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Report

on

Training cum Demonstration of the Process

of

10 - UNDECENOIC ACID FROM CASTOR OIL

to

M/s. DESIGN & RESEARCH INSTITUTE FOR PETROCHEMICAL ENGINEERING

of

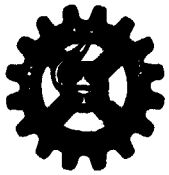
JILIN PROVINCE, CHINA

Under Contract
from
UNIDO
VIENNA, AUSTRIA

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY

(Council of Scientific & Industrial Research)

HYDERABAD, INDIA



March, 1994

106 p. tables

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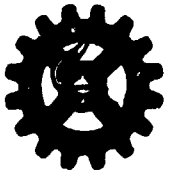

March, 1994

LETTER OF TRANSMITTAL

This report is submitted by the Indian Institute of Chemical Technology, Hyderabad, India (IICT) to the United Nations Industrial Development Organization, Vienna, Austria (UNIDO) in terms of Article 4(c) read with Article (g) of Annexure B of the Contract No. 93/042 between UNIDO and IICT.

The scope of IICT services as enjoined in the Terms of Reference of the above stated contract consisted of training two scientists from the Design and Research Institute for Petrochemical Engineering, Jilin, China (DRIPE) by and at IICT in the preparation of 10-undecenoic acid from castor oil. The two scientists from DRIPE, Mr. Li Huai and Mr. Li Huai Liang were at IICT from 7th January 1994 to 16th March 1994 for training. IICT trained the above named scientists from DRIPE during their working at IICT in preparation of 10-undecenoic acid from castor oil as stipulated in Article (c) of Annexure B of the said contract and to the full satisfaction of the scientists from DRIPE. The two scientists from DRIPE sign this letter of transmittal as a proof of their satisfaction of the training received by them from the IICT.

for and on behalf of DRIPE

Mr. Li Huai

Mr. Li Huai Liang

for and on behalf of the IICT

(T.N.B. KAIMAL)

प्रधान / HEAD
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SYNOPSIS

Mr. Li Huai and Mr. Li Huai Liang, scientists from the Design and Research Institute for Petrochemical Engineering (DRIPE), China, arrived at the IICT on January 7, 1994. After preliminary discussions, a plan of action was drawn up according to which a preliminary run followed by three demonstration runs were to be carried out by IICT scientists in one month's time. These runs have been successfully completed within the stipulated time at the scales and yields agreed upon in the contract. Results of these demonstration runs are summarized and given below. As the results show, all the contractual obligations have been fully met. Details of the runs along with the relevant data sheets are given under PART A. PART B gives the results of the runs conducted by the Chinese scientists themselves as part of the training programme. Their results further corroborated the results obtained during the demonstration runs.

Summary of Results of Process Demonstration:

10-UNDECENOIC ACID FROM CASTOR OIL

To M/s BRIPE, CHINA.

	DEMO1	DEMO2	DEMO3
I. METHYLATION OF CASTOR OIL	25/1/94	29/1/94	3/2/94
Wt. of castor oil (kg) :	45.1	44.9	45.1
Wt. of methanol (kg) :	9.0	9.0	9.0
Wt. of Me esters (CME) (kg) :	46.7	45.9	46.2
Moisture content of CME (%) :	1.8%	1.61	1.46
Wt. of dry CME (kg) :	45.86	45.16	45.52
Wt. wash water (kg) :	33.73	33.2	33.6
Glycerol cont. of wash water :	11.37%	11.42%	11.46
Glycerol recovered (kg)	3.83	3.79	3.86

II. PYROLYSIS OF CME (27/1/94)

Conditions:	27/1/94	1/2/94	7/2/94
Temperature (°C) :	588	590	595
Feed rate (kg/h) :	1.14	1.13	1.15
Steam/feed ratio :	1.7	1.69	1.6
Residence time*(s) :	1.43	1.48	1.53
Total run time (h) :	36	34.43**	36
Stable run time (h) :	34	32.43	34

Time (h)	Pyrolyzed product (kg)			Water collected (kg)		
	I	II**	III	I	II**	III
2	2.04	2.04	1.89	4.07	3.92	3.71
7	5.00	5.02	5.08	9.98	9.57	9.25
12	5.14	5.18	5.06	9.90	9.83	9.00
17	5.20	5.24	5.26	9.86	9.54	9.28
22	5.28	5.18	5.43	9.81	9.42	9.36
27	5.30	5.14	5.14	10.03	9.56	8.96
32	5.06	4.86	5.20	9.87	9.56	9.26
36	4.28	2.62	4.31	8.24	4.85	7.66
	37.30	35.28	37.37	71.76	66.25	66.48

*Based on the specific vol. of steam only, at pyrolysis temperature.
**Corresponds to a run time of 34.43 hours due to mechanical breakdown of boiler.

Total CME pyrolyzed[a]	:	40.26 kg	38.27	40.87
less first 2 h	:	(-)2.06 kg	(-)2.22	(-)2.27
		38.20	36.05	38.60
Total pyrolyzed product (kg)	:	35.63	33.24	35.48
Moisture content (%)	:	0.75	1.05	0.84
Pyrolyzed product, dry wt.(kg)	:	34.99	32.89	35.18
Loss on pyrolysis (kg)	:	3.21	3.16	3.42
Throughput (kg/h)	:	1.020	1.023	1.029

III. DISTILLATION OF PYROLYZED PRODUCT

BEND 1

DIST1. (28/1/94)

DIST2 (2/2/94)

Wt. of pyrolyzed product distilled : 2.9775 kg

Frn No.	Frn. wt (g)	Composition, Wt. (GC)			
		HA	MU	16+18	Me Ric
1	20.0	Discarded			
2	668.4	93.93	-	-	-
3	68.5	81.5	11.92	-	-
4	1294.0	3.8	95.34	-	-
5	13.0	-	68.37	12.66	2.29
Residue	828.0	-	-	29.5	68.03

Wt. of fractions excluding Frn. 1 : 2871.9g

Loss on distillation: 2977.5 - 2871.9 = 105.6g

Frn No.	Frn. wt (g)	Composition, Wt. (GC)			
		HA	MU	16+18	Me Ric
1	13.9	Discarded			
2	735.4	99.2	-	-	-
3	57.8	79.46	6.8	-	-
4	1234.6	-	98.7	-	-
5[a]	48.99	-	19.4	22.2	4.4
Residue	807.6	-	-	24.72	73.39

[a]Also contained 42.5% undecenoic acid

Wt. of fractions excluding Frn. 1 : 2884.39

Loss on distillation: 2977.5 - 2884.39 = 93.1g

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	668.4	627.8	-	-	-
3	68.5	55.83	8.16	-	-
4	1294.0	49.17	1233.7	-	-
5	13.0	-	8.9	1.6	0.3
Residue	828.0	-	-	244.3	563.3
	2871.9	732.8	1250.8	245.9	563.6
				Others:	78.8g

[a]All values expressed on moisture-free basis.

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	735.4	729.5	-	-	-
3	57.8	45.93	3.93	-	-
4	1234.6	-	1218.55	-	-
5	48.99	-	31.89	10.87	2.15
Residue	807.6	-	-	199.64	592.7
	2884.39	775.45	1254.37	210.51	594.85
				Others:	49.23g

DEMO 2

Dist. 1 (3/2/94)

Wt. of pyrolyzed product distilled : 2.9685 kg

Frn No.	Frn. wt (g)	Composition, Wt (GC)			
		MA	MU	16+18	Me Ric
1	13.0	Discarded			
2	693.95	97.22	-	-	-
3	47.1	85.5	6.52	-	-
4	1235.0	1.54	97.29	-	-
5	70.54	-	75.74	18.12	1.5
Residue	791.22	-	-	30.89	68.79

Wt. of fractions excluding Frn. 1 : 2837.8g

Loss on distillation: 2968.5-2837.8 = 130.7g

Frn No.	Frn. wt (g)	Weight, g			
		MA	MU	16+18	Me Ric
2	693.95	674.66	-	-	-
3	47.1	40.27	3.07	-	-
4	1235.0	19.02	1201.53	-	-
5	70.54	-	53.43	12.78	1.06
Residue	791.22	-	-	244.41	544.28
	2837.81	733.95	1258.03	257.20	545.34
				Others:	43.45g

Dist. 2 (7/2/94)

Frn No.	Frn. wt (g)	Composition, Wt. (GC)			
		MA	MU	16+18	Me Ric
1	12.9	Discarded			
2	597.1	95.2	2.71	-	-
3	109.0	65.1	31.83	-	-
4	1200.4	0.2	98.49	1.15	-
5*	113.7	-	72.33	22.32	3.44
Residue	749.0	-	-	27.83	71.52

*Treated with diazoemethane to convert undecenoic acid present

Wt. of fractions excluding frn. 1 : 2769.2

Loss on distillation: 2968.5 - 2769.2 = 199.3

Frn No.	Frn. wt (g)	Weight, g			
		MA	MU	16+18	Me Ric
2	597.1	568.44	16.18	-	-
3	109.0	70.96	34.69	-	-
4	1200.4	2.40	1182.27	13.80	-
5	113.7	-	82.24	25.38	3.91
Residue	749.0	-	-	208.45	535.68
	2769.2	641.8	1315.38	247.63	539.59
				Others:	24.8 g

DEMO3 Distn 1

Wt. of pyrolyzed product distilled : 2.9748 kg (8/2/94)

Frn No.	Frn. wt (g)	Composition, Wt (GC)			
		MA	MU	16+18	Me Ric
1	11.85	Discarded			
2	581.40	92.28	7.72	-	-
3	66.69	75.47	23.90	-	-
4	1337.0	2.74	96.68	-	-
5	77.44	-	89.31	5.71	0.86
Residue	762.30	-	2.19	31.75	62.85

Wt. of fractions excluding Frn. 1 : 2824.83g

Loss on distillation: 2974.8 - 2824.8 = 150.0g

Frn No.	Frn. wt (g)	Weight. g			
		MA	MU	16+18	Me Ric
1	12.9	Discarded			
2	581.4	536.52	44.88	-	-
3	66.69	50.33	15.94	-	-
4	1337.0	36.63	1292.26	-	-
5	77.4	-	69.13	4.42	0.66
Residue	762.3	-	16.69	242.03	479.11
	2824.83	623.47	1439.28	246.45	479.77
				Others :	35.61g

DEMO3 Distn 2

Wt. of pyrolyzed product distilled : 2.9748 kg (17/2/94)

Frn No.	Frn. wt (g)	Composition, Zwt (GC)			
		MA	MU	16+18	Me Ric
1	19.:0	Discarded			
2	740.97	92.95	1.31	-	-
3	56.72	72.45	13.85	-	-
4	1299.0	1.52	97.47	-	-
5*	72.50	-	16.50	36.04	3.30
Residue	721	-	-	35.54	64.46

Frn No.	Frn. wt (g)	Weight, g			
		MA	MU	16+18	Me Ric
2	740.97	682.06	9.71	-	-
3	56.72	41.09	7.85	-	-
4	1299.0	18.68	1266.13	-	-
5	72.5	-	37.23	26.13	2.39
Residue	721.0	-	-	256.24	464.76
	2890.19	741.83	1320.92	282.37	467.15
				Others :	78.15g

Wt. of fractions excluding Frn. 1 : 2890.19g

Loss on distillation: 2974.8 - 2890.19 = 84.61g

*Also contained 32.42% undecenoic acid.

