

6-1954

The Catalytic Vapor Phase Butylation of Phenol

Nathan Lewis Zutty

Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Zutty, Nathan Lewis, "The Catalytic Vapor Phase Butylation of Phenol" (1954). *Honors Theses*. 2183.
<https://digitalworks.union.edu/theses/2183>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

THE CATALYTIC VAPOR PHASE BUTYLATION OF PHENOL

By

Nathan Lewis Zutty

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment for the degree of
Bachelor of Science with a Major in Chemistry.

By Nathan L. Zutty

Approved by Howard E. Sheffer

UNION COLLEGE
LIBRARY

June, 1954

8
UN92
Z96c
1954
c.2

Acknowledgment

To Doctor Howard E. Sheffer, whose
helpful guidance made this thesis
possible.

SEPT. 9, 1954

174435

Table of Contents	Page
Introduction	1
Historical	1
Experimental	4
Separation of Products	5
Distillation of Phenols	9
Distillation of Phenolic Ethers	9
Butylene Gas Analysis	10
Identification of Products	10
Summary	14
Appendix	16
Bibliography	24

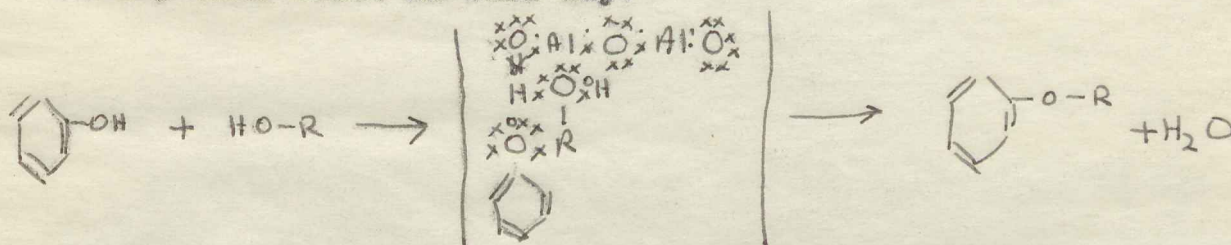
Introduction

The purpose of this experiment is to study the reaction between secondary butyl alcohol and phenol in the vapor phase. The effect of temperature upon the formation of different butyl phenols and butyl phenyl ethers was observed.

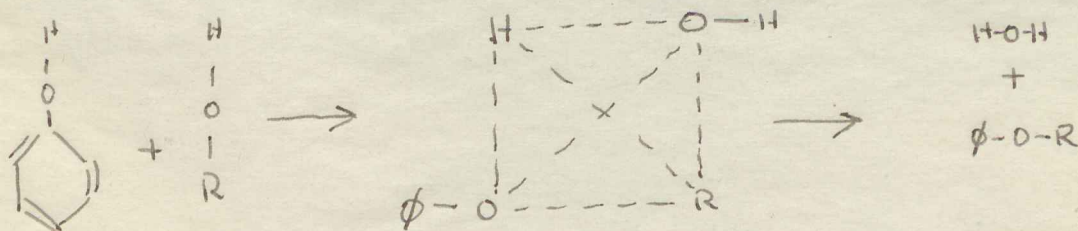
Historical

The principle products of the reaction between an alkyl alcohol and phenol over an activated alumina catalyst consist of mono-substituted alkyl phenols, alkyl phenyl ethers, and higher boiling fractions, consisting of polysubstituted alkyl phenols and ethers.

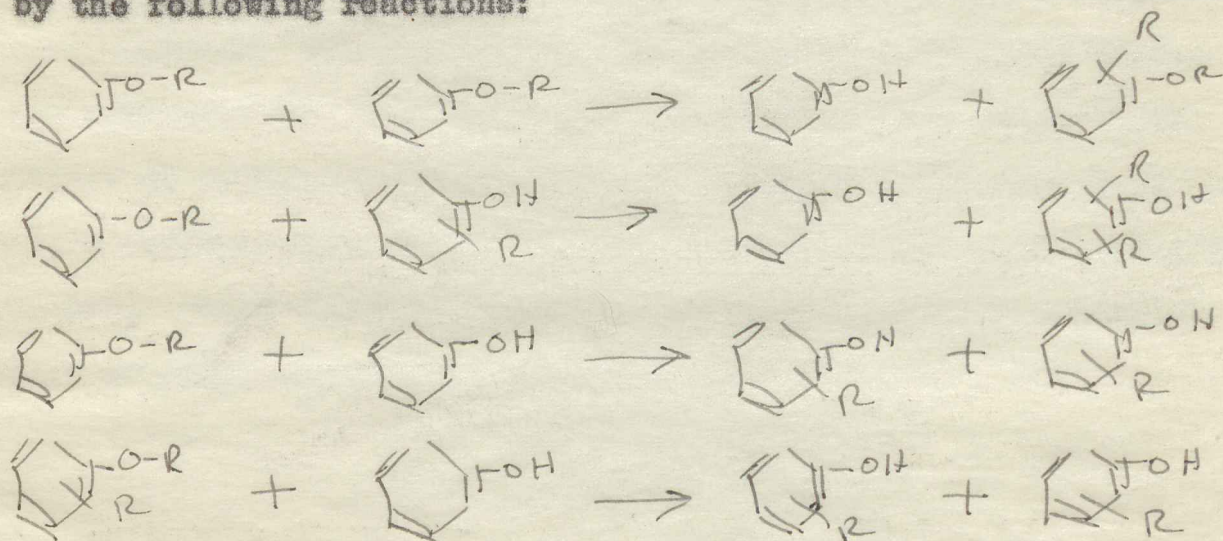
The mechanism of this reaction has not been conclusively proven, however it is supposed that all of the reaction products result from the rearrangement of an alkyl phenyl ether. This is in accordance with the activated complex theory of Eyring¹² and may come about in this way:



or more simply:



where the reacting molecules arrange themselves for reaction by means of a catalyst thru hydrogen bonding. From this phenyl ether the reaction can supposedly go in two ways: First by an intramolecular rearrangement where the alkyl group shifts to the ring and secondly, by an intermolecular rearrangement where the alkyl group of the ether reacts with another phenyl nucleus to give substituted alkyl phenols. The latter proposal has gained wider acceptance. It may be explained by the following reactions:

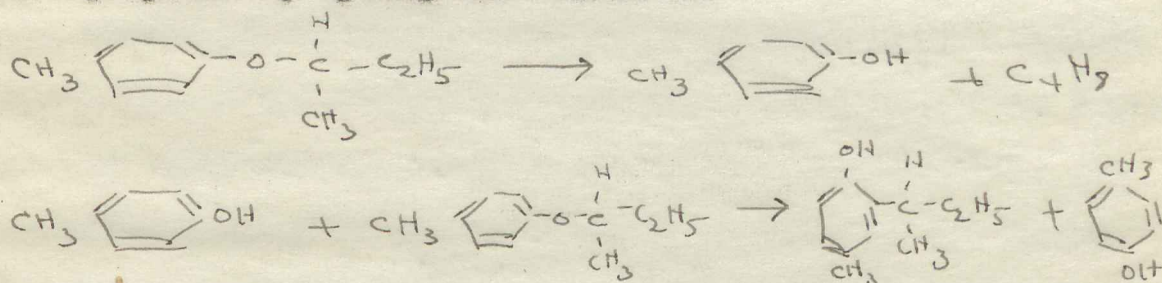


Where R is $\text{CH}_2\text{CH}_2\overset{\text{H}}{\underset{|}{\text{C}}}\text{CH}_3$.

