

## Pyrolysis of castor oil methylesters to 10-undecenoic acid and heptaldehyde<sup>†</sup>

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The results of the pyrolysis of methyl esters of castor oil in a continuous tubular reactor to produce methyl undecenoate and heptaldehyde are discussed. Flow rates of esters, pyrolysis temperature and ester to steam ratios have been investigated as the process variables to arrive at the optimum values. Moreover, the literature pertaining to pyrolysis of castor oil has been reviewed.

India is one of the major castor seed producing countries in the world. The seed is crushed for extraction of its oil. Castor oil is unique amongst vegetable oils due to its very high content of hydroxy unsaturated fatty acid (hydroxy monoethenoid acid) called ricinoleic acid. Due to the preponderance of this acid to the extent of 80-90% by weight, this oil serves as a useful raw material for the manufacture of number of organic chemicals.

Pyrolysis of castor oil or its fatty acids or its fatty acid esters under suitable conditions yields 10-undecenoic acid or its ester and heptaldehyde. These two products are important starting chemicals for the preparations of some valuable synthetic aromatic compounds.

10-Undecenoic acid is used extensively for the manufacture of nylon-11. It is also used in the preparation of fungicides, insecticides, detergents, wetting agents and waxes. Heptaldehyde obtained as a by product during pyrolysis of castor oil, is used primarily in rubber industry in the preparation of vulcanisation accelerators. The other important application of heptaldehyde is in the preparation of synthetic aromatics, particularly  $\alpha$ -amyl cinnamic aldehyde (synthetic jasmine), methyl heptene carboxylate, and methyl *n*-heptyl ketone, nonylic acid. Polymers can also be prepared from heptaldehyde. The cracking products of castor oil alongwith their physical and thermodynamic properties and uses are also reported<sup>1</sup>. However, most of these studies are exploratory in nature and are confined to laboratory scale preparations of these products. The scope of the present paper is to discuss the results obtained from continuous pyrolysis of methyl esters of castor oil in

a tubular reactor and to summarise the published literature on pyrolysis of castor oil, its fatty acids and esters.

Castor oil as such is not preferable for pyrolysis reaction because its glycerol portion will interfere with the main reaction of pyrolysis and forms a number of undesirable products such as acrolein, polymeric materials and acetolides, thereby, making the separation/recovery of product uneconomical. In order to overcome these difficulties, castor oil is processed according to one of the two schemes as shown in Fig. 1. In all the schemes, it is seen that glycerol is obtained as a valuable by product. Even though the undecenoic acid is directly obtained by using fatty acids, the scheme using esters as starting material is preferable because these are more stable under the prevailing conditions of pyrolysis.

Literature pertaining to pyrolysis of castor oil, its esters and fatty acids to produce 10-undecenoic acid and heptaldehyde has been summarized in Table 1. The reaction has been carried out with and without catalysts. Different types of catalysts are used such as Al, Tl, Ti, Ce, Th, W, Mo, glass, rosin, mastic and poly(vinyl chloride) under wide range of conditions of temperatures from 275-700°C and pressure from 5-760 mm Hg. Glass flasks, cylindrical vessel, tubular reactors packed with catalysts or tubular reactors with inert packing have been used. A maximum conversion of 88% with yields of 66% and 10-40% of undecenoic acid and heptaldehyde, respectively, was reported.

Heat treatment of castor oil at higher temperatures gives rise to fuel oils by cleavage of the fatty acid chain into hydrocarbons.

