

FRACTIONATION REQUIREMENTS FOR PRODUCING ANHYDROUS AMMONIA  
FROM AMMONIA-WATER VAPOR SYSTEMS

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In several proposed processes<sup>1, 2, 3</sup>\* for recovering ammonia from coke-oven gas, the ammonia is absorbed in an aqueous solution that is subsequently stripped of its absorbed ammonia. If the stripping operation is performed at the normal boiling point of the solution and if the absorbent used is nonvolatile, the vapors leaving the stripper will consist of ammonia and water at a pressure of 1 atmosphere. These vapors can then be fractionated to produce anhydrous ammonia. If the fractionation is performed at the original pressure of the vapor feed, the anhydrous ammonia leaving the top of the column would have to be condensed in a refrigerated condenser. The cost of refrigeration will in general make this process economically unattractive. Consequently, the anhydrous ammonia must be produced in a column operating at a pressure high enough to permit ordinary cooling water to be used to condense the ammonia. At 200 pounds per square inch gauge (psig), ammonia condenses at approximately 100 F. With 80 F cooling water, the ammonia leaving the top of a fractionator operating at 200 psig can be condensed in a condenser with a 10 F approach and a 10 F cooling-water rise. Since the bottoms of the fractionator will be essentially pure water, open steam would be used and, consequently, steam at approximately 200 psig could be used. (Steam at this pressure is available at many plants.) The fractionation of the vapor feeds, initially at a pressure of 1 atmosphere, in a column operating at 200 psig is complicated by the desire to utilize as much as possible of the latent heat already contained by the vapor but at the same time to avoid high vapor-compression costs. Several alternative methods of accomplishing the fractionation are possible. These are shown in Figures 1 through 4.

Method I

As shown in Figure 1 the vapor, originally saturated at 14.7 psia, is compressed directly into a fractionator operating at 200 psig to produce an anhydrous-ammonia overhead. The vapor leaving the compressor at 200 psig is assumed to be essentially saturated at that pressure.

Method II

As shown in Figure 2 the vapor, originally at 14.7 psia, is first compressed only to a pressure where it can be readily condensed, and the condensate is then pumped into a fractionator operating at 200 psig to produce an anhydrous-ammonia overhead. The condensate, pumped to 200 psig, is heated to its saturation temperature with the fractionator bottoms prior to entering the fractionator. It was chosen to compress the vapor to a pressure where the bubble point of its condensate is 100 F so that the vapor could be condensed with cooling water available at 80 F in a condenser with a 10 F approach and a 10 F cooling-water rise. As a limiting case of this method, the vapor can be totally condensed without any compression if it is lean enough. At a pressure of 1 atmosphere, a vapor containing 25 per cent ammonia can be totally condensed at about 100 F. Consequently, vapors containing 25 per cent ammonia or less would be totally condensed without any compression.

\* See references.

### Method III

As shown in Figure 3 the vapor is first partially condensed at atmospheric pressure, and the liquid and vapor portions are then pumped and compressed, respectively, into a fractionator operating at 200 psig to produce an anhydrous-ammonia overhead. The liquid portion, pumped to 200 psig, is heated to its saturation temperature with the fractionator bottoms prior to entering the fractionator. The vapor portion leaving the compressor at 200 psig is assumed to be essentially saturated at that pressure. It was chosen to partially condense the vapor to a point where the dew point of the vapor and the bubble point of the resulting condensate are 100 F so that the vapor could be partially condensed with cooling water available at 80 F in a condenser with a 10 F approach and a 10 F cooling-water rise. At a pressure of 1 atmosphere, a condensate containing 25 per cent ammonia has a bubble point of 100F. The vapor leaving the partial condenser will be in equilibrium with this condensate and will therefore contain 95.4 per cent ammonia. As one limiting case of this method, if the vapor contains 25 per cent ammonia or less, the partial condenser becomes a total condenser and no subsequent compression is required. Consequently, for feeds containing less than 25 per cent ammonia, this method degenerates to the same limiting case as did Method II. As the other limiting case of this method, if the vapor contains 95.4 per cent ammonia or more, no partial condensation will occur, and this method will become identical with Method I.

### Method IV

Instead of totally condensing feeds containing less than 25 per cent ammonia, as would be done in Methods II and III, or simply compressing them into the fractionator, as would be done in Method I, these lean feeds can first be fed to a pre-fractionator operating at atmospheric pressure and enriched to a composition that can still be totally condensed with ordinary cooling water as shown in Figure 4. The condensed overhead leaving this first unit would then be pumped to 200 psig and heated to its saturation temperature with the water waste from the high-pressure fractionator. It would then enter the high-pressure fractionator to produce an anhydrous-ammonia overhead.

In all four methods, the vapor feeds at 1 atmosphere were assumed to be at their saturation temperature. Actually, the ammonia-water vapors arising from the stripping of an ammonia-absorbing solution will often be somewhat superheated with respect to their own dew point. However, the small amount of additional sensible heat will have very little effect upon the condenser and fractionator calculations. The results of calculations, which are to follow, were all based upon producing 1 ton per hour of anhydrous ammonia.

In analyzing the four fractionation methods described to ascertain in what range of feed composition each is most economical, only utility costs were considered and capital costs were ignored. This could be done for two reasons. First, the capital costs were relatively small compared with the utility costs. For example, the cost of the fractionating tower in terms of its depreciation and maintenance per year, did not amount to more than 5 per cent of the utility costs per year. Also, the capital costs involved in all of the different methods, especially in the ranges of feed compositions where the methods were competitive with each other, were roughly equal, and thus were not a significant factor in evaluating the different methods.

The power requirements for compressing the vapor feed, originally at 0 psig, into a fractionator at 200 psig producing one ton per hour of anhydrous ammonia are shown in Figure 5. Since the ammonia content of the feed is essentially 1 ton per hour at all feed compositions, the feed rate will increase and the power requirements will correspondingly rise as the feed becomes increasingly lean in ammonia.

Shown in Figure 6 are the power requirements for compressing the vapor feed, initially at 1 atmosphere, to a pressure where the bubble point of its condensate is 100 F, and the cooling-water duty for subsequently condensing the partially compressed vapor. As seen, the pressure to which the vapor must be compressed becomes greater as the ammonia content of the feed increases above 25 per cent ammonia. This factor causes the power requirement to increase as the feed becomes increasingly rich in ammonia. However, at the same time the feed rate decreases and this factor causes the power requirement to decrease. Consequently, the curve showing the horsepower requirements will go through a maximum as seen in the slide. Vapor feeds containing 25 per cent ammonia or less can be totally condensed at a pressure of 1 atmosphere and, hence, the horsepower requirements reduce to the negligibly small amounts needed to pump the condensate into the tower. The cooling-water duty for condensing the vapor decreases as the feed becomes increasingly rich in ammonia, owing to the decreasing feed rate. The cooling-water duty curve changes from a concave to a convex shape at a composition of approximately 85 per cent ammonia because of the very rapidly decreasing heat of condensation of ammonia-water vapors richer than 85 per cent ammonia.

Shown in Figure 7 is the cooling-water duty required to partially condense the vapor feed at atmospheric pressure to a temperature of 100 F (that is, to a condensate containing 25 per cent ammonia) and the power requirement for compressing the vapor portion leaving the partial condenser to a pressure of 200 psig. Consistent with what has been said earlier, the fraction of the feed leaving the partial condenser in the vapor state varies between 0 at a feed composition of 25 per cent ammonia and 1.0 at a feed composition of 95.4 per cent ammonia. Hence, as the feed composition increases beyond 25 per cent ammonia, an increasingly large fraction of the feed must be compressed, but at the same time the total feed rate is decreasing. Hence, the horsepower curve is convex and goes through a maximum as seen. The cooling-water duty decreases as the feed becomes increasingly rich in ammonia, both because the feed rate decreases and because for feeds richer than 25 per cent ammonia the fraction of the feed that is condensed also decreases with increasing ammonia concentration. The cooling-water duty is zero for a feed composition of 95.4 per cent ammonia, since at this composition none of the feed is condensed.

Shown in Figure 8 is a comparison of the utility requirements for sending the feed, which is initially a vapor at atmospheric pressure, to a fractionator operating at 200 psig by means of Methods I, II, and III. Method IV will be considered separately later. Method I, in which all the vapor is compressed from 0 to 200 psig, entails the greatest consumption of power, as would be expected. However, since in Method I the feed is sent to the fractionator in the vapor state, it will entail the lowest steam consumption in the fractionator. As explained earlier, Methods II and III have identical requirements for feeds containing less than 25 per cent ammonia. For feeds richer than 25 per cent ammonia, Figure 8 shows that Method III entails a smaller condenser duty than does Method II because in Method III only part, rather than all, of the feed is condensed. It is also clear from Figure 8 that Method III entails a smaller power consumption than does Method II. Method III entails the compression of a relatively small amount of vapor through a relatively large pressure ratio, and Method II entails the compression of a relatively large amount of vapor through a relatively small pressure ratio. That Method III should require a smaller power consumption than Method II is not evident from any prior considerations but is a consequence of the particular properties of the ammonia-water system.

With the feeds now at 200 psig and at different thermal states depending on the method used to elevate their pressure, it remains to calculate the utility requirements for fractionating them. All fractionation requirements were based on producing 1 ton per hour of anhydrous ammonia and a water waste containing not more than 0.5 per cent ammonia. The steam and condenser-duty requirements were calculated by the Ponchon-Savarit Method since the widely different molar latent heats of ammonia and water render the McCabe-Thiele Method inapplicable to this system.

Fractionation requirements are usually calculated by first selecting an optimum reflux ratio. Although this can always be done by a balance of capital and operating costs, a rule of thumb that is often used is that the optimum reflux ratio will be about 1.5 times the minimum reflux ratio. This rule was found to be a poor guide for the ammonia-water system. A better guide was to first select an optimum number of theoretical plates.

