ALKALINE CONDENSATION OF ETHYL ALCOHOL

by

Jesse G. Pennepacker

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Bachelor of Science in Chemical Engineering

from the

Massachusetts Institute of Technology

Signature of Author Jesse G. Pennepacker

Signature of Supervisor E. R. Gilliland

Date Submitted May 25, 1953

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Date Submitted_________May 25, 1953_

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts
May 25, 1953

Professor E. R. Gilliland
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir,

This thesis entitled " Alkaline Condensation of Ethyl Alcohol " is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Jesse G. Pennepacker

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TABLE OF CONTENTS

SUMMARY

The object of this thesis was to attempt alkaline condensation of ethyl alcohol using sodium ethoxide and various hydrogenation- dehydrogenation catalysts.

Work was done by Weizmann in 1937 (1) using pressure to condense n-butanol in the presence of sodium and a copper bronze dehydrogenation catalyst.

Later work was done by the Carbide and Carbon Chemicals Corporation (2) using atmospheric or low superatmospheric pressures. Sodium ethoxide prepared in situ by refluxing with NaOH, and various metal and metal oxide dehydrogenation catalysts were used. The alcohols were n-butyl and higher.

In this condensation of ethyl alcohol, pressure was used principally to obtain a high enough temperature. The reaction was carried out in a batch reactor with no agitation. The alcoholate was made from sodfum and alcohol. Dehydrogenation catalysts used were Zn-ZnO, $ZnO-Cr_2O_3$, Ni, $ZnO-Cr_2O_3-CaO$, and none.

Yields of n-butanol were generally low, 0 - 7.6% based on starting alcohol. Undetermined by- products boiling in the range 80- 83 C were also formed. In the run where CaO was used, a large amount of this was produced, and it is thought to be the result of a dehydrating action. Small amounts of hydrocarbons were believed present as shown by varying degrees of turbidity formed upon adding the lighter fractions to water. Boiling point data including azeotropes were consulted,

and chemical tests made but the identity of this other substance or substances could not be definitely established.

Some organic acids were formed but quantitative data were not obtained.

It is believed that the temperature was not high enough, and the rate of reaction too slow in the runs made.

The best dehydrogenation catalyst of those used is Zn-ZnO. The initial course of run #3 and the higher yield in a shorter running time indicates that the reaction proceeds at a lower temperature and more rapidly than with the other catalysts.

It is believed that quantities of resinous products such as aldehyde resins were formed.

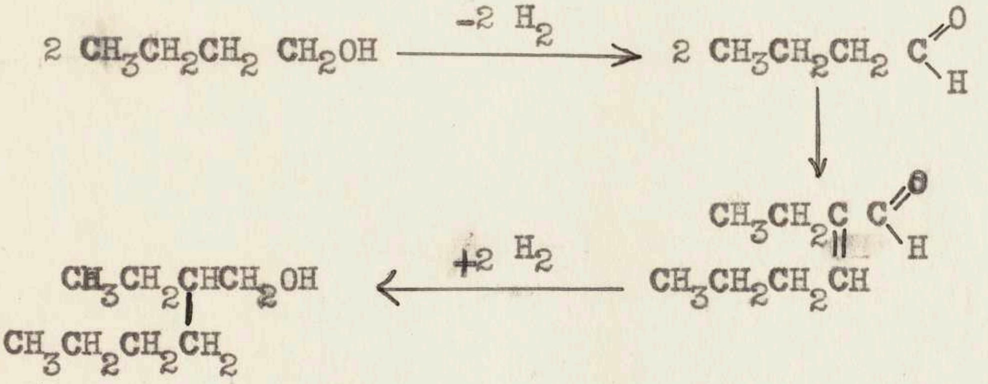
INTRODUCTION

The purpose of this thesis was to attempt to condense ethyl alcohol using sodium ethylate as a condensation catalyst and metallic and metal oxide hydrogenation-dehydrogenation catalysts.

