trioxide from the contact converters cannot be stated until the space-time-yield studies are completed.

Certain ores are readily chlorinated by the combined action of sulfur dioxide, air, and salt. The products, in general, are the anhydrous sulfates and chlorides. These anhydrous salts may have commercial value, even greater than their importance in chemometallurgy. In the case of the iron oxide ore the production of pure anhydrous ferric chloride by volatilization is handicapped by the unusually low vapor pressure of sodium chloride solutions in the product.

The accelerated attack of mixtures of sulfur dioxide and chlorine on ores might be used as a source of anhydrous sulfates. In this case chlorine acts only as an intermediate compound; for once the chloride is formed from the oxide, it is readily converted to the sulfate by gases rich in sulfur dioxide and oxygen, the chlorine being thereby regenerated. This mechanism prevails in the case of ferric oxide and apparently takes place to some extent with even more refractory ores such as zircon. The mechanism suggests that a continuous countercurrent process might be used in which the ore is fed into one end of a continuous shaft or rotary furnace while sulfur dioxide and air are blown into the other end. A small amount of sodium chloride or other chloride may be present with the ore, or some chlorine may be added with the gases. As the solid charge travels forward, the oxide is first converted to the chloride. At higher temperatures and in the presence of excess sulfur dioxide and oxygen, the chloride is converted to sulfate and chlorine travels with the gas to the oxide end of the furnace.

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Nitration of Benzene

CONTINUOUS PROCESS, USING NITRIC ACID ALONE

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DESPITE the importance of nitration processes, few changes in nitration methods have been proposed for years. The voluminous literature is concerned mostly with the determination of optimum conditions for the nitration of various substances, and with the use of mixed acid as the nitrating agent.

Although the function of sulfuric acid in mixed acid is not definitely known, it has been supposed to dehydrate the nitric acid, yielding what Hantzsch calls "pseudo acid" (*3*). This pseudo acid, $OH-NO_2$, is the stronger nitrating agent, while the more dilute acid $H-NO_3$ is an oxidizing agent. Intermediate concentrations will yield both oxidation and nitration products.

The free energy of the reaction between HNO_3 and benzene is about $-28,000$ calories per mole under standard conditions, and indicates that the reaction is essentially complete at equilibrium. Attempts have been made to hydrolyze nitrobenzene with water and dilute acid at 100° C. but have not resulted in detectable quantities of hydrolysis products. It is therefore evident that the nitration of benzene is an irreversible reaction, and that the rate of nitration is primarily a function of the effects of the nitration agent.

The actual mechanism of the reaction is open to question, although the most generally accepted is Wieland's addition-elimination theory (*2*); the nitric acid is considered as adding on to the benzene nucleus with subsequent elimination of water. Michael and Carlson (*4*) recently presented the theory that nitration may involve the addition of a nuclear hydrogen to the Δ-oxygen and of the aromatic residue to the nitrogen. Then water would be eliminated from the addition compound.

Although it has been known for some time that benzene and its homologs can be nitrated with nitric acid alone (*1*), little or no progress has been made with the reaction. Dilution of the acid by the water produced from the nitration decreases the rate of reaction to the point where it becomes uneconomical and impractical to operate. The dilute acid nitrates slowly and contaminates the end materials with oxidation products. To carry out the nitration within a reasonable time, large excesses of nitric acid are necessary, which increase the possibility of polynitro-compound formation as well as the cost of raw material.

Recently the substitution of a mechanical method of water removal to supplant chemical dehydrating agents has been mentioned (*5*, *7*). The basis for this method is the so-called partial pressure evaporation—i. e., the utilization of the addi-

tive vapor pressures of an immiscible entrainer and of the water formed during nitration. The mononitration of benzene is probably the most basic and familiar nitration process, and an entrainer (benzene) is present among the reacting materials. Therefore the removal of the water resulting from the nitration was approached with the knowledge that benzene and water form a constant-boiling mixture at approximately 69° C., and that each of the other materials present (water, benzene, nitrobenzene, and nitric acid, as well as the nitric acid–water constant-boiling mixture) boils at a higher temperature. Therefore the benzene-water constant-boiling mixture (C. B. M.) should be separable by distillation.

