

SYNTHETIC PHENOL

By

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An effort has been made to acknowledge by a foot-note all publications which were referred to in the preparation of this paper.

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SYNTHETIC PHENOL

Introduction

Until recent years the only source of phenol in the United States was the coal tar from by-product coke ovens. By means of fractional distillation there is separated from this tar what is commonly known as the carbolic oil fraction, which contains a number of important organic compounds belonging to the group called tar acids. Phenol, the most important of these compounds, is separated and obtained in a pure condition by means of further distillation and recrystallization. Before the year 1914 the use of phenol was limited to the manufacture of dyestuff intermediates and to the preparation of certain Pharmaceuticals. With the beginning of the war, however, the demand for this compound increased enormously as the allied countries, especially France, were using immense quantities of phenol in the manufacture of the explosive, picric acid. It at once became evident that the by-product industry could not satisfy these increased demands, and other means of producing phenol were therefore sought. Several plants were built to operate the old benzene-sulfonic acid process which had been known for some time but had never been used commercially in this country. The undesirable features of this latter process led to considerable research work on the production of phenol from the halogen derivatives of benzene, and in the course of this work several processes were developed and patented by which phenol could be produced from either chloro-benzene or bromo-benzene. The plants, which were immediately built to produce phenol by means of these new halogenation processes, were operated quite successfully in competition with plants which were using the old benzene-sulfonic acid process. The cessation of hostilities, however, threw on the

market large quantities of phenol which had been held in reserve by the United States government and this compelled all the war time plants to cease operation.

Nevertheless, the phenol question has taken a new and important turn which bids fair to put its manufacture on a firm peace basis. There is an ever increasing number of industrial and technical uses of synthetic phenol-formaldehyde resins of the Bakelite type. Also the dye industries, with the encouragement of a high protective tariff, are showing considerable growth. All of which forecasts a ready and sustained market for phenol in the future.

The purpose of this paper is to describe and discuss a series of experiments made by the writer on a new process for the production of phenol from either chloro-benzene or bromo-benzene. In the first part a number of the most important processes now in use for the manufacture of phenol will be briefly outlined. Following this the various experiments will be described, and the results tabulated. Then will follow the probable flow sheet of material for a plant which would operate this process, and finally, a general summary will be presented.

Phenol from Benzene by Sulfonation

Benzene is universally used as the starting material in manufacturing synthetic phenol. However, there is no method by which the hydroxyl radical can be substituted for a hydrogen atom in the benzene nucleus directly. This substitution is therefore made by indirect methods, such as sulfonation, chlorination, or bromination. Four important processes have been developed for the manufacture of phenol from benzene. They are,

- 1 - Benzene-sulfonic acid process
 - b-Vapor phase modification of the above
- 2 - The Dow Process
- 3 - Aylsworth Process
- 4 - Process of Meyer and Bergius.

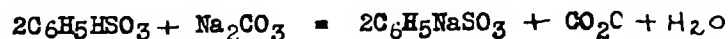
Benzene-Sulfonic Acid Process:¹

The reactions involved in the synthesis of phenol by means of this process, each of which is carried out in a separate plant unit, are:

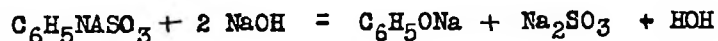
Sulfonation:



Neutralization:



Fusion:



Acidification:



¹Met. & Chem. Eng. - V.15 (1916) 185 - 186.

The first reaction, sulfonation, is carried out in lead lined tanks, where a mixture of sulfuric acid and benzene is allowed to react for a period of sixteen to twenty hours. The product of this reaction is benzene-sulfonic acid. However, only 60 per cent of the sulfuric acid present combines with benzene, the remaining 40 per cent is lost, as will be shown in the next paragraph.

From the sulfonators, benzene-sulfonic acid is pumped to lead lined neutralization tanks where it is first treated with lime to neutralize the excess acid. Sodium carbonate is then charged into the tanks. A saturated solution is used in order to keep the water content as low as possible. The product, sodium benzene sulfonate is then evaporated to dryness in multiple effect evaporators.