Earlier work relating to this problem was done by Weizmann (1) in 1937. In the self condensation of n-butanol, metallic sodium, a copper bronze catalyst and 74 grams of n-butanol were reacted in an autoclave at 160 atmospheres pressure for 12 hours. The products were:

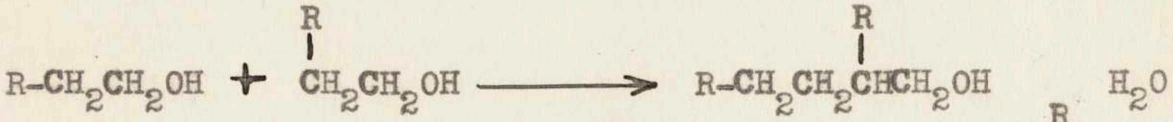
Unreacted n-butanol	16 gm.
butyl butyrate	4.4 gm.
2-ethyl hexanol	30 gm
2-(ethyl-hexyl) butyrate	5 gm
	55.4 gm.

The remainder of the alcohol unaccounted for (18.6 gm) is approximately equivalent to the 2 ethyl hexanol formed. The mechanism of the reaction was suggested to be:



It was stated that molecular hydrogen was not required in the last step and could be supplied at the expense of unreacted alcohol.

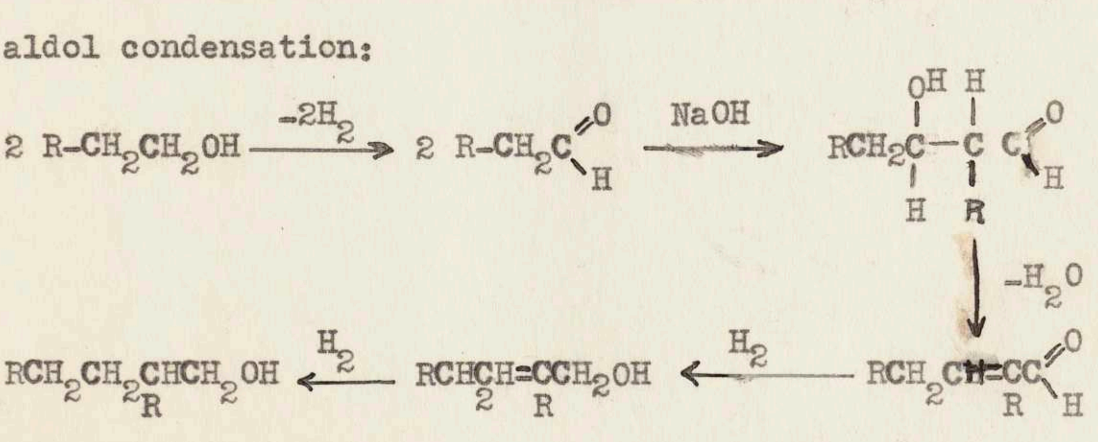
More recent work concerns a patent granted to the Carbide and Carbon Chemicals Corporation.(2) These condensations were carried out at atmospheric pressure or at low pressures ranging to 100 psig. The alcoholate was prepared in situ and in concentrations of 3-15% by refluxing the alcohol with caustic soda and removing the water as formed. n-butanol and higher alcohols were used. Various metal and metallic oxide dehydrogenation catalysts such as Raney nickel, Zn, Zn-ZnO, etc. were used. Conversions ranged from 1-4% per hour. The reaction times were from 14-33 hours and yields from 31-63%. In each case the products formed seemed to indicate a reaction of the general type:



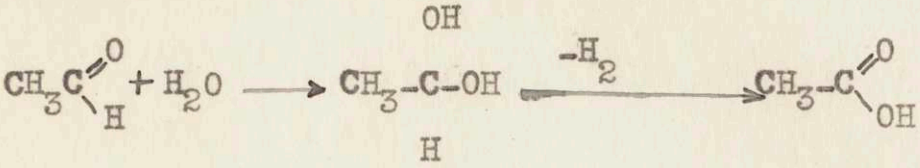
$$R\text{-}CH_2CH_2OH + \overset{R}{\overset{|}{C}}H_2CH_2OH \longrightarrow R\text{-}CH_2CH_2\overset{R}{\overset{|}{C}}HCH_2OH \quad H_2O$$

with small amounts of the unsaturated alcohol $R\text{-}CH_2CH{=}\overset{R}{\overset{|}{C}}\ CH_2OH$ also formed. It is claimed in the patent that the high ratios of acid salts to alcohols obtained in previous known alcohol condensation processes were due to the failure to remove water of condensation as rapidly as formed.