Perry¹³ reports that increasing the temperature of the reaction results in an increase in alkyl phenols and a decrease in phenolic ethers. This would be in support of the intermolecular rearrangement theory. Quite a bit is known about the

rearrangement of alkyl phenyl ethers. Claisen¹⁴ found that allyl phenyl ethers rearrange intramolecularly to allyl phenols. But Smith¹⁵ also noticed that iso, secondary, and tertiary butyl phenyl ethers rearrange all giving the same p-tert. butyl phenol when aluminum chloride is used as a rearranging agent. This indicates that the reaction is intermolecular instead of intramolecular as Claisen¹⁴ supposed.

A third possibility was proposed by Sprung and Wallis¹⁶ who said that alkyl phenols are not formed by an intramolecular rearrangement, but are produced by result of a reaction between two molecules of an ether. They prepared various butyl phenyl ethers in optically active forms and studied their rearrangements under various conditions. In each case the alkyl phenols formed retained their optical activity. The intermolecular rearrangement proposed by Sprung and Wallis is:



This type of reaction explains the presence of olefins in the catalytic vapor phase alkylation of phenol; and moreover the presence of poly-substituted phenols which are also formed.

Experimental

A diagram of the apparatus used in the reaction run appears in figure one. The phenol-sec. butyl alcohol feed is introduced into the reaction chamber by means of nitrogen pressure upon its surface. The pressure and hence the drop rate is controlled by means of a glycol pressure regulator which works by lowering or raising the center tube. The feed solution, in a 1:1 molar ratio, passes up thru a capillary tube and then drops into the reaction chamber. The drop rate can be observed in the glass tube which leads into the heated catalyst chamber. The reactants drop into a heated stainless steel tube, 3.5 feet long (figure two), vaporize and pass thru the catalyst chamber. They condense in the lower section of the tube, and are collected in a Grignard flask at the bottom. The reaction chamber was divided into three parts all heated and carefully controlled by means of two variacs and a rheostat. The temperature measured by means of a chromel alumel thermocouple which is placed at intervals along the reaction chamber in a tube concentric with it. The E.M.F. developed by this system is measured by a Leeds-Northrup potentiometer set up. The temperature may be controlled separately in either of the three sections by the voltage control apparatus which are connected to the heaters. Thirty-two grams of activated alumina catalyst are used for a six hour

run, this fills the catalyst bed to a depth of four inches and results in a contact time of approximately 3.5 seconds. 315 milliliters of feed were used for the run at an average temperature of 287^o centigrade. The temperature is measured at one inch intervals along the reaction tube and then averaged to find the temperature of the run. The gases formed during the reaction, including the nitrogen used to control the drop rate were collected in a twenty liter bottle for later analysis.

Separation of Butylphenols from Phenolic Ethers (13)

The crude product is treated with 600cc. of 20% sodium hydroxide. The two layers are separated and the alkaline layer is then washed four separate times with 50cc. of ethyl ether to remove any remaining phenolic ethers. These extractions are then combined with the original phenolic ether layer. The phenolic ethers are now treated with 50cc. of 20% sodium hydroxide. These extracts are combined with the original alkaline layer.

The phenolic ethers are now dried with anhydrous sodium sulfate. The alkaline layer is now acidified with concentrated hydrochloric acid (250cc.). After cooling the phenolic and aqueous layers are separated. The aqueous layer is washed four times with 50cc. of benzene each time.

The ethyl ether and benzene are roughly distilled from the ether and phenolic layers respectively, and the two are ready for fractional distillation.