Fusion takes place in cast iron fusion pots, which are provided with strong agitators, and heated by oil. When the strong caustic solution has reached a temperature of 300 degrees centigrade, the sodium salt from the neutralizers is pumped in. Fusion is continued with considerable agitation until the conversion of the sulfonate to sodium phenate is complete. The time required is from sixteen to twenty-four hours.

At the end of this time water is run into the pots to dissolve the phenate. This phenolic salt solution is then removed to another battery of tanks and brought just to the point of neutralization with sulfuric acid. Crude phenol separates from the aqueous layer, and is purified by distillation.

There are a number of undesirable features in this process. It requires a large plant and much costly equipment for operation. As it is not possible to remove the water which is formed in sulfonation, reaction

is slow, and results finally in a 40 per cent loss of sulfuric acid. Fusion with caustic soda is especially troublesome and costly, since the fusion pot must be replaced frequently.

Sulfonation in Vapor Phase¹

The vapor phase modification of the above is similar in every respect with the exception of the first step. Sulfonation is carried out by means of Tyrer's vapor phase process. The advantages of this are: It permits a higher working temperature, thus making it possible to carry the reaction to 95 per cent of completion; avoids the use of reflux condensers which are necessary in the old process; and, allows the removal of water as fast as it is formed, thus reducing considerably the time required for sulfonation.

¹Ind. & Eng. Chem. - Vol. 16 (1924) 1066.

Phenol from Benzene by Halogenation

The Dow Process¹

This is one of the three important processes for the manufacture of phenol from benzene by means of halogenation. Benzene as a starting material is first converted into the halogen derivative, bromo-benzene. This in turn is heated for eighteen to twenty-four hours with strong caustic solution in high pressure autoclaves at a temperature of 300 degrees centigrade. The products from this reaction are sodium phenate and sodium bromide. Upon acidification the former is reduced to phenol. A feature of this process is the fact that bromine is recovered as sodium bromide and is marketable. However, fusion with caustic at high temperatures and pressures, is here as in former processes, very objectionable.

The Aylsworth Process²

The principle involved in this process is the same as in the one above. However, fusion with caustic is carried out in especially designed autoclaves which are the invention of Aylsworth. These consist of heavy steel tubes immersed in niter cake, which at 400 degrees centigrade becomes viscous and boils. This serves to keep the temperature in the coils constant. By means of high pressure double entry pumps chloro-benzene and strong caustic solution are forced into the heated tubes under pressure of 3000 pounds per square inch. Under these conditions sodium phenate forms rapidly. The steps which must be taken to operate this process are;

¹ Dow Patent. —

² Jour. of Ind. & Eng. Chem. - 12 (1920) - 279 - 280.

- 1 - Chlorination of benzene
- 2 - Fusion with caustic
- 3.- Acidification
- 4 - Distillation

The advantages claimed for this patent are: Simplicity, small first cost of plant and equipment, and the speed of reaction. The chief disadvantages are: The difficulties and hazards of operating under such high pressure, and the cost of operating high pressure pumps.

Process of Meyer and Bergius¹

The plan of operation of this process is essentially the same as the preceding ones. However, only a ten per cent solution of caustic soda is used in the high pressure treatment with chloro-benzene or bromo-benzene and this results in considerable reduction in the cost of materials. The disadvantages are the same as those incurred in the Dow process.

¹Patent of Meyer & Bergius.

Phenol from Halogenated Benzene and Steam
in the Vapor Phase

The new process described in this paper differs from any of the above, and presents many advantages. In outline it is as follows: A mixture of chloro-benzene or bromo-benzene and steam is passed through a quartz tube containing a metallic gel such as silica gel or bauxite at a temperature of 600 degrees centigrade or above. Under these conditions phenol is formed together with an almost equal amount of black oily liquid. Some previous work has been done along this same line by Meyer and Bergius¹. They used only metallic oxides such as oxides of aluminium, iron, and copper, and did not realize the importance of using gels as catalytic agents. As will be shown in the following experiments these have a very marked effect upon the speed and completeness of the reaction.