The mechanism of the reaction might be explained by an aldol condensation:

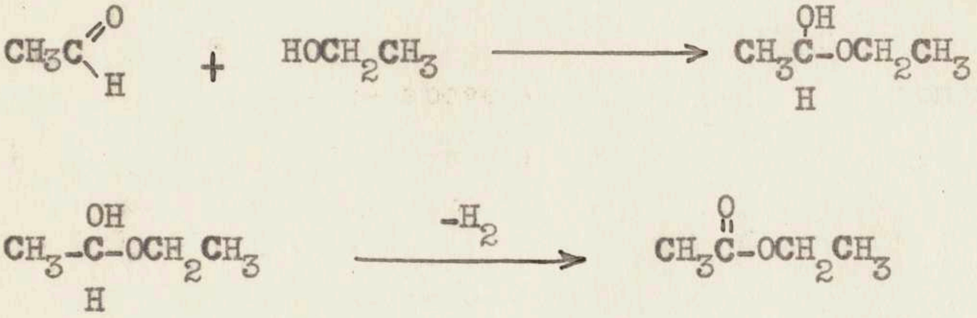


If it is necessary to remove water as formed, this might be explained by hydration of aldehydes and their subsequent dehydrogenation:



$$CH_3C\begin{smallmatrix}O\\H\end{smallmatrix} + H_2O \longrightarrow CH_3\text{-}\overset{OH}{\underset{H}{C}}\text{-}OH \xrightarrow{-H_2} CH_3\text{-}C\begin{smallmatrix}O\\OH\end{smallmatrix}$$

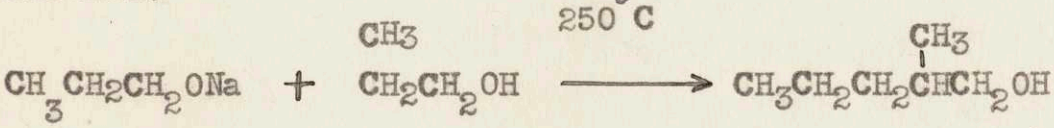
Analogous to the above would be the formation of esters through a hemiacetal; and their saponification:



$$CH_3C\begin{smallmatrix}O\\H\end{smallmatrix} + HOCH_2CH_3 \longrightarrow CH_3\overset{OH}{\underset{H}{C}}\text{-}OCH_2CH_3$$

$$CH_3\text{-}\overset{OH}{\underset{H}{C}}\text{-}OCH_2CH_3 \xrightarrow{-H_2} CH_3\overset{O}{\overset{\|}{C}}\text{-}OCH_2CH_3$$

Sodium ethoxide itself sometimes acts as a dehydrogenation catalyst in some organic reactions. In the case of n- propyl alcohol:



$$CH_3CH_2CH_2ONa + \overset{CH_3}{CH_2}CH_2OH \xrightarrow{250^\circ C} CH_3CH_2CH_2\overset{CH_3}{C}HCH_2OH$$

No other catalyst is necessary. The reaction is supposed to go completely when equimolal amounts of alcoholate and alcohol are used.(3)

In the case of n-pentanol:(3)

$$C_5H_{11}OH + C_5H_{11}ONa \xrightarrow{240^\circ C} C_5H_{11}.C_5H_{10}OH \quad NaOH$$

In all the examples given in the patent, Condensation took place in the α position. n- pentanol was not one of the alcohols used in these procedures, so it is not known whether the different conditions employed would have given the α condensation product.

Ethyl alcohol was chosen for the experimental procedures in this thesis. Since the α carbon atom is also the carbon atom at the end of the molecule, it was thoughtthat the condensation reaction might take place more readily due to less hindrance and the presence of three α hydrogen atoms rather than two. Also, the α hydrogens vary in activity with the radical attached. It was thought that this might tend to decrease any formation of esters and their saponification to acid salts. No literature record could be found concerning the condensation of ethanol.

If the elimination of water from the reaction phase were not necessary in this case,caustic soda and ethyl alcohol might be used to synthesize n-butanol and possibly higher alcohols in a batch reactor. If the alcoholate were only a condensation catalyst,there might be enough present even in the presence of water to cause condensation (of the acetaldehyde intermediate). Condensation to form ethyl acetate requires more drastic conditions.(4) If the aldehyde mechanism is correct,a controlling factor would appear to be dehydrogenation to aldehyde.

