METHYLATION OF PHENOL

by

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

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INTRODUCTION

The purpose of this investigation is to study the effect of temperature on the reaction between methyl alcohol and phenol over an activated alumina catalyst. This effect is determined by observing the difference in the amounts of phenolic and phenolic ether compounds formed at these temperatures, which range from approximately 325° c to 420° c.

HISTORICAL

Reacting methanol with phenol in the vapor state over activated alumina catalyst, results in the formation of anisole, cresols, and some higher boiling ethers and phenols.

Many proposals have been made as to the mechanism of the reaction, but no posative experimental evidence has been uncovered as to the true nature of the reaction. One of the most widely accepted theories is that anisole is produced first in the reaction and this then undergoes a rearrangement to form the cresols and other products. This theory is somewhat supported by the fact that if anisole is passed over the catalyst the same products, in similar yields, are formed as with the methanol and phenol. To account for these results it is proposed that a neutral methyl radical migrates from the anisole to some foreign nucleus. If this latter proposal is true then the reaction is actually not a true rearrangement, and is certainly not intramolecular in nature.

The production of phenols, cresols and anisoles can be accounted for by reactions of the following type.

$$C_6H_5OMe + C_6H_5OMe \rightarrow C_6H_5OH + MeC_6H_4OMe$$

$$C_6H_5OMe + MeC_6H_4OH \rightarrow C_6H_5OH + Me_2C_6H_3OH$$

$$C_6H_5OMe + C_6H_5OH \rightarrow C_6H_5OH + Me\ C_6H_4OH$$

$$MeC_6H_4OMe + C_6H_5OH \rightarrow MeC_6H_4OH + MeC_6H_4OH$$

EXPERIMENTAL WORK

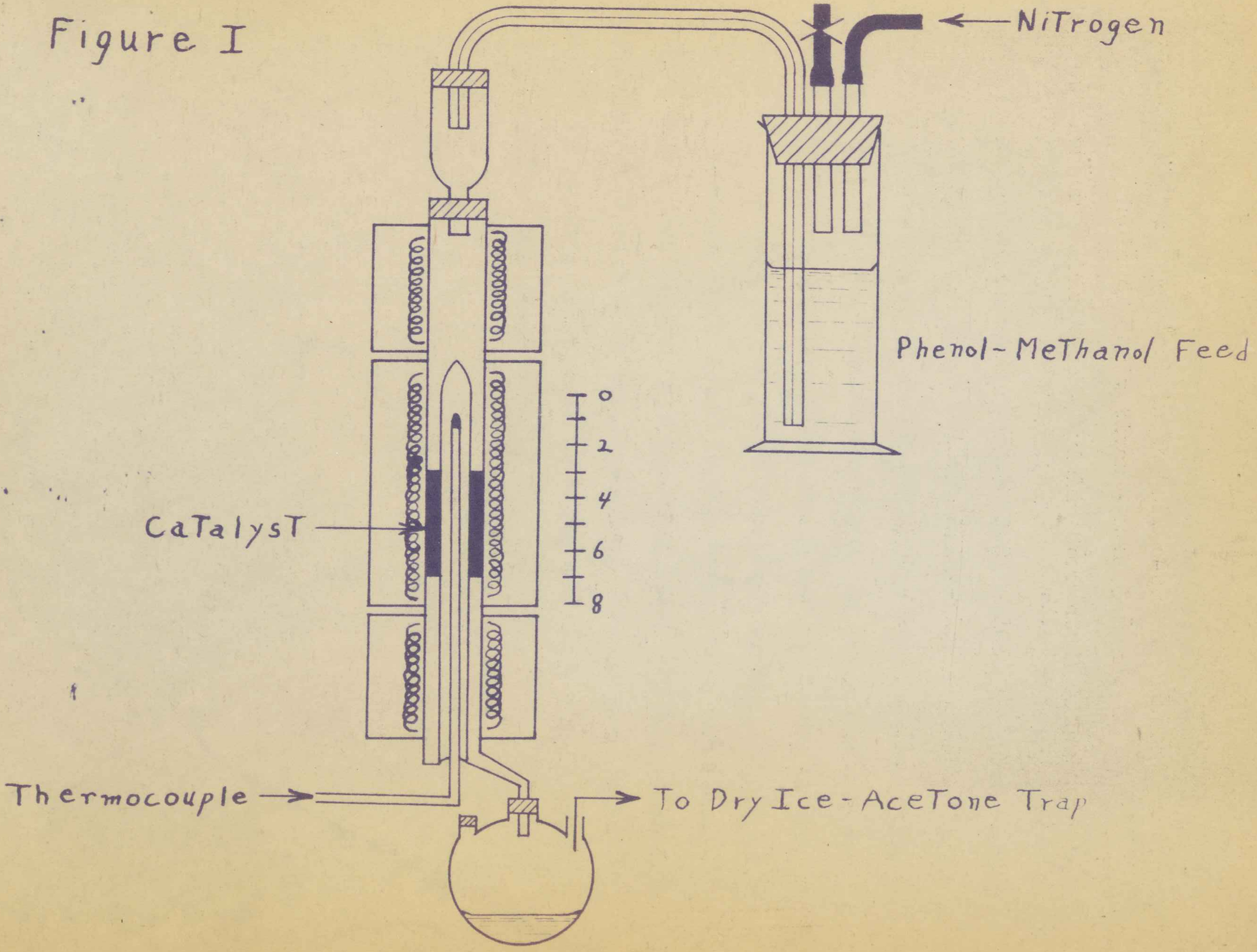
REACTION RUN

A diagram of the apparatus used for methylating the phenol is illustrated in Figure I on the following page. The converter shown is divided into three heated sections the first acting as a preheater, besides helping to keep the catalyst bed at a constant temperature. The temperature in each section is controlled separately by regulating the voltage supplied by two variacs and a rheostat. The catalyst bed is centrally located in a three and one half foot steel tube.