It has been stated that the fission of ricinoleic acid into heptaldehyde and undecenoic acid begins sharply at 285-290°C<sup>2</sup>. The yield being inde-

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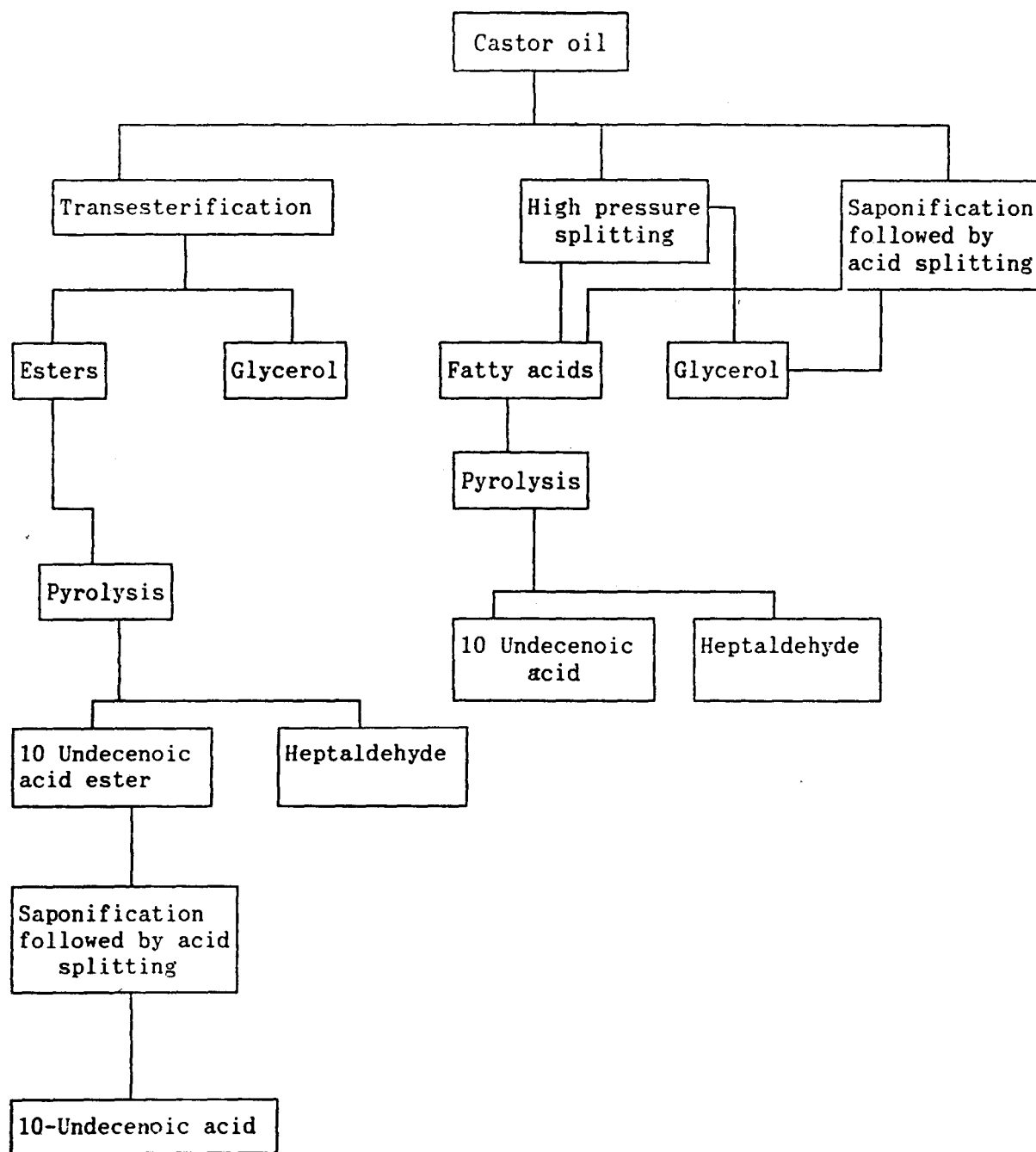


Fig. 1—Flow scheme for pyrolysis of Castor Oil

pendent of pressure, increases with increasing temperature, although the high temperature slightly reduces the yield of undecenoic acid by favouring its polymerisation. This is because of two simultaneous reactions, viz., dehydration to linoleic acid which then undergoes spontaneous polymerisation to a spongy residue and fission of ricinoleic acid into heptaldehyde and undecenoic acid. To explain these results, it is suggested that the tautomeric form of ricinoleic acid plays a major role in isomerisation of double bond and the pyrolysis reaction.