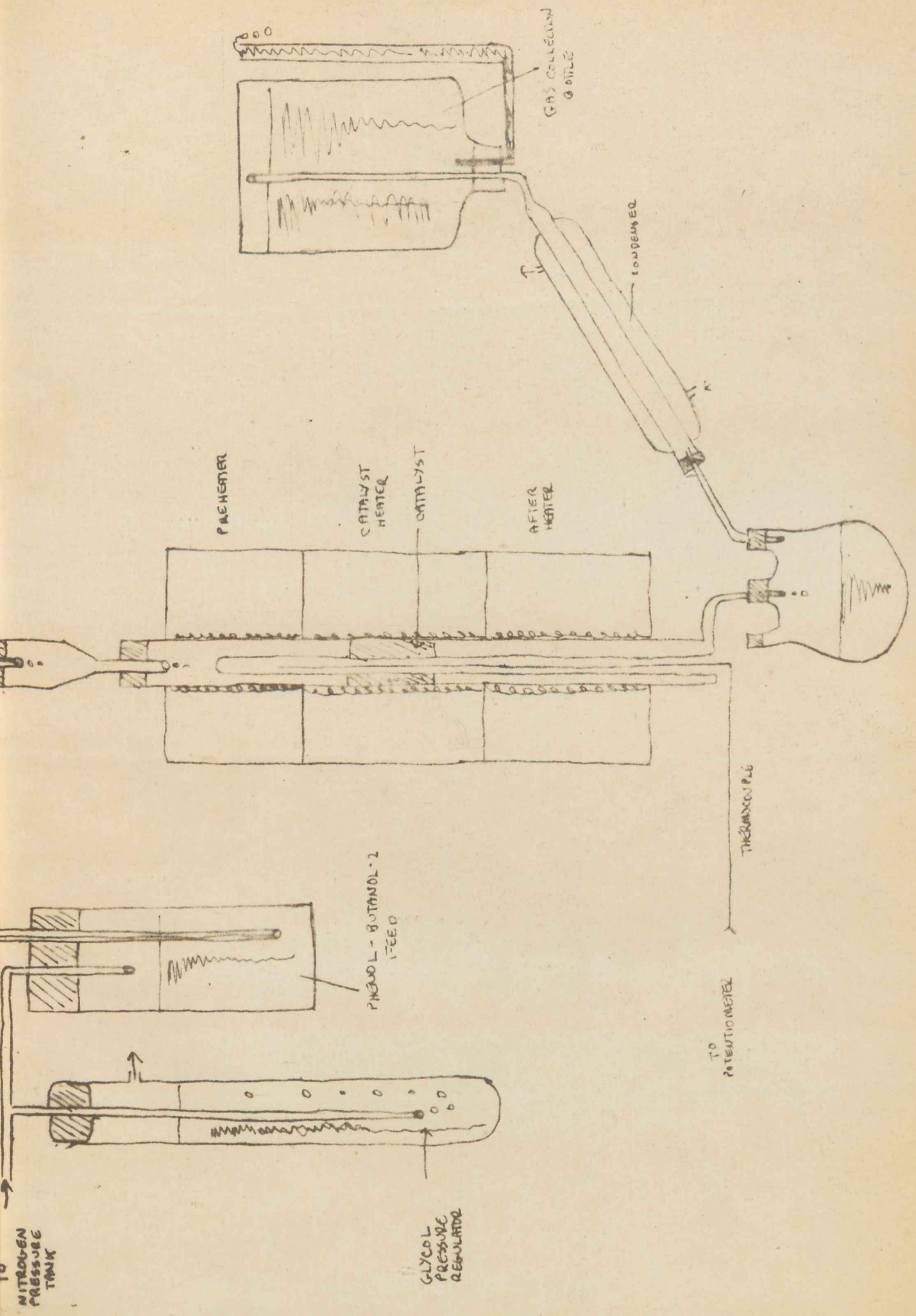


FIGURE II
DETAILED DIAGRAM OF REACTION TUBE

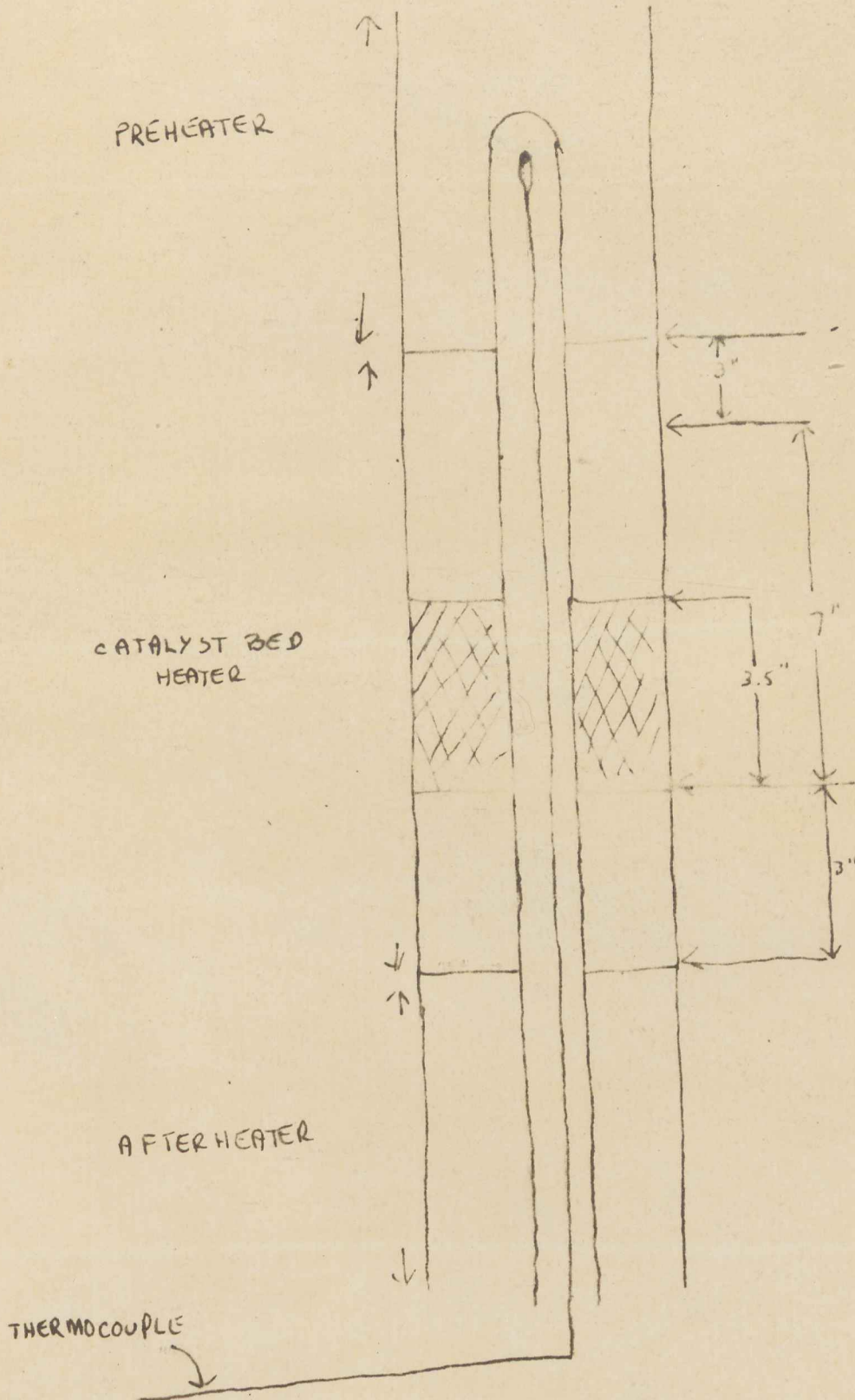
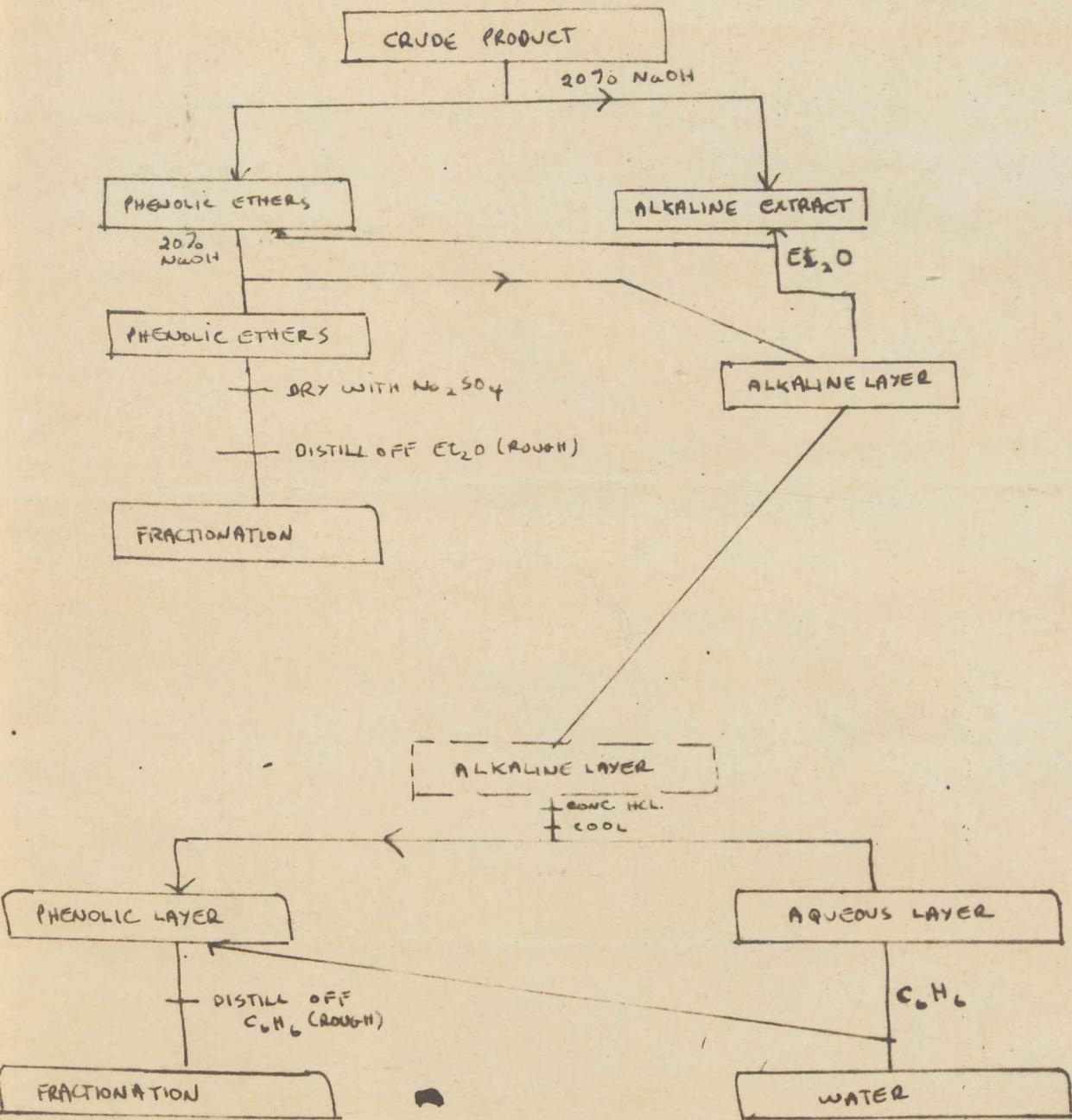