The temperature of the catalyst bed is measured by means of a chromel-alumel thermocouple and a potentiometer set up. The hot junction of the thermocouple is entered into the catalyst bed by means of a small steel tube inside of the larger steel tube. By moving the thermocouple wire up or down the temperature may be determined at any spot in the bed, or in the tube. The scale shown next to the converter on the diagram indicates the position of the thermocouple in the typical reaction run data sheet in the appendix.

In the alkylation run the phenol-methanol feed solution is forced out of the large graduated cylinder, thru the capillary tube, and into the converter by utilization of nitrogen under pressure. Varying the pressure applied to the surface of the feed solution is the method used to obtain the proper amount of feed entering the converter. In order to control this pressure to a greater degree, a glycol pressure aid is employed.

Figure I


Nitrogen
Phenol-Methanol Feed
0
2
4
6
8
Catalyst
Thermocouple
To Dry Ice-Acetone Trap

As the drops of solution enter the converter they are preheated for a very short period and then fall on the catalyst bed. The catalyst bed consists of thirty two grams of one eighth inch activated alumina pellets, which in the tube used, gives a depth of about three and three quarter inches. After passing thru the catalyst bed the product is collected in a round bottom flask. An outlet from this flask is led thru a trap, set in a dry ice-acetone bath, to catch any gaseous products such as dimethyl ether which may be formed in the reaction. In none of the three reactions carried out however was any dimethyl ether found in the trap. Each run takes three hours, and during this interval about 220 ml. of phenol-methanol feed pass into the converter. Two or three milliliters of product is lost in each run due to a slight leak in a joint of the steel tube.