The pyrolysis of castor oil has also been studied by heating the oil at various temperatures in a heated silica tube and it is found that the drop in saponification value at 425°C is the indication of first pyrolytic reaction to form acrolein and the drop in acetyl value and simultaneous increase in the acid value at a temperature of 450°C is the further indication of the disappearance of hydroxyl groups of the castor oil and formation of heptaldehyde and undecenoic acid, respectively<sup>3</sup>. It has been suggested that the H atom of the OH group attaches itself mesomerically to C atom in

Table 1—Summary of processes for castor oil pyrolysis into 10-undecenoic acid (I) and heptaldehyde (II)

Reactants	Temperature, °C	Pressure, mm Hg	Residence time	Catalyst	Product yield	Remarks	Ref.
Castor oil	550-570	—	—	Al	—	Copper-Tubular reactor is used	(7)
Castor oil	550-560	—	—	—	—	Electrical heated (nichrome) pipe in the absence of air or catalyst	(8)
Castor oil	500	—	—	Sand silica, MnO <sub>2</sub> , pumice, alimina, sodium silicate, borax, K carbonates and metal oxides of Zn, B, Tl, Ti, Ce, Th, W and Mo	24% of heptaldehyde was obtained with sand or silica	Mechanism of reaction is explained	(4)
Castor oil	275	625 5-10	—	—	—	Decomposition begins at 275°C and polymerization starts at 300°C	(9)
Methyl ricinoleate	350-650	—	—	Alternate layers of glass rings and glass wool or pumice coated with Na borate or NaPO <sub>4</sub>	—	Reaction carried out in a Glass tube  Best results obtained with temp. range of 500-600°C	(10)
Castor oil	300	30-40	—	—	—	Destructive distillation carried out in a batch process	(11)
Castor oil	300-340	Vacuum	—	—	—	A mixture of raw castor oil and an acidic resin such as ester gum is destructively distilled under vacuum	(12)
Castor oil	425-465	—	—	—	—	Reaction carried out in a SiO <sub>2</sub> tube	(3)
Esters of ricinoleic acid	400-650	—	Reactant was passed over a period of 5 h	Molten lead is filled in the reactor tube upto 50 mm	970 g total wt. g of product (i) 170 g heptaldehyde (ii) 300 g undecenoate (iii) 500 g Ricinoleate after recycling of 500 g of Ricinoleate yielded 41 g aldehyde and 92 g undecenoate	Reaction carried in a quartz tube 30 mm length in the presence of molten metals	(13)

Contd.

Table 1—Summary of processes for castor oil pyrolysis into 10-undecenoic acid (I) and heptaldehyde (II)—*Contd.*