Benzene was nitrated without sulfuric acid or other dehydrating agent, and the water of nitration was removed as an azeotropic mixture with benzene. This mixture boils at 69.25° C. The effect of acid concentration upon the rate of nitration was studied, with and without agitation of the benzene and aqueous acid layers. The effect of time upon conversion, using 68 per cent nitric acid, was determined.

In the preliminary runs the water and benzene removed as an azeotropic mixture contained considerable quantities of acid. Additional length of the distilling column reduced this acid, but the possibility of a ternary system was considered. An investigation of the system benzene-acid-water showed that 68 per cent nitric acid can be fractionated from the benzene-water azeotrope. A distribution curve of acid in water-benzene was plotted at room temperature. The benzene-nitrobenzene system was investigated, and the x–y diagram plotted.

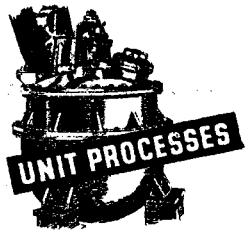
A series of continuous runs, using a feed of 61 per cent nitric acid was undertaken to obtain data of the effect upon percentage nitrated of varying the ratio of benzene to acid, the vapor rates, and the feed plate position. Further investigations were carried out with a feed of constant-boiling nitric acid vapor. Necessary design data were obtained for a two-column continuous system, which may be operated smoothly due to the large excess of benzene always present.

PHYSICAL DATA

The steps to be used later can be better understood if certain data regarding phase equilibria are available. Accordingly, the solubility of nitric acid in benzene at 20° C. (more exactly, the distribution curve) was determined by agitating equal weights of benzene and of a water solution of nitric acid at various concentrations in a separatory funnel. Samples of each layer were titrated, and the data are as follows:

% HNO_3 in Water Layer	% HNO_3 in Benzene Layer	% HNO_3 in Water Layer	% HNO_3 in Benzene Layer
6.3	0.0	47.5	2.9
7.6	0.0	49.0	3.0
40.0	2.6	58.0	4.16
43.5	2.7	61.3	4.45

In Figure 1 the acid concentration in the benzene layer is plotted against that in the water layer. The percentage of nitric acid in the benzene layer is negligible at lower concentrations of the water layer and becomes about a tenth of that in the water layer at strengths where nitration is later shown to proceed.



The vapor-liquid relation, which is important in the separation of benzene from nitrobenzene by distillation, was determined in the standard manner by the method previously described (*6*), and analysis was made by differences in density. Figure 2 is the equilibrium diagram. Only a few theoretical plates would be necessary in a distillation column exhausting benzene from a mixture of benzene and nitrobenzene, as shown by the wide divergence of the curve from the 45° line. This was to be expected, since the difference in boiling points at atmospheric pressure is about 130° C.

RATE OF NITRATION

Although the rate of nitration of benzene with nitric acid alone decreases with increasing dilution of the acid, it was felt that the quantitative effects of this dilution under the projected conditions of operation should be determined. Therefore 2.5 liters of benzene were charged to a flask fitted with a reflux condenser and sampling tube; when it was boiling freely, 250 grams of 61 per cent nitric acid (Commercial Acid) were introduced. Time was measured from this point. Samples of the lower acid and the upper benzene layers were removed periodically for the determination of acid concentration and amount of nitrobenzene formed.

