Technical News feature

High Pressure Splitting of Castor Oil

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ABSTRACT

The effects of variations in pressure (20-40 kg/cm^2), oil-to-water ratio (1:0.4-1:1, w/w) and time (0-8 hr) on the extent of hydrolysis of castor oil were studied. Higher pressure, lower oil-to-water ratio and longer duration gave higher percentage splits. At 40 kg/cm^2 pressure and an oil-to-water ratio of 1:1, ca. 92% split was obtained in 8 hr. When the oil was hydrolyzed in 2 stages at 20 kg/cm^2 with an oil-to-water ratio of 1:0.4, ca. 96% split was obtained in a total period of 10 hr. Splitting at 20 kg/cm^2 gave minimal amounts of dienoic acids because of the decomposition of estolides.

INTRODUCTION

High pressure hydrolysis of oils and fats with water is a normal commercial practice in manufacturing fatty acids (FA) with glycerol as a by-product. Oils containing hydroxy FA are also expected to yield, on hydrolysis, estolides because of intermolecular condensation between the hydroxyl and carboxyl groups of the FA as ricinoleic acid is known to form estolides (polyricinoleic acids) on heating or even when stored (1,2). Such estolide formation was observed during the splitting of castor oil at atmospheric pressure using a Twitchell catalyst (3) and of hydrogenated castor oil at high pressure (4). Estolides were further found to decompose at high temperatures (4,5). A systematic study of splitting of castor oil at high pressures appears, therefore, to be of interest. Such split products could be useful in manufacturing dehydrated castor oil (DCO) FA (6) and dimeric FA (7).

MATERIALS AND METHODS

Castor oil (acid value, 1.1, saponification value, 181.4; hydroxyl value, 162.1; iodine value, 83.2) was purchased from a local firm.

An electrically heated 2-L stainless-steel autoclave fitted with a turbine stirrer, safety valve, pressure gauge, temperature indicator and sampling device was used. Heating was controlled manually using a dimmerstat. The autoclave was charged up to 60% of its volume with predetermined quantities of castor oil and distilled water and heated to the desired pressure in 45-60 min. The time at which the contents attained the desired pressure was taken as the zero hour reaction time and the reaction was carried out at that pressure for the required period. The heating and stirring were stopped at the end of the reaction period and the autoclave was taken out of the heater jacket to facilitate faster cooling of the reaction product and to minimize further reaction. The products were washed with water and the washings added to the main sweet water. Glycerol was estimated by the periodate oxidation method of the American Oil Chemistis' Society (8). The products were extracted with diethyl ether, washed with water, dried under vacuum at 60 C and analyzed for acid. saponification and hydroxyl values according to the American Oil Chemists' Society procedures (8).

For detecting estolides in the initial stages of the reaction, the split products were dissolved in diethyl ether and the ethereal layer was treated with 3% aqueous potassium hydroxide solution. The resulting solution of soaps of free fatty acids (FFA) and estolides was separated and repeatedly extracted with diethyl ether to remove any unsplit glycerides. The solution was acidified with dilute sulfuric acid in the presence of diethyl ether. The liberated acids were isolated, dried under vacuum at 60 C and analyzed for acid values and for the presence of estolides by thin layer chromatography (TLC) on 0.25 mm layers of Silica gel G using a solvent mixture of gasoline (40-60 C)/diethyl ether/ethyl alcohol/acetic acid (60:40:4:1, v/v/v/v) (9). The separated components were detected by spraying the plates with 1% phosphomolybdic acid in isopropyl alcohol and heating the plates in an oven at 105 C for 15 min. The estolide contents in the final products, obtained by splitting for 8 hr at 20 kg/cm^2, 30 kg/cm^2 and 40 kg/cm^2 using an oil-to-water ratio of 1:0.8 (w/w), were calculated by multiplying the percentage split with the ratio of ester value (saponification value − acid value) to the saponification value of the acidic fraction separated from the total split products.

Single-stage splitting experiments were carried out using various ratios of oil-to-water (1:0.4, 1:0.6, 1:0.8 and 1:1, w/w) and pressures (20 kg/cm^2, 30 kg/cm^2 and 40 kg/cm^2). Two-stage splitting experiments were carried out at 20 kg/cm^2 using castor oil and water in the ratio of 1:0.4 (w/w).

The FA compositions of castor oil and the final split products were determined by saponification, acidification, conversion of the liberated acids to methyl esters and an-analysis by gas liquid chromatography (GLC) of the methyl esters as the trimethylsilyl ether derivatives using bis-(trimethylsilyl) trifluoroacetamide (Sigma Chemical Co., St. Louis, MO) for silylation. The analyses were carried out using a Hewlett-Packard 5840A unit equipped with a hydrogen flame ionization detector (FID), a data processor and a glass column (1.6 m × 2.5 mm) packed with 10% EGSS-X/Gas Chrom Q (80-100 mesh). The column, injection port and detector were maintained at 200 C, 250 C and 300 C, respectively. Nitrogen was used as a carrier gas at a flow rate of 30 mL/min.