Reactants	Temperature, °C	Pressure, mm Hg	Residence time	Catalyst	Product yield	Remarks	Ref.
Esters of ricinoleic acid	480-550	—	—	—	1000 g of oil gave 211 g heptaldehyde and 392 g of undecenoate	Pyrolysis carried out in the presence of metals such as stainless steel, quartz sand or molten Pb.	(14)
Castor oil (400g)	400	40-50	10 min	—	23% I	Reaction carried out in liter flask	(15)
Castor oil (389g)	450-470	40-50	Flow rate 3.2 g/min	—	13% I	Cylindrical iron vessel	(15)
Castor oil (304g)	540-550	40-50	Flow rate, 4 g/min	—	32% I 22% II	With varying flow rates of oil and residence time	(15)
Castor oil (475g)	540-550	15-20	Flow rate, 4.8 g/min	—	15% I	Porcelain packed tube reactor. Silica beads packing	(15)
Castor oil (375g)	540-550	15-20	Flow rate, 2.6 g/min	—	20% I 10% II	Porcelain reactor packed with iron borings	(15)
Castor oil (600g)	600-610	15-20	Flow rate, 3.3 g/min	—	36% I 18% II	Porcelain reactor packed with iron borings	(15)
Castor oil (198g)	590-600	10-15	Flow rate, 1.7 g/min	—	26% I 15% II	Empty silica tube reactor	(15)
Castor oil (213g)	590-600	15-20	Flow rate, 1.7 g/min	—	22% I 17% II	Empty iron tube reactor	(15)
Castor oil (34 g/h)	450	—	—	—	30% II 28% I	Carried out a number of experiments. Maximum yields under reported conditions	(16)
Castor oil	225-250	500	—	—	33% I 17% II 45% residue 18% I 17% II 60-65 residue	Laboratory scale experiments Pilot scale experiments	(17)
	325-350	atm pressure	—	—	Low yield and more residue	—	
Esters of ricinoleic acid (338g) crude	320	—	Flow rate, 15-20 g/min	—	108 g of undecomposed, 8.6 g of (II) 132.1 g of (I)	Pyrex tube in a Pb bath. Similar results obtained in Fe tube	(18)
Castor oil acid (338 g) crude	—	—	—	Rosin, Mastic, Sandarac, polyvinyl chloride, Pt or Zn powder	—	Good yields were obtained with poly(vinyl)chloride & in the presence of Zn the yields were decreased	(19)

*Contd.*

Table 1—Summary of processes for castor oil pyrolysis into 10-undecenoic acid (I) and heptaldehyde (II)—*Contd.*

Reactants	Temperature, °C	Pressure, mm Hg	Residence time	Catalyst	Product yield	Remarks	Ref.
Ricinoleic acid (a) or Esters of ricinoleic acid (b) or mixture of (a) and (b)	450-600	300	Less than 1 s with a flow rate of 0.1 g per s per cm <sup>2</sup> of tube	—	Products are separated in a fractionating column. Unreacted material recycled	Vapor phase reaction was conducted	(20)
Ricinoleic esters	400-600	—	8 kg/h/unit vol. of non-catalytic heated zone	—	The products are removed from the heated one as fast as they are formed and are rapidly cooled to condense them	Stainless steel reactor	(21)
Castor oil (1kg) and 20 g of water used in the form of emulsion	450-500	—	Passed into reactor in drop wise manner	—	950 g crude gave 270 g (90%) (II) and 380 g (80%) of (I) and rubber like residue	Reaction was conducted in a copper tube under vacuum	(22)
Methyl ricinoleates in the presence of steam (1 kg of esters dispersed in 1.3 kg of steam)	575 steam temp. of 350	—	1.5 s	—	From 1 kg of crude ricinoleate 79 g non-condensable 254 g (90.5% II) 442 g (99% of I) & 174 g of residue contg. 30% ricinoleate. From 1kg of propyl ricinoleate 80g gases 43g low molecular condensible 232g (96% of II) 465g (99% I) 180g (10% ricinoleate)	—	(23)
Castor oil fatty acids	550	360	500 g/h	—	26-27% (I) 16-17% (II)	Copper tube 25 mm dia X 1m length	(24)
Methyl esters of castor oil.	450-525	350-500	100-80 g/h	Pumice or brass ring packing as catalyst	70% of (I) 80-85% of (II)	1% of Cu. ricinoleate or undecenoate as catalyst increased the yields of II & I upto 20%. Coke formation was also increased	(25)
Methyl ricinoleate	460	—	—	Pb, Cu and steel	—	Percentage of yields of I & II observed to be higher in the presence of Pb than those obtd. over steel and Cu	(26)

*Contd.*

Table 1—Summary of processes for castor oil pyrolysis into 10-undecenoic acid (I) and heptaldehyde (II)—*Contd.*

