

# Heptaldehyde and Undecylenic Acid From Castor Oil

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**Castor Oil was pyrolyzed in a vertical stainless steel tubular reactor packed with 12.5-mm diameter mild steel balls in presence of 0.5% benzoyl peroxide. The operating parameters were optimized to obtain high yields of heptaldehyde and undecylenic acid. Heating at 550 C under reduced pressure of 45 mm (Hg) yielded 24.8% heptaldehyde and 36.0% undecylenic acid.**

Castor is an important, inedible oilseed crop of India. The country ranks second in and accounts for about 25% of the world production of this oilseed crop. The castor seed is crushed for extraction of its oil; however, the industry for production of castor oil derivatives is not yet well developed. Consequently, India imports castor oil derivatives in the forms of surface coating materials, textile auxiliaries, perfumery chemicals, polymeric compounds and surfactants. Thus, it is of considerable interest to develop castor oil derivatives and the industry for better utilization of castor oil to meet the domestic demand for speciality chemicals indigenously.

Pyrolysis of castor oil at higher temperature (>400 C) under reduced pressure yields heptaldehyde and undecylenic acid, which are sources of valuable perfumery, pharmaceutical and polymeric materials. Further, heptaldehyde serves as a solvent for rubber, resins and plastics and is a source of emulsifiers, plasticizers and insecticides. Similarly, undecylenic acid serves as a source of bactericides and fungicides (1-4).

Normally, castor oil pyrolysis is accompanied at lower temperatures by dehydration of the oil and other pro-dehydration conditions. The dehydrated oil is polymerized and results in a gelled and spongy product, difficult to analyze for its constituents (5). The extent of dehydration and other side reactions significantly affect the pyrolysis reaction and thus the yields of both the desired oleochemicals. The other side reactions cause impurity in the resulting product in the form of acrolein, ketonic compounds and other fatty acids. Several reports have considered pyrolysis of castor oil at 400-700 C under reduced pressure to obtain heptaldehyde and undecylenic acid in yields that range from 16.0-24.0% and 17.6-35.0%, respectively (6-14). Han Toe Li (15) used rosin, sandrac, PVC and zinc powder as a catalyst for the pyrolysis of castor oil to obtain better yields of heptaldehyde and undecylenic acid.

Normally, pyrolysis at higher temperatures proceeds through free radical formation as has been observed in the case of hydrocarbons. It is possible that pyrolysis reaction of ricinoleic acid derivatives may also involve a free radical mechanism (12). Also, the reaction in the presence of free radical-yielding initiators has been reported to be more effective in providing higher yields of the desired oleochemicals (16).

The reported conditions of pyrolysis in several of these studies, however, do not provide satisfactory yields of both the desired oleochemicals and thus lack techno-

economic feasibility. Consequently, this research was undertaken to optimize process parameters for pyrolysis of castor oil to obtain better yields of heptaldehyde as well as undecylenic acid.

## EXPERIMENTAL PROCEDURES

**Materials.** Raw grade castor oil was obtained from a local market. Laboratory Reagent grade benzoyl peroxide (Sarabhai M. Chemicals, Vadodara, India),  $\alpha$ - $\alpha'$  azoisobutyronitril (Merck, Schuchardt, West Germany) and Water White grade rosin (Indian Turpentine and Rosin Co., Bareilly, India) were used as initiators of pyrolytic reaction.

## METHODS

**Characterization of castor oil.** The physicochemical characteristics of castor oil (specific gravity, color, refractive index, optical rotation, acid value, saponification value and unsaponifiable matter) were assessed using standard AOCS procedures (17). The fatty acid composition of castor oil was determined by gas liquid chromatography of the methyl esters prepared according to the method of Jameison and Reid (18).

**Pyrolysis in glass assembly.** Castor oil samples in 500-g quantities were pyrolyzed at 320 C and 340 $\pm$ 2 C under 20-80  $\pm$  mm (Hg) pressure in the presence of benzoyl peroxide and rosin (1%, w/w) in a three-necked, two-l flask (batch process). The pyrolysis products were condensed and collected.

Alternatively, the reaction flask half-filled with porcelain powder (under 40 mesh) was preheated to 340 $\pm$ 2 C. While the temperature was maintained, castor oil containing benzoyl peroxide (1%, w/w) was introduced at a flow rate of 2-5  $\pm$  0.1 g/min (continuous process). The pyrolysis products were collected under 45 $\pm$ 5 mm (Hg) pressure.

**Pyrolysis in unpacked cylindrical reaction vessel.** An electrically-heated mild steel (MS) cylindrical vessel (38.1 cm deep  $\times$  10.2 cm i.d.) connected to a condenser was used for pyrolysis of castor oil containing benzoyl peroxide (1%, w/w). The samples were introduced into the preheated vessel at a flow rate of 5  $\pm$  0.1 g/min. and pyrolyzed at 450-600  $\pm$  5 C under reduced pressure of 45 $\pm$ 5 mm (Hg). The pyrolysis products were collected as before.