A large excess of benzene was used, since it was expected that in later work benzene would always predominate, and also in order to decrease any effect which the nitrobenzene formed might have in diluting the benzene phase. The concentration of nitrobenzene in the benzene layer was low, never over about 10 per cent. It was expected (and found) that the nitration process would never go too fast or get out of control in any way, especially since the low boiling point of

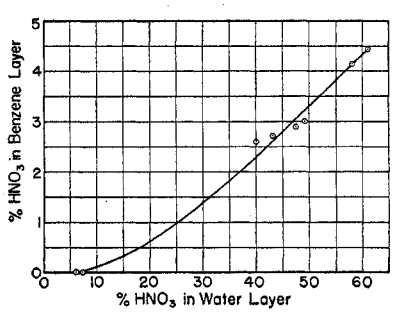


Figure 1. Distribution of Nitric Acid between Water and Benzene at 20° C.

the liquids and the accompanying vaporization of the C. B. M. served as a thermal control. The amount of nitrobenzene formed was determined by specific gravity measurement. These data give an indication of the rate of conversion under free-boiling conditions. As the amount of nitrobenzene formed during the reaction was measured, the amount and concentration of nitric acid in the acid layer could be calculated, since no water was removed from the system. This checked the actual titration value fairly closely. These data are given in Table I and plotted in Figure 3*A*.

Since in a heterogeneous system the area of mutual contact between the phases affects the rate of reaction in large meas-

TABLE I. REACTION DATA

Time, Min.	Nitrobenzene % HNO_3 conversion	Nitrobenzene Moles present	HNO_3 Concn. Observed	HNO_3 Concn. Calculated
		Without Agitation		
0	0	0	61.2	61.3
30	15.6	0.436	58.4	58.0
60	33.5	0.935	50.0	50.0
90	36.2	1.01	48.7	49.0
313	38.5	1.07	47.7	47.5
538	47.0	1.31	43.5	43.5
648	53.6	1.50	40.1	40.0
		Mechanical Agitation		
0	0	0	61.3	61.3
10	11.35	0.471	56.4	56.4
20	26.2	1.09	49.7	49.8
30	40.6	1.69	42.5	42.4
40	41.5	1.725	42.0	41.9
50	44.0	1.83	40.5	40.6
60	45.2	1.875	40.0	39.9
70	46.5	1.935	38.7	38.9
80	47.4	1.970	38.5	38.6
90	48.2	2.00	38.0	38.1
100	49.4	2.05	37.3	37.3
110	50.3	2.09	36.6	36.7
120	50.5	2.118	36.0	36.1
135	50.9	2.155	35.5	35.6
150	51.8	2.18	35.2	35.2

ure, the influence of mechanical agitation was studied. The same quantities of constituents were used; the only change in the apparatus was the addition of a stirrer to maintain a vigorous agitation of the two liquid phases. The results of these runs are shown in Table I, and the data are plotted in Figure 3*B*. As was to be expected, more rapid conversion and more consistent data were obtained. Here, as in Figure 3*A*, considerable nitrobenzene formed at the start when the concentration of acid was high. But the amount formed did not increase greatly after the acid concentration had dropped to a limiting value, and this acid concentration did not decrease greatly thereafter. Comparison of the reaction with and without agitation, however, shows that the surface contact in the second case is a determining factor in the total amount and speed of nitration.

To show the effect of acid concentration upon the rate of reaction, the curves of Figure 3 for the amounts of nitrobenzene formed were graphically differentiated to give the rates

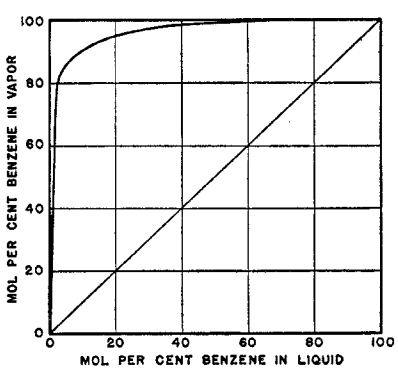


Figure 2. Composition of Vapors in Equilibrium with Boiling Binary Solutions of Benzene and Nitrobenzene

of nitration (in moles of nitrobenzene formed per minute) at different times throughout the runs. These rates of nitration are plotted in Figure 4 against the values of the instantaneous nitric acid concentration (found from the curves of Figure 3). Since cold acid was poured into the refluxing benzene, boiling stopped for a few minutes. This, combined with the fact that the reaction proceeded rapidly at the high concentration of acid, probably accounted for abnormal reaction rates at concentrations higher than 50 per cent. Therefore, the points for highest acid concentration in each run (near the start of the run) were disregarded.