Because of the very favorable vapor-liquid equilibrium of the ammonia-water system, it is extremely easy to fractionate ammonia from ammonia-water feeds, and it was found that a tower containing about 10 theoretical plates would require but slightly more steam and condenser water than would an infinitely high tower. Therefore, by providing the tower with more than 10 theoretical plates very little could be saved on steam and cooling water. However, if the number of theoretical plates were reduced substantially below 10, the steam and cooling-water rates would begin to increase more quickly. For the purposes of this paper it is assumed that a tower containing 10 theoretical plates represents an optimum installation. Consequently, the steam and cooling-water requirements were obtained by the Ponchon-Savarit Method to correspond to a fractionator containing 10 theoretical plates. For any given application it is necessary to more accurately establish the optimum tower size.

Shown in Figure 9 are the steam and condenser-duty requirements for a 10-theoretical-plate fractionator, operating at 200 psig and producing 1 ton per hour of anhydrous ammonia and a water waste containing not more than 0.5 per cent ammonia. Anhydrous ammonia contains no more than 0.3 per cent water. For both all-liquid and all-vapor feeds, the steam rate and condenser duty decrease as the feed becomes richer in ammonia primarily because of the decreased amounts of feeds that need be handled. For an all-vapor feed, the condenser duty required is higher and the steam rate is lower than for a liquid feed, as would be expected. For a liquid feed, the steam rate and condenser duty do not approach zero as the feed composition approaches 100 per cent ammonia. This is because as long as any fractionation at all is accomplished the feed must be vaporized and recondensed. Of course, when the feed composition reaches 99.7 per cent ammonia, no fractionation would be needed and all requirements would drop discontinuously to zero. For a vapor feed, the steam rate approaches zero as the feed composition approaches 100 per cent ammonia, since the feed already enters the column in a vaporized state. However, the condenser duty for a vapor feed does not approach zero as the feed composition approaches 100 per cent ammonia since the vapor feed must always be condensed to produce liquid anhydrous ammonia. The mixed vapor-liquid feed line shown indicates the steam rate and condenser duty required to fractionate feeds containing the proportions of liquid and vapor leaving the partial condenser in Method III. For each over-all feed composition, the fraction of the feed that will leave the partial condenser in the vapor state has been shown in Figure 7. As explained earlier, and as shown, the mixed vapor-liquid feed will become an all-liquid feed at a feed composition of 25 per cent ammonia, and will become an all-vapor feed at a feed composition of 95.4 per cent ammonia.

From the utility requirements shown on the previous two slides, Figures 8 and 9, the utility costs can be computed, the following assumed utility rates being used:

Power at 1 cent per kilowatt-hour  
Steam at 70 cents per thousand pounds  
Cooling water at 2 cents per thousand gallons

These are average utility rates applicable to many plants.

The cooling-water rate is computed from the condenser duty on the basis of a cooling-water rise that will yield a 10 F approach in the condenser. Consequently, the allowable cooling-water rise in the column condenser will be 10 F. For feeds containing more than 25 per cent ammonia, the allowable cooling-water rise in the feed condenser will also be 10 F because of the manner in which these feeds are handled.

Feeds leaner than 25 per cent ammonia have a bubble point higher than 100 F and, therefore, can be condensed with 80 F cooling water in a condenser with a 10 F approach and a cooling-water rise greater than 10 F. For these lean feeds, the allowable cooling-water rise was based upon a 10 F approach in the condenser, provided that the outlet cooling-water temperature did not exceed 125 F.

Shown in Figure 10 are the utility costs for producing 1 ton per hour of anhydrous ammonia from a vapor feed, initially at atmospheric pressure, by means of Method I. The steam cost for the column and the cooling-water cost for the column condenser (curves 2 and 3) were computed from the vapor-feed curves shown on the previous figure. The power cost for the compressor (curve 1) was computed from the power requirements shown earlier, Figure 5, for compressing the vapor from 0 to 200 psig. All of the utility costs increase and hence the total utility cost increases as the feed becomes increasingly lean in ammonia, primarily because of the increasingly larger amount of feed that must be handled.

Shown in Figure 11 are the utility costs for producing 1 ton per hour of anhydrous ammonia from a vapor feed, initially at atmospheric pressure, by means of Method II. Feeds containing less than 25 per cent ammonia will have a bubble point higher than 100 F at atmospheric pressure and therefore can be totally condensed without compression. The cooling-water cost for the feed condenser (shown by curve 1) is lower for a feed containing 20 per cent ammonia than it is for a feed containing 25 per cent ammonia, because of the greater cooling-water temperature rise that is allowable for the leaner feed. As the feed composition becomes leaner than 20 per cent ammonia, the cooling-water cost for the feed condenser increases, because of the overpowering effect of the increasing feed rate. For feeds containing more than 25 per cent ammonia, the allowable cooling-water temperature rise in the feed condenser will remain constant, since the vapor is always compressed to a pressure where the bubble point of its condensate is 100 F. Hence, the cooling-water cost for the feed condenser gradually decreases as the ammonia content of the feed increases above 25 per cent ammonia. The steam cost for the column and the cooling-water cost for the column condenser (curves 4 and 3) were computed from the liquid feed lines on the slide showing the fractionation requirements, Figure 9. The power cost for the compressor (curve 2) was computed from the power requirements, shown earlier, Figure 6, for compressing the vapor from atmospheric pressure to a pressure where the bubble point of its condensate is 100 F. It is seen that for lean feeds the total utility cost increases primarily as a result of the increasing steam cost for the column rather than as a result of increasing power costs as in Method I. As the feed composition increases beyond 25 per cent ammonia, the power cost for compressing the vapor increases more quickly than the steam and cooling-water costs decrease, and therefore the total utility cost begins to increase. As the power cost begins to level out, the decreasing steam and cooling-water costs then cause the total utility cost to decrease. Hence, the total utility cost goes through a maximum at a feed composition of 45 per cent ammonia. Therefore, if the fractionation were performed as prescribed in Method II, it would cost more to fractionate a vapor feed containing 45 per cent ammonia than a vapor feed containing 20 per cent ammonia, both initially at atmospheric pressure. This leads to the surprising conclusion that it would be advantageous to dilute the feed containing 45 per cent ammonia to a feed containing 20 per cent ammonia in a direct condenser, totally condense it, and pump the condensate into the high-pressure fractionator. It is clear from Figure 11 that this means of operation will be more economical than Method II for feed compositions covering the extent of the dotted line shown, namely from about 20 to 75 per cent ammonia. If the fractionation of these feeds is accomplished by this dilution method, the total utility cost involved will remain approximately constant at about \$4 per ton of ammonia produced.

Shown in Figure 12 are utility costs for producing 1 ton per hour of anhydrous ammonia from a vapor feed, initially at atmospheric pressure, by means of Method III. Feeds containing less than 25 per cent ammonia can be totally condensed at atmospheric pressure and hence no subsequent compression is required. The cooling-water cost for the feed condenser given by curve 1 decreases, then increases, and finally decreases

again for generally the same reasons as given for Method II. The steam cost for the column and the cooling-water cost for the column condenser (curves 4 and 3) were computed from the mixed vapor-liquid feed curves shown in Figure 9. As the feed composition increases above 25 per cent ammonia, the feed rate decreases and the fraction of the feed that enters the fractionator as a vapor increases. Consequently, as the feed becomes increasingly rich in ammonia, the steam cost for the fractionator decreases more quickly than in Methods I and II and the cooling-water cost for the fractionator condenser decreases more slowly than in Methods I or II. In Methods I and II, the thermal state of the feed entering the fractionator did not vary with the feed composition as it does in Method III. The power cost for the compressor (curve 2) was computed from the power requirements, shown earlier, Figure 7, for compressing the vapor fraction leaving the partial condenser from 0 to 200 psig. As the feed composition increases above 25 per cent ammonia, the power cost for compressing the vapor increases. However, the power cost increases slowly enough so that the decreasing steam and cooling-water costs are not offset, and hence, the total utility cost does not exhibit a maximum in this range, but decreases slowly with increasing ammonia content in the feed.

It was seen from the previous figures that it is relatively expensive to fractionate a lean vapor, either because of the compression cost if the vapor is compressed into the fractionator, Figure 5, or because of the steam cost in the fractionator if the vapor is condensed and then pumped into the fractionator, Figure 9. In Method IV, the lean vapor is first sent to a prefractionator where it is enriched to a composition that can still be readily condensed with available cooling water. The overhead from this first column is then pumped into the high-pressure fractionator to produce the anhydrous ammonia. If the lean vapor feed is handled in this manner, some of the latent heat already contained by the vapor can be utilized in its enrichment without incurring any compression costs. Hence, it may be anticipated that for lean vapor feeds Method IV will prove to be most economical.

Shown in Table I are the utility requirements and costs for producing 1 ton per hour of anhydrous ammonia by means of Method IV, from a saturated vapor feed at atmospheric pressure containing 5 per cent ammonia.

Table I

Requirements for Producing Anhydrous Ammonia by Means of Method IV  
From a Vapor Feed Containing 5% Ammonia

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Basis: 1 ton per hour of anhydrous ammonia produced

Prefractionator:

Pressure: 0 psig  
 Feed: Saturated vapor at 0 psig containing 5% ammonia  
 Distillate: Ammonia-water solution containing 15% ammonia  
 Waste: Water containing 0.2% ammonia

Main Fractionator:

Pressure: 200 psig  
 Feed: Saturated ammonia-water solution containing 15% ammonia  
 Distillate: Anhydrous ammonia  
 Waste: Water containing 0.5% ammonia

Utility Requirements and Costs Per Ton of Anhydrous Ammonia Produced

	Condenser Duty, Millions of BTU	Cooling Water Cost, \$	Steam Rate, Thousands of lbs	Steam Cost, \$
Prefractionator	43.6	2.33	1.4	0.98
Main Fractionator	2.8	0.67	4.4	3.08

Total Utility Cost = \$7.06

The distillate composition of 15 per cent ammonia, chosen for the prefractionator, results in the best balance of utility costs between the prefractionator and the main fractionator. If the distillate composition were made richer than 15 per cent ammonia, the cooling-water cost for the prefractionator condenser would increase because of the smaller allowable cooling-water temperature rise that would result. If it were made leaner than 15 per cent ammonia, the steam cost for the main fractionator would increase sharply. As seen in the next figure, the total utility cost of \$7.06 per ton of ammonia, which results from handling the vapor feed containing 5 per cent ammonia by means of Method IV, is considerably less than would result from handling the same feed by any other method.