FIGURE III

FLWSHEET FOR SEPARATION OF PHENOLS FROM PHENYL ETHERS



Distillation of Phenols

After the phenols are separated from the phenolic ethers they are fractionally distilled. A column of thirty theoretical plates is used (figure four). It is approximately four feet tall and one-half inch in diameter and is packed with 3/32 of an inch stainless steel helices. For fractionation a reflux ratio of 15:1 is used; this means that for every fifteen drops condensing at the top of the column, one is withdrawn. The column is insulated by an outer shell of diatomaceous earth. The column and stillpot are heated by means of variacs. Good control is obtained this way.

As the products distilling are high boiling and melting the outlet from the condenser was heated by an infra-red heat lamp to prevent clogging.

An inert chaser, diphenylamine, is added to the stillpot to insure complete fractionation.

Graphs and the data of this run are found in the appendix.

Distillation of Phenolic Ethers

The ethers contain water and must be azeotropically distilled with benzene to insure complete drying as the sodium sulfate was not effective. If this is not done the phenolic ethers form a constant boiling mixture with their water and fractionation could not be attempted.

Since the amount of ethers formed are small, a small

three bubble Snyder column is used. This corresponds to three theoretical plates and has no hold up. (figure 5) The column is wrapped in asbestos paper since the ethers are very high boiling. A good separation is obtained. Graphs and data of this distillation appear in the appendix.

Butylene Gas Analysis

The gas produced during is assumed to consist of butylenes. Since it comes over mixed with nitrogen, it was found necessary adsorb the gas in a solution of bromine in carbon tetrachloride to rid it of its nitrogen. The nitrogen is collected in a large bottle and the amount of butylenes produced are found by subtraction. The gas was passed thru the adsorbant twice to insure complete adsorption.

Total volume of gases collected during the run:	21.8liters
Volume of gases after adsorption:	13.1
Total volume of butylenes produced during run:	8.7

This volume of butylenes corresponds to 0.366 moles or 11.77 grams of gas produced. A diagram of the adsorption apparatus is shown in figure six.

Identification of Products

Derivatives were made from the cuts obtained during the fractional distillation. Since no literature values for derivatives of sec.-butyl phenols were found, it was found