Pressure was used in all but one run, both to obtain a high enough temperature and also because pressure often has the effect of increasing the surface activity of catalysts.

APPARATUS

The apparatus used was a bomb type reactor of about o.72 liters volume. It was fitted with a rupture (safety) disk at one end and a thermocouple well and pressure guage at the other end. A valve was also provided for venting the gas at the end of a run or if necessary, during a run to keep the pressure from rising too high. Heating was accomplished using a removeable resistance coil (insulated) which fitted around the reactor. Current was controlled with a variac. No agitation was provided.

PROCEDURE

The sodium was weighed and placed in a 1 liter flask. Ethyl alcohol, usually about one pint was added in small portions and allowed to react. Upon completion of the reaction, flask and contents were weighed. The mixture was poured into the reactor, the flask washed with a small measured volume of alcohol and the dehydrogenation catalyst added. The empty flask was then weighed. The reactor was sealed and connected to the pressure guage and thermocouple.

After heating to about 50 psig, the system was vented to remove air. The loss of alcohol in this preliminary venting was negligible.

It was usually attempted to get as high a temperature as possible consistent with preventing the pressure from becoming too high. Release of the pressure by vent control was only done when necessary to prevent rupture of the safety disk. Any liquid coming over was collected.

At the end of a run, the reactor was allowed to cool overnight and the gas pressure at room temperature noted. A sample of gas was collected over water and burned with a yellow flame, but no carbon was deposited. The gas was not tested for unsaturation but it is thought that some hydrocarbon gases were formed.

The reactor contents were weighed at the end of a run. About 100 ml. of water were added to the mixture, the liquid distilled from the solid residue, and the boiling range noted. The distillate was salted out with anhydrous K_2CO_3, the oil layer separated, redistilled over a steam bath and collected in fractions. The distillations were conducted slowly using a glass column of the Vigreaux type. The boiling points were checked using the standard ASTM technique.

Five complete ethyl alcohol runs were done under pressure and one run under reflux at atmospheric pressure. Three more pressure runs were started but trouble was experienced with leaks and rupture.

No attempt was made to recover and titrate the organic acids, since difficulty was experienced in attempts to determine with certainty the content of the lighter fraction of the alcohol distillate.

Testing of products- light fractions (78-84° C)

1. The lighter fractions gave varying degrees of turbidity when about 1 cc was added to 5 cc of water. The turbidity varied from run to run , and was generally greater with the fractions boiling at 80° C and higher. Turbidity varied fron barely noticeable to a chalk white. This is believed due to small amounts of hydrocarbons, soluble in alcohol but insoluble in water.
2. Solubility tests indicated complete solubility only in concentrated sulfuric acid. In most cases, a

deep red or orange coloration indicated polymerization.

3. Unsaturation was present in small or negligible amount as indicated by the Baeyer test.(5) Of the aliphatic hydrocarbons, only the unsaturated ones are soluble in sulfuric acid.

4. Tests for aldehydes and ketones were negative. These included Fehling's solution, 2,4 dinitrophenylhydrazine, and sodium bisulfite.

5. Saponification tests for esters gave no acids.

6. Acid hydrolysis (dilute HCl) may have yielded aldehydes but this is inconclusive(presence of acetals). The melting point observed(of the 2,4 dinitrophenylhydrazone derivative) was 190-200°C. It may have been a mixture.

7. Attempts to prepare dibasic acids by permanganate oxidation were unsucessful.

8. Tertiary butyl alcohol was thought unlikely since it probably would involve isomerization. An attempt to prepare a 3,5 dinitrobenzoate derivative was unsuccessful.

9. No test was made for isobutyl alcohol, which was considered unlikely based on structure.

No attempt was made to prepare derivatives of butyl alcohol, the boiling point being taken as sufficient indication. The 106-112° and the 103-106.5° fractions of runs 4 and 9 are transition fractions. A column of large holdup could not be used since yields were low.

RESULTS

General

As can be seen from the table, the conversions to butyl alcohol were very low. There are large discrepancies in the distillate recovered versus the alcohol charged.

It is thought that small amounts of alcohols higher than C_4 may have been formed.

Run #1

This reaction was done to get some indication of the yield, since the reaction is one that is supposed to go reasonably well. It is used industrially, probably employing caustic soda.(6) The yield is only equivalent to about 20% of the sodium used, but the reaction time was short.