Shown in Figure 13 is a comparison of the total utility costs involved in producing 1 ton of anhydrous ammonia by each of the different methods considered. It is evident that for lean feeds a large economic incentive exists for prefractionating the feed as described in Method IV. The total utility cost that results from handling a feed containing 5 per cent ammonia by this method is \$7.06. If this feed were totally condensed and the condensate subsequently pumped into the high-pressure fractionator, as in Methods II and III, a total utility cost of \$10.80 would result. Compressing the feed directly into the high-pressure fractionator, as in Method I, would result in a much higher cost than is involved in either of the two previously mentioned methods. In Method IV the lean feed is enriched to 15 per cent ammonia. Consequently, when the feed composition reaches 15 per cent ammonia, Method IV reduces to simply condensing the feed and pumping the condensate into the high-pressure fractionator. As explained earlier, for feeds containing less than 25 per cent ammonia, Methods II and III reduce to totally condensing the feed and pumping the condensate into the high-pressure fractionator. Hence, at a feed composition of 15 per cent ammonia, Method IV will become identical with Methods II and III.

Figure 13 shows that for feeds containing more than 25 per cent ammonia, Method III is more economical than Method II. For feeds ranging in composition from about 25 to 75 per cent ammonia, it is more economical to first dilute the feed to about 20 per cent ammonia, totally condense it, and pump the condensate into the high-pressure fractionator than it is to handle the feed by means of Method II. However, as can be seen, this method of diluting a rich feed to a composition that can be totally condensed at atmospheric pressure is never more economical than partially condensing the feed and then compressing the vapor leaving the partial condenser as is done in Method III. As explained earlier, for feed compositions richer than 94.4 per cent ammonia, Method III is identical with Method I and the vapor is simply compressed into the high-pressure fractionator.

If utility rates, cooling-water temperature, and steam pressure are significantly different from those assumed in this paper, not only will the utility costs change but the preferred method for handling a feed of a given composition will also change. For example, if the fractionation is performed in a location where power costs are unusually high, the costs of Methods II and III will increase since both involve compressing the vapor. However, the cost of diluting the rich vapor to a composition that can be totally condensed at atmospheric pressure and pumping the condensate into the high-pressure fractionator will remain approximately constant at the value indicated by the horizontal line, Figure 13. Consequently, where power costs are high, it would be more economical, at least over some range of feed compositions, to dilute a rich feed to a composition at which it could be totally condensed rather than handling it by means of Method III. The same procedure would also be used if the available cooling-water temperature is unusually high, for it would become necessary to operate the fractionator at a pressure significantly higher than 200 psig to condense the anhydrous ammonia. Consequently, the compression costs involved in Methods II and III will increase, and it might be most economical to dilute a rich feed to a composition that could be totally condensed at atmospheric pressure.

Summary

For the cooling-water temperature, steam pressure, and utility rates chosen in this paper, the preferred methods of producing anhydrous ammonia from ammonia-water vapors initially at atmospheric pressure are as follows:

1. Feeds containing less than 15 per cent ammonia are first sent to a prefractionator operating at atmospheric pressure in which they are enriched to a 15 per cent ammonia overhead. The distillate from the prefractionator is then pumped into the main fractionator operating at 200 psig to produce anhydrous ammonia.

2. Feeds containing from 15 per cent ammonia to 25 per cent ammonia are totally condensed at atmospheric pressure, and the condensate is pumped into a fractionator operating at 200 psig to produce anhydrous ammonia.

3. Feeds containing from 25 per cent ammonia to 95 per cent ammonia are first partially condensed at atmospheric pressure to a temperature of 100 F. The condensate and vapor leaving the partial condenser are then pumped and compressed, respectively, into a fractionator operating at 200 psig to produce anhydrous ammonia.

4. Feeds richer than 95 per cent ammonia are compressed into a fractionator operating at 200 psig to produce anhydrous ammonia.

Literature Cited

1. Bahr, H., German Patent No. 741,222 (1943).
2. Bergfeld, L., German Patent No. 270,204 (1911).
3. Societe Industrielle et Financiere de Lens, French Patent No. 857,242 (1940).

METHOD II - COMPRESSION FOLLOWED BY CONDENSATION

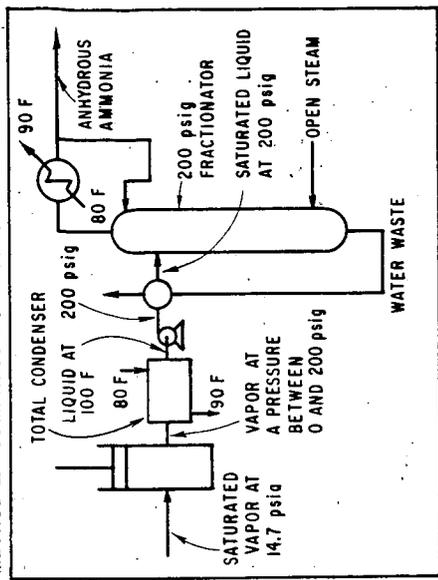


FIGURE 2

METHOD IV - PREFRACTIONATION

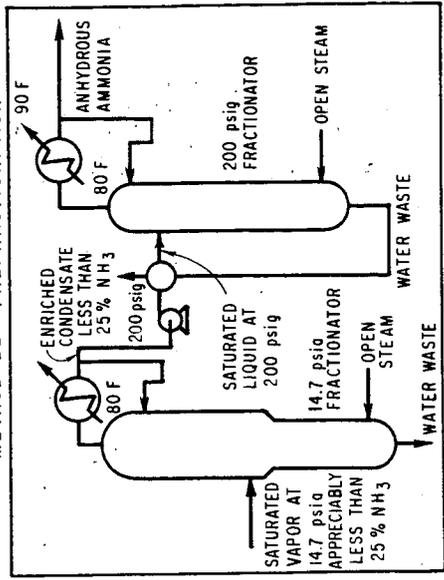


FIGURE 4

METHOD I - DIRECT COMPRESSION TO 200 psig

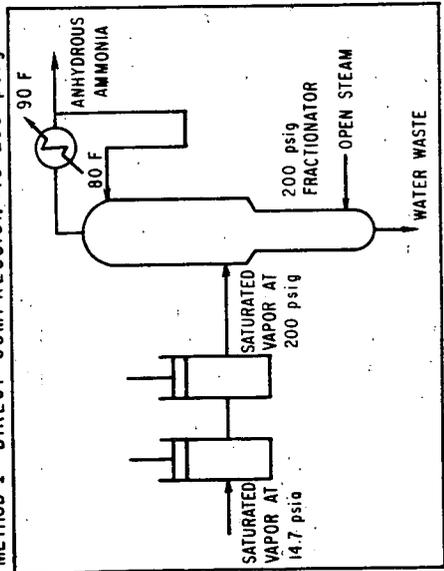


FIGURE 1

METHOD III - PARTIAL CONDENSATION FOLLOWED BY COMPRESSION

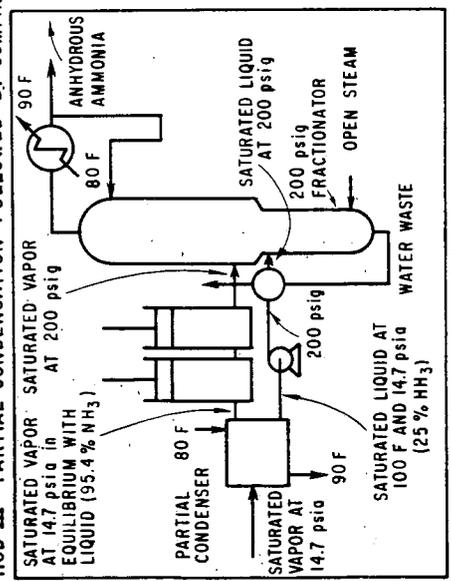


FIGURE 3

REQUIREMENTS FOR COMPRESSING ALL OF THE VAPOR INTO A 200 psig TOWER PRODUCING 1 TON/HR ANHYDROUS AMMONIA AS IS DONE IN METHOD I

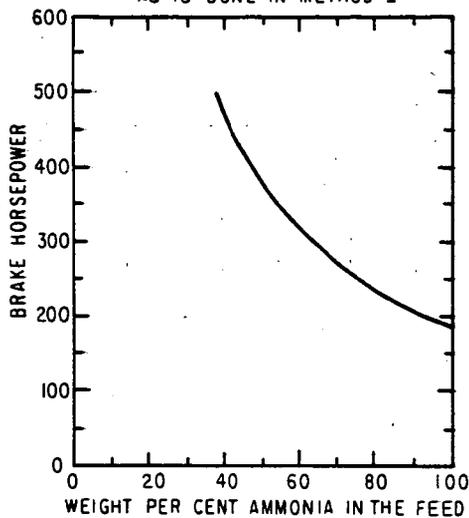


FIGURE 5

REQUIREMENTS FOR COMPRESSING THE VAPOR TO A PRESSURE WHERE ITS BUBBLE POINT IS 100 F AND THEN TOTALLY CONDENSING IT AS IS DONE IN METHOD II (BASIS: 1 TON/HR OF NH<sub>3</sub>)

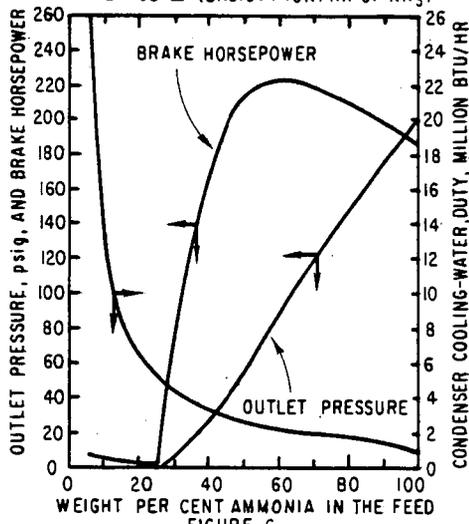


FIGURE 6

REQUIREMENTS FOR PARTIALLY CONDENSING THE VAPOR AT 1 ATM AND THEN COMPRESSING THE VAPOR PORTION INTO A 200 psig TOWER PRODUCING 1 TON/HR AMMONIA AS IS DONE IN METHOD III