STILL HEAD
THERMOMETER

COLUMN
THERMOMETER

CONDENSER

HEAT
LAMP

TO VARIAC

IV
ING COLUMN

GLASS SHELL

DIATOMACEOUS EARTH

NICHROME HEATING WIRE
FOR COLUMN

STAINLESS STEEL
HELICES

HEATING PAD FOR
STILL POT

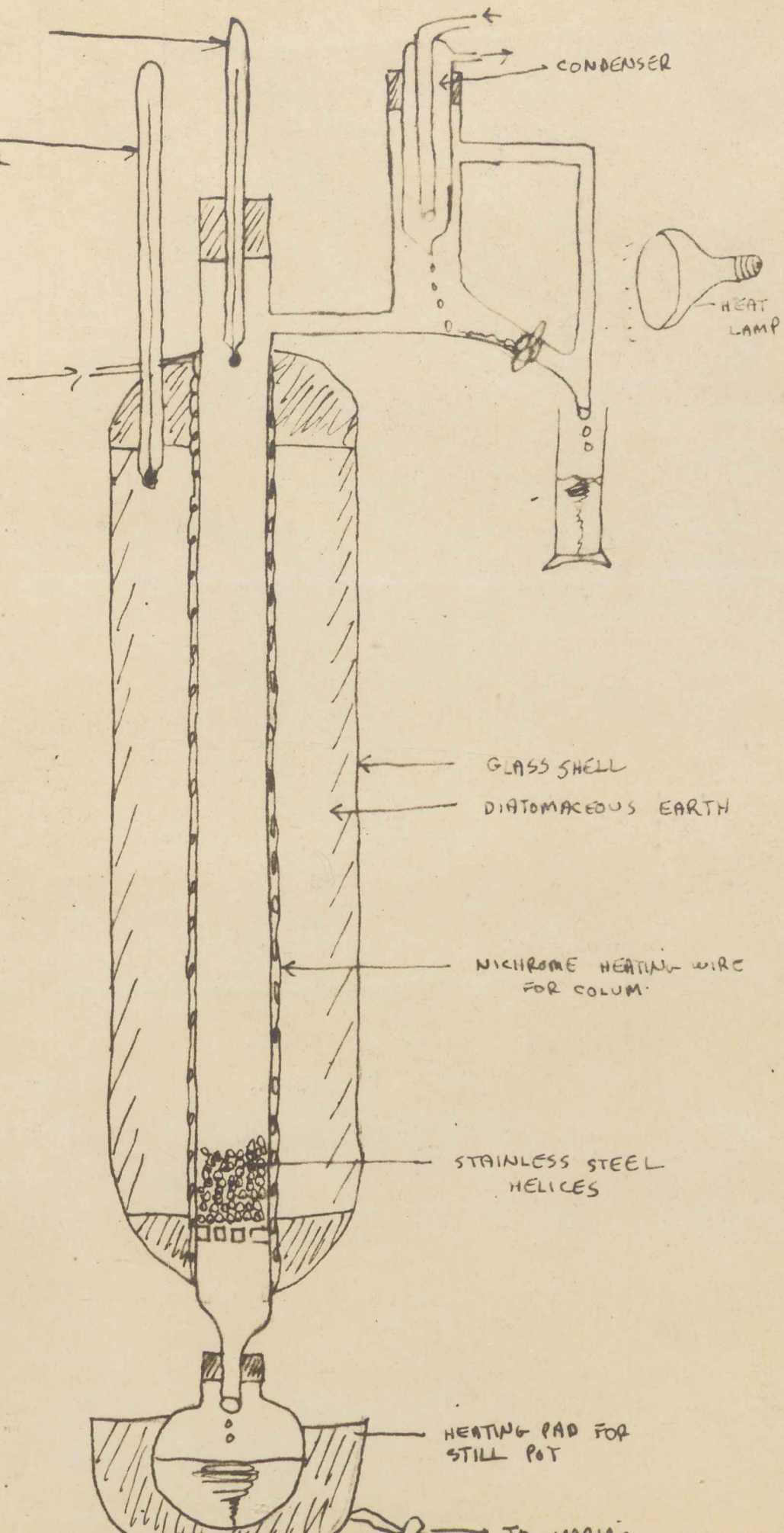


FIGURE V.
DISTILLATION OF PHENOLIC ETHERS.

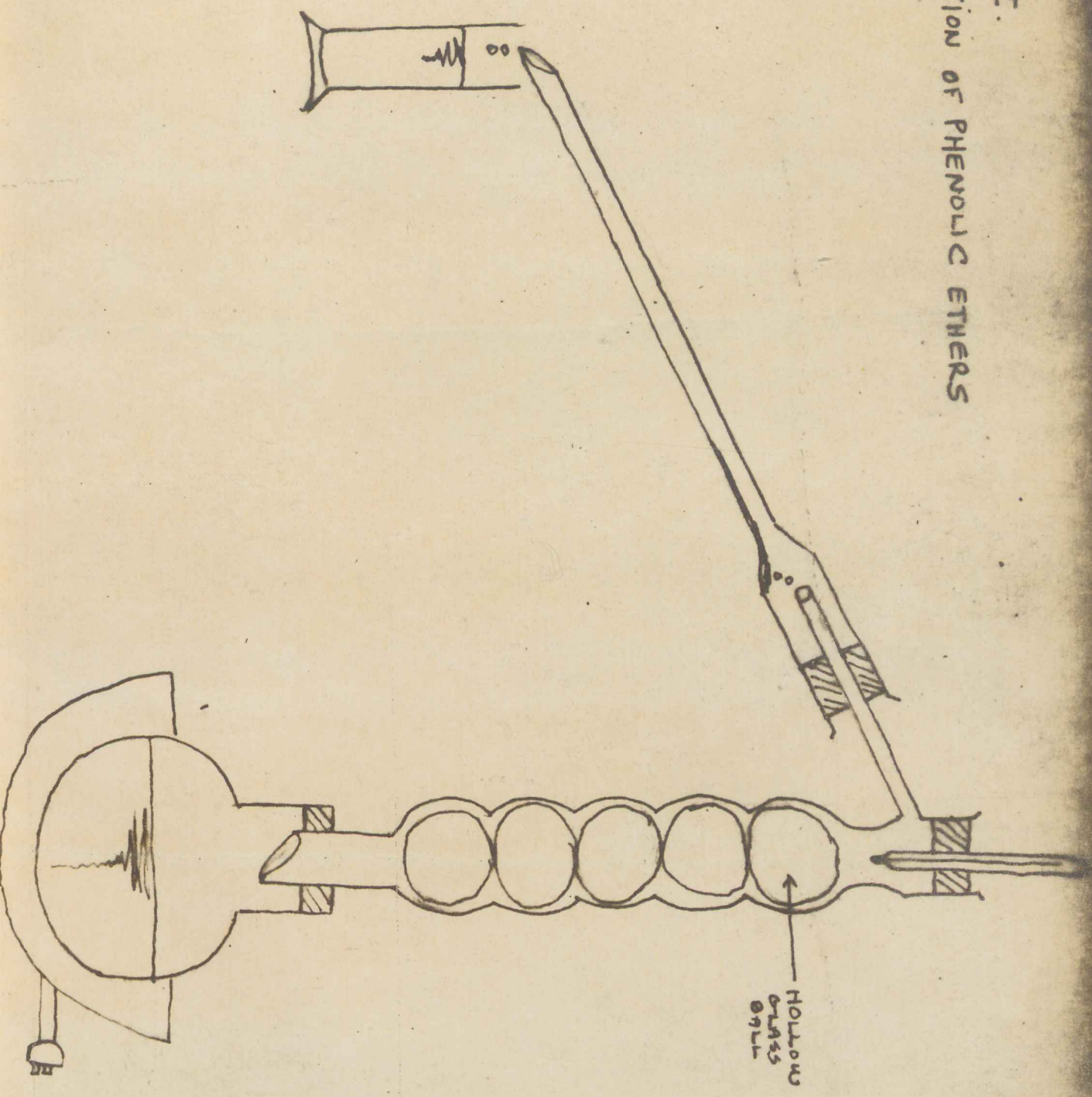
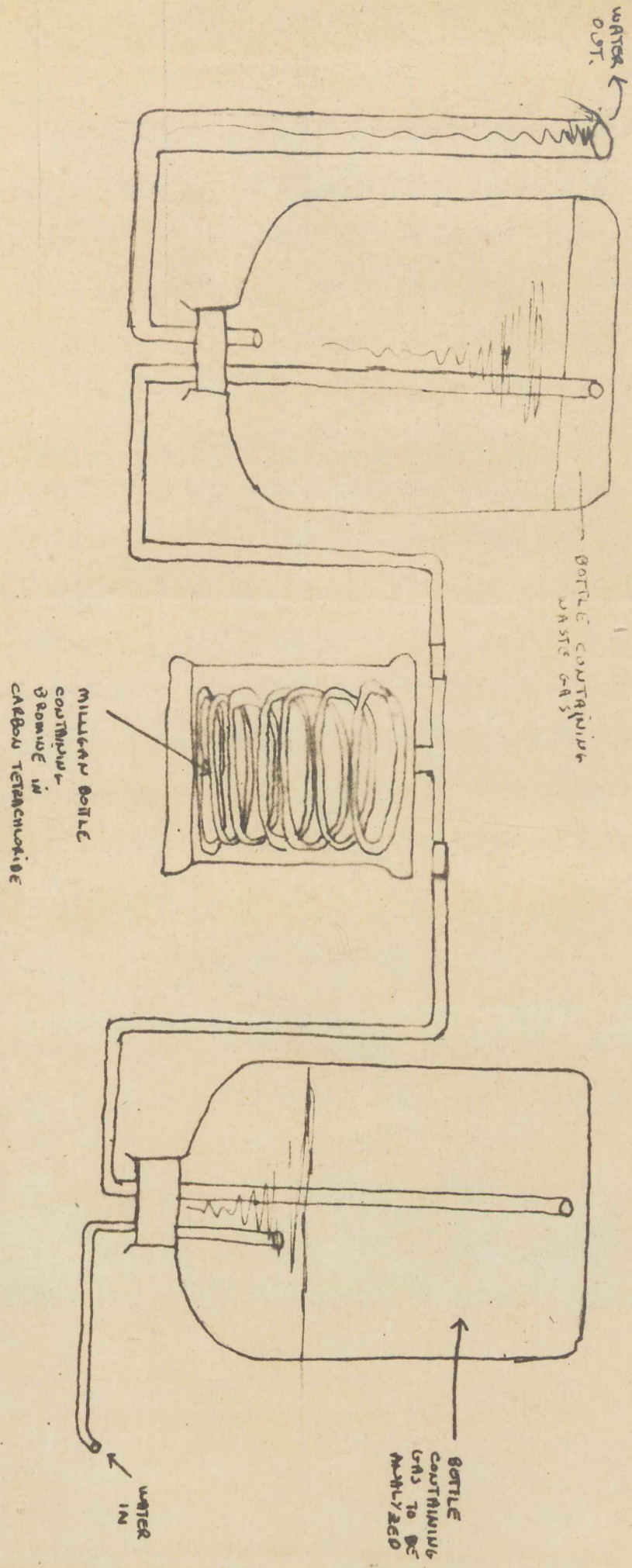