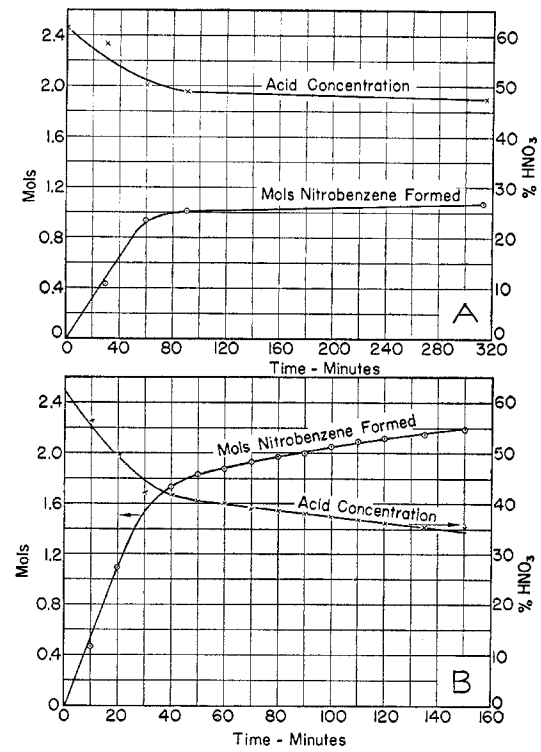


Figure 3. Conversion of Benzene and Nitric Acid to Nitrobenzene

A. Batch run without agitation.
B. Batch run with agitation

The curves of Figure 4 are similar in shape. But the one for the run without agitation shows that for effective conversion, the acid concentration must be much higher; even then the rate is much lower.

It can be seen that there is a critical acid concentration below which the rate of reaction falls off rapidly. These values are different, however, for the agitated and free-boiling experiments. The critical concentration for the agitated runs is about 38 per cent acid concentration, and that for the unagitated runs is about 48 per cent. These results would probably be greatly affected by the different degrees of agitation in other units of larger size having agitators of different types. However, they are probably indicative of the rates to be expected.

WITHDRAWAL OF WATER FORMED

Several runs were made in which the flask and condenser setup described above was fitted with a decanter to remove the water condensed in the reflux condenser, while allowing the benzene to return. Thus the benzene was used as a withdrawing agent during the nitration process to remove the water formed; and if the rate of formation was balanced by the rate of removal, the nitric acid in the pot could be maintained at any desired high concentration. In most cases the residual acid in the pot was about 68 per cent concentration. This is approximately the composition of the maximum-

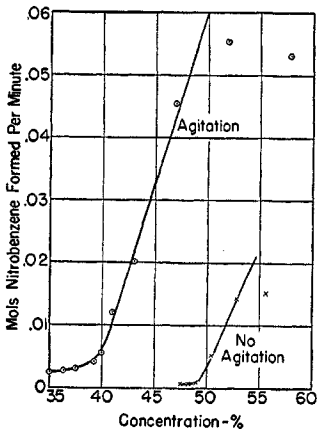


Figure 4. Rate of Formation of Nitrobenzene *vs.* Concentration of Nitrating Acid in Water Layer

boiling azeotrope of nitric acid and water. The water layer, however, distilled from the reaction flask containing large quantities of nitric acid (as high as 40 per cent concentration), as a result of the relatively high vapor pressure of nitric acid. In order to hold down the nitric acid, a packed glass column 1 inch (2.5 cm.) in diameter and 2 feet (61 cm.) high was installed; the condensed benzene (after separating and decanting the water) was used as reflux. This experiment showed that the accompanying rectification helped somewhat, but the water layer in the decanter still contained approximately 6 per cent nitric acid.