MATERIAL BALANCE

DEMO 1

I. INPUT (kg)

Me Ricinoleate:	34.0
Others :	4.2
	38.2

OUTPUT (kg)

	Dist I	Dist II
Heptaldehyde :	8.6	9.11
Me undecenoate:	14.70	14.74
C16+C18 :	2.89	2.47
Me Ricinol. :	6.64	6.99
Others :	0.93	0.58
Loss on pyrolysis :	3.21	3.21
Loss on distillation:	1.24	1.09
	38.21	38.19

DEMO 2

INPUT (kg)

Me Ricinoleate:	32.08
Others :	3.97
	36.05

OUTPUT (kg)

	Dist I	Dist II
Heptaldehyde :	8.13	7.11
Me undecenoate:	13.94	14.57
C16+C18 :	2.85	2.74
Me Ricinol. :	6.04	5.98
Others :	0.48	0.27
Loss on pyrolysis :	3.16	3.16
Loss on distillation:	1.45	2.21
	36.05	36.04

DEMO3

INPUT (kg)		OUTPUT (kg)		
Me Ricinoleate	: 34.35	Heptaldehyde	: 7.37	8.73
Others	: 4.25	Me undecenoate	: 17.02	15.79
	38.60	C16+C18	: 2.91	3.34
		Me Ricinol.	: 5.67	5.52
		Others	: 0.42	0.77
		Loss on pyrolysis	: 3.42	3.42
		Loss on distillation	: 1.77	1.00
			38.58	38.57

IV. HYDROLYSIS OF ME UNDECENOATE

	DEMO 1 (29/1/94)	DEMO2(4/2/94)	DEMO3(8/2/94)
Wt. of Me undecenoate	: 3.0 kg	3.0	3.0
Wt. of undecenoic acid	: 2.77 kg	2.76	2.77
Moisture content	: 1.27%	1.56%	1.31%
Wt. of dry undecenoic acid	: 2.73 kg	2.72	2.73
Acid value	: 299.45	290.37	296.5
Purity by Acid value	: 98.2%	95.23%	97.25
Purity by GC	: 98.45%		

	I		II		III	
CALCULATION						
Wt. of pyrolyzed product (kg)	34.99	34.99	32.89	32.89	35.18	35.18
Wt. of undecenoic acid (kg)	13.38	13.40	12.63	13.21	15.49	14.37
CME equiv. to pyrolyzed product	38.20 kg	38.20	36.05	36.05	38.60	38.60
Undecenoic acid obtd from 1kg CME :	0.3502kg	0.3508kg	0.3503	0.3664	0.4013	0.3722
OR						
Yield of 95% undecenoic acid from 100g CME	: 36.86 g	36.92 g	36.87	38.57	42.24	39.19

Conversion & Yield:	DEMO1	DEMO2	DEMO3
CME pyrolyzed (kg)	: 38.20	36.05	38.6
Me ricinoleate in CME[1](kg)	: 34.0 (108.97 g·mol)	32.08 (102.82 g·mol)	34.35 (110.11 g·mol)
Me ricinol. left unpyrolyzed	: 6.81 (21.82 g·mol)	6.01 (19.26 g·mol)	5.59 (17.92 g·mol)
Me ricinol. pyrolyzed	: 87.15 g·mol	83.56 g·mol	92.19 g·mol
CONVERSION	: 80.00%	81.27%	83.72%
Me undecenoate obtained from pyrolysis product	:14.72 kg (74.24 g·mol)	14.25 (71.96 g·mol)	16.40 (82.83 g·mol)
YIELD	:85.30%	88.56%	89.84%

[1]Me Ricinoleate content of CME = 89%

REPYROLYSIS OF DISTILLATION RESIDUE

Conditions of repyrolysis:

Temperature	: 594°C
Feed rate	: 1.143 kg/h
Steam/feed ratio	: 1.7
Product throughput	: 1.008 kg/h
Residence time	: 1.45 sec.
Total run time	: 6 h
Stable run time	: 4 h

Time (h)	Pyrolyzed product (kg)	Water collected (kg)
2	1.99	4.0
6	4.06	7.66

Wt. of residue pyrolyzed	:	6.86 kg
less first 2h	:(-)	2.286 kg
		4.57kg
Wt. repyrolyzed product	:	4.06 kg
Loss on repyrolysis	:	0.51 kg (11.16%)

Composition:

	Residue repyrolyzed	Product of repyrolysis
Heptaldehyde:	0.0	9.19
Me Undecenoate:	1.04	29.68
C16+C18:	34.41	45.28
Me Ricinoleate:	64.26	14.48
Others:	0.31	1.37

Distillation of repyrolyzed product:

Wt. of pyrolyzed product distilled : 3000.0 g

Frn No.	Frn. wt (g)	Composition, Wt (GC)			
		HA	MU	16+18	Me Ric
1	10.8	Discarded			
2	325.0	86.70	6.99	-	-
3	63.9	71.70	16.28	-	-
4	736.0	2.10	93.62	-	-
5*	70.6	-	54.24	7.71	14.08
Residue	1680.0	-	-	66.69	27.70

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	325.0	281.77	22.72	-	-
3	63.9	45.82	10.40	-	-
4	736.0	15.45	689.04	-	-
5	70.6	-	48.51	5.44	9.94
Residue	1680.0	-	-	1120.39	465.36
	2875.5	343.04	770.67	1123.83	475.30

Wt. of fractions excluding Frn. 1 : 2875.5g
Loss on distillation: 3000.0 - 2875.5 = 124.5g
Others : 160.66g
*Also contained 13.46% undecenoic acid.

Results of 9 distillations show an average of 26.67% of residue in pyrolysis product.
Wt. of residue repyrolyzed : 4.57 kg
Assuming 9% loss during first pyrolysis, 4.57 kg of residue = 17.14 kg of pyrolysis product = 18.83 kg CME
Wt. of undecenoate obtained from 3.0kg of repyrolysis product = 0.771 kg = 1.04 kg from 18.83 kg CME
Assuming a conversion figure of 0.9 (theoretical, 0.93), wt. of undecenoic acid obtainable : 0.936kg
Thus, 100g of CME may yield on repyrolysis of residue, an additional 4.97g of undecenoic acid (5.23g undecenoic acid of 95% purity).

CONCLUSIONS

A yield of 87.34g of undecenoic acid of 95% purity is realisable from 200g of castor oil against the contractual obligation of 70-72g/200g.

THUS, THE CONTRACTUAL OBLIGATIONS ARE FULLY MET.

SCOPE

IICT will train two scientists from DRIPE at IICT in preparation of 10-undecenoic acid giving a reaction yield of not less than 70-72 grams in conversion of castor oil to 10-undecenoic acid from 200 grams of castor oil containing not less than 85% of ricinoleic acid and free fatty acid not more than 2%, in the following manner:

Step 1 - Methanolysis - 37 kg castor oil per batch to obtain methyl esters.

Step 2 - Pyrolysis of castor methyl esters - 1.0 kg/hour continuous process to obtain pyrolysed products, 36 hours continuous operation.

Step 3 - Distillation of pyrolysed products - 1 kg/batch to obtain methyl undecenoate including free undecenoic acid, if any. Heptaldehyde is collected as a by-product.

Step 4 - Hydrolysis of methyl undecenoate - 1.0 kg/batch to obtain 10-undecenoic acid. Purity of 10-undecenoic acid obtained will be minimum 95% by GC analysis.

CONTENTS

PART A

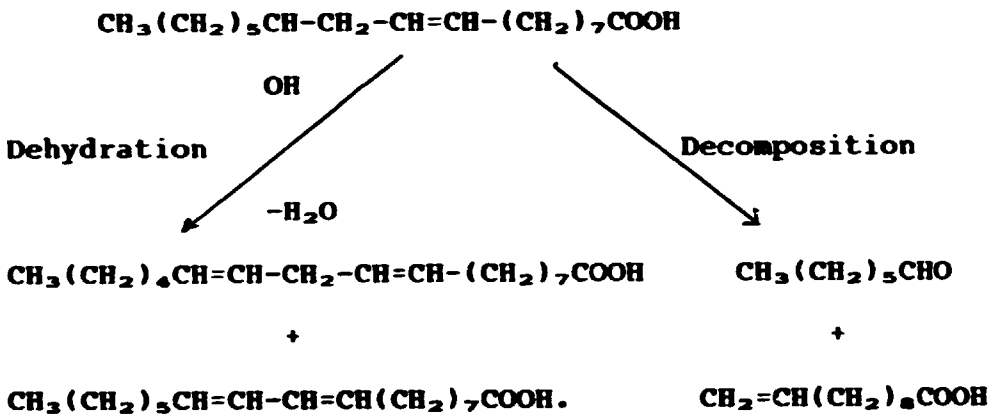
1. INTRODUCTION

Castor oil is unique in that it contains a high percentage of ricinoleic acid (12-hydroxy-*cis*, 9-octadecenoic acid). When heated to high temperatures (500-600°C) ricinoleic acid is pyrolysed into 10-undecenoic acid and heptaldehyde. Undecenoic acid is the precursor in the manufacture of Nylon 11 (Rilsan) via bromination, amination and polymerization. Rilsan is an engineering plastic used in the manufacture of automotive components, for electronic parts, in the sports goods industry, for rollers and bearings for conveyors, for flat and tubular films for packaging, for dry powder coatings, etc. Undecenoic acid can also be used in the manufacture of perfumery chemicals, such as γ-undecalactone, isojasmone and macrocyclic lactones and ketones. PEG monoesters of undecenoic acid and undecyl sulfate exhibit excellent surfactant properties. Undecenoic acid also finds use in the production of bactericides, fungicides and insect sprays.

Heptaldehyde is the starting material for valuable perfumery chemicals such as α-amyl cinnamaldehyde, methyl heptyne carbonate and nonalactone. Heptaldehyde can be easily oxidized to heptanoic acid, the esters of which with polyols are valuable lubricants. Heptylalcohol, produced by the reduction of heptaldehyde, is an industrial solvent for plastics and resins and is also used in cosmetics.

2. CHEMISTRY OF THE PROCESS

Pyrolysis of ricinoleic acid is believed to take place according to the following scheme:



According to this scheme, a tautomeric form of ricinoleic acid can undergo two reactions simultaneously. 1) dehydration to produce a mixture of conjugated and nonconjugated dienoic acids and 2) decomposition to heptaldehyde and undecenoic acid. Under the influence of the high temperature these primary products can further react to form polymeric and other products thus bringing down the yield of the desired products.

3.0 PROCESS DETAILS

Pyrolysis of castor oil can be divided into four steps namely:

a) Methylation of castor oil to produce the methyl esters,

b) Pyrolysis of methyl esters,

c) Distillation of the pyrolyzed products, to recover methyl undecenoate and heptaldehyde, and

d) Saponification of methyl undecenoate to produce undecenoic acid.

Operations (a), (c) and (d) are batch operations while (b) is a continuous one. The process is schematically described in the annexed flow sheet.

3.1 METHANOLYSIS OF CASTOR OIL

This step is carried out on 45 kg castor oil/batch scale in a 100 l glass reactor (R101) equipped with a turbine type stirrer, glass condenser (E101) and a glass coil which can be heated with steam and cooled with water. Castor oil (45 kg) is charged into the reactor along with about 6 kg methanol and heated under stirring to 40°C. Sodium hydroxide pellets (315 g) dissolved in about 3 kg methanol are added slowly to the reactor in 15 min. The temperature is maintained at *ca.* 40°C and the reaction mixture is stirred at this temperature for 3 h. Completion of the reaction is checked by TLC on silica gel coated microslides using the solvent system hexane-ether (70:30, v/v).

Sulfuric acid (215 ml) dissolved in one litre water is added to neutralize the sodium hydroxide and the steam heating is put on. The temperature is raised to 75 to 80°C and the pressure is reduced slowly to *ca.* 180 mm Hg to distil off the excess methanol. Tap water (10 kg) containing 15 ml sulfuric acid is then added under stirring. The stirring is continued for 5 min. at 80°C and the contents are then allowed to separate for 30 min. The acidic aqueous glycerol layer is drawn off and stored in a 50 l carbuoy. Hot water (10 kg) is added to the reaction product and mixed at 80°C for 5 min. The layers are allowed to separate (30 min.) and the wash water is drawn off and transferred to the carbuoy containing aqueous glycerol. This treatment is repeated till washings are neutral. Two washings are generally adequate. The contents of the reactor are then cooled to room temperature and the wet methyl esters are transferred to a storage tank (ST101), presently to a 50 l carbuoy and weighed. The composition of the methyl esters is determined by GC and its moisture content by Karl Fischer method. The glycerol content of the combined water washings is determined by AOCS method.

3.2 PYROLYSIS OF CASTOR METHYL ESTERS (CME)

A description of the pyrolysis reactor is given below and a detailed drawing is annexed.

The pyrolysis reactor (R201) is a tubular reactor consisting of a vertical SS 316 tube of dia 102 mm (i.d.) and length 408 mm. A discharge pipe (SS 316) with a valve is provided at the bottom

for cleaning and removal of material, if any, after pyrolysis. Inside the reactor, a concentric inner tube (SS 316, dia 28 mm (i.d.), length 245 mm open at the bottom and about 100 mm from reactor bottom and 55 mm from the reactor top is provided, and is connected to the feed inlet pipe (SS 316, 20 mm dia o.d.) at the top. A vapour outlet pipeline (SS 316, 20 mm dia, i.d.) is provided at the top of the reactor for conveying the pyrolysed product to the condenser. The reactor is placed in a square, box type, ceramic brick lined furnace (side: ca 178 mm height: ca 610 mm), each side of which is provided with resistance winding. Two adjacent sides are connected in series and each of the two heaters thus obtained has 25 ohms resistance. The clearance between the reactor and the furnace is 40 mm (min). The heat input to the reactor is controlled by the dimmerstats of the heaters. Thermowells are provided at suitable points in the reactor and the furnace to facilitate temperature measurement.

Castor methyl esters (CME), 4 kg from ST101 are charged into a stainless steel feed tank (ST201).