**Pyrolysis in packed tubular reactor.** An electrically heated stainless steel (SS) tubular reactor (76.2 cm long  $\times$  2.5 cm i.d.), packed with either SS pieces (0.6-0.8 cm long  $\times$  0.8-1.0 cm wide  $\times$  0.1 cm high) or SS borings or MS balls (10/12.5 or 14.0 mm in diameter), was installed over a condenser for continuous pyrolysis of castor oil at 450-650 $\pm$ 5 C under reduced pressure of 45-105  $\pm$  5 mm (Hg). The oil containing benzoyl peroxide up to 1.5% (w/w) or  $\alpha$ - $\alpha'$ -azoisobutyronitril up to 2.0% (w/w) was fed to the reactor at a flow rate of 1-4 g/min.

**Recovery of heptaldehyde and undecylenic acid.** Heptaldehyde and undecylenic acid were recovered from pyrolysis products of castor oil under reduced pressure of 20 mm (Hg) at 60-65 C and 160-170 C, respectively.

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TABLE 1

## Pyrolysis of Castor Oil in Glass Assembly

Process and run number	Pyrolysis Conditions				Yields (% w/w)		
	Temperature (°C)	Pressure (mm Hg)	Initiator (% w/w)	Feed rate oil (g/min)	Pyrolysis Product	Heptaldehyde	Undecylenic acid
Batch 1	320	20	-	-	56.7	8.0	11.4
2	320	20	1.0 <sup>a</sup>	-	56.0	8.2	10.3
3	320	20	1.0 <sup>b</sup>	-	62.8	8.2	11.6
4	340	20	-	-	56.0	8.1	12.0
5	340	40	-	-	57.8	7.9	11.9
6	340	60	-	-	52.6	6.8	10.1
7	340	80	-	-	53.5	7.2	9.0
8	340	20	1.0 <sup>b</sup>	-	64.8	9.0	12.4
Continuous							
9	340	45	-	2.0	68.0	11.2	15.4
10	340	45	1.0 <sup>b</sup>	2.0	74.3	12.0	16.3
11	340	45	1.0 <sup>b</sup>	3.0	72.9	11.7	15.9
12	340	45	1.0 <sup>b</sup>	4.0	75.0	10.1	15.3
13	340	45	1.0 <sup>b</sup>	5.0	78.1	9.6	15.0

<sup>a</sup>Rosin.<sup>b</sup>Benzoyl peroxide.

TABLE 2

Effect of Temperature of Pyrolysis of Castor Oil<sup>a</sup> in Unpacked Cylindrical MS<sup>b</sup> Reaction Vessel<sup>c</sup> on Yields of Oleochemicals

Temperature of pyrolysis (°C)	Pyrolysis product	Yields <sup>d</sup> (% w/w)	
		Heptaldehyde	Undecylenic acid
450	78.0	7.8	12.5
500	78.1	8.9	13.2
550	69.0 <sup>e</sup>	11.3 <sup>e</sup>	15.1 <sup>e</sup>
600	63.0	9.6	14.1

<sup>a</sup>Containing benzoyl peroxide (1% w/w).<sup>b</sup>MS, mild steel.<sup>c</sup>Feed rate of oil into the reaction vessel (38.1 cm high × 10.2 cm i.d.) was 5.0 ± 0.1 g/min.<sup>d</sup>Under 45 ± 5 mm Hg pressure.<sup>e</sup>Average of four runs.

The purity of heptaldehyde was assessed by hydroxyl amine hydrochloride and 2-4, dinitrophenyl hydrazine methods (19), as well as by synthesizing its derivatives, viz, nonenoic acid and 2-4, dinitrophenyl hydrazone, and checking their boiling and melting points, respectively. The purity of undecylenic acid was checked by assessing its iodine value and neutralization number (17) as well as by gas liquid chromatography (GLC) and boiling point of its methyl ester (20).

The identity of the above products was further confirmed by IR and NMR spectroscopy.

## RESULTS AND DISCUSSION

The castor oil used in the present work had all its physico-chemical characteristics within the normal limits (21), confirming that the samples were genuine.

TABLE 3

Effect of Temperature and Pressure of Pyrolysis of Castor Oil<sup>a</sup> in SS Tubular Reactor<sup>b,c</sup> on Yields of Oleochemicals

Pyrolysis condition	Yields (% w/w)			
	Temperature (°C)	Pressure (mm, Hg)	Pyrolysis product	Undecylenic acid
450		45	92.2	23.6
500		45	88.0	29.3
550		45	82.6 <sup>d</sup>	35.4 <sup>d</sup>
		65	79.3	34.8
		85	74.1	28.5
		105	68.5	26.1
600		45	69.4	30.0
650		45	50.0	15.1

<sup>a</sup>Containing benzoyl peroxide (1% w/w).<sup>b</sup>Feed rate of oil into the reactor (76.2 cm long × 2.5 cm diameter) was 3.0 ± 0.1 g/min.<sup>c</sup>Packed with MS balls of 12.5 mm diameter.<sup>d</sup>Average of two runs.