Materials

The alumina gel used in this work was prepared by heating the mineral hydroxide of aluminium until all the water had been driven out, leaving a hard porous structure.

The silica gel employed was obtained from the Silica Gel Corporation of Baltimore, Maryland. It had a hard glassy appearance, and was composed of small particles about .2 cm. in diameter. This was found to be more effective than the fine dust gel, since the latter did not permit the vapors to pass readily through the tube.

Silica gel may be prepared, according to Fels and Firth,²
in the following manner: To a volume of concentrated hydrochloric acid

¹Berichte der Deutschen Chem. Ges. (1914) 47, 3155.

²Journal of Physical Chemistry - 29 (1925) -241.

at the boiling point is added an equal volume of water glass (sodium silicate). Considerable agitation is necessary to insure uniform mixing. When this has been done, the mixture is allowed to stand quietly until there is formed a clear firm gel. The liquid is then poured off by decantation and the gel is broken into small bits and thoroughly washed to remove sodium chloride. After this it is slowly heated at gradually increasing temperatures until the water has been driven from the pores. It is then practically free from moisture and ready for use.

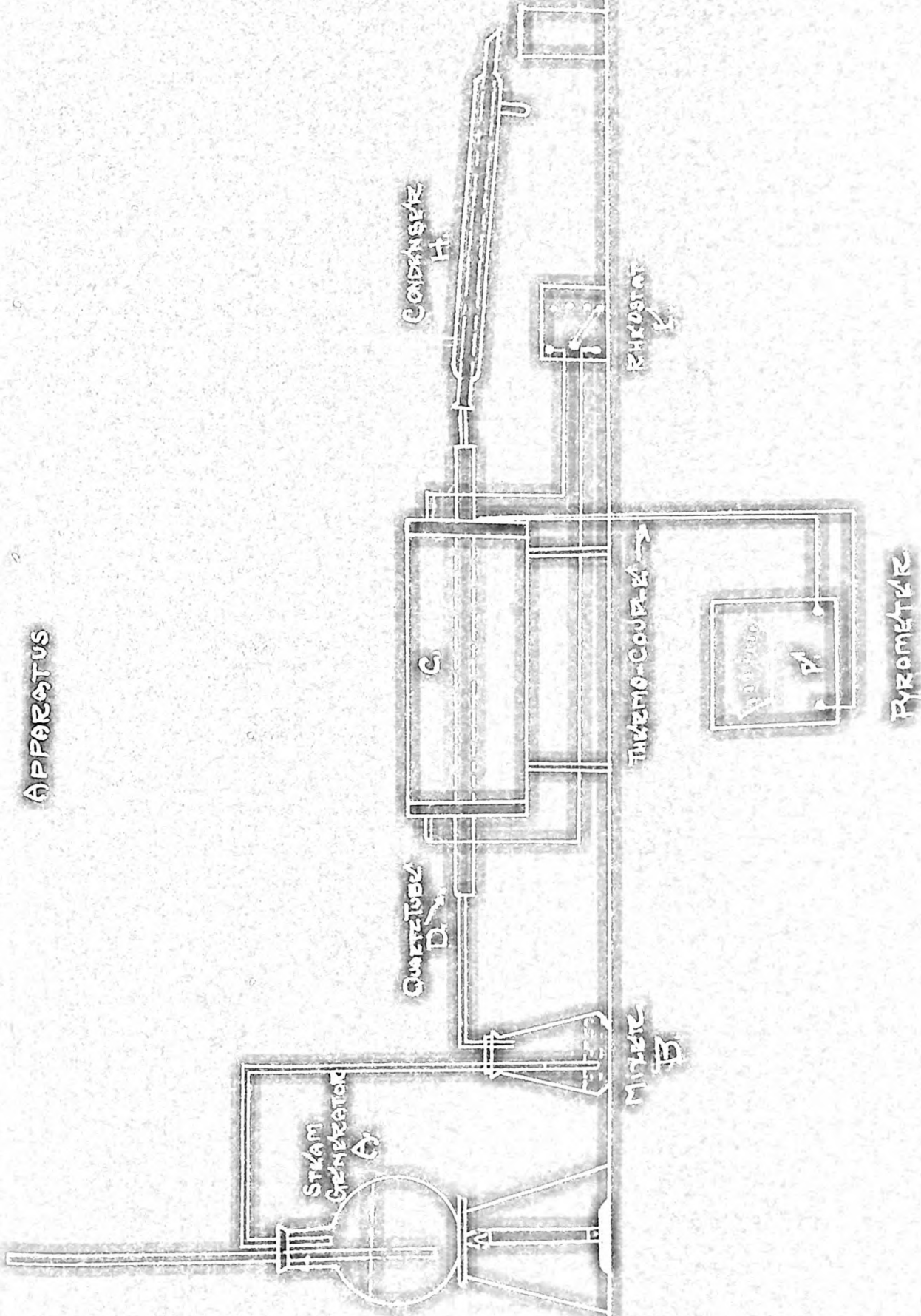
Description of Apparatus

The drawing on the following page is a detailed sketch of the apparatus employed in carrying out the experiments described below.

Symbol: A - Boiler for generating steam
B - Container for halogen compound (Mixer)
C - Small electric resistance furnace
D - 3/4" quartz tube containing gel
E - Rheostat for temperature control
F - Pyrometer and thermo couple
H - Simple water cooled condenser

Outline of operation: Steam from boiler A, passes through mixer B, and thence the mixture passes into the heated furnace and through the gel. As the vapors pass out of the furnace they are condensed to liquid by cooling in condenser H.

APPARATUS



G.S.B.

Experimental

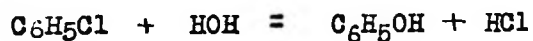
Experiment No. 1

A few grams of alumina gel prepared from bauxite were put into the quartz tube. A 50cc sample of chloro-benzene in the mixing tube B was passed through the tube by means of steam distillation while the temperature was held constant at 700 degrees centigrade. When the vapors had been condensed they separated into two layers, the upper one being aqueous.