The pyrolyser (R201) and steam superheater (H201) furnaces are heated to ca 700 and 550°C, respectively. Cold water (5-10°C) is circulated through the condenser (E201) and through the coil in the receiver (ST202). Saturated steam from the boiler is fed to the steam superheater (H201) from where it passes through the reactor (R201), to the condenser where it is condensed and collected in the receiver (ST202) along with the pyrolysis products. The flow of saturated steam is adjusted to

get the required CME: steam ratio (ca 1:1.6-1.7, w/w). The CME are pumped at a rate of ca 1.2 kg/h by a metering pump (P201) to a T-joint where they get mixed with the superheated steam. The mixture then passes through the inner tube of the pyrolyzer reactor and through the annular space between the inner and outer tube of the reactor to the condenser and receiver (ST203). The temperature in the annular space is maintained at 570-590°C by controlling the heat input to the furnace by means of dimmerstats. At this temperature pyrolysis of CME takes place. The vapour mixture is condensed in the condenser and collected in the receiving tank (ST202). The uncondensed gases, are led through an ice-cooled trap into water and then to vent. The pyrolysis products and condensed water are drawn off from the receiving tank (ST202), separated and the separated pyrolysis products are weighed and stored in a storage tank (ST203), presently in 50 l carbuoy.

3.3 DISTILLATION OF THE PYROLYSIS PRODUCT

Fractional distillation of the pyrolysed product is carried out in a 3 kg/batch all-glass distillation assembly. The assembly consists of a 5 l, two-necked flask (ST301) fitted with a glass column (T301).

The glass column is connected to an efficient condenser which in turn is connected to a Perkin triangle arrangement to collect the different distillate fractions without breaking the vacuum in the system. Cold water is circulated through the condenser. The flask is heated using an electrically heated oil bath. The glass

column is heated electrically. About 3 kg of the pyrolyzed product is charged into the flask and heated slowly to 60° at 30-40 mm Hg pressure to distill off moisture and low-boiling components. The different fractions collected are as follows:

Fraction	Temperature (°C)		Pressure
	Still	vapour	(mm Hg)
1	30-60	26-40	30-40
2	60-100	40-60	15-20
3	100-120	60-80	7-10
4	120-190	80-140	7-10
5	190-205	140-165	7-10

Each fraction and the residue was weighed and its composition determined by GC using methyl myristate as internal standard.

The pooled up residue from the distillation step is repyrolysed, if required.

3.4 HYDROLYSIS OF METHYL UNDECENOATE TO UNDECENOIC ACID

The hydrolysis is carried out in a 40 l polypropylene reactor (R401) equipped with an Inconel coil and a Teflon-covered stirrer. Three kilograms of the undecenoate from pooled fractions of the distillation step is charged into the reactor and heated

to 50° by passing steam through the coil, under stirring. A solution of NaOH (1070 g) dissolved in water (5.5 kg) is added over a period of 15 min. Stirring is continued and the temperature of the reaction mixture raised to 70° until the mixture is homogeneous (1 hour). Concentrated HCl (3.5 kg) dissolved in an equal amount of water was gradually added under stirring to a pH 3-4. The separated aqueous layer is drawn off and the organic layer washed with water to neutrality, weighed and stored in ST401, presently a 20 l carbuoy. The organic layer is dried and analyzed for purity.

4.0 RAW MATERIALS AND PRODUCT SPECIFICATIONS

4.1 RAW MATERIALS

4.1.1 Castor oil

Grade	: IS first special (BSS grade)
Appearance	: Pale yellow liquid
Density (25°C)	: 0.9562
Viscosity	: 6.51 poises
Acid value	: 2 max.
Saponification value	: 177-18
Iodine value	: 82-90
ricinoleic acid content	: 85% min.

4.1.2 Methanol

Appearance	: Clear colourless liquid with characteristic odour
Density (25°C)	: 0.791
Refractive index (20°C)	: 1.328
Distillation range	: 95% distills between 64.5 and 65.5°C
Moisture (% wt)	: 0.10

4.1.3 Sodium hydroxide (pellets)

Reagent grade, 96%.

4.1.4 Sulfuric acid (98%)

Sp. gr. 1.835

4.1.5 Hydrochloric acid (35-38%)

Sp. gr. 1.18

4.2 PRODUCTS

4.2.1 Heptaldehyde

Appearance	: Clear, pale yellow liquid with characteristic odour.
Purity	: 90% Min.
Density (20°C)	: 0.818
Refractive Index (20°C)	: 1.412 - 1.413
Distillation range	: 95% distills between 55-57° at 15 mm Hg pressure

4.2.2 Undecenoic acid

Appearance	: Clear, pale yellow liquid with characteristic odour.
Purity	: 95% Min.
Density (20°C)	: 0.87 - 0.91
Refractive index (20°C)	: 1.449 - 1.451
Distillation range	: 95% boils between 136-138°C at 2 mm Hg pressure

5 ANALYTICAL METHODS

5.1 RAW MATERIALS

5.1.1 Castor oil

5.1.1.1 Acid value: Acid value is determined according to the Official Method of the AOCS.

Apparatus: 250 ml Erlenmeyer flasks.

Reagents:

Ethyl alcohol 95%: The alcohol must give a distinct, sharp end point with phenolphthalein and must be neutralized with alkali to a faint but permanent pink colour just before use.

Phenolphthalein: 1% in 95% ethanol.

Potassium hydroxide solution: 0.1 N, accurately standardized.

Procedure: Weigh accurately 2-5 g of oil (0.1 to 0.2 g in case of fatty acids) into the Erlenmeyer flask. Add 50 ml of neutral alcohol and 2 ml of indicator. Warm the solution on a steam bath and titrate with standard potassium hydroxide solution while shaking vigorously until the appearance of the first permanent pink colour of the same intensity as that of the neutralized alcohol. The colour should persist for 30 sec.

Calculation:

$$\text{Acid value} = \frac{\text{Vol. of alkali x normality x 56.1}}{\text{wt. of sample}}$$

5.1.1.2 Fatty Acid Composition: Fatty acid composition of the oil was determined using an internal standard according to the Official Method 963.22 of the AOAC-AIUPAC (See below).

5.1.2 **Methanol**

5.1.2.1 Moisture content

Moisture content in methanol is determined by the Karl Fischer (KF) method as described in IS: 2362-1973, 6.2.2.

Apparatus: Karl Fischer automatic titrator model VEEGO/MATIC-1 or equivalent.

Reagents : KF reagent, twin pack.
methanol for KF titration.
Disodium tartarate dihydrate (AR)
KF reagent is standardized using crystalline disodium tartarate dihydrate to obtain the KF Factor (IS: 2362-1973, 6.2.1.2).

Procedure: Take 25 ml of methanol in the titration flask and neutralize with KF reagent. Then add 10 ml methanol to be tested and titrate with KF reagent till end point is reached. Note the titration value.

Moisture content % of the sample

$$\frac{\text{Titration value x KF Factor}}{\text{Vol of Sample x 10}}$$

5.1.3 **Castor oil methyl esters (CME)**

5.1.3.1 Moisture content

Moisture content was determined by KF method as described above.

5.1.3.2 Composition

This was determined by gas chromatography (GC) using an internal standard (see below).

5.1.4 Glycerol

Glycerol was estimated in the separated glycerol layer and water-washings after methanolysis by the AOCS method Ea 6-51.

This method determines glycerol and other polyols which react with sodium periodate in an acid solution forming aldehydes and formic acid.

Apparatus:

1. Buret, 50 ml. Delivery time must not be less than 90 sec. for 50 ml.
2. Pipet, 50 ml.
3. Variable speed stirrer, electrical or mechanical, with glass stirrer.
4. pH Meter with glass electrodes, calibrated.
5. Beakers, 500 ml.
6. Volumetric flasks, 250 ml.

Reagents:

1. Sodium periodate solution:

   (a) Dissolve 60 g sodium metaperiodate in distilled water containing 120 ml of 0.1 N sulfuric acid, total

volume 1 litre. If the solution is not clear, filter through sintered glass filter. Store in dark, in glass stoppered bottle. The acidity of this reagent may change slowly with time so a blank must be run each day that analyses are made. If $NaIO_4$ does not dissolve, it is not of reagent quality and a new supply must be obtained.

(b) Test for quality: Pipet 10 ml of the periodate solution into 250 ml volumetric flask, dilute to mark and mix thoroughly. To 0.5 to 0.6 g C.P. glycerine in 50 ml of distilled water add 50 ml of diluted periodate solution with a pipet. Prepare a blank using only 50 ml of distilled water. Allow to stand 30 min, add 5 ml of HCl, 10 ml of a 15% potassium iodide solution and mix. Allow to stand 30 min, add 5 ml of HCl, 10 ml of 15% potassium iodide solution and mix. Allow to stand for 5 min and then add 100 ml distilled water. Titrate with 0.1 N sodium thiosulfate solution, shaking continuously until yellow colour has almost disappeared. Add 1-2 ml of starch indicator solution and continue titration, adding the thiosulfate solution slowly until the blue colour has just disappeared. The sodium periodate is satisfactory when the titration solution containing glycerol divided by titration of the blank is between 0.750 and 0.765.

2. Sodium hydroxide solution, *ca* 0.1250 N, but

accurately standardized with potassium acid phthalate using phenolphthalein indicator.

3. Sodium hydroxide solution, *ca* 0.05 N.

4. Sulfuric acid solution, 0.2 N.

5. phenolphthalein indicator, 1% in 95% alcohol.

6. Bromothymol blue indicator solution, 0.1% in distilled water prepared as follows: Dissolve 0.1 g dry indicator in 16 ml of 0.01 N NaOH by grinding indicator with the alkali in a mortar. Transfer to a 100 ml volumetric flask, dilute to volume with distilled water and mix thoroughly.

7. Ethylene glycol solution, mix 1 volume of ethylene glycol (b. pt. 195-197°C) and 1 volume of distilled water.

8. Sodium thiosulfate solution, 0.1 N, accurately standardized.

9. Hydrochloric acid, Sp. gr. 1.19.

10. Starch indicator solution, 10 g soluble starch in 1 litre of boiling distilled water.

11. Potassium iodide solution, dissolve 150 g in

distilled water and make it to 1 litre.

12. Standard buffer solution: Dry 50 g of reagent potassium acid phthalate at 100°C and cool to room temperature in a dessiccator. Transfer 10.21 g of the dry potassium acid phthalate to a 1 litre volumetric flask. Dissolve in distilled water and mix thoroughly.

Preparation of sample:

Samples containing salt, sediment or suspended matter must be warmed and thoroughly mixed to ensure uniform distribution. Some sediment tends to cling to the bottom of the container and the viscosity of the glycerin retards rapid dispersion. Careful preparation of sample is necessary to obtain an accurate analysis.

Procedure:

1. Make all weighings accurately and rapidly into the 600 ml beaker. When sample contains less than 20% glycerol it may be weighed into a tared dish and then washed into the 600 ml beaker with distilled water. When sample is less than 500 ml, dilute to 50 ml with distilled water. For the most accurate results, the sample tested must contain between 0.32 and 0.50 g of glycerol. Use the following Table to determine the

correct sample size.

Glycerol (%) in product to be analyzed	Sample to be weighed (g)
100 or less	0.40 - 0.53
90 or less	0.45 - 0.55
80 or less	0.50 - 0.60
70 or less	0.55 - 0.75
60 or less	0.65 - 0.85
50 or less	0.80 - 1.00
40 or less	0.90 - 1.30
30 or less	1.20 - 1.80
20 or less	1.80 - 2.60
10 or less	4.00 - 5.00
5 or less	7.0 - 11.0
2.5 or less	16.0 - 20.0
1.0 or less	40.0
0.5 or less	80.0

When glycerol content is not known make a single preliminary test using the amount specified for 100% glycerol. From the results of this test the proper sample weight can be selected quite accurately.

2. Add 5-7 drops of bromothymol blue indicator to the sample in the beaker and acidify with 0.2 N H_2SO_4 to a definite green or greenish yellow colour. Neutralize with 0.05 N NaOH, to indicator end point, a definite blue free of green colour. When colour of the solution interferes with the detection of the colour change of the indicator, use the pH meter and adjust to pH 8.1 ± 0.1.

3. At this point prepare a blank containing 50 ml of distilled water but no glycerol and carry through simultaneously with the sample in an identical manner using the indicator to adjust the pH before adding the sodium periodate solution.

4. Add 50 ml of sodium periodate solution with a pipet, swirl gently to insure thorough mixing, cover with a watch glass and allow to stand for 30 min at room temperature (below (35°) in the dark.

5. Add 10 ml of 50% ethylene glycol-water solution and allow to stand 20 min.

6. Dilute to approximately 300 ml and titrate using a pH meter to determine the end point pH 6.5 ± 0.1 for the blank and 8.1 ± 0.1 for the sample. When

approaching the end point add alkali, a drop or part of a drop at a time.

7. Calculations:

$$\text{Glycerol, \%} = \frac{(S-B) \times N \times 9.209}{W}$$

S = ml of NaOH solution to titrate sample

B = ml of NaOH solution to titrate blank. B must not be less than 4.5 ml.

N = Normality of NaOH

W = Weight of sample in grams.