Run #2

This run was done using only sodium with the ethyl alcohol in an attempt to get a comparison with run # 1. The same temperature could not be approached because of the higher pressure required. The yield of n-butanol was negligible. Gas pressure on cooling would indicate that some reaction did take place, but it is believed small.

The boiling point of the product of run #2 was 78.3-78.5° C. Measured volumes of product and water were distilled, care being taken to avoid superheating etc.

This may indicate the presence of something other than ethyl alcohol and may be compared with the 80-84 fractions obtained in some of the other runs.

Run #3

This was the first run using hydrogenation - dehydrogenation catalysts. Both temperature and pressure are somewhat lower but the yield is higher. Also present is a detectable amount of an 82-83° fraction.

Run #4

Oxide catalysts were used in this run. The CaO was added added to determine if dehydration would increase the yield of n-butanol by preventing hydrolysis of the alcoholate. It seems to have caused side reactions as can be seen from the large amount of 80-90 fractions. The change in catalyst from run #3 could have affected the result, but it was thought that a better catalyst could be found.

Run #5

This run was done using a nickel powder catalyst, and no high boiling fractions were obtained. Some of the sample was distilled with a little water and gave a distribution in boiling range similar to run #2.

Run #9

This run was done at a higher pressure in order to get a higher temperature. Comparison with run #4 shows that the yield is lower

Run #10

This run was conducted for the same length of time as run #3, which seems to have the highest yield. It was done by refluxing the alcoholate solution and catalyst at atmospheric pressure. Although there was no high boiling fraction, a few cc of material partially soluble in water was salted out of the water coming over towards the end of the distillation.

RESULTS

Run #	EtOH (gm)	Na (gm)	Dehydr. Cat. Type	Dehydr. Cat. gm.	Time (hr)	Temp. (°C)	Press. (psig)	Vent.	Press. on cooling (psig)	B.P.R. °C (6)	gm.	%Conv. BuOH (1)	(2)
n-propanol 1	273.9	15.5	none	---	3¼	240-260	600-700	yes	---	@ 153	28.7	12.3	---
2	536.9	57.4	none	---	6.3	215-230	750-1000	yes	340	78.3-78.5	all	0	---
3	342.9	22.9	Zn ZnO	10.1 10.1	6½	190-200	400-880	yes	400	76.8-78 @ 78.3 78.3-79.8 82 - 83 119-120	37.3 98.9 70.3 15.8 21.1 243.4	7.6	340.6
4 (3)	302.8	23.6	ZnO Cr_2O_3 CaO	5.9 5.6 55.3	8½	175-190	500-800	no	260	78 -78.3 79 -83 @ 87 106-112 117-120	54.7 43.7 5.5 3.7 13.7 121.3	5.6-7.1	326.0
5	394.2	46.0	Ni	7.8	7 8	125-150 180-185	80-130 250-650	no no	0 310	79.6-79.7	398.2 (7)	0	416.1
9	332.0	22.1	ZnO Cr_2O_3	1.9 5.0	2 5½	200-215 200-225	1000-2500 1500-3000	no no	1400 1075	78-78.3 loss (4) 82.5-84 103-106.5 115-118	127.1 ---- 2.7 4.1 9.4 143.3	3.5-5	313.7
10 (5)	261.2	18.1	Zn ZnO	5.0 5.0	6½	boiling	atmos.	--	----	78.8-79.5 @ 79.5	124.5 82.1 206.6	0	-----

(1) Based on alcohol used
(2) Wgt. reactor contents and ventings at end of run
(3) Attempted ether extraction- losses-difficult sep'n.
(4) Sample bottle broken
(5) Run 10 not salted out
(6) Dehydrated before distillation, excepting run #10 and 5
(7) Run 5 not salted out

DISCUSSION OF RESULTS

1. It is not believed that the rate of reaction is a limiting factor in all cases, provided that the temperature is high enough and a satisfactory catalyst is used. Run #3 was heated up rapidly at the start until the pressure was about 450 psig, and the current turned off. The pressure rose rapidly to 1000 psig and the reactor had to be vented six times (to 750-900 psig) to keep the pressure below 1000 psig.