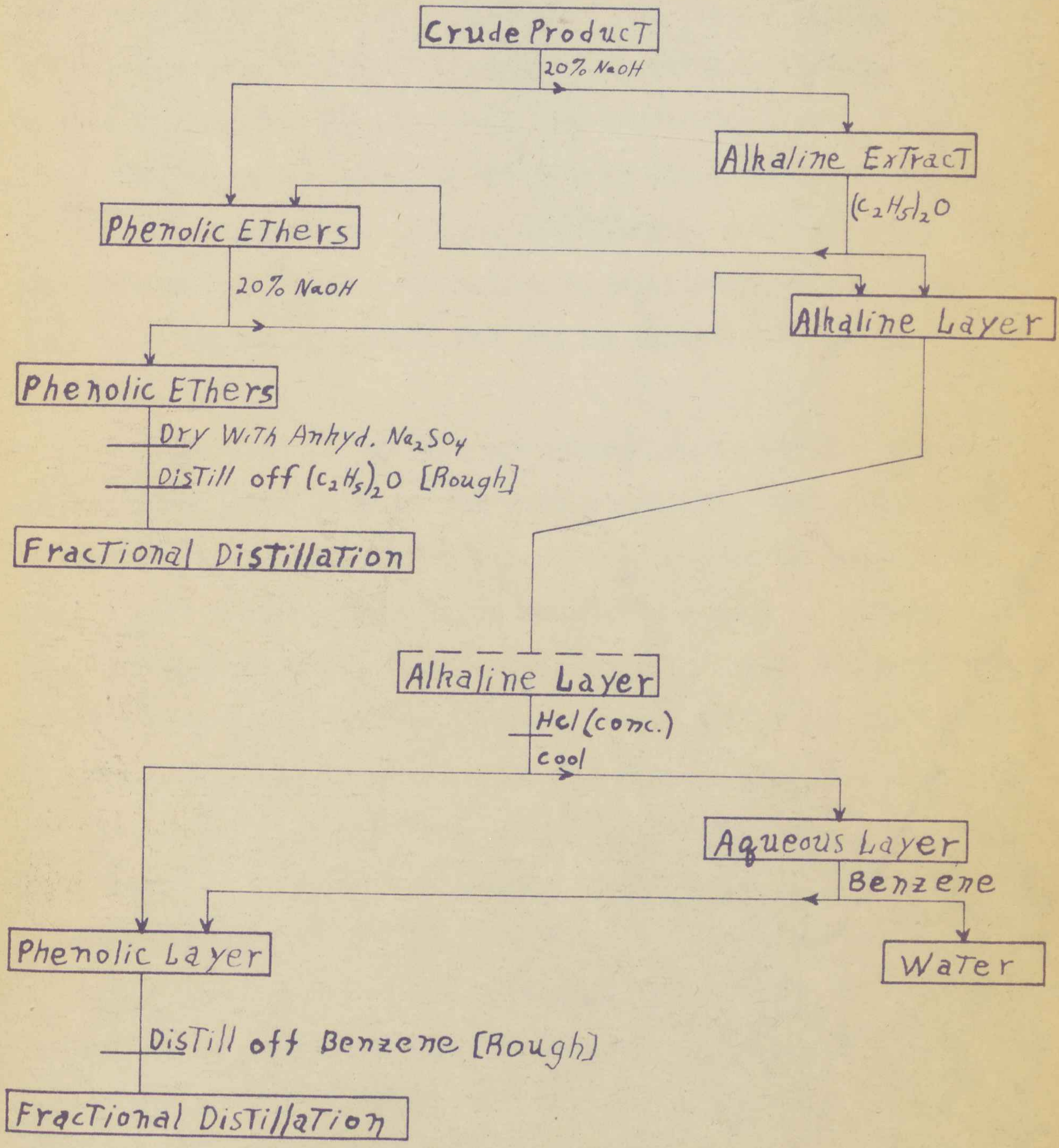
SEPARATION OF PHENOLS AND PHENOLIC ETHERS

The crude product is first treated with 600 ml. of 20 % sodium hydroxide. The two layers are separated and the alkaline layer is then washed four separate times with 50 ml. of ether to remove any remaining phenolic ethers. These extractions are combined with the original phenolic ether layer. The phenolic ethers are now treated with two separate portions of 50 ml. of 20 % sodium hydroxide. These extracts are combined with the original alkaline layer. The phenolic ethers are now dried with anhydrous sodium sulfate, filtered, and roughly distilled to remove the ethyl ether.

The alkaline layer is next acidified with concentrated hydrochloric acid and the phenolic and aqueous layers are separated. The aqueous layer is washed four times using 50 ml. of benzene and these extracts are combined with the previously separated phenolic layer. The phenols are now roughly distilled to remove most of the benzene.

Figure III

Flow Sheet of Separation



DISTILLATIONS

The phenols are fractionally distilled in the column illustrated in Figure III on the following page. This column is four feet high and is packed with one thirty second inch stainless steel helices. Operating at total reflux the number of theoretical plates is approximately twenty five. Both the column and the pot are heated electrically using two variacs as regulators. On one distillation the loss of product was computed and this amounted to approximately eight percent. Part of a typical distillation run is illustrated in the appendix.

A great deal of trouble was encountered with the glass ball socket joint between the column and pot. Using the type clamp (a), illustrated with the column, seemed to produce too much strain on the glass joint causing the neck of the pot to crack if the clamp was tightened too much. This presented a problem because unless the joint is tight a high distillation loss of product is incurred. It was finally discovered that by using a clamp of the type (b), illustrated, the strain was more evenly divided and the joint could be made fairly tight without cracking the neck of the pot.