**Pyrolysis in glass assembly.** The details of results obtained from pyrolysis experiments in laboratory glass assembly are indicated in Table 1.

**Batch process.** The yield of undecylenic acid was somewhat higher at 340 C under 20 or 40 mm (Hg) pressure than at 320 C. At 340 C, higher pressures (>40 mm Hg) resulted in decreased yield of pyrolysis product and its recoverable content of both oleochemicals. Between rosin and benzoyl peroxide, only the latter was observed to improve the yields of pyrolysis product and both oleochemicals.

**Continuous process.** The continuous process provided comparatively greater yields of pyrolysis product and oleochemicals in both the presence and absence of the initiator-benzoyl peroxide, perhaps because of the porous nature and large surface area of the porcelain matrix used for the reaction. An increase in feed rate from 2-3 g/min to 4-5 g/min improved the recovery of the pyrolysis product; however, the yields of oleochemicals decreased. Because the maximum yields of oleochemicals were far from satisfactory in the glass assembly and there were limitations of the glass assembly for providing still higher temperatures, the metallic reactors were considered for subsequent work on continuous pyrolysis of castor oil.

**Pyrolysis in unpacked cylindrical reaction vessel.** The results of experiments in pyrolysis of castor oil in unpacked cylindrical MS vessel showed that a reaction temperature of 550 C provided higher yields of heptaldehyde and undecylenic acid (Table 2). Because the yields of oleochemicals were considerably lower in the unpacked reaction vessel, it was prudent to modify and pack the reactor for subsequent experiments on pyrolysis of castor oil.

**Pyrolysis in packed tubular reactor.** The effect of temperature and pressure of pyrolysis of castor oil, containing benzoyl peroxide and fed to a SS tubular reactor (packed with MS balls 12.5 mm in diameter) at a flow rate

of  $3.0 \pm 0.1$  g/min, on the yields of pyrolysis product and oleochemicals, is shown in Table 3. The yield of the pyrolysis product decreased with an increase in reaction temperature, perhaps due to polymerization of some of the pyrolytic products. As expected, the recovery of the product of pyrolysis at a particular temperature decreased with increasing reaction pressure (Table 3).

The results of this set of experiments suggested that better yields of heptaldehyde and undecylenic acid were obtainable from the product of pyrolysis of castor oil at  $550 \pm 5$  C under  $45 \pm 5$  mm (Hg) pressure.

The effect of the initiator concentration and feed rate in pyrolysis of castor oil, under optimized conditions of temperature ( $550 \pm 5$  C) and pressure ( $45 \pm 5$  mm Hg) in the SS tubular reactor, on the yields of oleochemicals is indicated in Table 4. It is apparent that benzoyl peroxide was again a superior initiator of pyrolysis of castor oil than  $\alpha$ - $\alpha'$  azoisobutyronitril. The role of initiator in en-

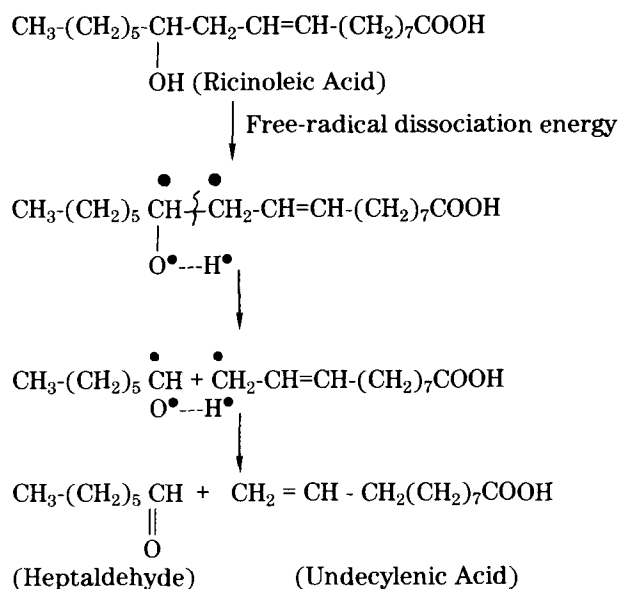


TABLE 4

Effect of Initiator Concentration and Feed Rate in Pyrolysis of Castor Oil<sup>a</sup> in SS Tubular Reactor<sup>b</sup> on Yields of Oleochemicals