At this stage it was not known whether a ternary C. B. M. existed. To obtain semiquantitative information regarding the vapor-liquid relations of the quaternary mixture under the conditions of operation, two simple experiments were carried out: In one, a glass still pot was fitted with a packed glass column, 1 inch in diameter and 5 feet (1.52 meters) long, arranged for total reflux. If a ternary constant-boiling mixture existed under total reflux, the vapors would show a constant acid concentration in the water, despite any length of fractionating column. A batch of 250 grams of 6.1 per cent nitric acid and 250 grams of benzene were refluxed under total reflux conditions until constant-temperature conditions prevailed. Samples were withdrawn and analyzed. Since no nitric acid was present, it was concluded that no ternary azeotrope of benzene, nitric acid, and water existed; and benzene and water could be completely removed from a mixture of the two and nitric acid by efficient fractionation. Thus, the column in the preceding run was simply not sufficiently long to accomplish the desired separation, and if an additional length (not more than 5 feet) had been added, no nitric acid would have come over.

Another experiment was carried out with approximately the same setup, except that the water distilled through the column was removed continuously, and only the benzene was returned to the system as reflux. This served in effect as a nitric acid concentrating system and gave a rough indication of the ease of removing pure water in its C. B. M. with benzene from dilute nitric acid solutions. The data showed that the vapors were free of acid until the pot concentration was about 6.5 per cent. At this point the percentage of acid in the water layer of condensate was only 0.2 per cent and gradually increased until, at a pot concentration of 65 per cent, it was 18 per cent; this is a rough indication of the separating efficiency of this column. The data are shown in the following table and in Figure 5:

% Acid in Water Layer in Pot	% Acid in Water Layer of Dist.	% Acid in Water Layer in Pot	% Acid in Water Layer of Dist.
5.05	0.0	10.1	0.6
5.34	0.0	16.0	1.0
6.00	0.0	19.5	1.8
6.48	0.2	31.0	4.0
7.46	0.4	68.0	18.2
8.73	0.6		

These runs showed that the benzene-water C. B. M. could successfully be separated from any concentration of nitric acid if a sufficiently long column were provided. Thus, in the present case a 5-foot column gave a separation, between the respective water layers, from 68 per cent in the pot to 18 per cent in the decanter. Figure 5 and the above table indicate that a second superimposed 5-foot column (operating with the same reflux, the benzene layer, in every case) would reduce the concentration from this 18 per cent in the water layer of the decanter to about 1.6 per cent; and another section, less than 5 feet long, would reduce the concentration of the water layer in the decanter to a negligible amount.

CONTINUOUS FEED RUNS

With the fact established that the acid loss in the water drawn off could be eliminated, the investigation proceeded to the study of continuous acid feed. For the merit of a process based on nitration by nitric acid alone would be in its adaptability to continuous operation.

Runs were performed to obtain qualitative data on the effect of varying the relative length of the stripping and receiving sections of a column on the composition and temperatures at the top and bottom of the column. The rate of feed was also varied at each feed position, as well as the vapor rate or boil-up through the column.

The setup shown in Figure 6 consisted of a column 1 inch in diameter and 4 feet (1.22 meters) long, and provided with feed taps every 4 inches (10.2 cm.). The column was provided with a reflux condenser which led into a decanter and was insulated with 1 inch of 85 per cent magnesia pipe insulation. A series of runs was carried out in this setup. The benzene was charged to the pot and was refluxing when the acid feed was started. A bottle provided with a pet cock supplied acid by gravity flow. In almost all cases nitric acid of 61 per cent strength was used as feed. This was adjusted for a given flow rate, and a substantially constant head was maintained by adding quantities of acid to the bottle as the run progressed. The desired rate of flow was maintained by counting the drops falling into the funnel connected through a trap to the feed tap. The acid was weighed before and after the run to get the average feed rate for the test period. This provided a check on the drop counting method.