Since the phenolic ethers consist of only a small amount of material a different distillation set up was used. This apparatus is illustrated in Figure IV. It consists of two 25 ml. distilling flasks held together in the manner shown. Cold water running over the receiving flask condenses the vapors very nicely. This does not by any means give a really

Figure III

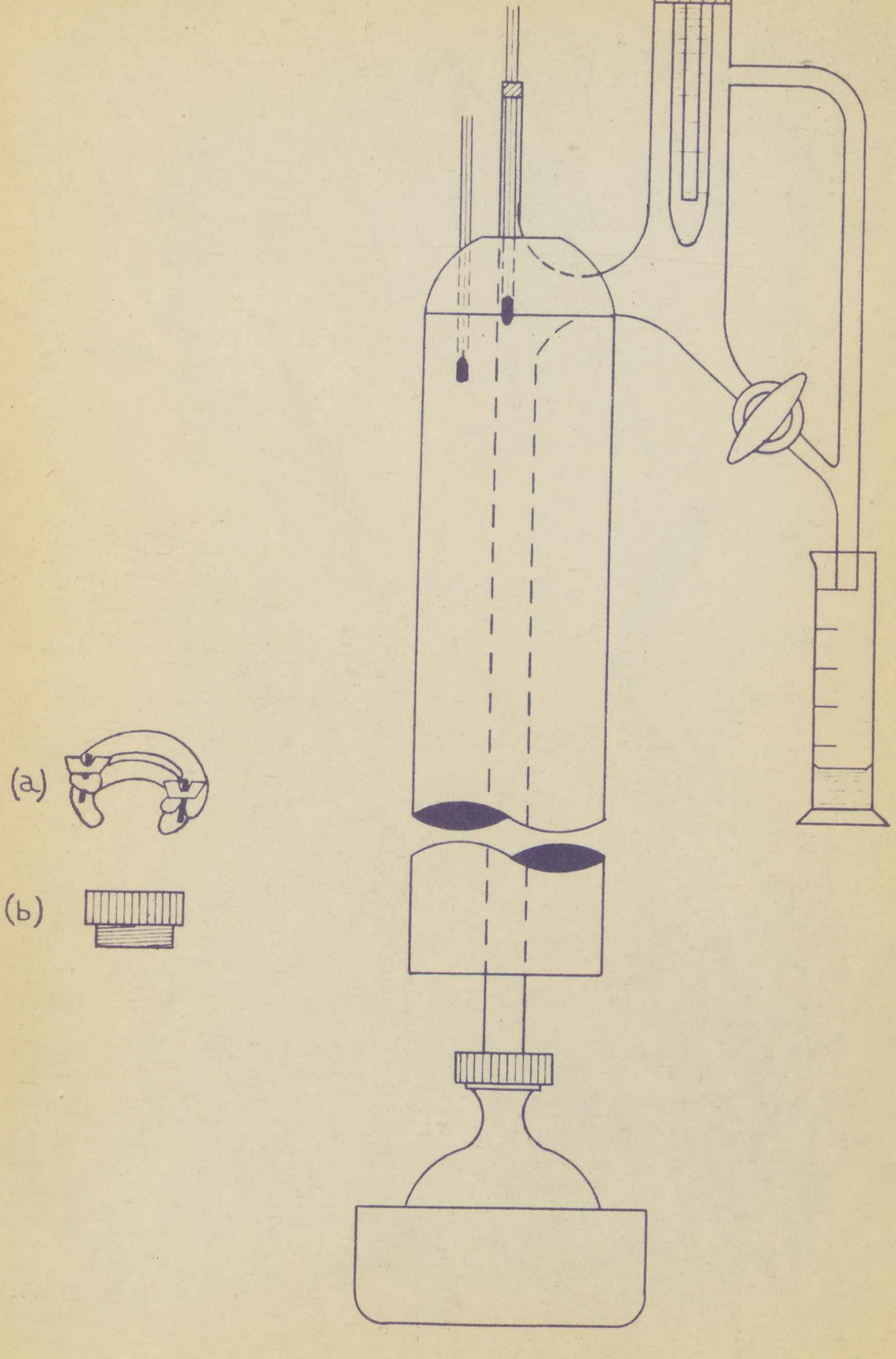
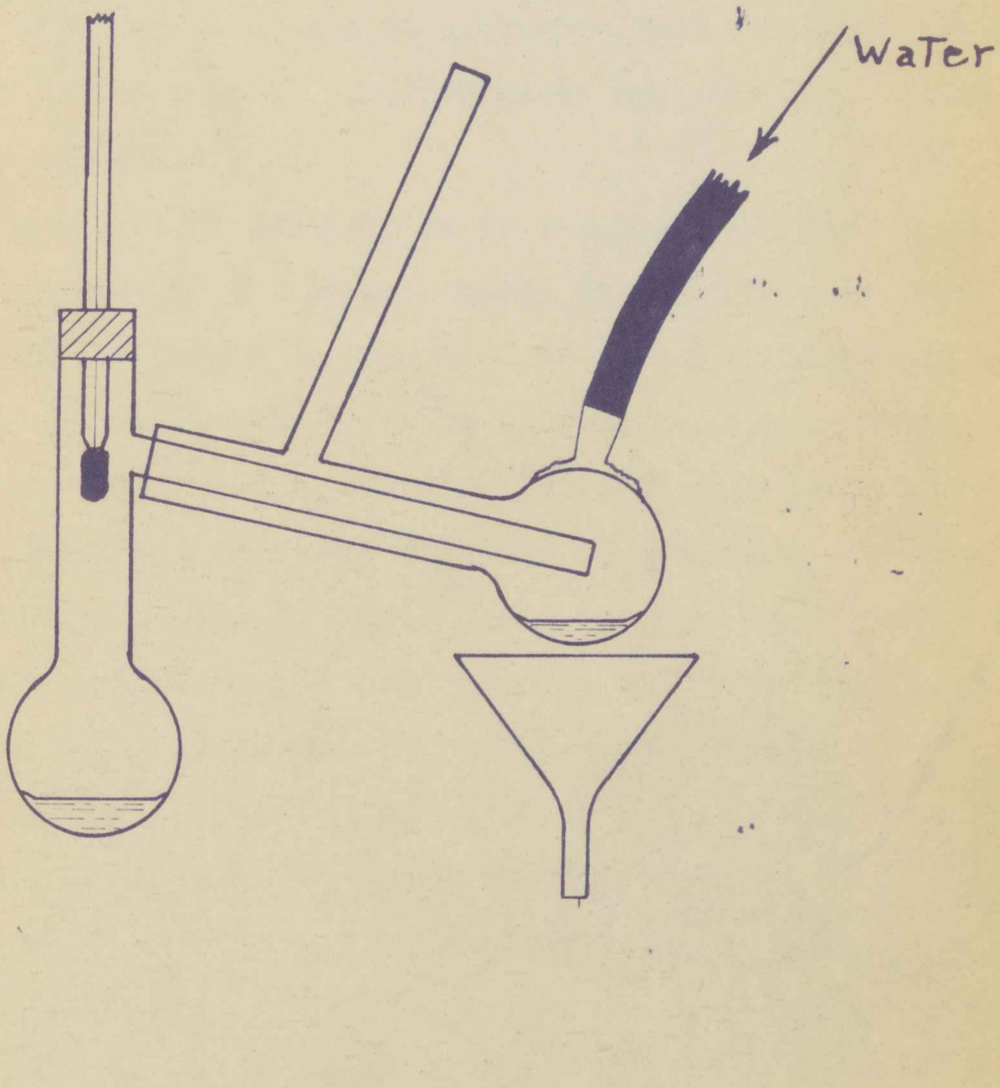