5.2 Pyrolysis PRODUCTS

5.2.1 Composition of distilled fractions.

The composition of the distilled fractions was determined by GC according to the Official Method 963.22 of the AOAC-AIUPAC. methyl myristate was used as an internal standard, where required.

A) Apparatus

a) Gas chromatograph. Equipped with a flame ionisation detector and electronic integrator. The instrument was operated under the following conditions.

i) Injection port - With minimum dead space in the injection system and maintained at 20-50° higher than column temperature.

ii) Column - 1-3 m x 2-4 mm (id) glass packed with 5% SE-30 on Chromosorb W HP (80/100 mesh). Condition the freshly packed column while disconnected from the detector at 300°C with a current of N_2 at 20-30 ml/min for ≥ 16 h.

b) Syringe - Maximum volume 10 µl graduated to 0.2 µl.

B) Reagents

a) Carrier gas - N, dried and containing less than 10 mg O/kg.

b) Other gases - H, 99.9% free from organic impurities. Air free from organic impurities.

c) Reference standards - A known mixture of heptaldehyde, methyl undecenoate, methyl palmitate, methyl stearate and methyl ricinoleate of a composition similar to that of pyrolysis products.

C) Operating conditions:

The instrument will be operated at following conditions:

Injection port - 250°C

Detector - 300°C

Column - 100°C (1 min) - 270°C (10 min) at 15°/min.

N - 30-40 ml/min.

H - 30-40 ml/min.

Air - 300 ml/min.

D) Performance Specification

Analyze an equal mixture of methyl undecenoate and methyl laurate at the above operating conditions. Adjust sample size, column temp. and carrier gas flow such that the methyl undecenoate peak is recorded at ca 7-10 min after solvent peak, ca 3/4 full scale. Measure the base widths in mm of Me undecenoate (W_1) and Me laurate (W_2) between points of intersection with baseline of tangents drawn to the inflection points of curves. Also measure retention distances in mm (S) from start to peak maximum for Me undecenoate and distance in mm between peak maxima for Me undecenoate and Me laurate, Y. Calculate theoretical plates, *n* (efficiency), and resolution, *R*:

$$n = 16\ (S/w_1)^2$$

$$R = 2Y/(w_1 + w_2)$$

Select conditions to obtain n in excess of 2000 and R 1.25. Columns will show gradual loss in R with use; when $R \leq 1.25$, replace.

E. Determination

With apparatus showing stable baseline, inject 0.2 to 2 µl of the sample solution in chloroform. Pierce septum of inlet port and quickly discharge the sample. Adjust sample size such that the major peak occupies not more than 80% of full scale.

F. Identification

Analyze reference mixture under the same operating conditions as for sample. Measure retention distances for known esters. The retention distances may be used to identify the major components present in the pyrolysis product.

H. Calculation

Because of the large differences in molecular weights of the products of pyrolysis and because of presence of secondary groups, correction factors must be used to convert peak areas into wt%. Determine

correction factors by analyzing known mixtures of composition similar to that of sample under identical operating conditions. For the reference standard,

% by wt of component i = $Bi \times 100/\Sigma BI$

where Bi is the wt. of component i in ref. std. and ΣBi is the total weight of all components in reference std. Calculate from the chromatogram,

% (area/area) of component i = $Gi \times 100/\Sigma Gi$

where Gi is the area of peak corresponding to component i and ΣGi is the sum of areas under all peaks. Calculate correction factor for each component,

$$Ki = (Bi/\Sigma Gi) \times (\Sigma Gi/Gi)$$

To calculate each component, multiply its area by appropriate correction factor and sum the corrected areas:

% by wt of component i = $(Ki \times Gi) \times 100/\Sigma (Ki \times Gi)$

In cases where all components are not eluted, as in the present case, use an internal standard S, such as C_{14} ester and determine its correction factor.

% by wt of component i = $(ws/w) \times (Ki/Ks) \times (Gi/Gs) \times 100$

where ws = mg internal standard and w = total mg of sample and subscript s refers to internal standard component. Reports results to two decimal places.

6. EQUIPMENT SPECIFICATIONS

Specifications for major equipments are given below. The unit numbers correspond to the numbers given in the flow sheet.

6.1 RFACTOR (R101)

Capacity : 100 litres

Type : Glass reactor fitted with turbine type stirrer and glass condenser.

6.2 Pyrolysis REACTOR (R201) : Vertical SS 316 tube of 100 mm dia and length 405 mm, with a discharge pipe (22.5 mm dia). The reactor has an inner tube (25.4 mm dia, 230 mm length) open at the bottom positioned about 100 mm above the reactor bottom. The reactor is provided with an outlet pipe (19 mm dia) at the top. The reactor assembly is housed in an electrically heated, box-type furnace.

6.3 REACTOR (R401)

Capacity : 40 litres

Type : Stirred tank polypropylene reactor (dia 400 mm; length 350 mm) with bottom discharge valve (glass). Inconel coil and Teflon-covered anchor-type stirrer.

Date: 25-1-94
Run No.: DEMO-1

METHANOLYSIS OF CASTOR OIL

Raw Materials:

	Moisture	Acid value
Castor oil	0.22%	1.8
Methanol	0.1%	

	Assay	Sp. gr.
NaOH	96%	
H_2SO_4	98%	1.835

(Representative, DRIPE)

(Representative, IICT)

Date: 25-1-94

Run No.: DEM0-1

METHANOLYSIS OF CASTOR OIL

Raw Materials	Weight (kg)	Volume (litres)
Castor Oil	45.1	
Methanol	9.0	
NaOH	0.315	
H_2SO_4	-	0.235

(Representative, DRIPE)

(Representative, IICT)

Date: 25-1-94
Run No.: DEMO 1

METHANOLYSIS OF CASTOR OIL

Time	Temperature °C	Operation	Remarks
2.30 PM	30	Castor oil + charcoal.	6 Kg MeOH
3.15	30	NaOH dissolved in 3 Kg. MeOH added.	
3.30	42	Alk addn over	
4.45	42	21 ml H_2SO_4 dissolved in 1 Lit water added in 5 min	
5.30	42	Steam heating increased & vac established slowly	
01.30	115	To recover MeOH	
2.50	95	Vac released Recovered MeOH weighed	
3.00	90	25 ml H_2SO_4 + 1 Lit water added & stirred for 10 min	
3.10	85	Stirring stopped	
3.40	70	Acidic glycerol layer taken out & weighed	
10.00	80	10 Kg hot water added & stirred for 5 min	
10.05	80	Kept for settling for 30 min	
10.40	80	Wash water removed & weighed	
10.45	80	10 Kg hot water added	
10.50	80	Stirred for 5 min & allowed to settle for 30 min.	
11.30	80	Wash water removed	
		Castor methyl ester separated & weighed	

(Representative, DRIPE)

(Representative, IICT)

Date: 25-1-94
Run No.: DEMO-1

METHANOLYSIS OF CASTOR OIL

Product Recovery:

	Weight (kg)
CME	46.70
Glycerol (in wash water)	3.83
Methanol	3.30

(Representative, DRIPE)

(Representative, IICT)

Date: 27-1-94
Run No.: DEMO-1

METHANOLYSIS OF CASTOR OIL

Product Analysis:

	Moisture content	Acid value
CME	1.8%	7.4

	Glycerol content
Wash water wt. 33.13 Kg	11.37%

(Representative, DRIPE)

(Representative, IICT)

Date: 27-1-94

Run No.: DEMO-1

METHANOLYSIS OF CASTOR OIL

CASTOR METHYL ESTERS (CME):

Moisture	1.8%
Acid value	7.4

Fatty acid Composition, wt%	C_{16}	1.16
	C_{18}	8.73
	C_{18}-OH	87.91

(Representative, DRIPE)

(Representative, IICT)

Date: 27.9.94
Run No.: 28-1 94.
DEMO1.

PYROLYSIS OF CME

Reaction conditions:

	Furnace, steam superheater	Superheated steam	Furnace, pyrolyzer	Pyrolyzer reactor	Feed
Temp. (°C)	488	407	683	588	72

Feed, CME (kg/h)	1.14
Feed, Steam (kg/h)	1.93.

(Representative, DRIPE)

(Representative, IICT)

Date: 27.1.94 & 28.1.94
Run No.: DEMO-1

PYROLYSIS OF CME

Time (h)	Temperature °C						Operation	Remarks
	Furnace, steam	Steam	Feed	Furnace, reactor	Reactor 1	Reactor 2		
0·0	414	373	76	633	573	554	Feed started	
2·0	503	436	75	679	591	581	Condensate discharged Separated & weighed.	
7·0	491	409	74	682	596	586		
12·0	513	421	72	683	595	588		
17·0	498	408	71	685	596	585		
22·0	470	387	68	685	593	586		
27·0	501	412	76	682	594	583		
32·0	488	404	71	670	585	573		
36·0	445	381	68	666	577	566		

(Representative, DRIPE)

(Representative, IICT)

Date: 27.1.94 & 28.1.94
Run No.: DAM01.

PYROLYSIS OF CME

Time (h)	Pyrolyzed Product (kg)	Water (kg)
2.0	2.04	4.67
7.0	5.00	9.98
12.0	5.14	9.90
17.0	5.20	9.86
22.0	5.28	9.81
27.0	5.30	10.03
32.0	5.06	7.87
36.0	4.28	8.24
	Total: 37.30	71.76

(Representative, DRIPE)

(Representative, IICT)

Date: 27.1.94 & 28.1.94
Run No.: DEMO 1.

PYROLYSIS OF CME

Total Run Time (h)	36
Stable Run Time (h)	34
Steam/Feed ratio	1.7
Residence time (sec.)	1.43
Product throughput (kg/h)	1.028

(Representative, DRIPE)

(Representative, IICT)

Date 27.1.94 & 28/1.94
Run No.: DEM01.

PYROLYSIS OF CME

CME Pyrolyzed (kg)	38.20
Pyrolysis Product (kg)	34.99
Loss on pyrolysis (kg)	3.21

Moisture content, (%) pyrolyzed product	0.75

(Representative, DRIPE)

(Representative, IICT

Date: 28.1.94
Run No.: DEMO.1 DIST.1

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
1 1.20 pm to 2.00 pm	1	35-50	100	30-40	35	
2 2.0 pm to 4.50 pm	2	50-80	100	40-60	20	
3 4.50 pm to 6.15 pm	3	80-90	120	62-80	8-9	
4 6.15 pm to 11 pm	4	90-150	120 - 160	80-140	8-9	
5 11 pm to 11.40 pm	5	150-190	180	140-165	8-9	

(Representative, DRIPE)

(Representative, IICT)

Date: 28.1.'94
Run No.: DEMO.1.DIST.1.

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt.	Remarks
1	20.0	
2	668.4	
3	68.5	
4	1294.0	
5	13.0	
Residue	828.0	
Total	2891.9	

Loss on Distillation	108.1

(Representative DRIPE)

(Representative IICT)

Date: 28-1-94
Run No.: DEMO-1
DISTILLATION-1

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	$C_{16} + C_{18}$	Me Ric	Others	
1						Discarded
2	93.93	-	-	-	6.07	
3	81.5	11.92	-	-	6.58	
4	3.8	95.34	-	-	0.86	
5	-	68.37	12.66	2.29	16.68	
Residue	-	-	29.5	68.03	2.47	

(Representative, DRIPE)

(Representative, IICT)

Date: 28-1-94
Run No.: DEMO-1
DISTILLATION-1

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	668·4	627·8	–	–	–	40·6
3	68·5	55·83	8·16	–	–	4·51
4	1294·0	49·17	1233·7	–	–	11·13
5	13·0	–	8·9	1·6	0·3	2·2
Residue	828·0	–	–	244·3	563·3	20·4
Total	2871·9	732·8	1250·8	245·9	563·6	78·84

(Representative, DRIPE)

(Representative, IICT)

Date: 2.2.'94
Run No.: Demo.1.DIST.2

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
12.05 pm 1 to 12.45 pm	1	35-45	100	26-40	35	
12.45 2 to 4.45	2	50-80	100	40-60	15-20	
4.45 3 to 5	3	80-90	120	62-80	8-9	
5 pm 4 to 10.45 pm	4	90-150	120-160	80-140	8-9	
10.45 pm 5 to 11.10 pm	5	150-190	180	140-165	8-9	

(Representative, DRIPE)

(Representative, IICT)

Date: 2.2.'94
Run No.: DEMO.1.DIST.2

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt. (g)	Remarks
1	13.9	
2	735.4	
3	57.8	
4	1234.6	
5	48.99	
Residue	807.6	
Total (g)	2898.29	

Loss on Distillation (g)	101.71

(Representative DRIPE)

(Representative IICT)

Date: 2-2-94
Run No.: DEMC-1
DISTILLATION-2

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	$C_{16} + C_{18}$	Me Ric	Others	
1						Discarded
2	99.2	-	-	-	0.8	
3	79.46	6.8	-	-	13.74	
4	-	98.7	-	-	1.3	
5	-	19.4	22.2	4.4	54.0	
Residue	-	-	24.72	73.39	1.89	

