

The following materials were examined as pyrolysis contacts: Iron sponge, coarse powdered aluminium (Al-grits), chamotte pearls, pumice with particle diameter of 0,3 to 1 cm, and pumice impregnated with borax solution. It was found that the nature of the heat transferring contact material had no significant role in the pyrolysis, but the area of the contact surface was of decisive importance. In agreement with the work of PANJUTIN [4], we found that the presence of metals and traces of mineral acids increase the tendency of tar formation. Chamotte pearl,

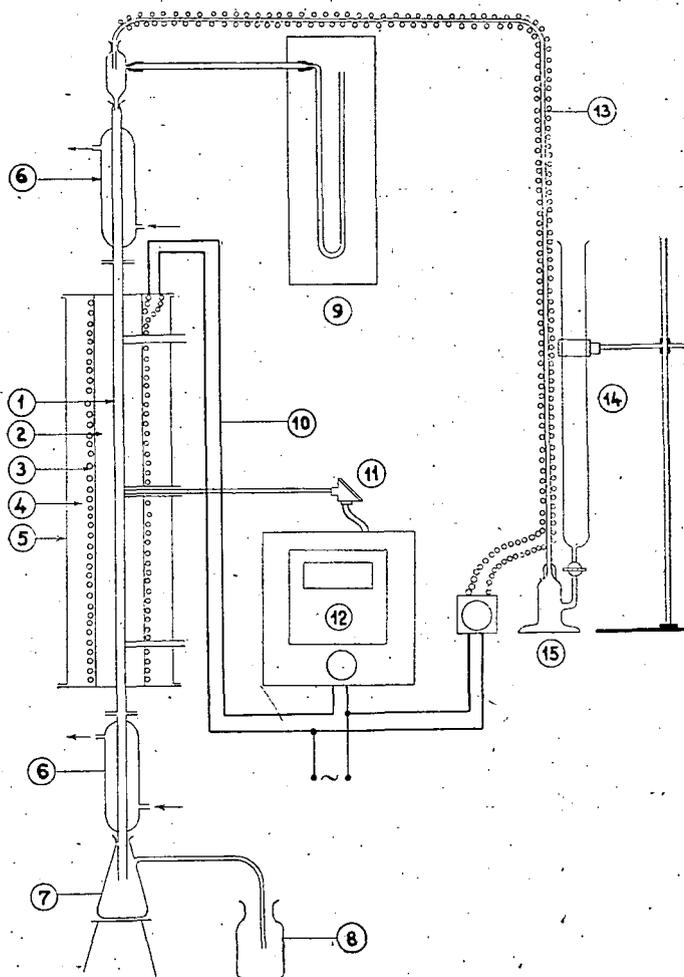


Fig. 1. Tube reactor for the preparation of methyl undecylenate. — 1. Reactor tube packed with contact in the heated zone. 2. Heat transferring aluminium block. 3. Heating filament. 4. Heat insulator (glass wool). 5. Tin-plate mantle. 6. Condenser. 7. Receiver. 8. Gas absorber. 9. Manometer. 10. Electric lines. 11. Thermocouple. 12. Automatic temperature controller. 13. Heated pressure feed line. 14. Feeding burette. 15. Feed pump.

pumice, and pumice impregnated with 10% borax solution were found to be the best contacts for this process among the materials examined and listed above. Yields and conversions, in percentages, of methyl undecylenate production are shown in Figs. 2., 3. and 4., at a feed rate of 200 ml per hour, and with various contacts.

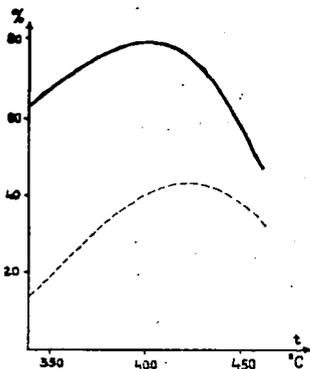


Fig. 2. Contact: Chamotte pearls. Length (volume) of the bed: 114 cm (157 cu. cm)

These diagrams indicate the following facts:

a) When different contact materials are used, the yields and conversions of methyl undecylenate production remain practically the same.

b) Higher temperatures bring about an increase of conversion and yield up to a certain maximum, then they are decreased with all contacts examined by us. The decrease of the formation of methyl undecylenate above a certain limiting temperature is due to too extensive pyrolysis and formation of tar at these temperatures.

c) When the volume (length of the bed) of the contact is increased, optimum conversions and yields are attained at lower temperatures, as a consequence of increased contact time.