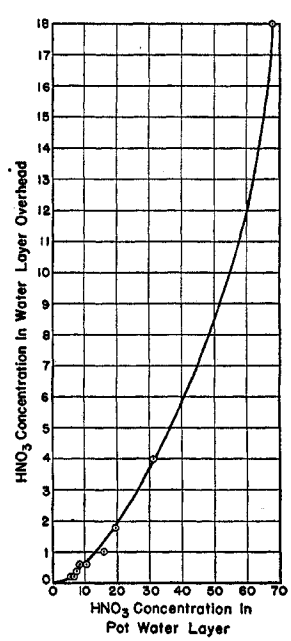


Figure 5. Concentration of Nitric Acid in Pot *vs.* Concentration in Decanter, Using Benzene as Entrainer

Run 16 will be discussed as an example. The feed position was 18 inches (45.7 cm.) from the pot. Benzene was added to make up the charge of 971 grams. The heat was turned on, and in about 20 minutes the benzene was refluxing at a constant rate. The pot temperature was 80°, and the top temperature was 78° C. The nitric acid feed was then started. Throughout the run the pot temperature varied from 80° to 83° C., and the top temperature fell to 73° C. At the end of the run the acid was shut off and the heaters were removed. Since the benzene layer in the decanter contained a dispersion of acid particles, it was found advisable to let this settle for 2 hours before analysis. Also, at the end of 2 hours the column was completely drained.

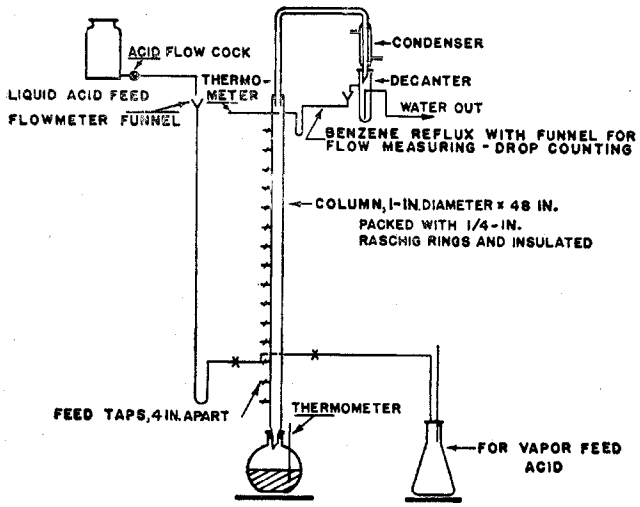


Figure 6. Laboratory Apparatus for Continuous Nitration of Benzene

The contents of the pot and of the decanter were each divided into two layers, aqueous and benzene. The benzene layer contained the relatively small amount of nitrobenzene formed. Most of this large excess of benzene and all of the dissolved nitric acid were separated from the benzene layer by distillation through a short column. Previous investigation as to the possibility of residual acid reacting to cause an increase in the quantity of nitrobenzene had shown that the 3 to 4 per cent acid dissolved in the benzene layer was insufficient to cause nitration. As a check on the amount of nitrobenzene actually formed, the specific gravity of the residue from this distillation was determined, and the amount of nitrobenzene present was calculated. In this manner a material balance could be made on each run; that of run 16 follows:

Grams Charged	% Converted to Nitrobenzene	% in Nitrobenzene Layer in Pot	% in Acid Layer in Pot	% in Benzene Layer Overhead	% in Acid Layer Overhead	% Unaccounted for
HNO_3, 77.8	45.2	13.1	22.1	Trace	18.0	1.6
Benzene, 971	4.5	79.0	Trace	15.5	Trace	<1.0

The unaccounted-for materials were probably lost by vaporization from the decanter, which ran warm, and by incomplete drainage of the column.