FIGURE VI
BUTYLENE GAS ANALYSIS APPARATUS



necessary to prepare derivatives of pure ortho and para secondary butyl phenol, and then compare these with those made of the cuts. Much difficulty was encountered in finding a solid derivative of these substituted phenols however, it was found that the p-nitrophenylurethan derivative gave reproducible results. These derivatives were made according to the method put forth by Shriner and Fuson¹⁶; however it was found that the addition of two drops of pyridine during the synthesis greatly increased the yield of derivative. The boiling points of the cuts obtained during fractionation were of some aid in identifying the products.

Thru derivatives and boiling points, ortho and para sec.-butyl phenol were shown to be formed. From boiling points alone, 2,4-di-sec.-butyl phenol, and ortho and para sec.-butyl phenyl-sec.-butyl ether were shown to be present.

Summary

The reaction between sec.-butyl alcohol and phenol in the vapor phase over an activated alumina catalyst at a temperature of 337°C. was studied.

Fifty per-cent of the phenol was converted; this is in agreement with Perry¹⁵, Lemieux¹⁷, and Putman¹⁸.

The effectiveness of the catalyst remained good for

the whole six hour run. The larger percentage of products formed consisted of substituted butyl phenols.

Since a large percentage of butyl phenols formed were high boiling and probably polysubstituted; it is recommended that for greater yields of monosubstituted butyl phenols a lower temperature should be used for the reaction.

APPENDIX

Reaction Run

Activated alumina is used as a catalyst; and a 1:1 molar ratio of sec.-butyl alcohol-phenol feed. A chromel-alumel thermocouple and a Leeds and Northrup potentiometer are used for temperature measurements.

1. weight of feed used	290 grams
2. volume of feed used	315 cc.
3. weight of product at finish	226 grams
4. volume of product at finish	228 cc.
5. volume of gas collected at finish	21.8 liters
6. weight of catalyst used	32.0 grams
7. volume of catalyst used	36.0 cc.

Data for the reaction run

Time	Feed Vol. (ml)	Drop Rate per min.	0" heated feed temp.	*3" (mv.)	**Variac #1 (volts)
10:15	435	33	9.8	9.5	65
10:20	420	27	11.0	11.0	65
10:35	400	19	11.2	11.2	65
10:50	395	25	11.4	11.4	65
11:10	375	20	11.5	11.5	63
11:22	365	25	11.3	11.3	63
11:36	360	23	11.1	11.1	63
11:48	355	30	11.5	11.5	63
12:00	355	34	11.1	11.1	63
12:11	325	25	11.5	11.5	63
12:20	315	26	12.0	12.0	57
12:30	305	24	12.0	12.0	53
12:36	300	22	11.6	11.6	53
12:47	295	23	11.5	11.5	50
1:07	280	26	11.0	11.0	52
1:15	275	24	10.8	10.8	52
1:25	263	28	10.5	10.5	52
1:35	255	26	10.5	10.5	54
1:43	245	28	10.5	10.5	54
2:00	235	22	10.5	10.5	55
2:07	230	22	10.5	10.5	55
2:16	223	26	10.3	10.3	55
2:26	212	24	10.2	10.2	55
2:40	201	22	10.0	10.2	55
2:50	195	20	10.2	10.2	57
3:00	190	20	10.0	10.0	57
3:20	160	24	10.0	10.0	57
3:27	155	24	10.0	10.0	57
3:45	140	26	10.2	10.2	57
4:00	135	16	10.2	10.2	57
4:15	120	50	10.0	10.0	57

The room temperature was 25°C. and the barometer read 750.0 mm/Hg.