The character of the reaction is primarily influenced by the length of the pyrolysing bed (volume of contact), by the feed rate of the starting material, and by the temperature used. These three factors show close relationship to each other,

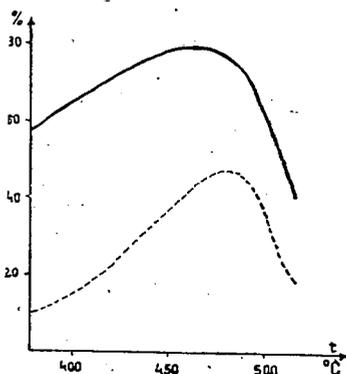


Fig. 3. Contact: Pumice. Length (volume) of the bed: 80 cm (110 cu. cm)

Conversion: -----

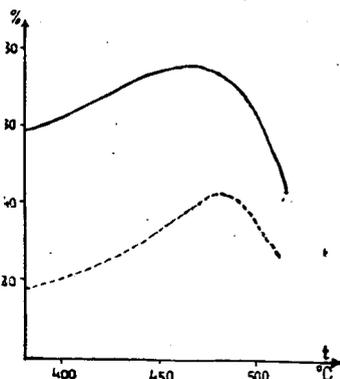


Fig. 4. Contact: Borax on pumice. Length (volume) of the bed: 80 cm (110 cu. cm)

Yield: _____

as it is seen from the Tables below, which show the variation of the conversions and yields of methyl undecylenate production with different lengths (or volumes) of contact (A), the effects of the temperature (B) and that of the rate of feed (C).

At constant temperature and with a constant rate of feed, the conversion and yield show changes of opposed direction when the length of bed of the contact is increased. Under the conditions specified in Table A, the conversion is increasing, at the same time the yield of methyl undecylenate is decreasing, which is indication of a more extensive over-pyrolysis of the formed products.

Table A

Length of bed (volume) cm (cu. cm)	Conversion %	Yield %
50 (70)	22	80
80 (110)	28	75
114 (157)	37	50

Temperature 430°C. Feed rate 200ml/h.

Table B

Temp. of decompn. °C	Conversion %	Yield %
380	11	58
430	28	75
510	24	45

Feed rate 200 ml/h.
Length of bed (volume) 80 cm (110 cu. cm)

Table C

Feed rate ml/h	Conversion %	Yield %
200	28	75
300	22	65
400	14	56

Length of bed (volume) = 80 cm (110 cu. cm).
Temperature 430°C

When the rate of feed and volume of contacting material are kept constant, lower temperatures produce changes other than required, leading to poorer yields and conversions. Increased temperatures result in improved values until an optimum is reached; above this temperature over-pyrolysis and polymerisation [5] is experienced.

With constant volume of contact material and constant temperature; an increase of the feed rate will bring about a decrease of contacting time; consequently conversions and yields will be decreased. It follows that, for the sake of economy, the temperature of pyrolysis must be increased near to the point of too extensive decomposition in such cases when the feed rate is increased, but the length (or volume) of contacting bed is kept constant.

Relationships among the feed rate of the starting material, temperature, and conversion or yield of methyl undecylenate are shown in the above Tables and in Figs. 5. and 6.

Besides the mentioned interdependence of feed rate and temperature of pyrolysis, the summarizing diagrams well indicate that at higher temperatures better conversions and yields for methyl undecylenate may be obtained if the pumice is impregnated with borax.

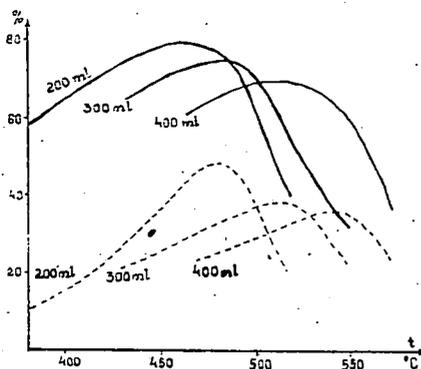


Fig. 5. Contact: Pumice. Length (volume) of the bed: 80 cm (110 cu. cm)
Conversion: -----

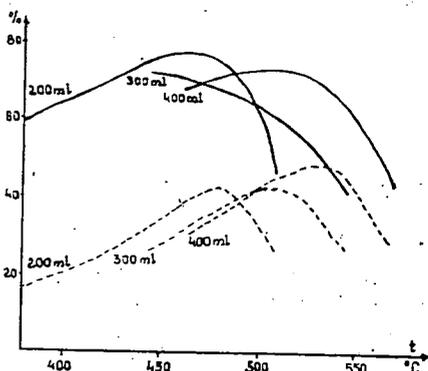


Fig. 6. Contact: Borax on pumice
Yield: -----

The experiments lead to the conclusion that when methyl ricinoleate is pyrolysed in a continuous tube reactor, optimum conversion (40–50%) and yield (75–80%) of methyl undecylenate may be obtained in the temperature ranges shown in Tables D and E, if the length of the contacting bed and the feed rate of the material are as indicated.