(Representative, DRIPE)

(Representative, IICT)

Date: 2-2-94
Run No.: DEMO-1
DISTILLATION-2

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	735.4	723.5	-	-	-	5.1
3	57.8	45.93	3.93	-	-	7.94
4	1234.6	-	1218.55	-	-	16.05
5	48.99	-	31.89	10.87	2.15	4.08
Residue	807.6	-	-	199.64	592.7	15.26
Total	2584.39	775.45	1254.37	210.51	594.85	49.23

(Representative, DRIPE)

(Representative, IICT)

Date: 28-1-94
Run No.: DEMO-1 HYDROL-1

HYDROLYSIS OF ME UNDECENOATE

Me undecenoate (kg)	3·0
NaOH (Kg)	1·07
Conc. HCl (kg)	3·50 LR Grade (36-38% Pure)

(Representative, DRIPE)

(Representative, IICT)

Date: 25-1-94
Run No.: DEMO 1

HYDROLYSIS OF ME UNDECENOATE

Time	Temp. (°C)	Operation	Remarks
2.30 PM	30	ME used charged with stirring & heating	
2.45	50	NaOH sol'n added	
3.00	60	Alk addn over	
3.15	110	Reqd temp attained	
4.20	110	HCl sol'n added	
4.35	60	Acid addn over	
5.00	60	Stirring stopped, kept for settling	
6.00	30	Acidic water removed	
6.05	30	5 Kg water added	
6.15	30	Stirred for 10 min kept for settling	
7.00	30	Ist wash water removed	
7.05	30	5 Kg water added	
7.15	30	washing contd	
7.45	30	IInd wash water removed	
7.50	30	5 Kg water added	
8.00	50	washing contd	
8.45	30	IIInd wash water removed	
8.50	30	5 Kg water added, heated to 70°C	
9.00	110	Kept for settling	
9.30 AM (29/1/94)	30	wash water and undecenoic acid separated and weighed	

(Representative, DRIPE)

(Representative, IICT)

Date: 29-1-94
Run No.: DEMO-1

HYDROLYSIS OF ME UNDECENOATE

Undecenoic acid recovered (kg)	2·77

Analysis:

Moisture content, %	1·27
Acoid value	299·45
Freezing point (°C)	19·5 - 21·0
Purity (by ~~ger~~ % A. Valu	98·20

(Representative, DRIPE)

(Representative, IICT)

Date: 29/11/94
Run No.: DEMO-2

METHANOLYSIS OF CASTOR OIL

Raw Materials:

	Moisture	Acid value
Castor oil	0.22%	1.8
Methanol	0.1 %	

	Assay	Sp. gr.
NaOH	96 %	
H_2SO_4	98 %	1.835

(Representative, DRIPE)

(Representative, IICT)

Date: 29-1-94
Run No.: DEMO·2

METHANOLYSIS OF CASTOR OIL

Raw Materials	Weight (kg)	Volume (litres)
Castor Oil	44·9	
Methanol	9·0	
NaOH	0·315	
H_2SO_4	-	0·235

(Representative, DRIPE)

(Representative, IICT)

Date: [illegible]
Run No.: [illegible]

METHANOLYSIS OF CASTOR OIL

Time	Temperature °C	Operation	Remarks
[illegible]	[illegible]	castor oil + 6 [illegible] added & heated [illegible]	[illegible] MeOH [illegible]
[illegible]	[illegible]	[illegible] added	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible] water	[illegible] added [illegible]
[illegible]	[illegible]	[illegible] applied slowly to [illegible]	[illegible]
[illegible]	[illegible]	Vac. released	
[illegible]	[illegible]	[illegible] stirred [illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible] hot water [illegible]	added, [illegible]
[illegible]	[illegible]	[illegible] wash [illegible]	[illegible]
[illegible]	[illegible]	[illegible] hot water [illegible]	added [illegible] stirred [illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible] hot water [illegible]	added [illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible] total [illegible]	[illegible]

[signature]
(Representative, DRIPE)

[signature]
(Representative, IICT)

Date: 29/1/94
Run No.: DEMO 2

METHANOLYSIS OF CASTOR OIL

Product Recovery:

	Weight (kg)
CME	48.9
Glycerol (in wash water)	3.79
Methanol	4.39

(Representative, DRIPE)

(Representative, IICT)

Date: 31-1-94

Run No.: DEMO-2

METHANOLYSIS OF CASTOR OIL

Product Analysis:

	Moisture content	Acid value
CME	1.61%	

	Glycerol content
Wash water wt. 33.2 Kg	11.42 %

(Representative, DRIPE)

(Representative, IICT)

Date: 31-1-94

Run No.: DEMO-2

METHANOLYSIS OF CASTOR OIL

CASTOR METHYL ESTERS (CME):

Moisture	1.61 %
Acid value	

Fatty acid Composition, wt%	C_{16}	1.16
	C_{18}	8.93
	C_{18}-OH	89.91

(Representative, DRIPE)

(Representative, IICT)

Date: 1.2.94 & 2.2.94

Run No.: DEMO2

PYROLYSIS OF CME

Reaction conditions:

	Furnace, steam superheater	Superheated steam	Furnace, pyrolyzer	Pyrolyzer reactor	Feed
Temp. (°C)	493	419	683	590	70

Feed, CME (kg/h)	1.13
Feed, Steam (kg/h)	1.92

(Representative, DRIPE)

(Representative, IICT)

Date: 1.2.94 2.2.94
Run No.: DEMO-2

PYROLYSIS OF CME

Time (h)	Temperature						Operation	Remarks
	Furnace, steam	Steam	Feed	Furnace, reactor	Reactor 1	Reactor 2		
0·0	463	414	79	620	568	549	Feed started.	
2·0	493	425	71	682	596	586	Condensate discharged Separated and weighed	
7·0	477	405	73	682	594	585	Do	
12·0	456	393	71	684	598	586	Do	
17·0	485	420	68	684	593	584	Do	
22·0	494	421	74	681	595	584	Do	
27·0	500	419	68	682	593	587	Do	Temp at 28 hrs
32·0	513	430	69	684	598	589	Do	
34·43	523	439	68	681	594	587	Do	

(Representative, DRIPE)

(Representative, IIT)

Date: 1.2.94 & 2.2.94.
Run No.: DEMO 2

PYROLYSIS OF CME

Time (h)	Pyrolyzed Product (kg)	Water (kg)
2.0	2.04	3.92
7.0	5.02	9.57
12.0	5.18	9.83
17.0	5.24	9.54
22.0	5.18	9.42
27.0	5.14	9.56
32.0	4.86	9.56
34.43	2.62	4.85
	Total: 35.28	66.25

(Representative, DRIPE)

(Representative, IICT)

Date: 12.9.94 & 2.9.94

Run No.: DEMO 2

PYROLYSIS OF CME

Total Run Time (h)	34.43
Stable Run Time (h)	32.43
Steam/Feed ratio	1.69
Residence time (sec.)	1.48
Product throughput (kg/h)	1.023

(Representative, DRIPE)

(Representative, IICT)

Date 1.2.94 & 2.2.94
Run No.: DEMO2

PYROLYSIS OF CME

CME Pyrolyzed (kg)	36.05
Pyrolysis Product (kg)	32.89
Loss on pyrolysis (kg)	3.16

Moisture content, (%) pyrolyzed product	1.05

(Representative, DRIPE)

(Representative, IICT

Date: 3.2.'94
Run No.: DEMO 2 DIST. 1

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
12 noon 1 to 12.45 pm	1	36-60	100	30-40	31	
12.45 2 to 4.45 pm	2	60-80	100	40-64	20	
4.45 3 to 5.15 pm	3	80-120	120	64-80	8-9	
5.15 4 to 1 am 4.2.'94	4	120-190	120-160	80-145	8-9	
1 am 5 to 1.15 am 4.2.'94	5	190-205	180	145-165	8-9	

(Representative, DRIPE)

(Representative, IICT)

Date: 3.2.'94
Run No.: DEMO-2 DIST. 1.

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt. (g)	Remarks
1	13.0	
2	693.95	
3	47.1	
4	1235.0	
5	70.54	
Residue	791.22	
Total(g)	2850.81	

Loss on Distillation (g)	149.19

(Representative DRIPE)

(Representative IICT)

Date: 3-2-94
Run No.: DEMO-2
DISTILLATION-1

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	$C_{16} + C_{18}$	Me Ric	Others	
1						Discarded
2	97.22	–	–	–	2.88	
3	85.5	6.52	–	–	7.98	
4	1.54	97.29	–	–	1.17	
5	–	75.74	18.12	1.5	4.64	
Residue	–	–	30.89	68.79	0.32	

(Representative, DRIPE)

(Representative, IICT)

Date: 3-2-94
Run No.: DEMO-2
DISTILLATION-1

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	693.95	674.66	-	-	-	19.29
3	47.1	40.27	3.07	-	-	3.76
4	1235.0	19.02	1201.53	-	-	14.55
5	70.54	-	53.43	12.78	1.06	3.32
Residue	791.22	-	-	244.41	544.28	2.53
Total	2837.81	733.95	1258.03	257.20	545.34	43.45

(Representative, DRIPE)

(Representative, IICT)

Date: 7.2.'94
Run No.: DEMO 2 DIST. 2.

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
10.50 1 am to 11.35	1	34-60	100	30-40	30	
11.35 2 to 3.15	2	60-80	100	40-62	18	
3.15 3 to 4.30	3	80-120	120	62-80	8-9	
4.30 4 to 10.10	4	120-190	120 - 160	80-145	8-9	
10.10 5 to 11.25 pm	5	190-205	180	145-165	8-9	

(Representative, DRIPE)

(Representative, IICT)

Date: 7.2.'94
Run No.: DEMO 2. DIST 2.

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt. (g)	Remarks
1	12.9	
2	597.1	
3	109.0	
4	1200.4	
5	113.7	
Residue	749.0	
Total (g)	2782.1	

Loss on Distillation (g)	217.9

(Representative DRIPE)

(Representative IICT)

Date: 7-2-94
Run No.: ~~DE~~ MO-2
DISTILLATION-2

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	C_{16} + C_{18}	Me Ric	Others	
1						Discarded
2	95.2	2.71	–	–	2.09	
3	65.1	31.83	–	–	3.07	
4	0.2	98.49	1.15	–	0.16	
5	–	72.33	22.32	3.44	1.91	
Residue	–	–	27.83	71.52	0.65	

(Representative, DRIPE)

(Representative, IICT)

Date: 7-2-94
Run No.: DCMO-2
DISTILLATION-2

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	537.1	568.44	16.18	—	—	12.48
3	107.0	70.96	34.69	—	—	3.35
4	1200.4	2.40	1182.27	13.80	—	1.93
5	113.7	—	82.24	25.38	3.91	2.17
Residue	749.0	—	—	208.45	535.68	4.87
Total	2769.2	641.8	1315.38	247.63	539.59	24.8

(Representative, DRIPE)

(Representative, IICT)

Date: 4-2-94
Run No.: DEMO-2

HYDROLYSIS OF ME UNDECENOATE

Me undecenoate (kg)	3.0
NaOH (Kg)	1.07
Conc. HCl (kg)	3.50 LR Grade (36-38% Pure)

(Representative, DRIPE)

(Representative, IICT)

Date: 4-2-94
Run No.: DEMO-2

HYDROLYSIS OF ME UNDECENOATE

Time	Temp. (°C)	Operation	Remarks
12.30 PM	30	Me und. charged under stirring	and steam heating
12.35	50	NaOH Solution added in 10 min.	
12.45	70	Req'd temp. attained.	
1 45	70	HCl Solution added.	
2.00	60	Addn over.	
2.45	60	Stirring stopped kept for settling	and
3.15	50	Acid layer removed	
3.25	50	5 kg hot water (Steam condensate) added	
3.35	50	Stirred for 10 min. kept for settling	
4.05	50	I wash water removed	
4 10	50	5 kg. hot water added & Washing Process repeated	
5.00	50	II wash water removed.	
5.05	50	5 kg hot water added Washing Process repeated.	
6.00	50	III wash water	removed
6.05	50	5 kg. hot water added. Washing Process	repeated
9.30 AM	30	Wash water and wet	
(5-2-94)		Undecenoic acid separated	
		and acid weighed.	

