillation follows immediately after the final acetic acid recovery: a vacuum of 1–10 mm. was used for the triacetin distillations in the four runs of Table I, and the triacetin yields were 17.6, 17.7, 17.7, and 18.0%, w/w on the hardened tallow.

Fatty Acid Isolation

The crude fatty acids produced by the acetolysis process contain diacetomono-glycerides, acetodiglycerides, and also acetoxyacids if an unsaturated fat has been used. The acetoxyacids boil some 30°C. and the diacetoglycerides some 60°C. above their parent fatty acids, so that considerable co-distillation of both components will occur unless a fractionating column is used. Acetoxystearic acids (A.V. 164, S.V. 328) are not particularly undesirable impurities, and their concentration would build up on recycling, but the diacetoglycerides (A.V. nil, S.V. 350–400) have a severe effect on the analytical constant of the distilled fatty acids. It was found that the diacetomonoglycerides were easily removed by quite low efficiency columns, and that they are broken down to more fatty acids and triacetin on recycling. The effect of using a 12-in. x 1-in. Vigreux column, with natural reflux, is shown in Table I. In the particularly good run No. II, where the vacuum held very steady, 98% of the fatty products were distilled leaving only 2% residue, and the last fraction to be distilled was a 9% yield analyzing 85% diacetoglycerides with only 15% fatty acids. A cut of some 10% of quite high purity diacetoglycerides could clearly be taken with a better column. Alternatively, with a simple column, an 80% yield of 98% purity fatty acid and 20% of still bottoms can be obtained.

Recycling of Still Bottoms

Analysis of typical experiments shows a glycerol balance of some 70% as isolated triacetin, 25% as acetoglycerides, and up to 5% unaccounted for. The bulk of the acetoglyceride glycerol should be recoverable as more triacetin by its further reaction with acetic acid. This was checked by combining three lots of distillation bottoms (averaging 12% w/w on hydrogenated tallow used), distilling again to recover diacetomonoglycerides and to concentrate the acetodiglycerides in the residue, and then reacting this residue with more acetic acid. See Tables II and III. The initial redistillation was carried to 220°C., overhead and 280°C. bottoms at 1 mm., and shows the considerable thermal stability of the materials, the distillate being 90% diacetoglycerides and only 3% of the initial ester value being unaccounted for on balance. The results of the re-acetolysis demonstrate the effectiveness of the recycling of still bottoms, though the high figure of 36% residue indicates an accumulation of high molecular weight material which is not broken down by acetolysis. This also indicates a need for performing this recycling as a separate re-run, so that these materials can be purged from the cycle.

TABLE I
Vacuum Distillation of Fat Products at 1–5 mms. Hydrogenated Tallow Reacted 24 Hours, 115°C., with 3 Vols. 98% Acetic Acid

	Yield[d]	S.V.	A.V.	Ester V	% FFA	% GAc2-St[c]
I. No Column Fraction						
1	5	....	....	....	....	....
2	54	219	196	23	94	6
3	8	....	175	....	86	14
4	27	236	156	80	78	22
Residue	6	....	....	....	....	....
II. 12 in. Vigreux[a] Fraction						
1	8	....	....	....	....	....
2	63	205	200	5	98.5	1.5
3	17	232	157	75	80	20
4	10	349	31	318	15	85
Residue	2	....	....	....	....	....
III. 12 in. Vigreux[a] Fraction						
1	71	211	202	9	98	2
2	17	222	188	34	91	9
3	2	314	69	245	37	63
Residue	10	309	24	275	12	....[e]
IV. 12 in. Vigreux[b] Fraction						
1	0.2	....	214	....	....	....
2	67	210	204	6	98.5	1.5
3	14	211	189	26	93	7
4	9	263	129	134	66	34
Residue	10	307	26	281	13	....[f]

[a] + 2% w/w on fat TolSO$_3$H.
[b] + 1% w/w on fat MeSO$_3$H.
[c] Calc. from ester value.
[d] % w/w on fatty products.
[e] Approx. 35% Ac$_2$MG + AcDG.
[f] Approx. 41% Ac$_2$MG + 46%AcDG.