Table D

Feed rate ml/h	Optimum pyrolysis temp. °C
100	390–410
200	420–440
300	440–460

Length (volume) of contact bed = 114 cm (157 cu. cm)

Table E

Feed rate ml/h	Optimum pyrolysis temp. °C
100	430–450
200	460–480
300	490–510
400	510–530

Length (volume) of contact bed = 80 cm (110 cu. cm)

2. Pyrolysis of methyl ricinelaideate

The pyrolysis of methyl ricinelaideate was the subject of a study, conducted parallel with that of methyl ricinoleate. Such experiments have not been reported with the former compound. The material was prepared by us from methyl ricinoleate, following the principle of PLAYFAIR's synthesis [6], [7]. The experiments with this trans compound obtained thus, led to the following conclusions.

The course of the pyrolysis is somewhat different from that of methyl ricinoleate, which is explained by the different spatial arrangements and stabilities of the compounds. With chamotte pearl contact and under identical conditions, con-

versions and yields of methyl undecylenate production are lower in the case of the trans compound. This is probably due to the fact that the dehydration and polymerisation reactions of methyl ricinelaide are favoured in the presence of chamotte pearl contact. When pumice, or even more, when pumice impregnated with borax is used, decomposition of methyl ricinelaide to methyl undecylenate and n-heptaldehyde (oenanthole) becomes the main reaction, especially at higher temperatures. A probable explanation of this behaviour is the assumption of a trans-cis rearrangement taking place above some defined temperature (about 450° C); subsequently, the product undergoes pyrolysis. This mechanism of reaction readily explains the fact that conversions and yields are lower with the trans than with the cis compound if lower temperatures are applied, as a consequence of slower isomeric rearrangement. This is shown in the diagrams below.

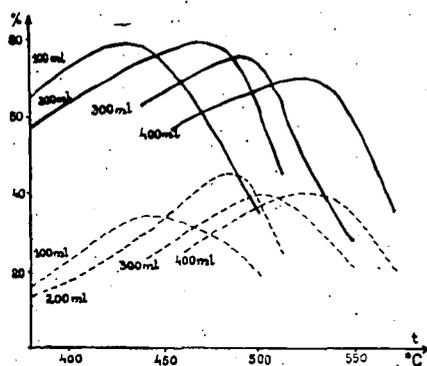


Fig. 7. Pyrolysis of methyl ricinoleate. Conversions and yields. Length (volume) of contact bed: 80 cm (110 cu. cm)
Conversion: -----

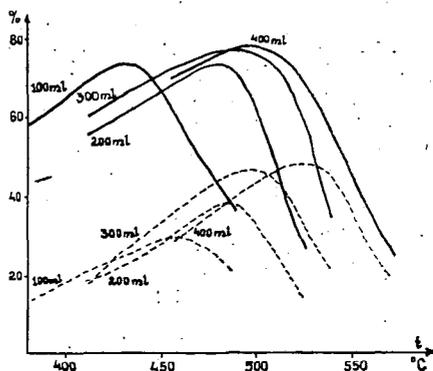


Fig. 8. Pyrolysis of methyl ricinelaide. Conversions and yields

Yield: _____

These figures show the average conversions and yields for methyl undecylenate obtained with pumice and borax on pumice at different feed rates (ml/hour), and as a function of temperature.

The other principal product of the pyrolysis of both methyl ricinoleate and ricinelaide is n-heptaldehyde. Conversions and yields for this compound correspond to the formation of methyl undecylenate until the point of over-pyrolysis is reached. At higher temperatures, due to its higher thermal stability, n-heptaldehyde becomes preponderant in comparison with methyl undecylenate.

Our experiments led to the following main conclusions concerning the preparation of methyl undecylenate by pyrolysis:

1. The most important factor in the pyrolysis is the surface area of the contact.
2. Borax-on-pumice is an advantageous contact for the reaction.
3. When the volume of the contact is increased, optimum pyrolysis temperature becomes lower, as a consequence of increased contact time.
4. With higher feed rates the temperature must be increased in order to maintain good conversions.

5. Optimum pyrolysis temperatures on borax on pumice catalysts for methyl ricinelaide are higher than for methyl ricinoleate, due to the higher thermal stability of the former compound.

6. According to our experiments, when reaction conditions are properly chosen, methyl undecylenate can be prepared with a conversion of 40 to 50%.

Experimental

Methyl ricinoleate

The compound was prepared according to the method of FALKAY and KRÁMER [8].