A higher temperature (around 230-240° C) may be necessary. This is usually the range of temperature required for the condensation of an alcohol and alcoholate using no catalyst.(3) It would seem that the catalyst does not lower the temperature required, but does increase the rate. In run #2 practically no reaction took place although the temperature was 215-230° C.

2. There are possible side reactions which could occur and nothing much can be concluded regarding this. The acids were not recovered and titrated, but it is known that there was only a small amount of acid in run #4.

3. Run #10 was not salted out, yet there is a difference of 55 grams between the alcohol used and the product distilled. Handling losses inthis run were low since distillation was directly from the reaction flask. Little if any acid was produced. There may have been polymerization to form aldehyde resins. Resinous products which could not be distilled without decomposition were observed

CONCLUSIONS

1. Zn-ZnO appears to be the best of the dehydrogenation catalysts used. Even in this case, the reaction did not proceed very far, probably because the temperature was too low during most of the run. The rate was too slow at the temperatures used.

2. No quantitative data were obtained on acids formed, but the reaction did not even proceed far enough to amount to a yield equivalent to the alcoholate.

3. The use of CaO in run #4 seems to have increased a side reaction. No definite conclusion could be reached regarding the composition of the 82-83° fraction. It may result from dehydration. It may be ethyl alcohol with some impurities, small in amount.

4. It seems certain that some resinous material was formed. Acetaldehyde can polymerize rapidly in the presence of strong alkali and heat. It would appear from the fact that some unsaturation was present in the patent procedures (2) That the aldehyde group is more easily re-hydrogenated. If the rate of hydrogenation to alcohol were not rapid enough to stop polymerization into long chains, aldehyde resins might result.

5. Small amounts of hydrocarbons (unsaturated) were formed. There may also have been small amounts of high molecular weight ethers which could result from dehydration.

RECOMMENDATIONS

1. Zn-ZnO or Zn may be the best catalyst for further work. Atemperature as high as 250°C may be desireable. Referring to run #9 , this may require a pressure of 3500-4000 psig as an approximation.

2. The use of less alcoholate, or the substitution of NaOH may be possible at the higher temperature using the Zn-ZnO catalyst, or using a Zn catalyst. KOH is more soluble in alcohol.If dehydrating conditions cause a side reaction, excessive dehydration conditions may be undesireable.

3. Better catalysts might be found.

4. Venting during a run should be avoided.It is believed that venting results in the formation of more acid, though no quantitative data were taken.

5. Agitation might give better results. Much of the dehydrogenation could have taken place near the reactor walls, resulting in high local concentrations of aldehyde intermediate and polymerization into resins.

6. A reaction time of only a few hours may be necessary using a high enough temperature and a satisfactory catalyst.

7. The lowest temperature possible using a satisfactory catalyst would be desireable since under the more vigorous conditions side reactions (as ester formation) might increase.

APPENDIX

DISTILLATION OF LIGHTER FRACTIONS WITH WATER

BOILING RANGE vs VOLUME

Run #5 fract #2

B.P. most @ 78.4 C
some @ 79.1-79.7 C
20cc and 5cc H_2O

79.5 C-------first drop
79.5-80 C ----6.1cc
80.5-81.5 C---5.0
81.5-82.5 ---0.8
to 86 C----- 1.5
to 99.5 C----1.3
to 100 C---- 2.0

Run #5 fract #1

B.P. most @ 78.4-78.5 C
dryness 79 C
20cc and 5cc H_2O

78.3 C-------first drop
78.3-79 -----1.1 cc
79-80 -------5.9
80-81 ------10.1
81-82 ------ 0.9
to 89 C----- 1.3
to 99.5 ---- 0.9
dryness----- 2.0

Run #2 fract #1

B.P. most @78.3-78.5 C
dryness 79 C
20cc and 5 cc H_2O

79 C -------first drop
79.5-80 C---- 2.7cc
80 -81 ----- 14.3
81-82.5 ----- 2.1
82.5-86 ----- 0.9
to 100 C---- 1.7
dryness ----- 1.6

Run #10 fract #2

B.P. most @ 79.5 C
dryness-- 79.8 C
20cc and 5 cc H_2O

79.5 C ---- first drop
79.5-80 -----0.6cc
80-80.5 ---- 4.4
80.5-81 ---- 7.2
81-82 ------3.4
82-84.5----- 1.4
to 88.5 C --0.8
to 96 C --- 1.o

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