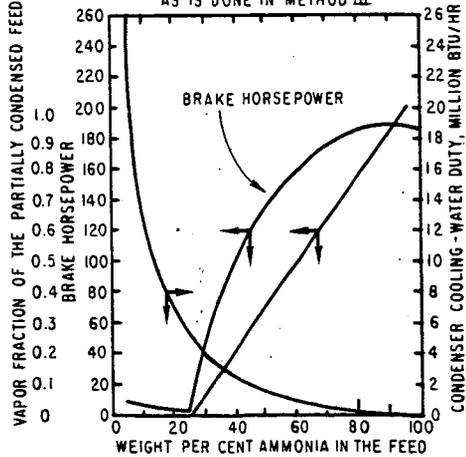


FIGURE 7

UTILITY REQUIREMENTS FOR SENDING THE FEED TO A FRACTIONATOR OPERATING AT 200 psig BY MEANS OF METHODS I, II, AND III

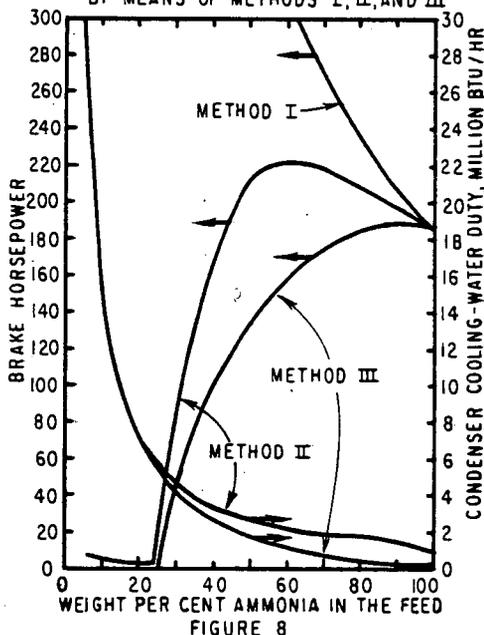


FIGURE 8

STEAM AND CONDENSER-DUTY REQUIREMENTS FOR A FRACTIONATOR AT 200 psig PRODUCING 1 TON PER HOUR ANHYDROUS AMMONIA AND A WATER WASTE CONTAINING NOT MORE THAN 0.5 PER CENT AMMONIA

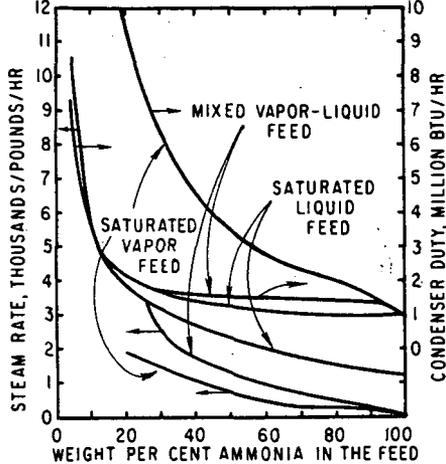


FIGURE 9

UTILITY COSTS FOR PRODUCING 1 TON/HR OF ANHYDROUS AMMONIA BY MEANS OF METHOD I  
 ① POWER FOR COMPRESSOR  
 ② STEAM FOR COLUMN  
 ③ COOLING WATER FOR COLUMN CONDENSER

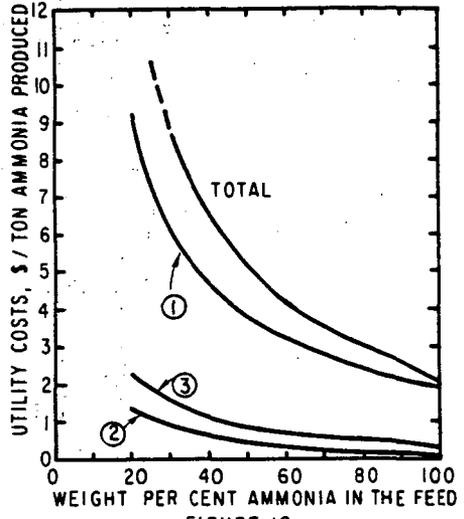


FIGURE 10

UTILITY COSTS FOR PRODUCING 1 TON/HR OF ANHYDROUS AMMONIA BY MEANS OF METHOD II

- ① COOLING WATER FOR FEED CONDENSER
- ② POWER FOR COMPRESSOR
- ③ COOLING WATER FOR COLUMN CONDENSER
- ④ STEAM FOR COLUMN

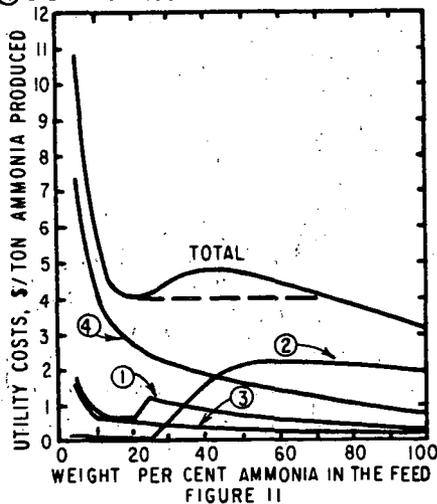


FIGURE 11

UTILITY COSTS FOR PRODUCING 1 TON/HR  
ANHYDROUS AMMONIA BY MEANS OF METHOD III

- ① COOLING WATER FOR FEED PARTIAL CONDENSER
- ② POWER FOR COMPRESSOR
- ③ COOLING WATER FOR COLUMN CONDENSER
- ④ STEAM FOR COLUMN

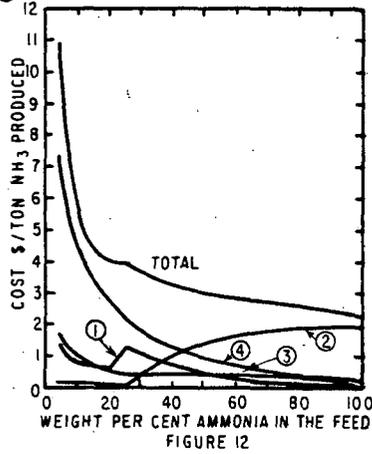


FIGURE 12

COMPARISON OF THE TOTAL UTILITY COSTS INVOLVED  
IN PRODUCING ONE TON OF ANHYDROUS AMMONIA  
FROM AN AMMONIA-WATER VAPOR FEED AT ATMOSPHERIC  
PRESSURE BY MEANS OF METHODS I, II, III, AND IV

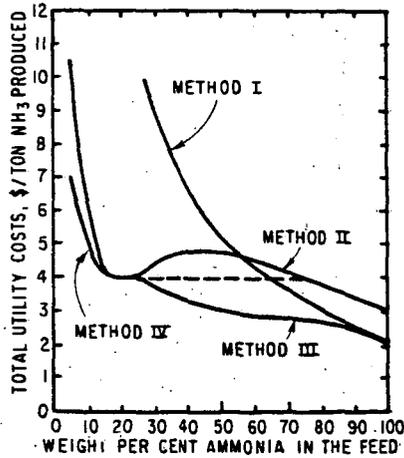


FIGURE 13

## THE ROLE OF CORROSION TESTING IN THE COAL-CHEMICAL PLANT

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### Introduction

It is a well-known fact that corrosion of plant equipment is costing the chemical producers millions of dollars annually. In the coal-chemical industry, as in any other industry today, it is imperative to minimize maintenance and replacement costs and to insure uninterrupted production to remain competitive. Although the high cost of corrosion cannot be entirely eliminated, it can be greatly reduced by the proper selection of constructional materials, by modifications in equipment design and operating procedure, and by the proper selection and application of protective coatings and inhibitors. However, the answer to a corrosion problem, whether it lies in replacement of the present materials of construction or in a modification in design, is usually not simple and cannot be readily ascertained without firsthand knowledge of the problem. This data can best be developed by conducting a well-planned corrosion-testing program.

Such a program can best be defined as one that will provide the most reliable data and the most convincing data from a given set of conditions. In planning a corrosion-testing program, both laboratory and plant tests should be considered. The laboratory test provides the closest control of the important variables and permits individual study of each variable. However, it is extremely difficult to duplicate in the laboratory the combination of effects, such as solution concentration, temperature, velocity, viscosity, that takes place under actual operating conditions in a chemical plant. The limited quantity of solution used in the laboratory test restricts the number and size of the materials in test. Further, unless the test solution is continuously renewed, it is difficult or impossible to maintain a constant concentration of known corrosive constituents in the solution, and thus the results may be erroneous. In a plant test, however, all the above variables are present. As a result, data obtained from plant tests with operating equipment are considered more reliable and are more convincing than laboratory data where plant conditions can only be approximated.

These remarks are not meant to suggest that laboratory data are misleading and have no place in a well-planned corrosion-testing program. On the contrary, laboratory tests can be used to screen a series of materials or inhibitors prior to being plant-tested, to provide data for comparison purposes, or to supplement plant data. In the development of new processes where previous corrosion experience is lacking or in plant corrosion problems where the equipment is inaccessible for corrosion testing, the corrosion engineer must often turn to laboratory data for guidance in selecting suitable constructional materials. When a new process is being developed and a pilot plant is to be constructed, corrosion tests should also be conducted in these facilities. Inasmuch as pilot facilities are often small, arrangements should be made early in the design stage to include adequate corrosion-testing locations. However, the data obtained from either laboratory or laboratory and pilot-plant studies should be used judiciously in selecting construction materials for a full-size piece of equipment.