* This is the temperature at the top of the catalyst bed in millivolts. Additional readings were taken every inch along the reaction tube. Since this is a typical set there is no need to repeat other groups of data.

** Variac #2 corresponded to the readings on variac #1, so again there is no need to present its figures. The rheostat read 3.5 inches throughout the run.

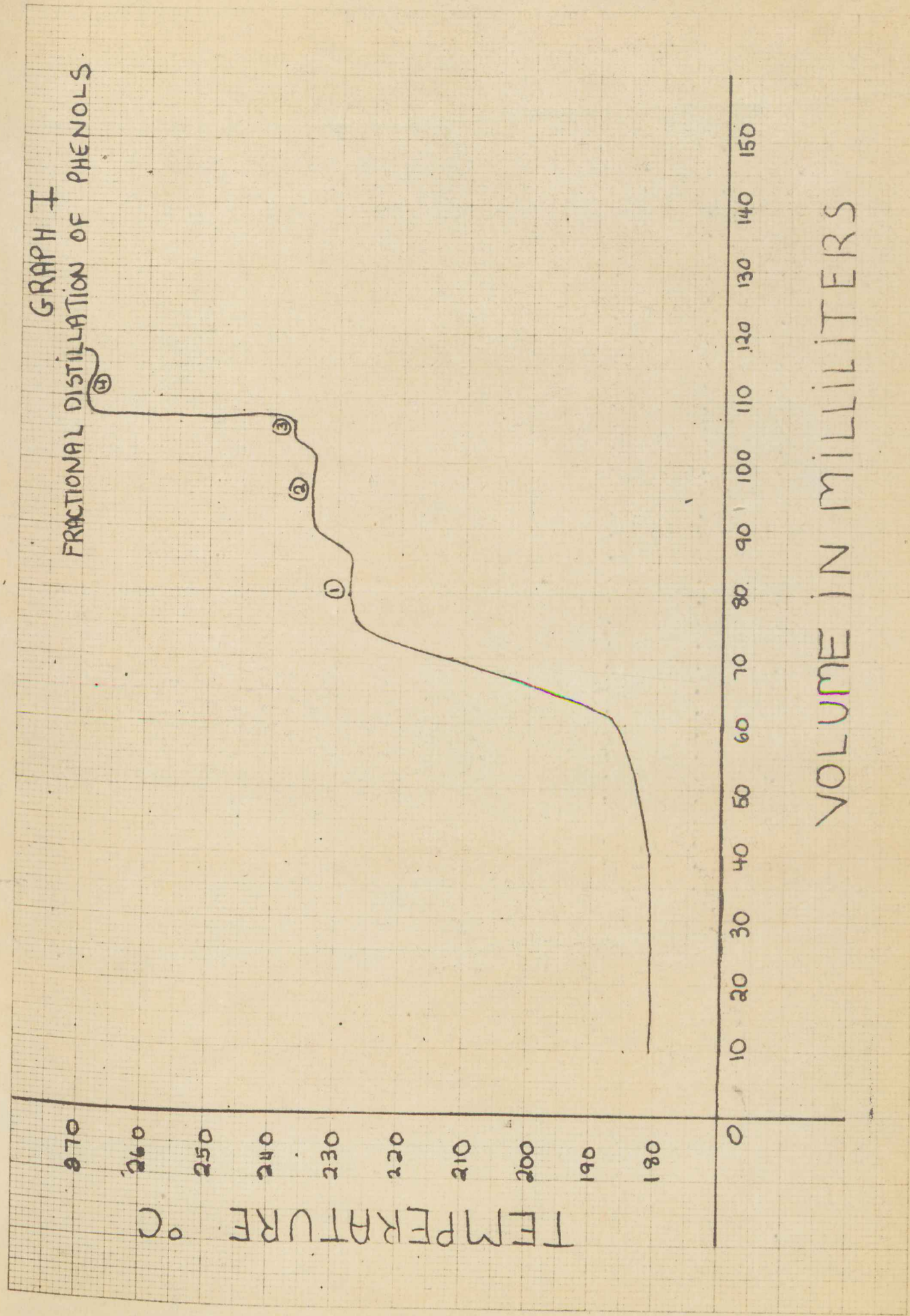
Data for the Fractional Distillation of the Phenols

Time	Temperature		Variacs		Cut#	(ml.)		(gn.) Wt.
	Column	Head	Column	Pot		(ml.) Vol.	Total Vol.	
3:20	175	182	120	80	1	10	10.0	
3:30	175	182	120	80	1	10	20.0	
3:40	174	183	100	70	1	12	22.0	
3:50	180	182	106	75	1	7.0	29.0	
4:00	180	182	110	76	1	6.0	35.0	
4:13	181	183	110	72	1	9.0	44.0	58.5
9:53	180	183	114	90	2	3.0	47.0	
10:00	177	185	113	70	2	7.0	54.0	10.1
10:10	181	185	120	74	3	1.5	55.5	
10:16	185	188	118	80	3	2.5	58.0	1.3
10:27	190	192	118	70	4	3.0	61.0	1.9
10:32	192	208	120	78	5	4.0	64.0	1.9
10:40	207	212	120	90	6	1.8	66.0	2.5
10:45	209	218	120	90	7	3.0	69.8	1.1
10:47	213	227	90	90	8	3.0	72.8	2.0
10:50	230	227	90	75	9	2.0	75.8	
10:55	230	227	94	75	9	2.5	77.8	
11:00	225	227	100	90	9	2.7	80.3	
11:08	225	231	100	101	9	3.5	83.0	6.5
11:15	225	233	100	101	10	5.0	88.5	2.2
11:18	229	233	100	101	11	2.5	91.5	
2:05	230	233	120	110	11	2.0	94.0	6.7
10:00	232	233	110	110	12	2.0	96.0	
10:12	233	233	110	110	12	2.0	98.0	
10:20	233	236	115	118	12	1.5	100.0	
10:25	238	236	115	118	12	2.5	101.5	3.8
10:42	239	269	130	120	13	1.0	104.0	2.7
10:45	275	269	130	120	14	1.5	105.0	
10:50	276	269	130	120	14	1.0	106.5	
11:05	280	269	130	120	14	1.5	107.5	
11:12	274	269	130	118	14	2.0	109.0	4.9
11:20	282	303	130	122				

25.0 grams of diphenylamine were added as a chaser (B.P. 302°C).
At the end of the distillation 24 grams of diphenylamine
were left in the stillpot. The barometer read 756mm/Hg.