Reactants	Temperature, °C	Pressure, mm Hg	Residence time	Catalyst	Product yield	Remarks	Ref.
Castor oil	450	—	34 g/h 100 g/h	—	30.3% of II 27.7% of I	—	(27)
Methyl esters of castor oil	500	—	—	—	66% of I	Metal melt bed reactor	(28)
Methyl ricinoleate 1:26 mole ratio Ester:water	580	—	28.3 mol/h/L of space velocity	—	—	Optimal conditions 560°C temperature 31.44 mol/h/L and moleratio of ester:water is 1:24.27	(29)
Castor oil	450	100-200	—	Porcelain beads	38 to 40% I and 20 to 25% II	Spongy mass, carbon deposition in the reac- tor observed to form during the reaction and they were minimized by carrying out the reaction under low pressure and by send- ing the steam along with oil	(1)
Castor oil	320-340	20-80	—	1% w/w of Rosin and Benzoylperoxide	Yield of (% w/w) I:9-12 II:6.8-9	(i) Batch process in three necked two liters capacity flask	(6)
Castor oil	340	45	2-5 g/min	Benzoylperoxide	I:15-16 II:9-12	(ii) Continuous process	
Castor oil	450-600	45	5 g/min	Benzoylperoxide	I:12-15 II:7.8-11.3	Unpacked cylindrical Ms reaction vessel. 38.1 cm deep × 10.2cm i.d.	
Castor oil	450-650	45-105	1-4g/min	Benzoylperoxide	I:15-35.4 II:12.3-24.6	Stainles steel tubular reactor 76.2 cm long × 2.5cm i.d. packed with either SS borings or Ms balls	

the molecule to form a six membered ring, which, during heating, is broken between, C<sub>3</sub> and C<sub>4</sub> and between the O and H linkage of the six-membered ring to give Me (CH<sub>2</sub>)<sub>5</sub> CHO and H<sub>2</sub>C:CH CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub> CO<sub>2</sub>H<sup>4</sup>. This is a kind of McLafferty rearrangement.

A concerted mechanism for the thermal decomposition of castor oil to 10-undecenoic acid and heptaldehyde has also been proposed<sup>5</sup>. Moreover, the pyrolysis reaction has been studied in batch and continuous processes using benzoyl peroxide as initiator to enhance the yields of products and it is found that the reaction proceeds via a free radical mechanism<sup>6</sup>.

Discrimination and evaluation of these mechanisms for practical use can be made only with the detailed kinetic study of the process.

### Experimental Procedure

**Methyl esters**—The methyl esters used in the experiments were prepared in a conventional way of transesterification and they were found to contain 85% of methyl ricinoleate.

**Steam generation**—The steam which was used as a diluent was generated in a 10 mm o.d. and 6mm i.d. stainless steel tube. The temperature of steam was maintained at 150-200°C by heating the tube electrically. Necessary amount of steam was generated by sending required amount of water using a metering pump.

The preliminary experiments of pyrolysis of castor oil methyl esters were performed in a packed bed reactor of 25 mm diameter and 100cm length using porcelain and glass beads as inert packing material, mainly to provide more heat transfer area. The deposition of carbon and polymerized material on packing, and walls of the

reactor tube indicates the occurrence of side reactions during the pyrolysis reaction. The reaction tube had to be cleaned very frequently to avoid choking. By and large, the yields of products from these experiments were found to be very low. Later, the reactor was modified. The pyrolysis was carried out with and without using steam as a diluent.

The experimental set up in the present study consists of an empty tubular reactor housed in an electrically heated silica tube, feed system and product collection assembly. The reactor tube is made of SS 316 with 15 mm i.d. and 19 mm o.d. and 600 mm length. Two heating nichrome coils of 900 and 1200 watts were wound over the tube to maintain temperatures in preheating and reaction zones, respectively. To the bottom end of the reactor tube the thermocouple sheath (6 mm o.d. and 3 mm i.d.) was welded to measure axial temperature profile by means of iron constantan thermocouple. Temperature was recorded by using of a digital temperature indicator. The set up is shown in Fig. 2.

The pyrolysis experiments were conducted by passing the preheated (250°C) methyl esters of castor oil in the up flow tubular reactor at the desired reaction temperature. The products from reactor were passed through bypass trap till steady state was attained. The temperature profiles were measured by adjusting the thermocouple position in the thermowell.