### Plant Corrosion-Testing Methods

In plant corrosion testing, various methods are utilized depending upon the objective. The tests most frequently used are those described below:

#### Corrosion-Specimen Test

The corrosion-specimen test is probably the best known and most widely used method in the coal-chemical industry. The test consists of obtaining cleaned and weighed specimens of various materials, including the materials in the piece of equipment to be tested, and exposing them in the liquid and vapor space of the operating unit for a given period of time. The test specimens are normally welded to obtain information on the effect of welding on the corrosion performance of the material, which is an important factor in choosing materials of construction for equipment. Moreover, in certain environments, it is often desirable to expose stressed specimens in the equipment to develop information on the susceptibility of the various construction materials to stress-corrosion cracking.

Although the specimens can be individually suspended in the unit, they are normally placed in a specimen holder and separated with insulating material to prevent direct contact except when galvanic effects are being studied. Figure 1 shows a typical corrosion-test rack and its various components. (Special types of rack may have to be designed for units difficult in accessibility.) Although it is usually necessary to shut down the operating unit to install or remove a test rack, retractable holders can be constructed to permit testing during normal operations. However, this method limits the number of materials that can be tested at one time. If the unit is inaccessible, the specimens can usually be installed in the related piping, though the data will not be as representative as data obtained from the actual operating unit. In testing in a pipeline, the specimens are mounted on a pipe plug and placed in a tee in the line. However, care must be taken to install the specimens parallel with the flow so as not to cause a restriction in the line. Figure 2 shows a mounted pipe-plug specimen and method of installation. In special cases, the materials to be evaluated can be obtained in pipe form, and short sections of each can be installed in the line. Much like the test specimens, these sections should be cleaned and weighed prior to exposure and should be insulated from each other.

After exposure, the test specimens are carefully cleaned and reweighed, and their corrosion rates calculated from the weight losses. Care should be taken to examine the specimens for local effects, such as pitting, grooving, and cracking. The data obtained from this test method will provide information on the expected service life of the unit, type of corrosion occurring, and suitable replacement materials.

#### The Electrical-Resistance Method

The electrical-resistance method is a direct means of measuring corrosion continuously and is used in the chemical industry to follow the progress of corrosion in operating equipment.<sup>1</sup>\* A special probe and meter are utilized in conducting these measurements. Figure 3 shows an electrical-resistance probe, and Figure 4 shows a portable meter and a typical installation. Several of these corrosion-monitoring devices are commercially available. In making measurements, the probe containing an element of the material to be tested is placed in the system under study and is then electrically connected to the meter. The meter measures the change in electrical resistance of the probe element as the cross-sectional area of the element is reduced by corrosion. The amount of corrosion can then be read directly from the meter in microinches penetration of the probe element.

\* See References.

With the electrical-resistance method, corrosion data can be obtained in a few hours, whereas with weight-loss measurements data sometimes cannot be obtained for months because the removal of specimens is governed by plant operations. Unlike the use of corrosion-test racks, the electrical-resistance method does not require shutting down the operating unit to remove or change probe elements. The measurements are not affected by the accumulation of most corrosion products or sludge. However, the measurements are affected by corrosion products that carry current, such as sulfides. Like any test, this method also has its undesirable features in that it is limited to measuring a uniform type of corrosion and it is necessary to visually examine the probes to determine the presence of local forms of corrosion, such as pitting.

Probably the most widespread use of the electrical-resistance method is in the evaluation of corrosion-preventive measures, such as inhibitors. In addition, this method is especially useful for correlating corrosion with changes in operations.

#### Service Test

The service test is the most satisfactory method of corrosion testing. In this test, sections of the equipment to be tested are replaced with full-size experimental parts. Probably the most frequent use of this method is with heat exchangers and pumps, both of which are normally inaccessible for corrosion-rack testing. For example, in evaluating materials for replacing heat-exchanger tubes, full-size tubes constructed of various materials are placed in the tube bundle for testing. After a sufficient operating period (six months to one year), the tubes are removed from the exchanger and examined. In a test of this type, where large pieces of equipment are often handled, the examination of the equipment usually consists of a visual inspection. However, for some equipment—tubes, for instance—the thickness of the parts can be measured with a micrometer prior to and after exposure to determine change in dimensions as a result of corrosion.

Unlike the other methods previously mentioned, this method will readily detect local points of corrosion. Unfortunately, this method is often impractical and expensive.

#### Visual-Inspection Method

Visual inspection is probably the most common method of evaluating the performance of a piece of equipment. However, it usually requires a complete shut-down and clean-out of the unit. The data obtained from visual inspection plus ultrasonic measurements of wall thickness provide convincing information on the service life of a unit. As a result, this method is widely used by insurance and state inspectors in examining pressure-coded equipment and by maintenance personnel in conducting preventive corrosion programs.

#### Nondestructive Testing Method

In nondestructive testing, two of the more widely used pieces of equipment are the ultrasonic thickness gauge and the magnetic-particle inspection equipment for detecting surface discontinuities, such as cracks. The ultrasonic thickness gauge is an instrument for the nondestructive measurement of an unknown wall thickness from one side. This instrument utilizes the principle of ultrasonic resonance in measuring thickness. Several portable, battery-operated gauges are commercially available. Figure 5 shows the ultrasonic thickness gauge and method of application. This method is especially useful in determining the wall thickness of inaccessible equipment where visual inspection cannot be made. The magnetic-particle inspection method has been very useful on occasion in determining the integrity of high-pressure equipment.

### Corrosion-Testing Applications

The corrosion-detection methods discussed above are the major plant tools which the corrosion engineer has to work with in his endeavor to control corrosion. Examples of how some of these methods have been used in solving specific corrosion problems in U. S. Steel's coal-chemical plants are given below. For each of the examples, a brief description of the process as it concerns certain pieces of plant equipment is given. Several additional examples of how corrosion testing has solved specific corrosion problems in coal-chemical plants have been presented by Larrabee and Mathay.<sup>2)</sup>

#### Corrosion-Rack Tests in Tar-Distillation Equipment

One area in the coal-chemical plant that has caused operators considerable corrosion trouble is the tar-distillation plant. In this operation, the tar removed from the coke-oven gas in the collecting mains is placed in decanters to permit separation of the flushing liquor and finely divided carbon that are carried along with the tar from the collecting mains. After decantation, the tar is washed and centrifuged to reduce the moisture and inorganic salt content of the tar. The tar leaving the centrifuge is then placed in storage tanks until further processing. Upon demand, the tar is pumped into a dehydrating flash drum, where it is further dehydrated and preheated to a high temperature. The tar leaving the flash drum enters the tar still (carbon-steel shell lined with AISI Type 316 stainless steel, with Type 316 internal parts), where it is fractionated into tar acid oils and pitch. The acid oil is further treated by distillation for the recovery of naphthalene and solvents.

Corrosion of the tar-distillation facilities is essentially controlled by the decantation, washing, and centrifuging operations. The agents in coal tar that are believed to be responsible for corrosion are the inorganic salts, ammonium chloride and ammonium thiocyanate.<sup>3)</sup> The tar-handling operations minimize the concentration of these contaminants. Of the two corrosion constituents, ammonium chloride is the most aggressive. The individual effect of thiocyanate and chloride compounds in acid oil on the corrosion of carbon steel was studied in laboratory tests. The results of these tests, Table I, show that operating problems with the tar-handling facilities can lead to serious corrosion problems as a result of large quantities of these corrosive constituents entering the tar-distillation equipment.

Recently, at one of the coal-chemical plants where serious operating problems were encountered in the tar-handling system, extensive corrosion of distillation equipment occurred. Interior inspection of the primary naphthalene fractionator revealed that the carbon-steel shell and AISI Type 410 stainless-steel internals of the fractionator were corroding. (The function of the primary naphthalene fractionator is to concentrate the crude naphthalene in the acid oil received from the tar still.) The corrosion attack was most severe at the top of the column where ammonium thiocyanate and ammonium chloride were found to concentrate. Following the inspection, the top of the column was lined with cement. At the same time, corrosion-test racks containing various metals were placed in the unit to determine suitable replacement materials, and the unit was again placed into operation. The types and chemical composition of the test materials contained in the racks are shown in Table II. After six months of operation, the fractionator was shut down and the test racks were removed. The results of these tests, Table III, show that AISI Types 304 and 316 stainless steels and USS TENELON stainless steel were practically unattacked.

Visual inspection of the unit revealed that the corrosion of the shell and internals had progressed to the point where replacement was necessary. On the basis of the above results, the corroded unit was recently replaced with a new AISI Type 316L stainless-steel fractionator. The low-carbon-grade Type 316L stainless steel was used in the construction to obtain maximum corrosion resistance at the weld areas.

Reducing the carbon content of the low-carbon stainless steels to the solubility limit of about 0.02 per cent minimizes or prevents carbide precipitation in the heat-affected zone of the metal during welding. As a result, the low-carbon stainless steels are less susceptible to intergranular corrosion at the weld areas.

#### Service Test in Wash-Oil System

In another coal-chemical plant, 150 million gallons of river water are used daily for cooling purposes. Although the water is treated with lime to raise the pH from about 3.8 to about 4.5 (further treatment being uneconomical because the water is not recirculated), the carbon-steel condenser tubes in the wash-oil regenerating system of the plant are corroded seriously and fail after about four months of service. (Wash oil is used to absorb from the coke-oven gas those constituents having boiling points below 200 C, such as benzol, toluene, and xylol.) The wash-oil condenser receives wash-oil vapors from a Dowtherm heat exchanger, which partially condenses the oil vapors coming from the wash-oil still. As shown in Figure 6, the hot oil flows through the shell side of the wash-oil condenser and is cooled by river water flowing through the tubes. The temperature of the oil is about 350 F. The cooling water enters the condenser at about 80 F and leaves at about 180 F.