Figure IV



efficient separation, but it does serve to indicate what components may be present in the phenolic ethers. This distillation was carried out for only one run (#3), and the data for this distillation may be found in the appendix.

CLOUD POINT DETERMINATION OF O-CRESOL IN PHENOL, O-CRESOL MIXTURES

Since some o-cresol is found even in the pure phenol cut it was decided to analyze all of the distillation cuts from 180° to 190° for o-cresol to determine just how much o-cresol existed in the phenol. This complete analysis was carried out for run #3.

The method of analysis is to weigh out accurately seven or eight grams of the phenol sample in an eight inch test tube. If the sample is suspected of having a fair percentage of o-cresol the sample is mixed with reagent pure phenol so that the weighed sample actually contains only five or ten percent of the phenol from the cut. To the sample an amount of distilled water, in milliliters, is added equal to 1.857 times the weight of the sample. This will give a mixture containing 35% of the phenol sample and 65% water.

The tube is then placed in a water bath at 75° - 80° and the contents are stirred until the solution is clear. A thermometer with one tenth degree divisions is immersed in the sample and the tube is then placed inside a larger tube which is immersed in a water bath at about 65°. The larger tube serves as an air jacket for the smaller tube containing the sample. The mixture is stirred well and as it cools a cloudiness sets in. An abrupt opacity of the mixture is the cloud point. Repeating this procedure gives several readings of which an average is taken. The percent of o-cresol is given by the following equations:

For cloud points up to 70.25°c

$$\%\ \text{o-cresol} = \frac{\text{cloud point } (^\circ c) - 66.40}{1.326}$$

For cloud points between 70.25° and 73.5°c

$$\%\ \text{o-cresol} = \frac{\text{cloud point } (^\circ c) - 66.81}{1.167}$$

IDENTIFICATION OF PRODUCTS

Derivatives were made of the fractions from the distillation of the phenols which were thought to be the purest in phenol, o-cresol and p-cresol. Phenoxyacetic acid derivatives were prepared by reacting the phenols with chloroacetic acid in the presence of sodium hydroxide at 100°. The components of the distillation are identified from the melting points of the derivatives. A table of these derivatives is located in the appendix.

RESULTS

The results of the three runs are tabulated on the following page. In the analysis the percents are weight percents of the feed solution, which entered the converter, and were determined by estimation from the graph in the appendix. The percent phenol converted to ethers and cresols are mol percents of the phenol in the feed which entered the converter. The losses are not only those due to extractions and distillations, but also include the water which is formed in the reaction.

Run number		1	2	3
Temperature	°C	327°	361°	421°
Catalyst		A-1	A-1	A-1
Contact time	sec.	2.34	2.28	2.09
Feed phenol alcohol ratio	$\frac{\text{mol}}{\text{mol}}$	1:1	1:1	1:1
Analysis				
phenyl ether	wt. %	12.8	6.4	3.2
other ethers				
phenol	"	41.3	41.9	34.6
o-cresol	"	6.6	10.2	13.7
m-cresol	"	3.3	5.3	8.0
p-cresol				
higher phenols	"	1.7	3.5	1.6
residue	"	--	--	5.5
losses	"	34.3	32.7	33.4
Phenol converted	mol %	44.9	44.1	53.3
Phenol converted to ether	"	14.8	7.4	3.7
Phenol converted to other ethers				
Phenol converted to o-cresol	"	7.6	11.8	15.8
Phenol converted to m-cresol	"	3.8	6.2	9.2
Phenol converted to p-cresol				
o-cresol m&p-cresol ratio	$\frac{\text{mol}}{\text{mol}}$	2.0	1.9	1.7

SUMMARY

In all of the runs at various temperatures, approximately half of the phenol is converted. At the lowest temperature studied the yield of cresols and higher phenols is rather low. At the highest temperature studied it was found that the yield of cresols and higher phenols is about doubled. On the other hand the study shows that in going from the low temperature to the higher temperature the yield of ethers is decreased by a factor of four.

The conclusion to be drawn from this study is that increasing the temperature of the reaction, between methanol and phenol in a one to one molar ratio, over the range of temperatures studied will result in an increase of phenolic products and a decrease in phenolic ethers.

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2. Cullinane and Chard - J. Chem. Soc. 148 821-3(1945)

3. Lemieux - Thesis presented to Chem. Dept. of Union College

4. Seaman, Norton and Foley -
Ind. and Eng. Chem. Anal. 15 159(1943)

5. Shriner and Fuson - Identification of Organic Compounds

APPENDIX

Typical Reaction Run Data

Example Run #3 Average Temperature 421°c

Time	Feed	Drop Rate	Heated Feed Temp. 0"	Catalyst Bed Temperature					Below Cat. Bed Temp. 8"	Variacs		Rheostat From Top
				3"	4"	5"	6"	7"		Pre-heater	Bed	Inches
1:49	425 ml	6/10 drops/sec.	402°c	422°c	430°c	426°c	416°c	400°c	382°c	64	65	3"
2:00		6/13	394°	438°	440°	426°	413°	397°	380°	64	65	3"
2:30		6/13	378°	422°	426°	418°	404°	390°	374°	64	65	2 3/4"
2:45	358	6/14	384°	426°	432°	426°	411°	391°	378°	64	65	2 3/4"
3:00		6/13	387°	428°	438°	430°	416°	400°	382°	63	65	2 3/4"
3:15	325	6/14	387°	430°	440°	430°	416°	402°	384°	60	63	2 3/4"
3:30		6/13	382°	426°	440°	432°	418°	402°	382°	60	63	2 3/4"
3:45	289	6/15	382°	426°	438°	434°	421°	402°	387°	60	63	2 3/4"
4:00		6/12	378°	421°	438°	434°	421°	402°	384°	58	61	2 3/4"
4:15	250	6/12	370°	416°	428°	432°	421°	404°	390°	58	61	2 3/4"
4:30		6/11	360°	411°	428°	430°	421°	404°	390°	58	61	2 3/4"
4:49	206	6/13	360°	411°	426°	428°	421°	402°	387°	58	61	2 3/4"
		Average		423°	434°	429°	417°	400°				