(Representative, DRIPE)

(Representative, IICT)

Date: 4-2-94
Run No.: DEMO-2

HYDROLYSIS OF ME UNDECENOATE

Undecenoic acid recovered (kg)	2·76

Analysis:

Moisture content, %	1·56
Acoid value	290·37
Freezing point (°C)	19·5 - 21·5
Purity (by ~~Acid~~ Value) %	95·23

(Representative, DRIPE)

(Representative, IICT)

Date: 3-2-94
Run No.: DEMO 3

METHANOLYSIS OF CASTOR OIL

Raw Materials:

	Moisture	Acid value
Castor oil	0.22 %	1.8
Methanol	0.1 %	

	Assay	Sp. gr.
NaOH	96 %	
H_2SO_4	98 %	1.835

(Representative, DRIPE)

(Representative, IICT)

Date: 3-2-94
Run No.: DEMO-3

METHANOLYSIS OF CASTOR OIL

Raw Materials	Weight (kg)	Volume (litres)
Castor Oil	45.1	
Methanol	9.0	
NaOH	0 315	
H_2SO_4		0.235

(Representative, DRIPE)

(Representative, IICT)

Date:
Run No.:

METHANOLYSIS OF CASTOR OIL

Time	Temperature	Operation	Remarks

(Representative, DRIPE)

(Representative, IICT)

Date: 3-2-94.
Run No.: DEMO-3.

METHANOLYSIS OF CASTOR OIL

Product Recovery:

	Weight (kg)
CME	46.20
Glycerol (in wash water)	3.86
Methanol	4.50

(Representative, DRIPE)

(Representative, IICT)

Date: 5-2-94
Run No.: BEMO-3

METHANOLYSIS OF CASTOR OIL

Product Analysis:

	Moisture content	Acid value
CME	1.46%	

	Glycerol content
Wash water wt. 33.6 Kg	11.46 %

(Representative, DRIPE)

(Representative, IICT)

Date: 5-2-94

Run No.: BEMO-3

METHANOLYSIS OF CASTOR OIL

CASTOR METHYL ESTERS (CME):

Moisture	1.46 %
Acid value	

Fatty acid Composition, wt%	C_{16}	1.16
	C_{18}	8.73
	C_{18}-OH	89.71

(Representative, DRIPE)

(Representative, IICT)

Date: 7.2.94 & 8.2.94

Run No.: DEM03

PYROLYSIS OF CME

Reaction conditions:

	Furnace, steam superheater	Superheated steam	Furnace, pyrolyzer	Pyrolyzer reactor	Feed
Temp. (°C)	501	418	687	595	72

Feed, CME (kg/h)	1.15
Feed, Steam (kg/h)	1.84

(Representative, DRIPE)

(Representative, IICT)

Date: 7.2.94 & 8.2.94
Run No.: DEMO-3

PYROLYSIS OF CME

Time (h)	Temperature °C.						Operation	Remarks
	Furnace, steam	Steam	Feed	Furnace, reactor	Reactor 1	Reactor 2		
0·0	423	382	79	618	556	535	Feed started	
2·0	508	432	78	687	603	594	Condensate discharged, separated & weighed	
7·0	476	402	72	686	598	592	do	
12·0	494	412	66	690	600	594	do	
17·0	531	440	73	687	595	590	do	
22·0	499	410	70	686	596	599	do	
27·0	506	413	73	688	598	593	do	
32·0	486	405	74	686	599	594	do	
36·0	513	434	72	691	602	595	do	

(Representative, DRIPE)

(Representative, IICT)

75

Date: 7.2.94 & 8.2.94
Run No.: DEMO 3

PYROLYSIS OF CME

Time (L)	Pyrolyzed Product (kg)	Water (kg)
2.0	1.89	3.71
7.0	5.08	9.25
12.0	5.06	9.00
17.0	5.26	9.28
22.0	5.43	9.36
27.0	5.14	8.96
32.0	5.20	9.26
36.0	4.31	7.66
	Total: 37.37	66.48

(Representative, DRIPE)

(Representative, IICT)

Date: 7.2.94 & 8.2.94

Run No.: DEMO3

PYROLYSIS OF CME

Total Run Time (h)	36
Stable Run Time (h)	34
Steam/Feed ratio	1.6
Residence time (sec.)	1.53
Product throughput (kg/h)	1.029

(Representative, DRTPE)

(Representative, IIT)

Date 7.2.94 & 8.2.94
Run No.: DEMO 3

PYROLYSIS OF CME

CME Pyrolyzed (kg)	38.60
Pyrolysis Product (kg)	35.18
Loss on pyrolysis (kg)	3.42

Moisture content, (%) pyrolyzed product	0.84

(Representative, DRIPE)

(Representative, IICT

Date: 8 2 94
Run No.: DCMO 3 DIST 1

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
11 am to 11.40	1	35-50	100	30-40	30	
11.40 to 2.45 pm	2	50-75	100	40-62	19	
2.45 to 3.05 pm	3	75-120	120	62-80	7-9	
3.05 to 7.45	4	120-170	120 - 160	80-140	7-9	
7.45 to 8.30 pm	5	170-200	160 - 190	140-160	7-9	

(Representative, DRIPE)

(Representative, IICT)

Date: 8.2.'94
Run No.: DEMO 3 DIST. 1

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt.	Remarks
1	11.85	
2	581.40	
3	66.69	
4	1337.0	
5	77.4	
Residue	762.3	
Total (g)	2836.64	

Loss on Distillation (g)	163.6

(Representative DRIPE)

(Representative IICT)

Date:
Run No.:
DISTILLATION-I

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	$C_{16} + C_{18}$	Me Ric	Others	
1						Discarded
2	72.28	1.72	–	–	–	
3	15.47	23.70	–	–	0.65	
4	2.74	76.65		–	0.55	
5	–	87.31	5.71	0.56	4.12	
Residue	–	2.17	31.25	62.55	3.21	

(Representative, DRIPE)

(Representative, IICT)

Date: 5 2 74
Run No.: DEMO 3
DISTILLATION-1

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	551.4	536.32	44.55	–	–	
3	66.69	50.55	15.74	–	–	
4	1337.0	56.63	1232.24	–	–	
5	77.4	–	67.13	4.42	6.66	
Residue	762.3	–	11.61	242.03	477.11	
Total	2824.53	623.48	1439.25	246.45	477.77	55.61

(Representative, DRIPE)

(Representative, IICT)

Date : 17-2-94
Batch No. : DEMO 3 DIST 2

DISTILLATION OF FRACTION PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Plate position	Vapour		
10.45 am to 11.35	1	30-50	100	30-40	35	
11.35 to 2.50 pm	2	50-113	110	40-64	20	
2.50 to 3.10	3	114-120	110 - 120	64-80	9-15	
3.10 to 8.40	4	120-190	120 - 160	80-140	8-9	
8.40 to 9.20 pm	5	190-200	160 - 180	140-170	8-9	

(Representative, DKTE)

(Representative, [illegible])

Date: 17.2.94
Run No.: DEMO 3. DIST 2

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	3.0

Fraction No.	Fraction Wt.(g)	Remarks
1	19.10	
2	740.97	
3	56.72	
4	1299.0	
5	72.5	
Residue	721.0	
Total(g)	2909.29	

Loss on Distillation (g)	90.71

(Representative DRIPE)

(Representative IICT)

Date: 12-2-94
Run No.: PLMC-3
DISTILLATION-2

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	$C_{16} + C_{18}$	Me Ric	Others	
1						Discarded
2	72.03	1.31	-	-	6.64	
3	72.45	13.55	-	-	13.7	
4	1.52	77.47	-	-	1.01	
5	-	16.30	36.04	3.30	44.16	
Residue	-	-	35.54	64.46	-	

(Representative, DRIPE)

(Representative, IICT)

Date: 17-2-94
Run No.: DLMC 5
DISTILLATION-2

DISTILLATION OF PYROLYSED PRODUCTS

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mus	$C_{16} + C_{18}$	Me Ric	Others
1						
2	240.17	60.66	2.71	–	–	
3	56.72	41.61	2.85	–	–	
4	1255.0	13.65	1266.3	–	–	
5	12.5	–	59.23	26.13	2.4	
Residue	221.0	–		256.24	464.5	
Total	2510.17	741.83	1326.12	282.37	467.2	13.15

(Representative, DRDE)

(Representative, IICT)

Date: 8-2-94
Run No.: DEMO-3

HYDROLYSIS OF ME UNDECENOATE

Me undecenoate (kg)	3.0
NaOH (Kg)	1.07
Conc. HCl (kg)	3.50 LR Grade (36.38% PWW)

(Representative, DRIPE)

(Representative, IICT)

Date:
Run No.:

HYDROLYSIS OF ME UNDECENOATE

Time	Temp. (°C)	Operation	Remarks
12.40 PM	30		
12.45	50		
1.05	60		
2.00	60		
2.15	60		
3.00	60		
3.15	50		
3.20	50		
3.35	50		
4.05	50		
4.10	50		
5.00	50		
5.05	50		
6.00	50		
6.05	50		
10.00 AM	30		
11.30			

(Representative, DRIPE)

(Representative, IICT)

Date: 8-2-94
Run No.: DEMO-3

HYDROLYSIS OF ME UNDECENOATE

Undecenoic acid recovered (kg)	2·77

Analysis:

Moisture content, %	1·31
Acoid value	296·50
Freezing point (°C)	-
Purity (by ~~e~~ Acid Value) %	97·25

(Representative, DRIPE)

(Representative, IICT)

Date: 15.2.94

Run No.: DEN04

REPYROLYSIS

~~PYROLYSIS OF CME~~

Reaction conditions:

	Furnace, steam superheater	Superheated steam	Furnace, pyrolyzer	Pyrolyzer reactor	Feed
Temp. (°C)	490	395	687	594	76

Feed, ~~CME~~ Dethr. Resi. Frac (kg/h)	1.143
Feed, Steam (kg/h)	1.943

(Representative, IPPE)

(Representative, IIC)

Date: 15.2.94
Run No.: DEMO 4

REPYROLYSIS

~~PYROLYSIS OF CME~~

Time (h)	Temperature °C.						Operation	Remarks
	Furnace, steam	Steam	Feed	Furnace, reactor	Reactor 1	Reactor 2		
0·0	448	384	73	620	563	545	Feed started	
2·0	494	402	74	687	597	588	Condensate discharged, separated and weighed.	
3·0	490	403	74	686	596	586	-	
4·0	490	403	76	688	597	593	-	
5·0	492	399	78	686	594	589	-	
6·0	485	388	78	689	599	599	Condensate discharged, separated and weighed.	

(Representative, DRIPE)

(Representative, IICT)

Date: 15.2.94
Run No.: DEMO 4

REPYROLYSIS
~~PYROLYSIS OF CHR~~

Time (h)	Pyrolyzed Product (kg)	Water (kg)
2.0	1.99	4.00
6.0	4.06	7.66
	Total: 6.05	11.66

(Representative, DPIPE)

(Representative, [illegible])

Date: 15.2.74
Run No.: DEMO 4

REPYROLYSIS
~~PYROLYSIS OF CHE~~

Total Run Time (h)	6.0
Stable Run Time (h)	4.0
Steam/Feed ratio	1.7
Residence time (sec.)	1.45
Product throughput (kg/h)	1.008

(Representative, [illegible])

(Representative, [illegible])

Date 15.2.94
Run No.: DEMO 4

REPYROLYSIS

~~FOR LEVEL OF CMP~~

CMP Pyrolyzed (kg)	4.57
Pyrolysis Product (kg)	4.06
Loss on pyrolysis (kg)	0.51

Moisture content, pyrolyzed product	

(Representative, DRIPE)

(Representative, IICT

Date: 16 - 94
Run No.: DL MK -

DISTILLATION OF PYROLYSIS PRODUCT

Time	Fraction No.	Temperature (°C)			Pressure (mm Hg)	Remarks
		Still	Still Dimmer position	Vapour		
1 h 12.35 pm	1	50 60	100	50 - 50	35 - 37	
2 h 2.40	2	60 - 80	100	50 62	18	
3 h 3.00	3	80 - 120	120	62 - 82	8 - 9	
4 h 7.15	4	120 - 153	120 - 150	82 - 142	8 - 9	
5 h 7.55 pm	5	153 157	170	142 - 162	8 - 9	

(Representative, DRIPE)

(Representative, IICT)

Date: [illegible]
Run No.: [illegible]

DISTILLATION OF PYROLYSIS PRODUCT

Pyrolysis product (kg)	[illegible]

Fraction No.	Fraction Wt.	Remarks
1	[illegible]	
2	[illegible]	
3	[illegible]	
4	[illegible]	
5	[illegible]	
Residue	[illegible]	
Total	[illegible]	

Loss on Distillation	[illegible]

(Representative [illegible])

(Representative [illegible])

Date:
Run No.:

DISTILLATION OF PYROLYSIS PRODUCT

Analysis (GC):

Fraction No.	Weight %					Remarks
	HA	MU	C_{16} + C_{18}	Me Ric	Others	
1						
2						
3						
4						
5						
Residue						

(Representative, DRDE)

(Representative, IICT)

Date:
Run No.:

DISTILLATION OF PYROLYZED PRODUCT

Composition of fractions:

Fraction No.	Fraction Weight g	Weight, g				
		HA	Mix	$C_{16} + C_{18}$	Me Ric	Others
1						
2				—	—	
3						
4						
5						
Residue						
Total						

(Representative), IIT

(Representative), IIT

PART B (TRAINING PROGRAMME)

After conclusion of the demonstration runs, the Chinese Scientists, Mr. Li Huai and Mr. Li Huai Liang themselves conducted the various steps of the process with the following modifications:

a) The second step of the process, viz., pyrolysis of CME was run for a total time of 6 h instead of 36 h, and

b) The last step of the process, viz., hydrolysis of methyl undecenoate, being a simple one, was omitted.