In an effort to reduce the high maintenance and replacement costs caused by the rapid failure of carbon-steel condenser tubes, a service test was initiated to determine the suitability of stainless-steel tubes in the wash-oil condenser.<sup>4)</sup> Four AISI Type 304 stainless-steel tubes and four carbon-steel tubes were installed in the tube bundle of the condenser at the same time. After four months of exposure, the carbon-steel tubes failed because of severe pitting by the cooling water. After six months of exposure, two of the Type 304 tubes removed from the condenser were practically unattacked. Figure 7 shows a section cut from the center of each type of tube after the service test. (The marks on the interior surface of the Type 304 tube are fabrication marks.) The remaining two Type 304 tubes were removed after one year of exposure and were also found to be in excellent condition. Because of the excellent resistance of the Type 304 tubes to corrosion by the low pH river water, Type 304 tubes will be installed in the entire condenser. The use of Type 304 tubes should result in a substantial yearly savings through decreased maintenance costs.

#### Corrosion Monitoring of Foul-Gas Line

In the utilization of coke-oven gas as a fuel for the open hearth, soaking pits, and reheating furnaces, it is desirable to remove the sulfur from the gas as it constitutes an unwanted contaminant in steel. At one of the coal-chemical plants, a portion of the coke-oven gas is processed for the removal of sulfur and other contaminants prior to sending the gas to the open-hearth melting furnace. In this process, the coke-oven gas leaving the gas line enters an absorption tower, where the gas is scrubbed counter-currently with a sodium carbonate solution to remove hydrogen sulfide, hydrogen cyanide, carbon dioxide, and other contaminants. The desulfurized coke-oven gas leaves the top of the tower and is sent to the open-hearth furnace. The foul solution is removed from the bottom of the tower and pumped into a stripping column, where it is regenerated by steam distillation and recycled to the absorber. The foul gas leaving the top of the column is sent to the open-hearth shop, where it is used as fuel for the boilers. The service life of the carbon-steel line carrying the foul gas to the open-hearth boilers is usually about two years. A corroded portion of the pipe after two years of service is shown in Figure 8.

An electrical-resistance probe with a carbon-steel element was installed in the foul-gas line to ascertain the effect of operating variables on the rate of corrosion of the line. Corrosion readings with the resistance meter were taken over

a period of 15 days during which time the progress of corrosion was determined when (1) steam was being fed to the steam tracers, (2) steam was not being fed to the steam tracers and, (3) the line was being steamed out. A graph of penetration (microinches) of the probe element versus time, Figure 9, shows that an increase in corrosion takes place only during steam-out periods. The corrosion attack is believed to be the result of hydrogen sulfide, hydrogen cyanide, and thiocyanate attack in the presence of water. The corrosion rate of carbon steel based on the resistance readings for the first steam-out period was 964 mils per year and that for the second steam-out period was 526 mils per year. This investigation also showed that the use of steam tracers for maintaining temperatures higher than about 150.F (normal gas temperature) on the line seemed to have no effect on the corrosion rate of the line. As a result of the investigation, the number of steam-outs was reduced.

#### Summary

The examples cited above represent only a few of the corrosion studies conducted in the Corporation's coal-chemical plants to determine suitable materials of construction for withstanding the extremely corrosive environments normally encountered. To give some idea of the extent of corrosion testing within the Corporation's plants since 1954, over 3500 corrosion specimens have been exposed in about 150 process units. In this same period of time, detailed corrosion inspections have been conducted on 110 process units.

As a result of these corrosion studies, suitable materials have been determined for the replacement of 21 major operating units and 39 smaller units. In addition, the corrosion data have enabled the Corporation to assist customers in selecting materials for the construction of new chemical plants.

#### References

1. A. J. Freedman, E. S. Troscinski, and A. Dravnieks, "An Electrical Resistance Method of Corrosion Monitoring in Refinery Equipment," Corrosion, 14, No. 4, pp. 29-32 (April 1958).
2. C. P. Larrabee and W. L. Mathay, "Controlling Corrosion in Coal-Chemical Plants," Corrosion, 14, No. 4, pp. 37-40 (April 1958).
3. D. McNeill, "Causes and Prevention of Corrosion in Tar Stills," Corrosion Technology, November 1957, p. 385.
4. R. J. Schmitt, "Behavior of Carbon and Stainless Steels in Acid Waters," Corrosion, 14, No. 10, p. 15 (October 1958).

Table I  
Corrosion Rate of Carbon Steel Exposed to Samples  
of Tar Acid Oil at 220 C

Thiocyanate Concentration, grams per liter	Chloride Concentration, grams per liter	Corrosion Rate, mils per year	
		Vapor	Liquid
*	*	3	5
5	0	13	40
0	5	42	184

\* Present in residual amounts.

Table II  
Types and Composition of Test Materials  
Exposed in Primary Naphthalene Fractionator

Material	Per Cent									
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	N
Carbon steel	0.18	0.50	0.930	0.03	0.043	0.05	0.03	0.02	*	*
AISI Type 410 stainless steel	0.06	0.48	0.022	0.005	0.55	*	0.32	12.2	0.03	*
AISI Type 201 stainless steel	0.10	6.0	0.038	0.015	0.40	*	5.4	16.7	*	0.15
AISI Type 304 stainless steel	0.08	1.2	0.022	0.014	0.51	*	9.0	18.5	*	*
AISI Type 316 stainless steel	0.06	1.5	0.03	0.014	0.46	0.23	13.4	17.8	2.3	*
USS TENELON stainless steel	0.08	14.2	0.024	0.008	0.79	*	0.29	16.6	*	0.32

\* Not determined; present in residual amounts.

Table III  
Corrosion-Rack Tests in Primary Naphthalene Fractionator

Material	Rack Location in Fractionator	Corrosion Rate, mils per year
Carbon Steel	Top	*
	Middle	106
AISI Type 410 stainless steel	Top	16
	Middle	1
AISI Type 304 stainless steel	Top	<0.1
	Middle	<0.1
AISI Type 316 stainless steel	Top	<0.1
	Middle	<0.1
USS TENELON stainless steel	Top	<0.1
	Middle	<0.1

\* Specimen completely disintegrated.

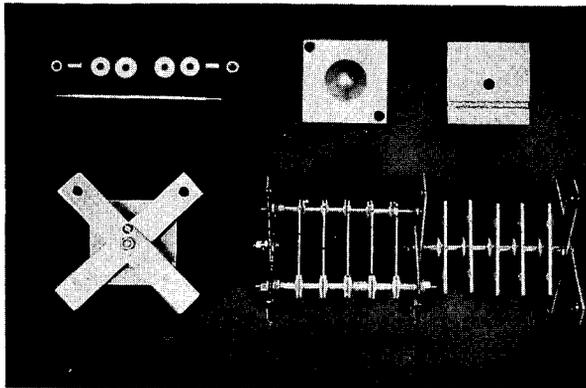


Figure 1. Corrosion-Test Rack and Component Parts.

Magnification: 0.125X

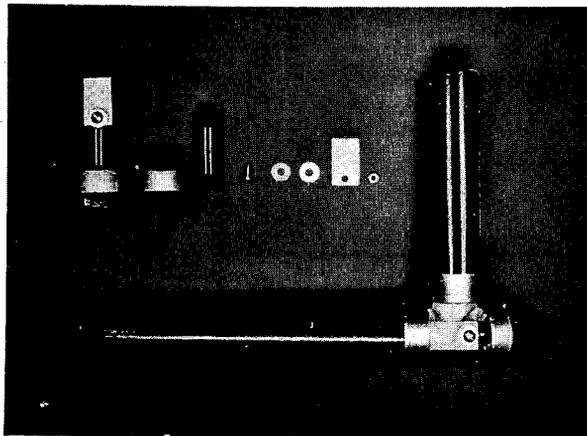


Figure 2. Mounted Pipe-Plug Specimen and Method of Installation.

Magnification: 0.125X

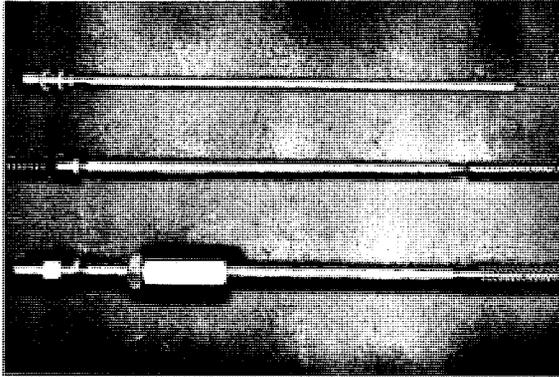


Figure 3. Electrical-Resistance Probe.

Magnification: 0.0625X



Figure 4. Portable Electrical-Resistance Meter and Typical Installation.

Magnification: 0.0625X

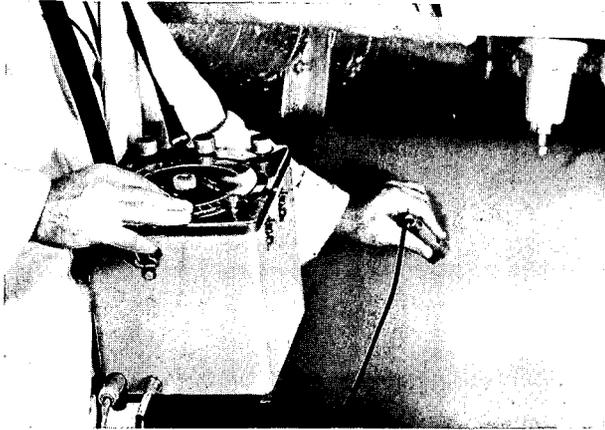


Figure 5. Ultrasonic Thickness Gauge and Method of Application.

Magnification: 0.125X

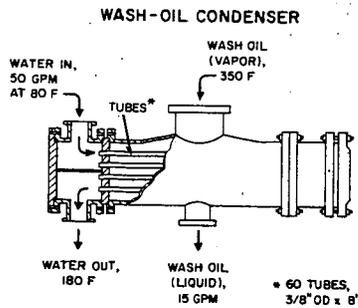


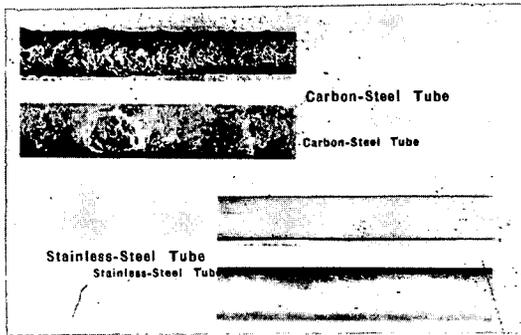
Figure 6.