RESULTS AND DISCUSSION

In the initial stages of splitting, estolides were found to be present only in minor quantities by TLC. This was confirmed by comparing the acid value of the free acidic material separated from the split products with the acid value of the castor oil FA; e.g., this was ca. 177 vs 187 in the case of samples having maximum hydroxyl values. Hence the percentage split was calculated from the saponification and acid values of the split products (10) until the hydroxyl values started falling. From then on the percentage split was calculated from the glycerol content in sweet water.

The effects of pressure, ratio of oil-to-water and reaction time on the pattern of splitting are shown in Tables I-III and Figure 1. In the initial stages of single-stage splitting of castor oil, the acid values and hydroxyl values of the products increased as a result of hydrolysis as well as the formation of di- and monoglycerides. The gradual increase

TABLE I

Single-Stage Splitting of Castor Oil at Different Pressures[a]

Time (hr)	20 kg/cm^2 (213 C)				30 kg/cm^2 (234 C)				40 kg/cm^2 (250 C)			
	AV[b]	SV[b]	HV[b]	Split (%)	AV	SV	HV	Split (%)	AV	SV	HV	Split (%)
0.0	2.8	181.2	164.3	1.5[c]	7.2	181.6	173.2	4.0[c]	16.2	181.9	171.3	8.9[c]
0.5	6.7	181.5	165.2	3.7[c]	29.7	182.4	178.2	16.3[c]	86.4	183.1	209.5	47.2[c]
1.0	15.0	182.1	168.7	8.3[c]	79.3	183.2	195.3	43.3[c]	132.0	–	161.0	66.9
2.0	75.1	183.0	178.3	41.0[c]	106.2	183.8	170.5	65.4	134.9	–	144.5	80.0
3.0	112.9	183.6	192.0	61.5[c]	107.5	–	–	78.5	–	–	–	–
4.0	112.5	–	161.0	72.9	112.2	–	–	83.6	132.1	–	129.6	87.5
5.0	114.1	–	–	79.8	116.0	–	–	86.0	–	–	–	–
6.0	111.2	–	–	83.3	117.3	–	–	87.5	131.3	–	130.0	90.0
8.0	104.0	–	–	86.4[d]	119.4	–	–	88.8[d]	131.2	–	109.0	91.5[d]

[a] Oil/water, 1:0.8 (w/w).

[b] AV, acid value; SV, saponification value; HV, hydroxyl value.

[c] Percentage split was calculated on the basis of acid and saponification values of the corresponding products. In the remaining samples percentage split was calculated from glycerol content in sweet water.

[d] The products obtained at 20 kg/cm^2, 30 kg/cm^2 and 40 kg/cm^2 contained 31.5%, 31.0% and 24.5% estolides, respectively.

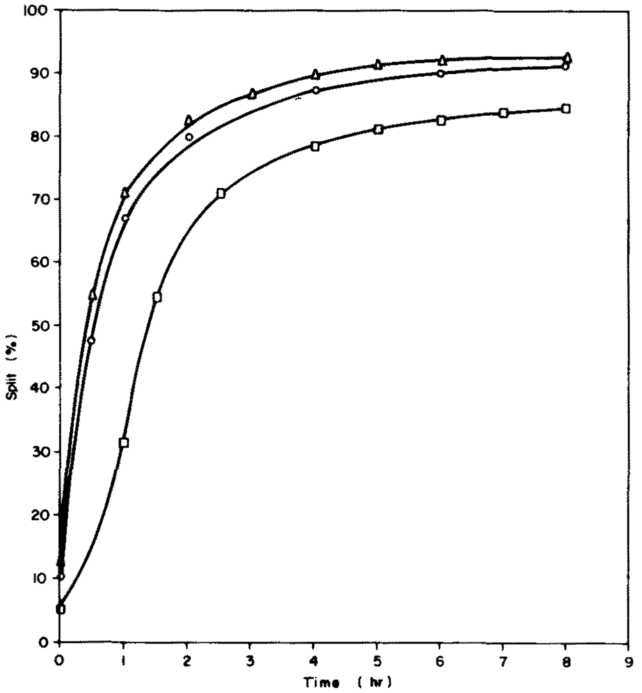

FIG. 1. Splitting of castor oil at 40 kg/cm^2 (250 C) using oil and water in the ratio of 1:1 (△), 1:0.8 (○) and 1:0.6 (□).