Part of Data For a Typical Phenolic Distillation Run

Example Run #3

Time	Temperature		Variacs		Cut No.	Volume of Cut	Total Volume
	Column	Head	Column	Pot			
2:05	182.0°C	180.0°C	90	105	4	3.4 ml.	55.8 ml.
2:15	182.0°	180.5°	91	105	4	6.8	59.2
2:25	183.0°	182.0°	91	105	4	9.8	62.2
2:35	184.5°	183.0°	91	105	5	3.5	65.7
2:45	184.5°	184.0°	91	105	5	7.0	69.2
2:55	185.5°	185.0°	92	105	5	10.0	72.2
3:05	186.5°	186.0°	92	105	6	3.5	75.7
3:15	187.0°	187.0°	92	106	6	6.8	79.0
3:25	189.0°	188.0°	93	106	6	9.9	82.1
3:35	189.5°	189.0°	93	106	7	3.3	85.4
3:45	191.0°	189.5°	94	106	7	6.7	88.8
3:55	191.0°	190.5°	94	106	7	9.9	92.0
4:05	193.0°	191.5°	95	106	8	3.4	95.4
4:15	193.5°	193.5°	95	106	8	6.8	98.8
4:25	196.0°	195.0°	95	108	9	3.4	102.2
4:35	198.0°	196.0°	95	108	9	6.8	105.6
4:45	200.0°	198.0°	95	108	9	10.0	108.8