FOUL-GAS LINE AFTER TWO YEARS OF SERVICE

Figure 7.

Magnification: 0.50X



TUBES AFTER EXPOSURE IN A WASH - OIL CONDENSER

Figure 8.

Magnification: 1X

CORROSION-PROBE MEASUREMENTS  
IN FOUL-GAS LINE

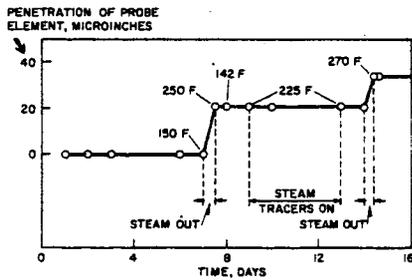


Figure 9.

## NAPHTHALENE DESULFURIZATION WITH SODIUM

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Improving the quality of coke oven naphthalene by treating the product with sodium to remove sulfur compounds and other impurities is of commercial importance to phthalic anhydride producers and other consumers of naphthalene. The treatment of naphthalene with sodium is disclosed in a patent issued in 1930 to G. Schroeter (U. S. Patent 1,763,410). Sodium has been used commercially to remove sulfur compounds, such as thionaphthenes, for a number of years. The available data, however, are inadequate to serve as the basis for designing a continuous process for large-scale operation. This study was undertaken to develop data on reaction rates and other factors essential in preparing preliminary design for a continuous process.

### AMOUNT OF SODIUM REQUIRED FOR DESULFURIZATION

In the initial series of tests, crude coke oven naphthalene (74°C melting point) was treated with different amounts of sodium to determine the amount required to achieve essentially complete desulfurization under batch conditions. A 100 g. sample of the naphthalene was added to a 500-ml. round-bottom flask equipped with a heating mantle and reflux condenser. After the naphthalene had reached a temperature of about 210°C, the sodium was added. The mixture was maintained at the reflux temperature of about 217°C. during the reaction period. The contents were then rapidly distilled and the sodium-treated naphthalene was analyzed for sulfur using the Parr bomb method.

The results are given in Table I. In the first four experiments, the sodium used was in dispersion form; in the last three tests, the sodium was in 1/8-in. to 1/4-in. cubes. The results show that 2% by weight of sodium added as a dispersion is very effective in reducing the sulfur. The sulfur is reduced from 8000 ppm. to about 70 ppm. in 30 min. In 60 min., it is reduced to about 5 ppm. The poor results obtained with solid sodium can be attributed to the small surface area of sodium in direct contact with the naphthalene.

Additional tests were made to determine amounts of sodium required to desulfurize higher purity 78°C. naphthalene. Results obtained with 1% and 2% by weight of sodium as a dispersion are shown graphically in Figure 2. These tests were conducted at 187°C. as compared with the reflux temperature of 217°C. in the earlier experiments. The addition of 1% sodium, based on weight of crude naphthalene, reduces the sulfur content from 5000 ppm. to approximately 160 ppm. in 70 min. This is equivalent to removing 98.6% of the sulfur. The reduction in sulfur, as expected, was greater with 2% by weight of sodium.

### INFLUENCE OF SODIUM PARTICLE SIZE ON DESULFURIZATION

Additional tests were made to obtain more data on the influence of the particle size of sodium. Crude naphthalene melting over the range of 74° - 78°C. serves as an ideal medium for dispersing sodium. The impurities or foreign components function as very effective dispersing agents. Dispersions containing 50% sodium/50% naphthalene were prepared by subjecting the mixture to high shear agitation with the temperature maintained at 110° - 120°C. The particle size was regulated by using different proportions of purified and crude naphthalene. Apparatus illustrated in Figure 1 was used for these tests. The samples were taken at selected intervals by applying a vacuum to withdraw the vapors from the reaction flask. The vapors were condensed in the sample bottle shown in the flask to the left.

The marked effect of the sodium particle size is illustrated by the data plotted in Figure 3. The reaction proceeds very rapidly with the 20-micron sodium dispersion. For example, the sulfur is reduced to 250 ppm. in 6 min. This is equivalent to removing 99.6% of the sulfur. A reaction period of 125 min., however, is required with the 150-micron sodium dispersion to reduce the sulfur to the same level.

### CONTINUOUS DESULFURIZATION WITH OVERFLOW TYPE REACTOR

Data derived from batch-type experiments and reaction rate studies indicated that the sulfur should be reduced to a low concentration with a continuous feed, continuous overflow reactor having an average hold-up time of 3 hr. A series of tests was made by continuously feeding crude naphthalene and 2% by weight of sodium (added as a 50% dispersion in naphthalene) to a well-agitated reactor having an average hold-up time of 3 hr. A resin kettle of 1500 ml. capacity, of the type previously described in Figure 1, was used for this series of tests. The crude 74°C. naphthalene and the 50% sodium dispersion were fed into the reactor by gravity from graduated cylinders. Samples of the overflow product were collected at intervals and analyzed for sulfur.

The results given in Table II show that very effective desulfurization can be obtained with this type of continuous system.

### CONCENTRATING THE RESIDUE FROM THE SODIUM-TREATED NAPHTHALENE

The sodium-treated naphthalene contains about 4% - 8% residue and high boiling fractions depending on the degree of purity of the crude naphthalene. Substantially all of the pure naphthalene content of the crude must be recovered for economic reasons. However, no data have been available on the heat transfer and physical characteristics of the mixture containing a relatively high percentage of residue.

The natural circulation evaporator used to boil off naphthalene from the mixture is shown in Figure 4. The rapid circulation is accomplished by applying the required heat in the exchanger indicated by (x). Naphthalene vapors pass overhead and are recovered from the condenser (y) shown on the left. The unit was operated until the mixture in the reboiler contained about 75% residue and 25% naphthalene. The heat transfer conditions in the heat exchanger were good under these conditions of high residue operation. With a properly designed, forced circulation unit, substantially all of the naphthalene could be recovered.

#### CHARACTERISTICS OF THE SLUDGE

All of the naphthalene from the 75% residue/25% naphthalene mixture obtained from the natural circulation reboiler just described was recovered by further evaporation in a distillation flask. The viscosity characteristics of the sludge after removing substantially all of the naphthalene are shown in Figure 5. The sludge upon cooling is very fluid at temperatures above 100°C. but the viscosity increases rapidly below this value. At room temperature, it may be described as semirigid in consistency.

#### COMMERCIAL EQUIPMENT FOR DESULFURIZATION

A wide variety of types of reactors for desulfurizing naphthalene can probably be considered in view of the rapid desulfurization rates achieved using fine particle size sodium dispersions. For example, the rate studies indicate that the hold-up time provided in a distillation column may, in some cases, be adequate. This presentation, however, is restricted to an evaporator type of reaction system. The major steps in the process are listed in Table III. The first step consists of preparing a 50% dispersion of sodium in crude naphthalene. The dispersion is mixed with the crude naphthalene feed which is then continuously fed to a desulfurization reaction vessel. High residue bottoms from this reactor are pumped to a second evaporator to recover the remaining naphthalene. The residue is discharged periodically from this vessel. The three major steps of the process are:

##### (A) Dispersing Liquid Sodium in Naphthalene

The basic equipment required for this step in the process is illustrated in Figure 6. The high-shear dispersion unit is charged with approximately equal parts of liquid sodium and crude naphthalene. Fine particle size dispersions are readily prepared by agitating the contents of the vessel for periods of 5-10 min. The dispersion is then discharged to a holding tank. A continuous feed from this tank is combined with the main naphthalene feed stream and introduced into the evaporator or desulfurization vessel.

### (B) Evaporator-Type Desulfurization Reactor

The second step of the process, illustrated in Figure 7, is essentially a continuous flow system. The incoming feed (A) and the vaporized naphthalene (B) plus the side stream (C) going to the second evaporator are regulated to maintain approximately a 50% residue/50% naphthalene mixture in the reactor. The vessel is designed to provide an average product hold-up time of 3 hr. Through-put at this hold-up time with a 2500 gal. vessel is about 30 million lb./yr. of naphthalene, assuming 300 operating days. The mixture is pumped through the external heat exchanger at a rate of about 500 gal./min. which provides extremely turbulent mixing. Volume turnover in the reactor is approximately 18 times/hr. The bottoms from the reactor are pumped to a second smaller evaporator to recover the balance of the naphthalene. Assuming 5% residue including high boilers in the sodium-treated naphthalene, the bottoms flow rate is approximately one-tenth the incoming feed rate.

### (C) Final Naphthalene Recovery and Residue Separation

The second evaporator shown in Figure 8 strips essentially all of the remaining naphthalene from the 50% naphthalene/50% residue mixture. It is operated on a semicontinuous basis. When the residue level in the evaporator approaches the capacity of the vessel, the feed from the first evaporator is shut off to permit discharging the vessel. With an 800-gal. capacity evaporator and a through-put rate of 30 million lb./yr., clean out will be required at approximately 8-hr. intervals.

The residue is fluid at the operating temperature and can be discharged by vacuum to a portable tank for conveyance to an incinerator. If the residue is transferred to a slag pile or other area for disposal, it is advisable to destroy small amounts of sodium in the mixture prior to discharging the residue from this evaporator. Although massive amounts of sodium will, under certain conditions, react rather violently with water, commercial experience has demonstrated that finely divided sodium mixed with inert material will react safely with superheated or dry steam in the presence of nitrogen and no hazards are involved. The reaction of sodium with steam to form caustic soda is completed in a matter of minutes.

### CONCLUSIONS

Rapid reaction of the fine particle size sodium dispersions with the sulfur compounds present in crude coke oven grade naphthalene have been demonstrated. Basic data have been translated to preliminary design for a continuous process for desulfurizing coke oven grade naphthalene.