TABLE II

Two-Stage Splitting of Castor Oil[a]

Time (hr)	AV[b]	SV[b]	HV[b]	Split[c] (%)
First stage				
0	1.4	181.1	163.2	0.8
1	15.2	181.7	169.7	8.4
2	61.8	182.3	201.2	33.9
3	99.1	182.5	204.4	54.3
4	109.1	183.5	173.2	64.3
5	–	–	–	74.0
6	–	–	–	77.0
Second stage				
1	–	–	–	89.4
2	–	–	–	94.8
4	–	–	–	96.0
6	–	–	–	96.5

[a] Oil/water, 1:0.4 (w/w); 20 kg/cm^2 pressure (213 C).

[b] Av, acid value; SV, saponification value; HV, hydroxyl value.

[c] Percentage split was calculated on the basis of acid and saponification values of the corresponding products for samples up to 3 hr and in the remainder from glycerol content in sweet water.

TABLE III

Fatty Acid Composition[a] of Castor Oil and Products of Split Castor Oil at Different Pressures

		Products of castor oil split[b] at			
Fatty acid	Castor oil	20 kg/cm^2 (213 C)	30 kg/cm^2 (234 C)	40 kg/cm^2 (250 C)	20 kg/cm^2 (2 stages)
16:0	0.9	1.0	1.0	1.2	1.1
18:0	1.0	1.1	1.1	1.1	1.2
18:1	3.1	3.0	3.5	3.4	3.4
18:2	3.2	3.3	8.4	12.8	4.0
18:1 (monohydroxy) + 18:0 (dihydroxy)	90.8	90.2	79.0	69.0	88.3
18:2 (conjugated) + 18:3	1.0	1.4	7.0	12.5	2.0

[a] The fatty acid composition was determined by GLC after saponification, acidification, esterification and silylation.

[b] Oil/water, 1:0.8 and 8 hr for single-stage and oil/water 1:0.4 and 10 hr for 2-stage splitting.

in acid values during the initial stages of splitting was caused by the predominance of formation of FA over the disappearance of carboxyl group by estolide formation. The time through which the hydroxyl value reached a maximum varied in different experiments and depended on the experimental conditions of splitting. Whereas maximum hydroxyl value was attained in 0.5 hr at 40 kg/cm^2 (250 C), it was reached in 1 hr at 30 kg/cm^2 (234 C) and 3 hr at 20 kg/cm^2 (213 C). Afterwards, first a sudden fall occurred in the hydroxyl value while acid value increased as a result of the disappearance of partial glycerides, then a slight increase or stabilization in the acid value occurred as a result of simultaneous formation of FA and estolides (Table I). The estolide contents, even in the final products obtained by splitting for 8 hr at 20 kg/cm^2 (213 C), 30 kg/cm^2 (234 C) and 40 kg/cm^2 (250 C), were appreciable—31.5%, 31.0% and 24.5%, respectively. The data obtained in 3 series of experiments carried out at 3 different pressures, 20 kg/cm^2, 30 kg/cm^2 and 40 kg/cm^2 at a constant oil-to-water ratio of 1:0.8 are shown in Table I. With an increase in pressure, the rate of splitting increased considerably and the induction period decreased. Hence higher pressures are conducive to the quick attainment of the maximum degree of hydrolysis. Thus a split of ca. 92% was attained in ca. 8 hr at 40 kg/cm^2. Figure 1 shows that induction periods increased and percentage splits decreased when the oil-to-water ratios were increased. The FA composition of the split products obtained at 20 kg/cm^2, 30 kg/cm^2 and 40 kg/cm^2 showed the formation of ca. 1%, 10% and 20% dienoic acids (Table III). The decomposition of estolides to form dienoic acids was minimal at 20 kg/cm^2.

For direct use of the split products in the manufacture of DCO FA (6) and dimeric FA (7), the split product should contain the least amount of unsplit oil to minimize formation of side products and increase the yield of desired products. Therefore, splitting was carried out in 2 stages at 20 kg/cm^2 pressure using castor oil and water in a ratio of 1:0.4. The pattern of splitting and the data obtained are shown in Table II. The data show the a split of ca. 77% was obtained in 6 hr in the first stage. The sweet water was removed, the fatty layer and fresh water were taken in the ratio of 1:0.4 and a second splitting was carried out for different periods of time. Table II also shows that a split of ca. 96% was easily obtained in 4 hr in the second stage. Two-stage splitting would facilitate the use of lower pressures and higher oil-to-water ratios. The product obtained by splitting castor oil in 2 stages contained less than 1% conjugated dienoic acids (Table III) and could be conveniently stored without appreciable deterioration until further processing took place.

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