The upper layer gave a distinct acid reaction, turning blue litmus red. This acid was identified as hydrochloric acid by adding an excess of sodium hydroxide and concentrating the solution by evaporation. Upon cooling cubic crystals of sodium chloride crystallized out of solution. To another portion of the upper layer was added a small amount of bromine water. Immediately there was formed a white flocculent precipitate of tribrom-phenol, showing that phenol had been produced in the furnace.

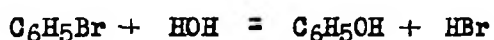
A portion of the chloro-benzene layer was shaken with caustic solution for several minutes. The caustic layer was then acidified and treated with bromine. The formation of tribrom-phenol again indicated the presence of phenol.

From the above results it is seen that phenol is produced when chloro-benzene and steam are passed over gel at a temperature of 700 degrees centigrade. The presence of phenol and hydrochloric acid in the condensates indicates that the equation which describes the reaction is:



Experiment No. 2.

The conditions named above were repeated in this experiment with bromo-benzene. The condensed liquid again gave an acid test denoting the presence of hydrobromic acid. Both the upper and lower layers gave the phenol reaction with bromine water. The equation which describes this reaction is:



It is of interest to note that iron was detected in the condensates. This is due to the fact that the bauxite contained some iron which was dissolved by the acid.

Experiment No. 3.

This experiment consisted of a series of runs, with 50cc each, and was made to find the most favorable temperature for converting chloro-benzene into phenol by this method. The most satisfactory temperature is that at which there is a maximum amount of phenol produced and a minimum amount of decomposed or charred chloro-benzene.

Temp. C.	$\text{C}_6\text{H}_5\text{Cl}$	Phenol	Phenol %
550	55	none	0
650	55	.038	.07
700	55	.0495	.09
850	55	.047	.08
950	55	trace	
1050	55	trace	

The lowest temperature at which the reaction will take place is 600°C. The most favorable working temperature is 650 to 700°C. Above this point charring increases rapidly until at 850°C. the condensed chloro-

benzene assumes a brown color, and above this temperature becomes black.