To obtain data useful in designing a large-scale unit for this process, a series of runs was made on the effect of varying independently the feed position for nitric acid and the rate of acid feed. These variables affect several factors, such as conversion yields and relative compositions, at different places in the system. The more interesting of these factors are: per cent nitric acid converted to nitrobenzene, per cent nitric acid feed which goes overhead, concentration of nitric acid in water layer of decanter, and per cent nitric acid feed which goes to still pot.

Table II. Vapor Feed of Nitric Acid

Run number	40	41	42
Rate of feed, g./min.	5.83	5.83	1.52
Total acid feed, g.	700.0	706.0	111.0
Time, min.	119.0	120.0	120.0
Benzene charged, g.	918.0	992.0	971.0
Temp. of vapors, ° C.	73	76	72
Temp. of pot, ° C.	82	82	82
% of acid feed going to pot			
Water layer	9.8	8.7	7.8
Benzene layer	21.2	18.7	14.0
% of acid feed going to decanter			
Water layer	6.2	7.3	6.0
To benzene reflux	0.0	1.0	0.2
% of acid feed converted to nitrobenzene	61.0	64.0	63.0
% of benzene charged			
Going to pot	47.2	46.0	76.8
Going to reflux	14.7	15.2	16.1
Converted to nitrobenzene	35.0	34.0	8.5
% unaccounted for			
Acid	1.8	0.3	0.9[a]
Benzene	3.1	4.8	1.4[a]
Rate of benzene reflux, g./min.	5.0	20.0	5.0
Ratio, benzene reflux/acid feed	0.863	3.44	3.29

[a] Sum of products greater than sum of reactants, due to analytical errors.

The conclusions reached in evaluating the data obtained may be presented qualitatively only, because of the small size of the experimental unit. The effect of increasing rates of acid feed, at constant benzene vapor rate and at the same feed position, usually showed an increase in the amount of nitrobenzene produced, a slight decrease in the total acid and per cent acid overhead, and an increase in acid passing to the pot. With greater rectifying length of column (i. e., a lower feed position) the influence of the rate of feed on the overhead was less than where greater stripping length was used. The converse must, of course, be true; and the amount of acid going to the bottoms for a given feed rate was found to be less with a longer exhausting section.

At the same feed rate, increased rectifying length favored a more complete reaction, while decreasing the amount and concentration of acid overhead and increasing the amount of residual unreacted acid in the bottoms. The ratio of weight of benzene vaporized and returned to the column per unit time to the weight of acid fed to the column per unit time did not seem to affect greatly the percentage of acid converted to nitrobenzene.

In these runs usually only a few per cent of the benzene was converted to nitrobenzene. This is not important in a continuous system, since a large excess of benzene is desired at all times, and the benzene-nitrobenzene mixture is readily separable by distillation, in order to recover the latter and return the former. The fact that, in the usual case, less than half the nitric acid is converted in the system, is also relatively unimportant since this may be regarded merely as a first pass, and the aqueous or acid layer may be immediately separated by decantation and again fed into the system. Or the column volume and its holdup (to increase the time of passage) may be increased to allow the reaction to proceed further. In any case, neither nitric acid nor benzene need be lost in any important quantities.

VAPOR FEED

Hantzsch (*2*) states that nitric acid vapor is made up entirely of pseudo acid and is thus a stronger nitration agent