The above modifications were made at the request of the Chinese scientists. Consequently, the following programme was gone through:

a) Methylation of castor oil; 45 kg/batch; one run

b) Pyrolysis of CME; three runs of 6 h each

c) Distillation of pyrolysis products, three runs.

The results, summarized below, corroborates the earlier results obtained in the demonstration runs.

PART II. TRAINING PROGRAMME

RESULTS OF EXPERIMENTS CARRIED OUT BY *DRIPE* SCIENTISTS

I. METHANOLYSIS OF CASTOR OIL

Wt. of castor oil (kg)	: 45
Wt. of methanol (kg)	: 9
Wt. of methyl esters (CME)	: 46.1
Moisture content of CME	: 1.49
Wt. of dry CME	: 45.41
Wt. of wash water	: 49.05
Glycerol content of wash water	: 7.9
Glycerol recovered	: 3.87

II. PYROLYSIS OF CME

Conditions:	I	II	III
Temperature (°C)	596	598	594
Feed rate (kg/h)	1.157	1.145	1.152
Steam/feed ratio	1.578	1.7	1.69
Residence time (sec.)	1.54	1.44	1.45
Total run time (h)	6	5.5	6
Stable run time (h)	4	4	4

Time (h)	Pyrolyzed product (kg)			Water collected (kg)		
	I	II	III	I	II	III
2	2.09	1.5 (1.5h)	1.93	3.67	3.24 (1.5h)	3.90
6	4.20	4.07	4.10	7.38	7.47	7.89
	6.29	5.57	6.03	11.05	10.71	11.79

Total CME pyrolyzed*:	6.90	6.21	6.81
less first 2 h :	2.28	1.69	2.27
	4.62	4.52	4.54
Total pyrolyzed product (kg):	4.20	4.07	4.10
Moisture content (%):	0.79	0.75	0.74
Pyrolyzed product, dry wt. (kg):	4.17	4.04	4.07
Loss on pyrolysis:	0.45	0.48	0.47
Throughput of product (kg/h):	1.04	1.01	1.02

*All values expressed on moisture-free basis.

III. DISTILLATION OF PYROLYZED PRODUCT

EXPT. I

Wt. of pyrolyzed product distilled : 2976.3g

Frn No.	Frn. wt (g)	Composition, Zwt (GC)			
		HA	MU	16+18	Me Ric
1	22.0	Discarded			
2	794.8	92.17	4.58	-	-
3	1362.5	2.90	95.92	-	-
4*	53.0	-	26.35	26.95	1.47
Residue	679.2	-	-	45.09	54.35

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	794.8	732.57	36.40	-	-
3	1362.5	39.51	1306.91	-	-
4	53.0	-	31.56	14.28	0.78
Residue	679.2	-	-	306.25	369.14
	2889.50	772.08	1374.87	320.53	369.92

Wt. of fractions excluding Frn. 1 : 2889.5
Loss on distillation: 2976.3 - 2889.5 = 86.8g
Others : 53.23g
*Also contained 30.89% undecencic acid.

EXPT. II

Wt. of pyrolyzed product distilled : 2977.5g

Frn No.	Frn. wt (g)	Composition, Zwt (GC)			
		HA	MU	16+18	Me Ric
1	14.27	Discarded			
2	816.36	94.72	3.29	-	-
3	38.58	64.60	24.38	-	-
4	1373.69	1.42	97.61	-	-
5*	60.7	-	5.95	32.00	0.13
Residue	590.7	-	-	49.67	2.32

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	816.36	773.26	26.86	-	-
3	38.58	24.92	9.40	-	-
4	1373.69	19.51	1340.86		
5	60.7	-	36.83	19.42	0.08
Residue	590.7	-	-	293.40	13.70
	2880.00	817.69	1413.95	312.82	13.78

Wt. of fractions excluding Frn. 1 : 2880.0g
Loss on distillation: 2977.5 - 2880.0 = 97.5g
Others : 321.79g
*Also contained 50.9% undecenoic acid.

EXPT. III

Wt. of pyrolyzed product distilled : 2977.8g

Frn No.	Frn. wt (g)	Composition, Iwt (GC)			
		HA	MU	16+18	Me Ric
1	17.0	Discarded			
2	892.7	95.23	2.73	-	-
3	1262.6	-	98.89	-	-
4*	76.65	-	2.85	39.93	-
Residue	642.2	-	-	40.87	49.28

Frn No.	Frn. wt (g)	Weight, g			
		HA	MU	16+18	Me Ric
2	892.7	850.12	24.37	-	-
3	1262.6	-	1248.58	-	-
4	76.65	-	41.62	30.61	-
Residue	642.2	-	-	262.47	316.48
	2874.15	850.12	1314.57	293.08	316.48

Wt. of fractions excluding Frn. 1 : 2874.15
Loss on distillation: (2977.8 - 2874.15) = 103.65
Others : 102.31g
*Also contained 47.85% undecenoic acid.

MATERIAL BALANCE

EXPT. 1

INPUT (kg)		OUTPUT (kg)	
Me ricinoleate	4.16	Heptaldehyde	1.08
Others	0.46	Me undecenoate	1.92
	4.62	C16+18	0.45
		Me ricinoleate	0.52
		Others	0.07
		Loss on pyrolysis	0.45
		Loss on distillation	0.12
			4.61

EXPT. 2

INPUT (kg)		OUTPUT (kg)	
Me ricinoleate	4.07	Heptaldehyde	1.11
Others	0.45	Me undecenoate	1.92
	4.52	C16+18	0.43
		Me ricinoleate	0.02
		Others	0.43
		Loss on pyrolysis	0.48
		Loss on distillation	0.13
			4.52

MATERIAL BALANCE (Contd.)

EXPT. 3

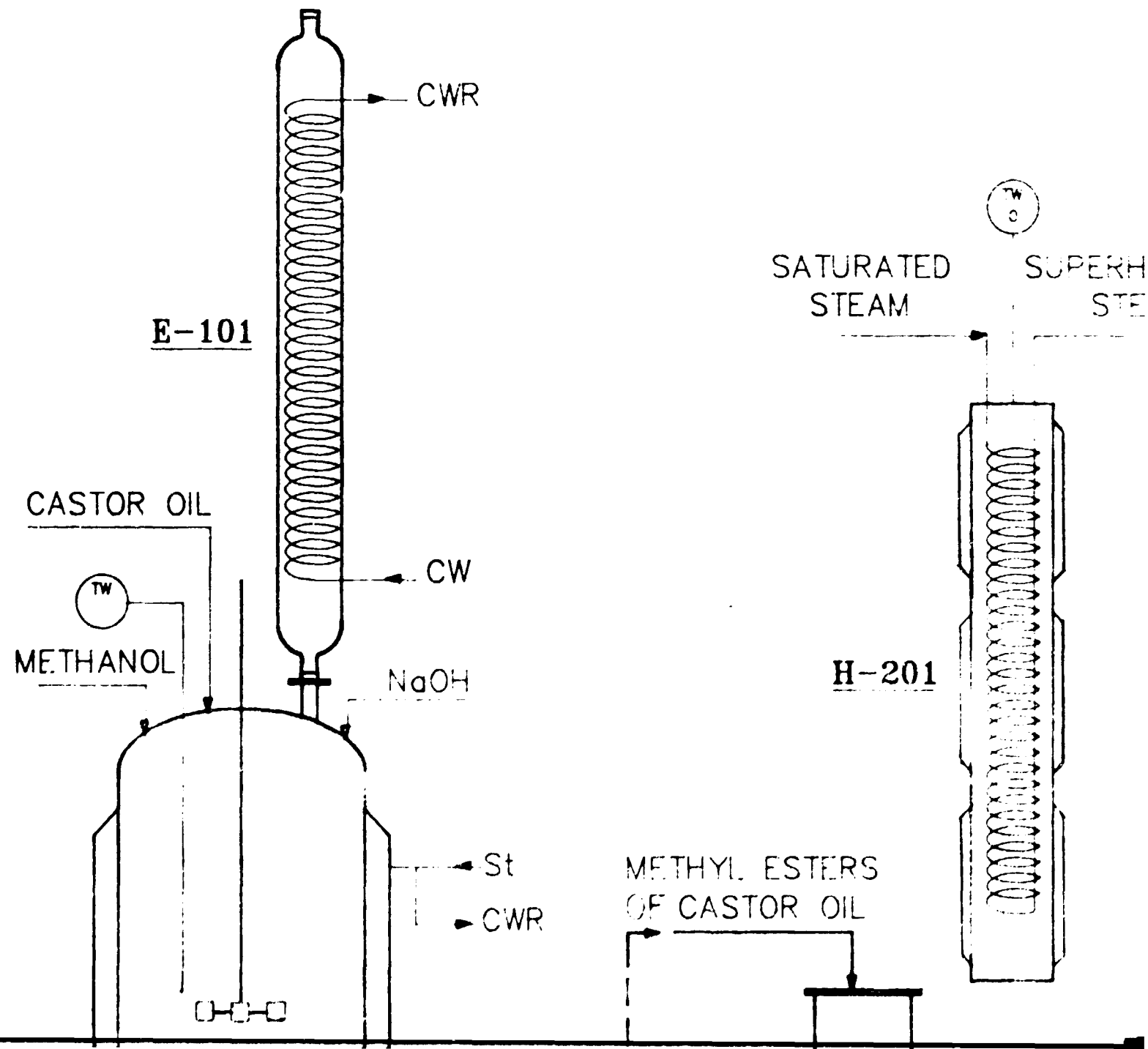
INPUT (kg)		OUTPUT (kg)	
Me ricinoleate	4.09	Heptaldehyde	1.16
Others	0.45	Me undecenoate	1.80
		C16+18	0.40
	4.54	Me ricinoleate	0.43
		Others	0.14
		Loss on pyrolysis	0.47
		Loss on distillation	0.14
			4.54

CALCULATION:

	EXPT. 1	EXPT. 2	EXPT.3
Me undecenoate from 100g CME :	41.56g	42.48g	39.65g
Undecenoic acid, assuming a factor of 0.9:	37.40g	38.23g	35.68g
Undecenoic acid, 95% pure :	39.37g	40.24g	37.56g

Repyrolysis of the distillation residue was not carried out.