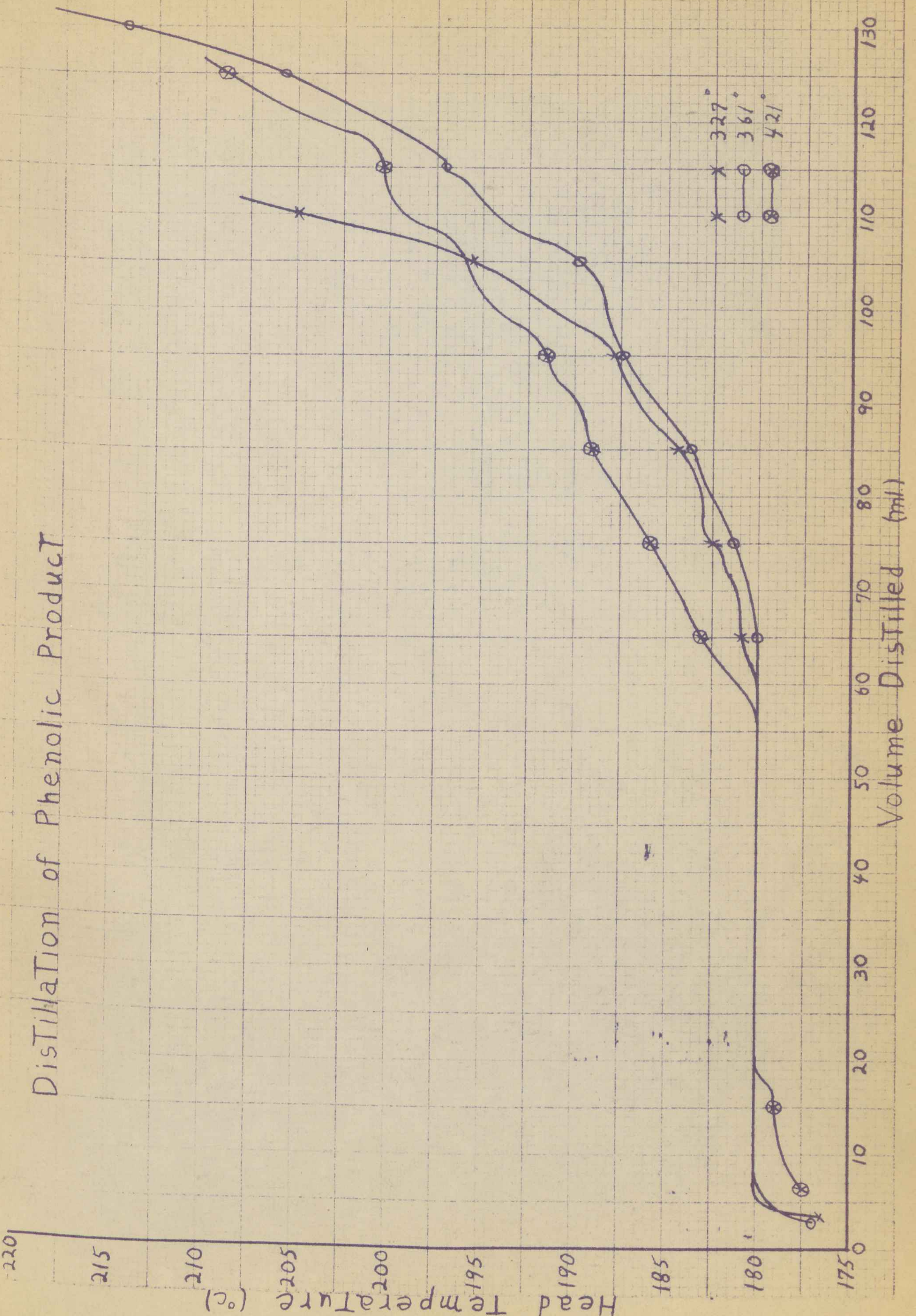
DISTILLATION OF PHENOLS

It is to be noted that not a very good separation of the phenolic products was accomplished in the distillations. From the graph on page V it can be seen that inflections or very small plateaus, other than the large phenol plateau at 180°, occur at several points on each distillation curve. If a good separation had taken place a fair sized plateau would show up at about 190°. The reason for the poor separation is that the column thermometer was not reading the true column temperature, thus a fraction consisted of not only the phenol at the particular temperature, but a fair amount of higher boiling phenols.

The above theory on the poor separation is supported by the fact that in the cloud point analysis of the cuts, from the phenol boiling point range to the o-cresol boiling point range, a large amount of o-cresol is contained in the cuts below the temperature at which o-cresol should come over.

Table of cuts for run #3.

Boiling Range	Cut Number	Running Volume
→ 177.5°	1	6.6 ml.
177.5° - 178.5°	2	9.9
178.5° - 181.5°	3	52.4
181.5° - 182.0°	4	62.2
182.0° - 185.0°	5	72.2
185.0° - 188.0°	6	82.1
188.0° - 190.5°	7	92.0
190.5° - 193.5°	8	98.8
193.5° - 198.0°	9	108.8
198.0° - 200.0°	10	112.4
200.0° - 203.5°	11	119.5
203.5° - 210.0°	12	126.6


DisTillaTion of Phenolic ProducT
Head TemperaTure (°C)
Volume DisTilled (ml.)
175
180
185
190
195
200
205
210
215
220
0
10
20
30
40
50
60
70
80
90
100
110
120
130
327°
361°
421°

Data on phenolic ether distillation of run #3

Total volume to be distilled equals approximately 7.0 ml.

Temperature (°C)	Cut	Volume of cut
149° - 178°	1	0.9 ml.
172° - 210°	2	1.0
210° - 235°	3	1.1
235° - 260°	4	0.7
260° - 300°	5	1.0
	Total Volume	4.7 ml.

One of the most probable products in the above distillation is diphenyl ether which boils at 259° C.

Determination of o-cresol in phenol, o-cresol cuts.

The o-cresol was determined for cuts numbered 3, 4, 5, 6 and 7 of the phenolic distillation of run #3. The sample calculation is given for cut number 3.

9.00 grams of reagent pure phenol is added to 1.00 grams of the cut giving a 10% sample of the phenol in the cut. To 7.01 grams of this is added 13.04 grams of distilled water which gives a mixture of 35% sample and 65% water.

Cloud Points	67.00° C
	66.95°
	67.00°
average	66.98°
with thermometer correction average	67.60° C

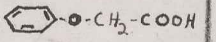
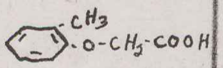
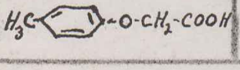
$$\% \text{ o-cresol} = \frac{\text{cloud point } (^\circ\text{C}) - 66.40}{1.326}$$

$$= \frac{67.60 - 66.40}{1.326} = 0.905\%$$

% o-cresol in cut number 3 = 9.05%

Cut Number	% o-cresol
3	9.05
4	33.6
5	48.5
6	83.0
7	96.6

Table of derivatives - run #3

Cut Number	Derivative	% yield	Corrected M.P.(°C)	Literature M.P. (°C)
3		53.0	103° - 105°	99°
7		18.3	151° - 155°	152°
10		15.0	136° - 140°	136°