Experiment No. 4.

This experiment was made to find how the quantity of alumina gel to which the vapors were exposed affected the amount of phenol produced. The amount was therefore increased until there was now in the quartz tube about 4 cubic inches of broken alumina gel. Two separate runs were made and the total amount of phenol produced in each case was determined.

Temp. C.	C ₆ H ₅ Cl	Phenol	Phenol %
700	55 gr.	.075 gr.	.137
800	55 "	.065 "	.118

These results show that an increase in the amount of heated gel to which the vapors are exposed gives a corresponding increase in the amount of phenol formed.

Experiment No. 5.

This experiment consisted of a series of runs which were made in an effort to find some other catalytic agent more effective than alumina gel. Runs were made using aluminagel, kaolin, limonite and silica gel. Equal volumes of each were placed in the furnace for each run.

Limonite	750°C	55 gr.	C ₆ H ₅ Cl	.038 gr.	C ₆ H ₅ OH
Kaolin	"	55 "	"	.044 "	"
Bauxite	"	55 "	"	.06 "	"
Silica Gel	"	55 "	"	.30 "	"

From these results it is seen that silica gel is much more effective than any of the others used. It is of interest to note here that the porosity of silica gel is much greater than that of bauxite (alumina gel), and that

this in turn has greater absorbing power than limonite or kaolin. As the results on the preceding page will show, the phenol yield is greater with the more porous oxides. This is in keeping with the fact that an increase in the amount of gel used in the furnace causes an increase in the phenol produced.

Experiment No. 6.

In the preceding experiment only a small quantity of silica gel was used as it was only desired to get a comparison with the other oxides. The amount was accordingly increased and a 50cc sample was passed through with steam just as in previous work. With silica gel as with alumina gel, the phenol yield increases as the quantity of heated gel increases.

Temp.	C ₆ H ₅ Cl	Phenol	Phenol %
750°C	55 gr.	.715 gr.	1.26

Experiment No. 7.

A slight variation was made in carrying out this run. At frequent intervals pure steam was passed through the furnace while chlorobenzene was being distilled through as in previous experiments. In other words, the gel was frequently swept out by means of super heated steam. Two runs were made, first using alumina gel, and second, silica gel.

Alumina gel	750°C	55 gr.	C ₆ H ₅ Cl	Phenol %	.55
Silica gel	"	" "	"	"	3.88

These results show that the passage of steam through the gel at frequent intervals during operation is an effective way of increasing the phenol yield. Also, the superiority of silica gel over bauxite is again exemplified.

Experiment No. 8

The object of this experiment was to determine whether chloro-benzene or bromo-benzene was best suited for the production of phenol by means of this process. A run was made of each under like conditions and the amount of phenol produced in each case determined.

C_6H_5Cl	700°C	55 gr. (50cc)	Phenol 2.5 gr. or 4.72 %
C_6H_5Br	700°C	75 " (50cc)	" 1.98 " " 2.64 %

The percentage by weight of phenol produced from chloro-benzene is greater than the percentage produced from bromo-benzene. Also, these increasing percentages show that phenol can be produced in considerable amount by means of this process.

Experiment No. 9

Two furnaces were connected in series and the quartz tube in each one was filled with silica gel. A 50cc sample of chloro-benzene was then passed through with steam, the gel being intermittently swept out with steam as described in Experiment No. 7. After this run had been completed, the furnaces were filled with alumina gel and another run was made under the same conditions as the previous one.

Silica gel	700°C	55 gr. C_6H_5Cl	Phenol 4.15 gr. 7.55%
Alumina gel	"	" " "	" .544 " .99

The results here shown again indicate the great advantage obtained by using silica gel instead of alumina gel. The use of steam for sweeping out the gel is also important. It is also interesting to note that, by using two furnaces, and consequently a greater quantity of gel, the phenol is considerably increased.