TABLE II
Redistillation of Bottoms

Material	Yield %	A.V.	S.V.	E.V.
Bottoms	....	16	309	293
Distillate	55	19	353	334
Final residue	45	8	246	238

TABLE III
Distillation of the Re-acetolyzed Still Bottoms

Fraction	Yield %	A.V.	S.V.	E.V.
Triacetin	21.2[a]	......	764	......
Fatty acids I	54[b, c]	191	212	21
Fatty acids II	10[b, d]	145	250	105
Residue	36[b]	22	303	281

[a] % w/w on still bottoms charged.
[b] % w/w on fatty products.
[c] Range 170–200°C./1 mm.
[d] Range 200–238°C./1 mm.

TABLE IV
The Acetolysis[a] of Rendered Beef Fat[b]

Fraction	Range, °C. at mm.	Yield %[c]	I.V.	S.V.	A.V.	E.V.
Triacetin	105-107/1.6	18.0	......	737	3	734
Fatty acids I	107-130/1.8	0.1	......	......	......	......
Fatty acids II	130-193/1.7	49.0	26.6	223	208	15
Fatty acids III	193-206/1.4	30.0	37.5	232	189	43
Fatty acids IV	206-212/0.9	11.0	23.4	328	99	229
Residue	......	10.0	27.0	287	16	271

[a] Refluxed 24 hr. with 3 vol. 98% HAc + 2% TolSO$_3$H w/w on fat.
[b] I.V. 37.0, S.V. 206, A.V. 1.5.
[c] w/w on tallow.

Acetolysis of Tallow

The use of hydrogenated tallow simplified the system by isolating the acetolysis reactions from the side reaction of acetic acid addition to double bonds. After the simpler case had been used to investigate the main process variables, some straight tallow batches were run in order to evaluate the effect of the side reaction on process operation and product quality. See Tables IV and V.

The low saponification values of the triacetins obtained in these runs indicate 2.8 acetyl groups per glycerol residue; this was due to the catalyst being inactivated before acetic acid recovery. The reactylation is usually performed by delaying the catalyst

TABLE V
The Acetolysis[a] of No. 1 Tallow[b]

Fraction	Range °C. at mm.	Yield %[c]	I.V.	S.V.	A.V.	E.V.
Triacetin	105-130/2.2	18.5	......	734	4	730
Fatty acids I	130-195/1.8	41.0	24.7	222	211	11
Fatty acids II	195-205/1.1	22.0	37.9	218	196	22
Fatty acids III	205/1.2	15.0	39.8	230	185	45
Fatty acids IV	205-206/1.0	7.0	29.2	282	148	134
Fatty acids V	206-212/0.9	5.0	19.5	352	87	265
Residue	......	9.0	29.1	291	16	275

[a] Refluxed 24 hr. with 3 vol. 98% HAc + 2% TolSO$_3$H w/w on tallow.
[b] I.V. 38.2, S.V. 198, A.V. 3.0.
[c] w/w on fat.

TABLE VI

Corrosion Tests in 1 Part Hydrogenated Tallow, 3 Parts 98% Acetic Acid Containing 1% Perchloric Acid at 100°C.

Material	Duration of test (weeks)	Penetration (mm./yr.)
304 S.S.	4	1.2
Carpenter 20	4	0.3
316 S.S.	4	0.1
Haynes 25	10	0.02
Hastelloy C	10	0.001

inactivation until the aqueous acetic acid has been removed in the first part of the distillation. This would raise the triacetin yield by about 1%, w/w on fat charged, due to the molecular weight increase resulting from the re-acetylation.