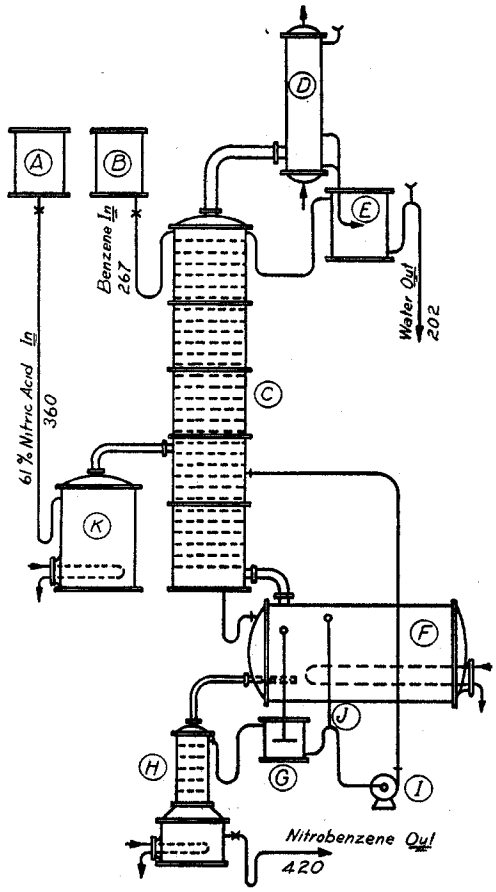


Figure 7. Flow Sheet for Nitration of Nitric Acid and Benzene to Nitrobenzene in Plant with Capacity of 5 Tons Nitrobenzene per Day

(Figures refer to pounds of material flowing per hour)

A. Nitric acid storage (61 per cent HNO_3)
B. Benzene storage
C. Nitrating column (approximately 30 inches in diameter)
D. Hot condenser
E. Decanter for separating hot benzene and water condensate
F. Distilling kettle with heating coils for steam
G. Decanter for separating the nitric acid and benzene-nitrobenzene layers leaving the distilling kettle
H. Distilling column for separating benzene and dissolved nitric acid from nitrobenzene, equipped with base heater
I. Pump for recycling nitric acid and water layer back to nitrating column
J. Vent line to distilling kettle

than the liquid acid. For this reason and because it is assumed that vapor will diffuse to give a uniform mixture, whereas cold liquid feed is bound to channel to some extent, a series of runs was made with nitric acid vapor as the feed. The apparatus for the continuous runs with liquid feed was used, and another boiling flask was added to supply vapor feed. The drops of feed went into a funnel leading to this flask, and boiled off continuously and uniformly to pass to the column through the desired feed tap. The results showed a marked improvement in the conversion yields, as shown in Table II; the conclusions concerning efficiency of nitration which were made for the liquid feed apply equally in this case.

In the continuous runs using liquid feed, the conversion of nitric acid to nitrobenzene was in the neighborhood of 45 per cent of the acid fed to the system; in the runs using vapor feed, the conversion increased to approximately 60 per cent of the total acid charged. The amount of acid fed to the same column during a given period was also higher than was possible in the liquid feed runs; and the amount of nitrobenzene formed in this column per time unit was about twice as high as in the liquid feed runs.

DESIGN OF PLANT

On the basis of this work, a layout is suggested for a plant producing nitrobenzene continuously. Figures are included for a plant to produce 5 tons of nitrobenzene per day for comparison. Since the boiling point of nitrobenzene (208° C.) is higher than the temperature of steam usually available in a plant, it might be preferable to reduce the benzene content of the bottoms product to about 5 per cent in the small column shown (at which composition the boiling temperature is about 118° C.) and to steam distill the balance of the benzene in a subsequent distilling column. Obvious advantages of this plant over the batch process are greater production capacity per man-hour and per square foot of floor space, as well as freedom from use and rehandling of mixed acid. The raw material costs are also lower, due to practically quantitative conversion. The major disadvantage is the comparative expensiveness of the materials of construction of the equipment required. In the batch process, where mixed acid is used, little corrosion occurs. In the continuous process any portion of the unit in contact with the nitric acid must be of suitable construction (stainless steel or other resistant material).

The main distilling unit is constructed to allow substantial holdup of the reactants so that the reaction has enough time to be completed. It is fitted with trays and bubble caps, and proper design allows for considerable agitation of the two liquid layers by the vapor bubbles released on each plate, to secure a high rate of reaction.

The plant would consist of a relatively small reaction tower, a nitrobenzene stripper and the accessory storage, and heat transfer equipment, as shown in Figure 7. A tentative estimate of the production costs indicates improvement over the present-day batch process.

The processes described above are the subject of patent applications of the Autoxygen Company of New York.

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