The product samples were drawn at regular time intervals after steady state conditions were established and analysed for methyl undecenoate, heptaldehyde and unconverted methyl ricinoleate.

**Product analysis**—Hewlett packard 5840 A Gas Chromatograph using flame ionization detector attached with data processor was used for analy-

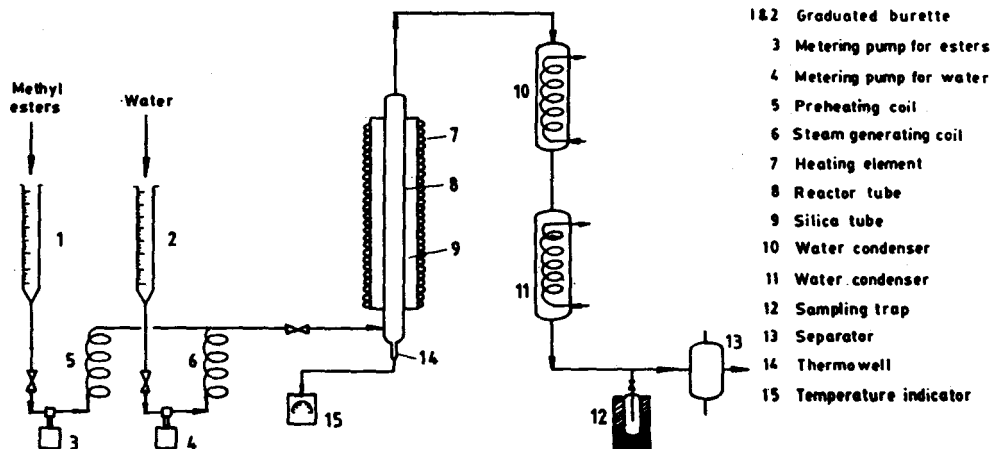


Fig. 2—Line diagram of experimental set-up

Table 2—Influence of temperature and flow rate of methyl esters on conversions

$y_1$  = Percent conversion based on heptaldehyde  
 $y_2$  = Percent conversion based on methylundecenoate  
 $y_3$  = Overall percent conversion based on methyl ester

Run No.	Methyl esters flow rate, g/h	$y_1$	$y_2$	$y_3$	6	69	42.37	40.00	78.00
					7	85	39.45	38.94	74.25
400°C									
1	20	8.53	9.28	98.82					
2	30	3.61	5.59	100.00	1	30	45.31	36.19	64.99
3	38	2.79	7.71	100.00	2	35	29.23	31.38	75.67
4	43	5.15	23.32	52.25	3	42	42.98	33.56	65.29
5	50	56.63	51.64	93.21	4	43	45.70	33.48	66.66
6	53	66.91	50.55	69.96	5	54	59.81	31.40	69.52
7	57	58.00	34.66	53.70	6	57	69.11	64.45	90.32
8	69	48.98	30.08	49.35	7	69	42.97	21.90	50.95
9	85	21.40	10.57	21.39	8	79	16.15	14.81	21.80
					9	85	16.69	25.24	42.36
500°C									
450°C									
1	30	9.47	5.48	14.78					
2	43	38.59	28.84	82.22					
3	49	31.95	33.77	48.73	1	35	49.49	58.52	77.79
4	57	69.26	51.05	73.47	2	43	42.18	32.21	80.38
5	69	63.78	44.75	79.31	3	57	41.57	38.49	69.12
6	85	31.61	20.25	57.11	4	85	33.78	31.42	55.04
520°C									
540°C									
1	30	49.11	59.67	100.00	1	35	68.43	60.05	80.94
2	38	40.93	43.24	99.96	2	43	50.73	47.98	75.36
3	43	55.57	47.98	73.36	3	57	49.44	45.92	79.29
4	49	47.55	32.44	66.08	4	85	39.45	38.94	74.25
5	57	51.38	45.92	79.29					

sis of the products. Nitrogen was used as carrier gas maintaining flow rates in the range of 33.70-40.80 mL/min. Columns used was Chromosorb-WHP (80-100 mesh) with two different specifications, i.e., DEGS (diethylene glycol succinate) 10% polar column (6 mm i.d.) and SE-30 (silicon elastomer) non-polar (6 mm i.d.).