Experiment No. 10.

The effectiveness of silica gel decreases with use. That is to say, a second sample passed through the same gel would not show as high a yield of phenol. This is due to the fact that the pores of the gel become clogged up with a carbonaceous substance which is formed by the decomposition or charring of chloro-benzene. However, the passage of steam through the gel at high temperature is effective in increasing the life or period of usefulness of it. It was also found that by passing oxygen or air through this charred gel at a temperature of 600°C. the carbon in the pores could be burned out and thus leave the gel in good condition for future use in phenol production. The following data will give an idea of the effect of using oxygen for cleaning out the gel. Run No. 1 was made with fresh gel, being the same run as shown in experiment No. 9. Run No. 2 was made with a fresh sample of chloro-benzene, which was passed through the same gel under like conditions. After this run was completed pure oxygen was passed through the hot gel in order to burn the carbonaceous substance from the pores. A third sample of chloro-benzene was then passed through this same gel. The amount of phenol produced in each run was then determined.

Run No. 1	55 gr	C_6H_5Cl	Phenol	4.15 gr.	7.55 %
" " 2	55 "	"	"	3.2 "	5.8 %
" " 3	55 "	"	"	3.63 "	6.60 %

Experiment No. 11.

This experiment was made with the object of finding the amount of chloro-benzene which was decomposed when subjected to the conditions under which this process is carried out. A 50cc sample was passed through

the furnace as in previous experiments and the amount of hydrochloric acid contained in the condensates was determined by means of titration with caustic solution, using methyl orange as an indicator. This result together with the amount of phenol produced is given in the following data:

Temp. 700°C	55 gr. C ₆ H ₅ Cl	2.55 gr HCL	2.86 gr. Phenol
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From these data several inferences may be made. First, that the chlorine atom was removed from 7.8 grams of chloro-benzene but in only 3.4 grams of this amount was the hydroxyl radicle substituted for the halogen atom. The remaining 4.4 grams of chloro-benzene went partly to form the charred substance which as before mentioned is deposited in the pores of the gel and partly to form the black oil in the condensate. This oil is found dissolved in the lower layer of the condensate, from which it may be separated by distilling off the chloro-benzene. Upon distillation 42 cc of chloro-benzene were recovered from the condensates from the above run, which of course, could be used again for the production of phenol. It is interesting to note that 7.8 grams of chloro-benzene were consumed in producing 2.86 grams of phenol; or in other words, a 35 per cent yield of phenol was realized.

Summary

1. Phenol can be produced by means of this process from either chloro-benzene or bromo-benzene, the former being preferable.

2. Silica gel, alumina gel, or limonite may be used as the catalytic agent in the furnace, but the first named is by far the more effective of the three.

3. The most favorable temperature for the phenol reaction is 650 to 750° Centigrade.

4. A greater yield of phenol is realized when steam is passed intermittently through the gel in order to keep the pores in as clean a condition as possible.

5. An increase in the amount of heated gel to which the vapors are exposed gives a corresponding increase in the amount of phenol produced, which fact is encouraging to large scale production.

6. The effectiveness of the gel gradually decreases due to the deposition of char in its pores. This condition however, can be remedied by the passage of oxygen through the heated gel.

7. In addition to the phenol formed by this process there is an oil formed which is not a halogen compound.

8. When the phenol and this oil have been removed from the condensed chloro-benzene, the latter may again be used for the production of phenol.

Conclusion

The probable outline of operation of this process is:

1. Chlorination of benzene.
2. Production of phenol from chloro-benzene and steam in an electric furnace containing silica gel.
3. Distillation.

Although it is impossible to predict just what difficulties might arise, this process seems worthy of investigation on a larger scale. It offers many advantages over the processes now in use, some of which are: Simplicity, low cost of plant equipment; low cost of operation, since it offers especially low labor costs; avoids the necessity of high pressure fusion with caustic soda, which has proved so troublesome in other processes; and speed of reaction.

Respectfully submitted to the faculty of the Chemical Department
and the Graduate Committee by,

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