SECTION 1


CWR
E-101
CW
CASTOR OIL
TW
METHANOL
NaOH
St
CWR
TW
SATURATED
STEAM
H-201
METHYL ESTERS
OF CASTOR OIL

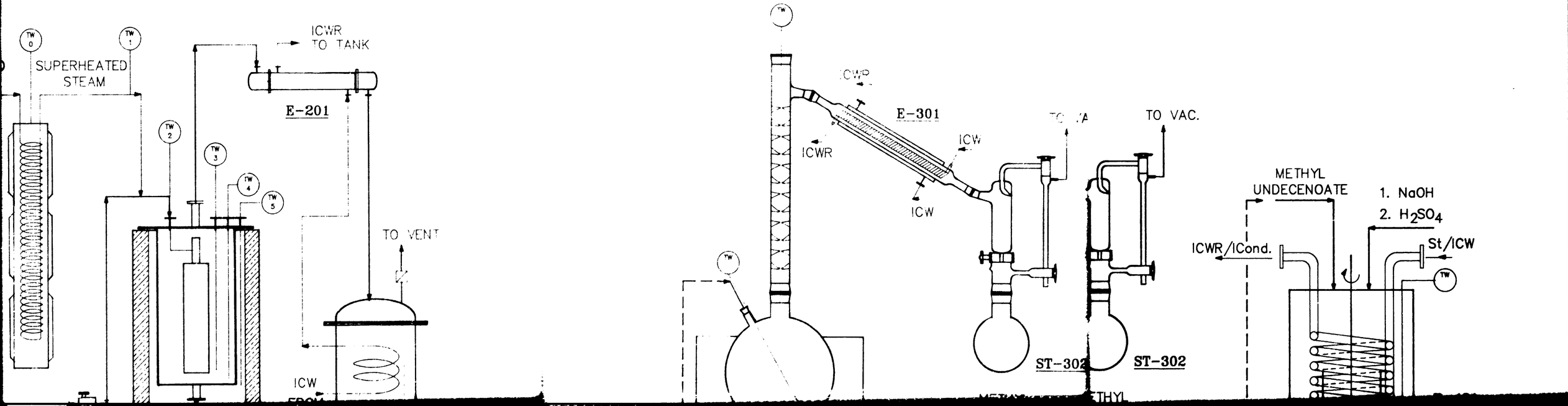
Rev.	Rev. No.	Description	By	Date

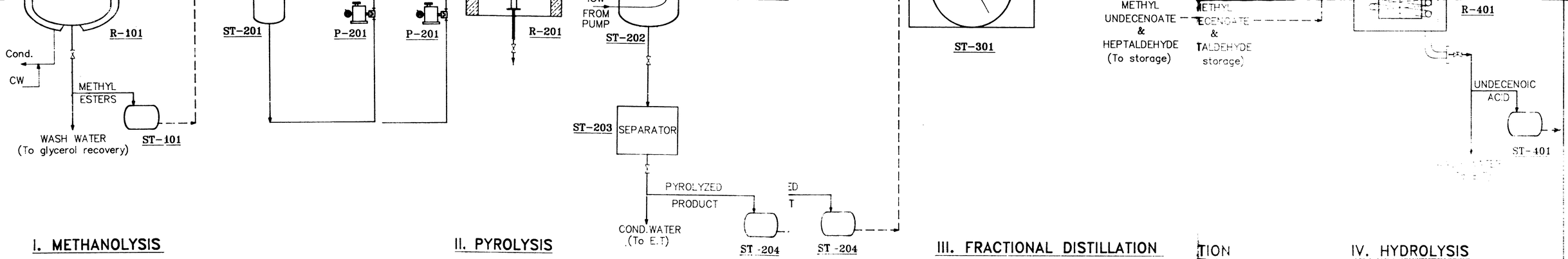
SECTION 2

SECTION 3

SECTION 4

UNDECENOIC ACID FRO FROM CASTOR OIL





I. METHANOLYSIS

SECTION 5

II. PYROLYSIS

SECTION 6

III. FRACTIONAL DISTILLATION

SECTION 7

TION

IV. HYDROLYSIS

	TRAP		TRAP
TW	THERMO	TW	THERMOWELL
CW	COLD W	CW	COLD WATER
CWR	COLD W	CWR	COLD WATER RETURN
ICW	ICE COL	ICW	ICE COLD WATER
ICWR	ICE COL	ICWR	ICE COLD WATER RETURN
E.T	BY	E.T	BY-PRODUCT TREATMENT

OF CHEMICAL TECHNOLOGY
HYDERABAD 500 00

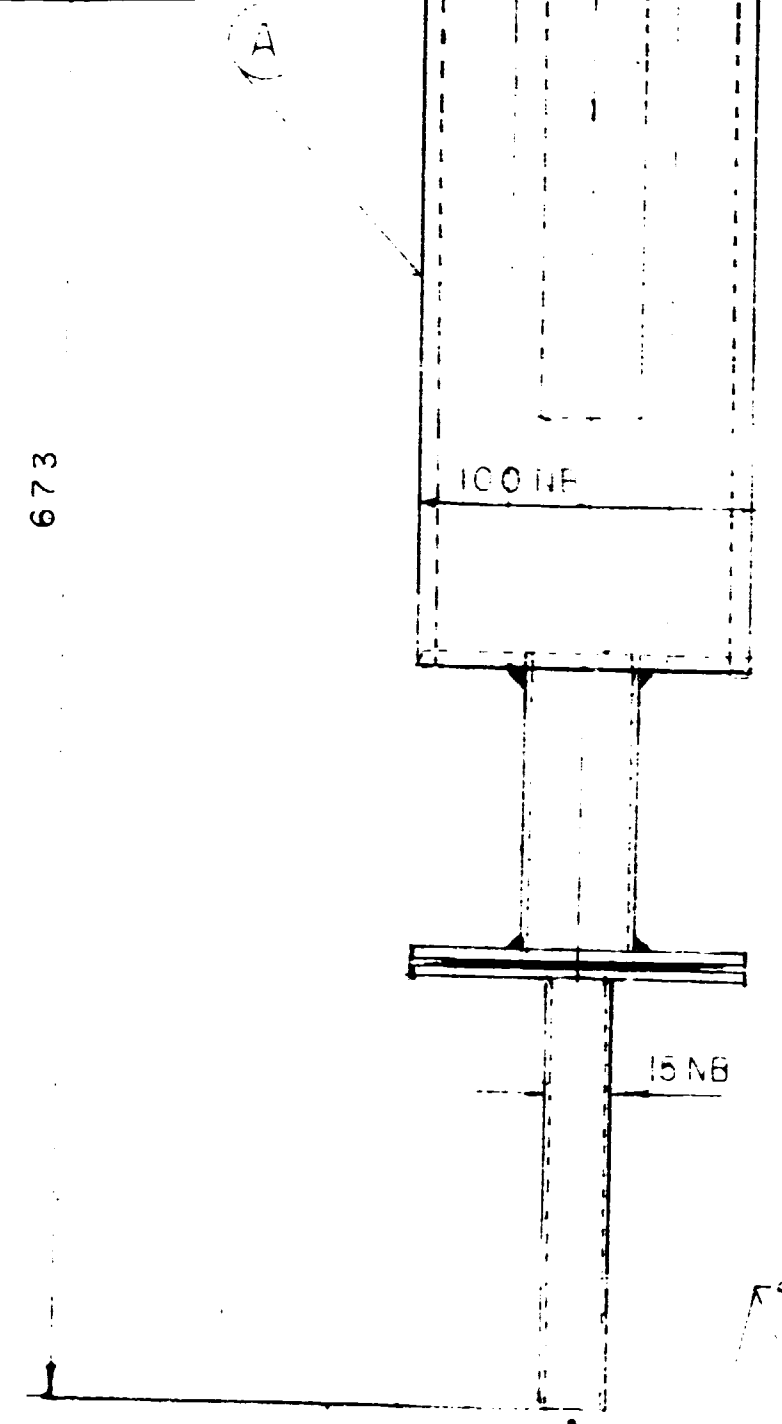
	Name	Date
DSN		
DRN	S.	3.3.94
TRD		
CHD		
APP		

Scale :

Rev. :

Drg. No. : TDF - MISC 001-467

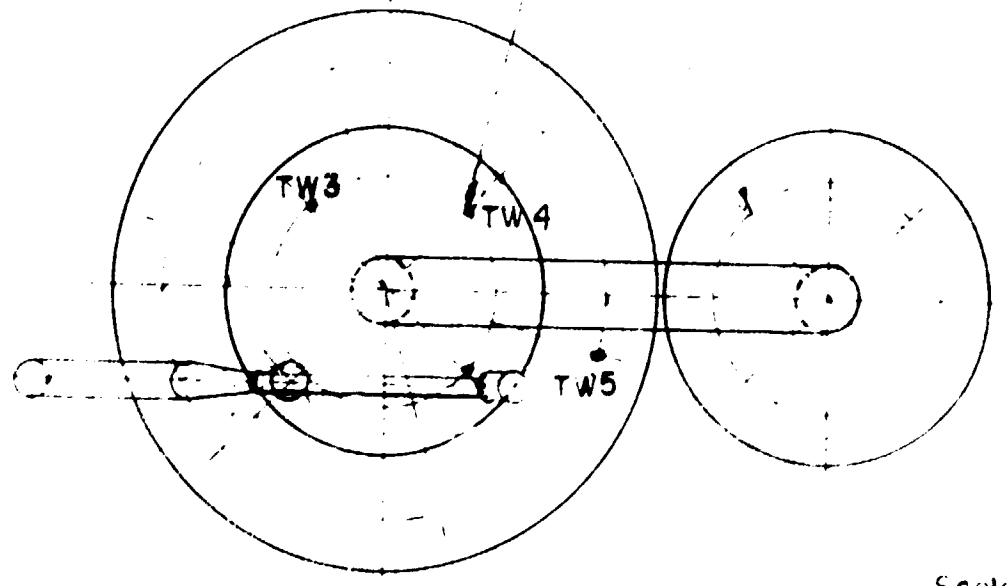

Drg. No. DE-MISC-001-451
REVISIONS
S. No
DATE
SECTION 1
SECTION 2
SECTION 3
SECTION 4
78 BCD
Ø 105
TW2
15 NB (1/2") BALL VALVE
1/2"x1/4"
20 NB
OD = 21
6-Ø 7/16" HOLES FOR Ø 3/8"x30L BOLTS
4-Ø 7/16" HOLES FOR Ø 3/8"x30L BOLTS
Ø 190
155 BCD
OD = 115
ID = 102
38 OD
31 ID
15 NB
OD = 35
ID = 20
OD = 20
L = 75
OD = 19
L = 25
OD = 33
ID = 28
LENGTH "L"
TW5 410
TW4 400
TW3 295



4-Ø7.6 HOLES FOR Ø3/8"x30L. BOLTS

"HOLES FOR x30L. BOLTS

SECTION 5



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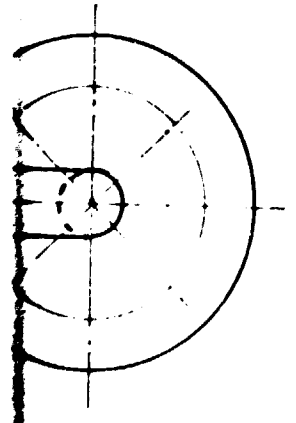

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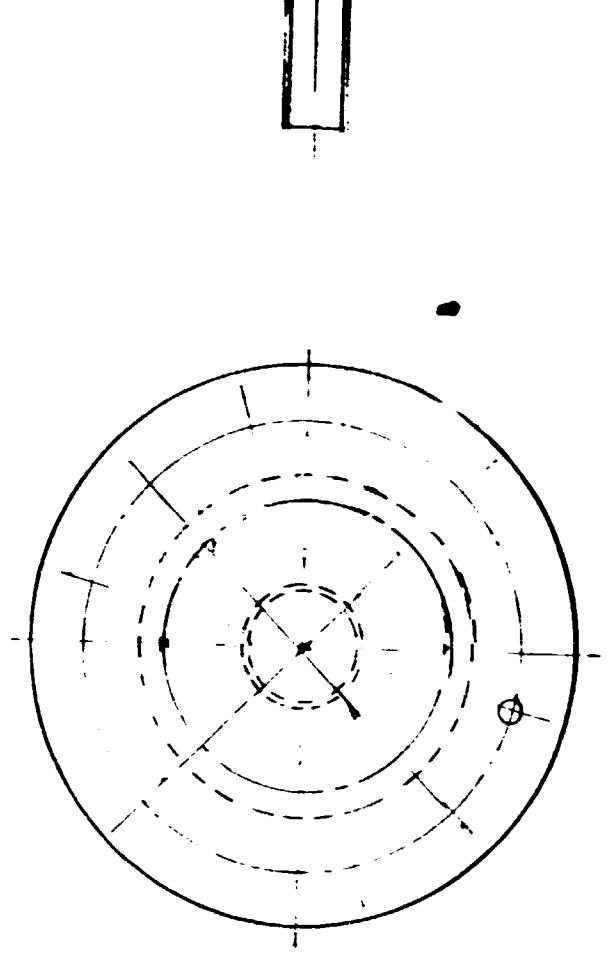
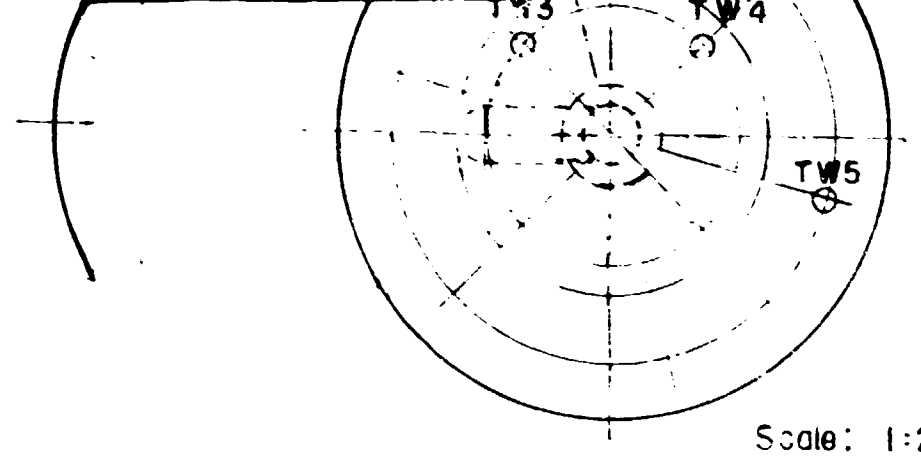


Scale: 1:2·5

SECTION 6



Scale: 1:2·5

SECTION 7

SECTIONS

Part No	Description	Material Specifications	No. reqd	Remarks

INDIAN INSTITUTE OF CHEMICAL TECHNOLOGY
HYDERABAD-500009

CSIR

	NAME	DATE
DSN		
DRN	B.V.	93-09-02
TPD		
CHD		
APD		

PYROLYSIS REACTOR

All dimensions are in mm unless otherwise specified

Scale:- 1:2.5 & 1:1