One part of castor oil was mixed with 0,4 parts of methyl alcohol, and 10% sodium hydroxide was added to adjust a 0,4% alkali hydroxide content in the mixture, calculated for castor oil. The mixture was refluxed for 30—40 minutes with occasional shaking. Then it was neutralized with diluted sulphuric acid and the excess methyl alcohol distilled off. After cooling, the reaction mixture separated to two layers. The lower layer consisted mainly of concentrated glycerol. It was separated, and the methyl ester layer was washed with water until free of mineral acid. Then it was dried by drawing air through the mixture, and finally distilled. B. p. 185—190° C at 2 mm; 209—211° C at 7 mm; 238—242° at 10 mm. The product was a water-white oil. The yield was almost theoretical. Analysis:

	Acid value	Ester value	Iodine value
Required for $C_{19}H_{36}O_3$ (312,48)	—	179,58	81,3
Found	4.8—4.9	177,76	87,2

Two hydroxy acids were isolated from the crude methyl ricinoleate with the melting points of 114—115° C (*A*) and 145—147° C (*B*), their structure, however, has not been investigated. Analysis showed the following values: For material *A*, C 69,57%; H 10,66%. Molecular weight 250—270. For material *B*, C 68,75%; H 11,00%. Molecular weight 220—250.

Ricinelaic acid

Ricinelaic acid was prepared by isomerizing ricinoleic acid according to the method of KASS and RADLOVE [7]. The product consisted of pale yellow crystal needles, m. p. 49—51° C.

Methyl ricinelaide

Ricinelaic acid was dissolved in three to five times the calculated amount of methanol, and the solution saturated with dry hydrogen chloride under cooling in ice. The solidified material was filtered and washed until free of mineral acid. B. p. 202—203° C at 4 mm; 211—213° C at 5—6 mm; 250—253° C at 10 mm. Yield of the pale yellow liquid was 70—75%. The product solidified on standing

at room temperature, m. p. 32—33° C. The material had the following characteristics:

	Acid value	Ester value	Iodine value
Required for $C_{19}H_{36}O_3$ (312,48)	—	179,58	81,3
Found (for distilled material)	3,15	168,9	80,5

Analysis after recrystallisation from methanol: $C_{19}H_{36}O_3$ (312,48) requires C 73,03; H 11,61%. Found: C 73,10; H 11,80%.

Pyrolysis of methyl ricinoleate and methyl ricinelaide

Systematic pyrolysis experiments were carried out in a continuous tube reactor of 110 cm length and 1,55 cm diameter. 70—120 g of the raw material was processed in each run, over various contacts. The length (volume) of the bed was 114 cm (157 cu. cm) when chamotte pearl was used, and 80 cm (110 cu. cm) when pumice or borax on pumice was employed. Feed rates of 70, 100, 200, 300, and 400 ml/hour and temperature ranges of 220—550° C were tried. With a given rate of feed, the temperature of pyrolysis was, in general, increased by degrees of 50° C, up to the point when excessive decomposition (fuming) was experienced. Two or three experiments were always carried out under identical conditions. The diagrams and tables show average results.

After switching on the electrical heating and adjusting the automatic temperature controller, the material to be pyrolysed was fed into the reactor tube at an exactly determined rate, by the aid of an automatic feeder.

The product of the pyrolysis was a more or less coloured reddish-brown fluorescent liquid, the colour being dependent on the conditions of the experiment and on the nature of the starting material. The yield varied between 60 and 100%. The pyrolysed material was fractionated by distilling it first under atmospheric, and from above 180° C under reduced pressure. The products could be purified by repeated atmospheric distillation.

The following products were obtained:

- Fore-run, to b. p. 70° C.
- Aldehyde — n-heptaldehyde fraction, boiling range 70—220° C. The yield varied within wide limits, depending on the reaction conditions. The aldehyd content of the fraction was 40—60%.
- Methyl undecylenate fraction, boiling range 230—260° C. Yield 10—52% of the theoretical.

Analysis:

	Acid value	Ester value	Iodine- bromine value
$C_{12}H_{22}O_2$ (198,29) requires	—	282,92	80,6
Found	8—15	245—264	80—96

Repeated fractionated distillation gave uniform methyl undecylenate in a yield of 60—70%. B. p. 248° C at 760 mm.

d) Distillation residue. This material consisted mainly of unreacted methyl ricinoleate and its amount varied between 10 and 85%.

The distillation residue of the trans compound obtained when the pyrolysis was carried out at 430—480° C solidified on cooling, and its distillation gave methyl ricinelaideate. With higher pyrolysis temperatures a residue distilling at the boiling point of methyl ricinoleate was obtained, which, however, has not been identified so far.

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ПИРОЛИЗ МЕТИЛ-РИЦИНОЛАТА И ЕТИЛ-РИЦИНЕЛАИДАТА. ЭКСПЕРИМЕНТЫ ИЗОЛИРОВАНИЯ МЕТИЛ-УНДЕЦИЛЕНАТА

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Авторами было исследовано соотношение между склонностью к крекированию метилового эфира рициноловой и рицинелайдиновой кислот и изомерией цис и транс.