Weight of product before fractionation: 182 grams
Total weights of cuts 1-14: 166 grams
Weight loss due to benzene: 76 grams

GRAPH I
FRACTIONAL DISTILLATION OF PHENOLS



VOLUME IN MILLILITERS

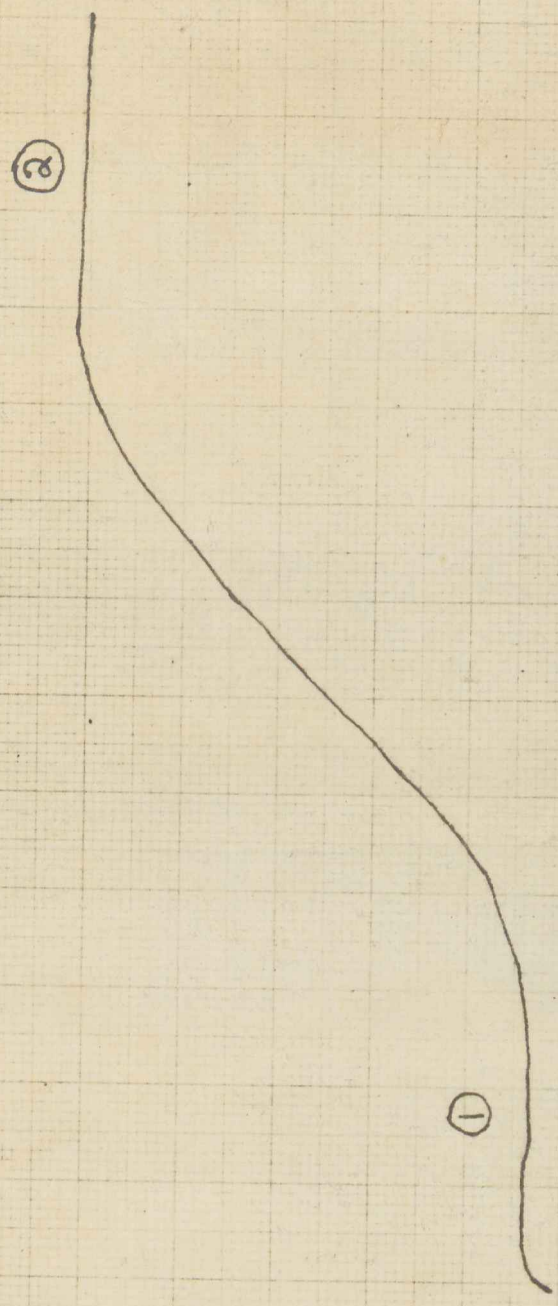
GRAPH 2
FRACTIONAL DISTILLATION OF PHENYL ETHERS

TEMPERATURE °C

260
255
250
245
240
235
230
225

VOLUME IN MILLILITERS

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
---	---	---	---	---	---	---	---	---	---	----	----	----	----	----	----



Fractionation of Phenolic Ethers

Cut #	Temp. °C.	Vol. (ml.)	Total Vol. (ml.)	Wt. (gms.)
1	228	2.2	2.2	2.5
2	228	2.2	4.4	2.3
3	235	3.0	7.4	2.7
4	250	4.0	11.4	3.1
5	250	3.9	15.2	3.0

At start ethers weighed: 86.5 grams
 Weight of butylphenyl ethers: 15.4 grams
 Weight loss due to water and ethyl ether: 73.1 gms.

Derivatives

I. From pure compounds:

Compound	Melting Point	% Yield
p-nitrophenylurethan of o-sec.-butyl phenol	130°C.	92.0
p-nitrophenylurethan of p-sec.-butyl phenol	170	35.0

II. The p-nitrophenylurethan of:

Cut#	Vol.	Boiling range	M.P. of Derivative	% Yield
9-10	8.7 ml.	227-230°C	137-145	12.5
11-12	6.0	255	137-138	10.0
13	4.0	238-259	166-168	5.0
14	7.0	275-282	170	10.0

Physical Constants

I. Butyl phenols

Butyl phenol	M.P.	B.P.	D	n_D^{25}	Der.	M.P.	Ref.
o-n		234-7	.975	1.5205	h		1,2,5
m-n		247-9	.974		a	67-8	1,5
p-n	22	248	.978	1.4981	a b c	27 81 115	1,2,5
O-sec.		228-51 226-8	.975	1.5200	b c d e f a	oil oil oil oil 138 oil	thesis, 5,7,8,9
p-sec.	61-2 53-4	240-2 239-42 236	.966 .986	1.5150 1.5182	a b f g	Oil oil 170 54-5	thesis, 5,7,8,9,11
2,4-di-sec.		265-7	.934	1.5072			8
O-tert	96						5
m-tert	40.6	240					5,6
p-tert	99	236-3 232-5 230	.906	$\frac{114}{4}$	a b	81-2 86.5	5,8,10,11
O-iso							
m-iso							
p-iso		235-9	.980	1.5319	b	124-5	

II. Ethers

Butyl phenyl ether	B.P.	D	n_D^{25}	Der.	M.P.	Ref.
n	206	.9515	1.5019	h	163-4	2,3,4
sec.	193	.973	1.4943			11
tert.	192					11
iso	196	.924	1.4932			11

Code for derivatives:

a	benzoate
b	aryloxyacetic acid
c	phenylurethan
d	α -naphthylurethan
e	diphenylurethan
f	p-nitrophenylurethan
g	p-chlorobenzoate
h	sulfonamide
i	picrate

All densities are taken at 20°C. with respect to water at 4°C.
except where otherwise noted.

Bibliography

1. Read and Mullin, J.A.C.S. 50 1764(1928)
2. Smith, Ibid. 56 1419(1934)
3. Baril and Megrdichian, Ibid. 58 1415(1936)
4. Huntress and Carten, Ibid. 62 603(1940)
5. Miller, Ibid. 54 1196(1932)
6. Carpenter, Easter, and Wood, J. Org.Chem. 16 586(1951)
7. Monroe and Hand, J.A.C.S. 73 487(1951)
8. Croxall, Sowa, and Niewuland, J.Org.Chem. 2 254(1937)
9. Read, Hewitt, and Pike, J.A.C.S. 54 1194(1932)
10. Hutson and Maieh, Ibid. 55 3720(1933)
11. Smith, Ibid. 55 3720(1933)
12. Gilman, "Organic Chemistry" Volume 1
13. Perry, Thesis presented to Union College Chemistry Dept.
14. Claisen and Kisleb, Ann. 401 21(1913)
15. Smith, Ber. 55 3718(1933)
16. Shriner and Fuson, "Identification of Organic Compounds"
17. Lemieux, Thesis presented to Union College Chemistry Dept.
18. Putman, Ibid.
19. Sprung and Wallis, Ber. 56 1715(1934)