Unconverted methyl ricinoleate was estimated after silylating the product samples with bis-trimethyl trifluoro acetamide using DEGS column at 190°C and methyl undecenoate and heptaldehyde were estimated using SE-30 column at 130°C. The saturated esters of  $C_{17}$  and  $C_{10}$  (100% pure) fatty acids were added as internal standards for quantitative estimation.

## Results and Discussion

The process variables such as flow rate of methyl esters, temperature, dilution ratio (esters to steam weight basis) are expected to have pro-

found influence on the reaction and hence the effect of these parameters was studied.

The temperature and flow rate of esters were maintained within the range of 300-600°C and 20-85 g/h, respectively. At lower temperature, i.e., below 400°C the yields of products were observed to be low with the simultaneous dehydration of methyl ricinoleate. Above 550°C, the charring of products and more volatiles and non-condensable gases were observed. Therefore, a temperature range of 400-540°C was chosen to investigate the effect of flow rate of esters, and presence of steam on the pyrolysis reaction.

The temperature range of 400-500°C appears to be conducive for pyrolysis reaction. Results are summarized in Table 2. It is observed that the fractional conversions based on the formation of heptaldehyde ( $y_1$ ) and methyl undecenoate ( $y_2$ ) increase with temperatures. However, at temperatures beyond 500°C, a dark coloured product was



Table 3—Influence of dilution ratio on conversion at 450°C

Run No.	Flow rate of esters, g/h	Flow rate of water, g/h	Ester: steam volume basis	$y_1$	$y_2$	$y_3$
1	103	45	0.41	39.94	23.64	68.23
2	85	45	0.50	44.76	37.17	63.78
3	64	44	0.64	19.36	15.42	46.57
4	56	47	0.79	60.08	43.44	78.34
5	56	48	0.81	56.46	41.69	68.79
6	70	60	0.82	38.29	26.02	39.72
7	56	88	0.82	56.47	41.69	65.28
8	50	50	0.95	45.06	33.34	53.22
9	85	90	1.00	16.23	10.95	31.21
10	42	45	1.06	57.13	35.03	67.67
11	30	45	1.41	20.45	14.67	60.53
12	42	136	3.11	21.71	15.55	60.53
13	33	110	3.15	16.84	16.23	74.30

observed accompanied by low yields of heptaldehyde and undecenoate. Charred particles were also noticed in the product stream.

The over all conversion based on the unconverted reactant was observed to be more than the fractional conversions indicating the occurrence of side reactions.

The flow rate of methyl esters varied from 20-85 g/h. It is evident from the results that there is a gradual increase in the formation of products with flow rates. Relatively low conversions are obtained at high flow rate of methyl esters (85 g/h). Lower residence times of the order of 0.90-1.15 h (corresponding to flow rates of 50-60 g/h) appear to be favourable for pyrolysis reaction.

The presence of steam reduces the partial pressures of methyl esters and minimizes the formation of dehydrated products. The influence of dilution ratio (esters to steam on volume basis) at a temperature of 450°C is shown in Table 3. Dilution ratio around 0.8 at flow rates of methyl esters around 40-55 g/h appears to be optimum for the pyrolysis reaction. This indicates that a minimum residence time of esters is essential for sufficient conversions. The quality of product in the presence of steam was found to be good.

### Conclusions

The present study revealed that flow rate of esters to be 40-70 g/h and temperature of 400-500°C are favourable for pyrolysis reaction. This temperature range can be lowered if the reaction is conducted at low pressures. The effect of dilution of methyl esters of castor oil with steam is not very significant although it improves the product quality by minimizing the carbon deposition

on reactor walls and prevents charring of products.

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