Initiator Concentration (% w/w)	Feed rate oil g/min	Yields (% w/w)		
		Pyrolysis product	Heptaldehyde	Undecylenic acid
-	3.0	67.2	22.4	32.4
0.3 <sup>c</sup>	3.0	79.6	23.6	32.8
0.5 <sup>c</sup>	3.0	82.6	24.8	36.0
1.0 <sup>c</sup>	3.0	82.6	24.6	35.4
1.5 <sup>c</sup>	3.0	83.1	24.8	36.0
0.5 <sup>d</sup>	3.0	72.4	22.0	32.0
1.0 <sup>d</sup>	3.0	70.9	23.9	33.0
1.5 <sup>d</sup>	3.0	71.0	23.8	33.1
2.0 <sup>d</sup>	3.0	72.1	23.9	33.0
0.5 <sup>e</sup>	1.0	68.6	19.1	28.5
0.5 <sup>e</sup>	2.0	74.5	21.2	30.9
0.5 <sup>e</sup>	4.0	83.0	22.4	31.4

<sup>a</sup>At  $550 \pm 5$  C under  $45 \pm 5$  mm (Hg) pressure.

<sup>b</sup>Reactor in 76.2 cm long  $\times$  2.5 cm diameter packed with MS balls 12.5 mm in diameter.

<sup>c</sup>Benzoyl Peroxide.

<sup>d</sup> $\alpha$ - $\alpha'$ -azoisobutyronitril.

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TABLE 5

Effect of Packing Materials in Pyrolysis<sup>a</sup> of Castor Oil<sup>b,c</sup> in SS Tubular Reactor<sup>d</sup> on Yields of Oleochemicals

Packing materials	Yields (% w/w)		
	Pyrolysis product	Heptaldehyde	Undecylenic acid
SS pieces <sup>e</sup>	75.1	15.5	27.6
SS borings	68.4	13.1	24.2
MS balls (diameter)			
10.0 mm	74.2	21.6	29.0
12.5 mm	82.6	24.8	36.0
14.0 mm	86.4	19.2	26.3

<sup>a</sup>At 550 ± 5 C under 45 ± 5 mm (Hg) pressure.

<sup>b</sup>Containing 0.5% (w/w) benzoyl peroxide.

<sup>c</sup>Oilfeed rate; 3.0 ± 0.1 g/min.

<sup>d</sup>76.2 cm long × 2.5 cm diameter.

<sup>e</sup>0.6-0.8 cm long × 0.8-1.0 cm wide × 0.1 cm high.

hancing the yields of the desired product is, however, not very explicit from the literature. However, the reaction can be explained from the follow mechanism.

The differences in the yields of pyrolysis products and oleochemicals in experiments with castor oil containing 0.5, 1.0 and 1.5% (w/w) levels of benzoyl peroxide were insignificant. When the feed rate to the reactor was varied, it was incidentally found that the pre-selected oil flow rate of 3.0 ± 0.1 g/min was apparently optimum.

The effect of packing materials in pyrolysis of castor oil under optimized conditions of temperature (550 ± 5 C), pressure (45 ± 5 mm Hg), initiator concentration (benzoyl peroxide 0.5%, w/w) and feed rate (3.0 ± 0.1 g/min), in the tubular reactor, on the yields of oleochemicals is shown in Table 5. The reactor packing with MS balls of 12.5 mm diameter provided maximum yields of heptaldehyde and undecylenic acid. The other packing materials, viz, SS pieces, SS borings and MS balls of 10 and 14 mm diameter provided lesser yields of these oleochemicals, perhaps because of some clogging of the reactor.

The purity of heptaldehyde assessed by hydroxylamine hydrochloride and the 2-4 dinitrophenyl hydrazine method was found to be 96.3% and 98.1%, respectively. The high purity of this oleochemical was confirmed by the boiling point of nonenoic acid (140 C under 25 mm Hg) and melting point of 2-4 dinitro-hydrazone (106 C), which were synthesized from experimental and authentic

samples of heptaldehyde. Similarly, the purity of undecylenic acid assessed by neutralization number and iodine value was found to be 97.2% and 96.4%, respectively. The high purity of this oleochemical was confirmed by detection of the only peak in the chromatogram of its methyl ester. Further, the boiling point of experimental methyl undecylenate was 124 C under 10 mm Hg pressure which coincided with that of the pure methyl undecylenate (20).

The results of this study suggest pyrolysis of castor oil containing 0.5% benzoyl peroxide at a flow rate of 3.0 ± 0.1 g/min and at 550 C under 45 ± 5 mm Hg pressure in a SS tubular reactor (76.2 cm long × 2.5 cm i.d.) packed with MS balls (12.5 mm in diameter) to obtain as much as 24.8% heptaldehyde and 36.0% undecylenic acid of average 97.2% and 96.8% purity, respectively.

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