About 20% of the original unsaturation disappears during the reaction and most of this can be accounted for by the appearance of excess ester value in the products, conversion efficiency of unsaturation to acetoxy being generally around 90%. The high ester value of the earlier distilled fractions shows that the acetoxy acids fail to separate as a clear fraction, and the analyses of the later fractions show that no diacetoglyceride fraction of over 50% concentration was obtained. A redistillation of Fraction IV of Table IV into two equal fractions gave little advance over this figure. While the acetoxy acids do not interfere with the separation of unsubstituted fatty acids from diacetoglycerides, they clearly contaminate both fractions.

Material of Construction

Corrosion tests were carried out at 100°C. using the most severe conditions, i.e., perchloric acid as catalyst, and with daily replacement of the catalyzed reaction mixture. See Table VI.

The first two materials consumed enough catalyst to slow the reaction, and were severely attacked. Type 316 stainless steel did not affect the reaction or show visible pitting, but enough nickel and chromium dissolved to color the test solution at the start. This marginally possible material merits further test with less highly corrosive catalysts. The last two alloys were fully satisfactory. The distillation processes present no novel problem once the catalyst has been inactivated, S.S. 316 being an established satisfactory material.

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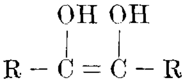
Citric Acid: Inactivating Agent for Metals or Acidic Synergist in Edible Fats?[1]

J. C. COWAN, PATRICIA M. COONEY, and C. D. EVANS,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Oxidative stabilities of soybean oil and lard are improved by the addition of either sorbitol or citric acid. Sufficient sorbitol gives enough improvement in stability so that added citric acid gives no increased stability. Unless sorbitol acts as a neutral synergist, forms a powerful acidic synergist in trace amounts or a new antioxidant, the antioxidant activity of citric acid appears to come from its inactivating capacities for metals.

THE MODE OF ACTION that various minor constituents or small amounts of additives have on the oxidative stability of vegetable oils, animal fats, and their derivatives, has been investigated extensively during the past 20 years. These investigations disclose that a series of phenolic derivatives like hydroquinone, catechol, and butylated hydroxyanisole are effective antioxidants for fats (12, 15) and that certain acidic compounds not phenolic in nature, like phosphoric, citric, and carboxymethyl mercaptosuccinic acids, are effective aids to stabilization (2, 8, 12). All the phenolic and related derivatives that are effective antioxidants appear to be enediols  $R-\overset{OH}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-R$ or vinylogs thereof (12). All acidic compounds that are effective appear to have another property in common, *i.e.*, they are effective inactivating agents of trace metals (2, 3, 5, 15, 18).

Fats are remarkably sensitive to trace amounts of metals, particularly if no natural or added metal-inactivating agent is present. This sensitivity appears to depend in part on the type of unsaturation present in the oil; for example, soybean oil is more sensitive to trace metals than is cottonseed oil (5). Only 0.01 p.p.m. of copper or 0.1 p.p.m. of iron is enough to make an appreciable difference in the rate of autoxidation of soybean oil whereas this amount of added iron may have little effect on cottonseed oil.

Olcott and Mattill (14) found that both a phenolic and an acidic "antioxidant" used together gave unusual stability under certain circumstances. They called this phenomenon a "synergistic effect." At that time Olcott and Mattill were not familiar with the metal-inactivating properties of the acidic compounds because this reaction had not yet been established with certainty. Although Evans (6) suggested that the antioxidant properties of phosphatides in fats and oils were probably based on their metal-inactivating capacities, this inactivation of metals by these acidic compounds was not generally recognized until later. Riemenschneider (15) and Dutton (2) reported data which clearly showed that these acidic compounds could act as metal-inactivating agents.

Lemon (10) examined this problem and concluded that citric acid was both a synergist and a metal inactivator. His conclusion was based primarily on studies with distilled peanut fatty esters. These studies showed that citric acid did improve the stability of the purified (distilled and chromatographed) esters, consequently the acid was considered to be a

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[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.