### ACKNOWLEDGEMENT

We are indebted to H. F. Porter of Du Pont Engineering Department for his assistance in developing some of the basic design features of the process.

REFERENCE

1. Schroeter, G. (to Newport Manufacturing Co.) U. S. Patent 1,763,410 (June 10, 1930).

TABLE I  
DESULFURIZATION OF NAPHTHALENE

<u>Run No.</u>	<u>Type Sodium Added</u>	<u>% Sodium Added</u>	<u>Treating Time, Min.</u>	<u>PPM. Sulfur After Treatment*</u>
1	Dispersion	2	30	50-70
2	Dispersion	2	60	5
3	Dispersion	3	30	10
4	Dispersion	4	30	Non-detectable
5	Solid	2	60	4900
6	Solid	3	60	4300
7	Solid	4	60	3900

\* Sulfur Content of 74°-75°C Naphthalene Before Treatment-8000 ppm.

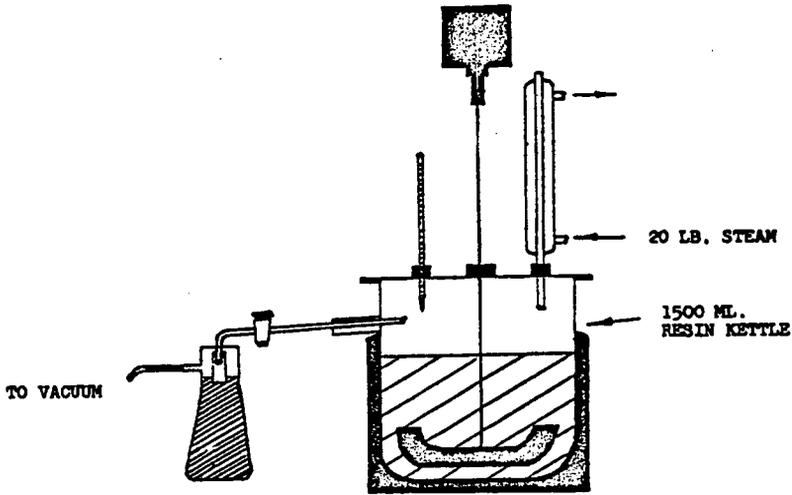
TABLE II  
DESULFURIZATION WITH 3-HOUR AVERAGE HOLD UP TIME

<u>Reactor Temperature</u>	<u>Sulfur Content, ppm.</u>		<u>% Sulfur Removed</u>
	<u>Feed</u>	<u>Product</u>	
190°-200°C	3200-6200	30	99-99.8

TABLE III  
PROCESSING STEPS IN DESULFURIZING

1. Dispersing the Liquid Sodium
2. Desulfurizing in an Evaporator Vessel
3. Recovery of Remaining Naphthalene
  - (A) Residue Separation

FIGURE 1



DESULFURIZATION APPARATUS

FIGURE 2

DESULFURIZATION RATES

78°C NAPHTHALENE  
@ 187°C, 350 mm Hg

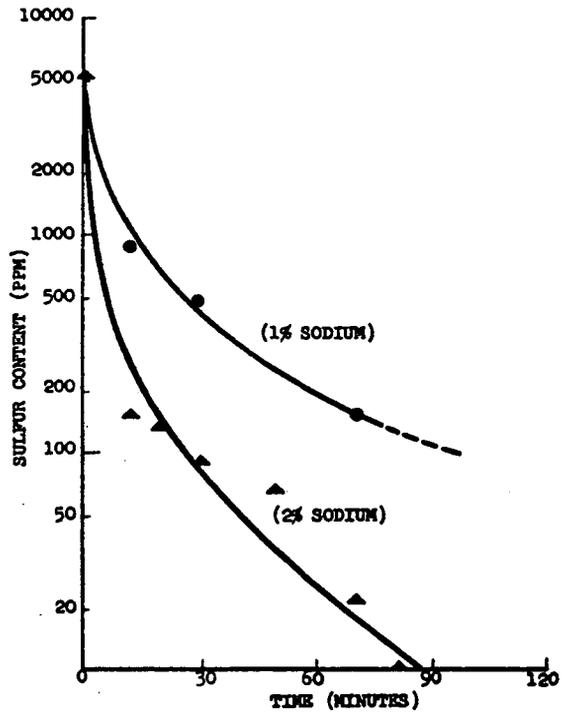


FIGURE 3

DESULFURIZATION RATES  
WITH VARYING  
SODIUM PARTICLE SIZE

78° NAPHTHALENE  
TEMPERATURE 217° C

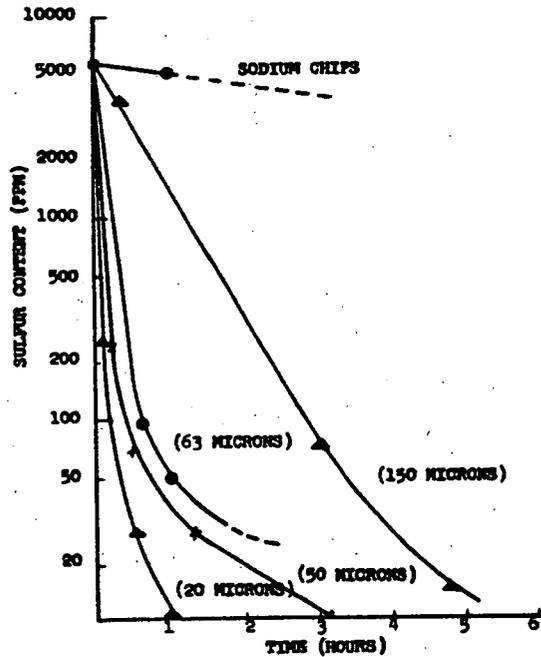
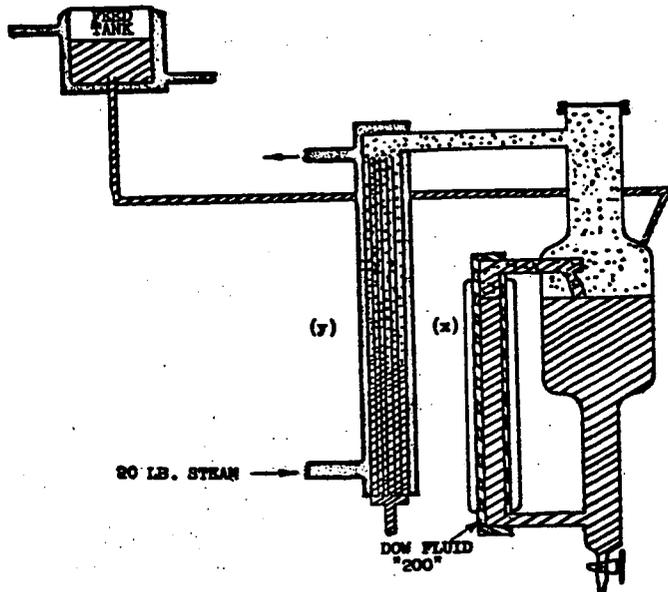


FIGURE 4



NATURAL CIRCULATION REBOILER

FIGURE 5

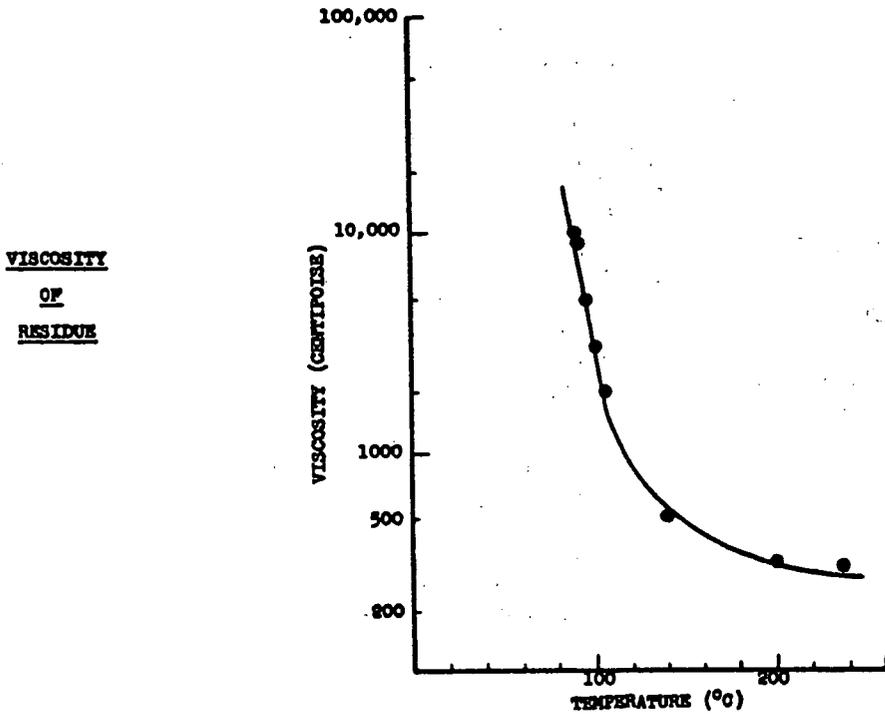
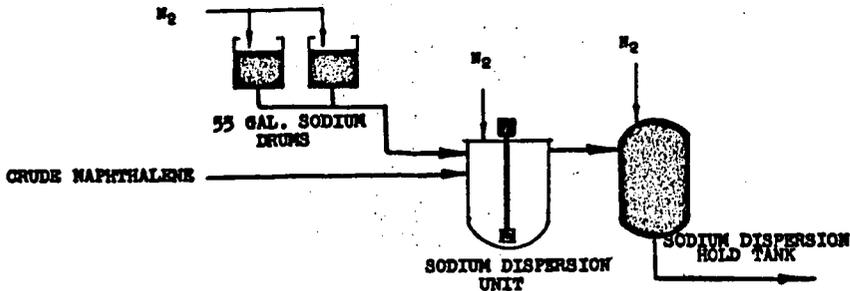


FIGURE 6



DISPERSING LIQUID SODIUM

FIGURE 7

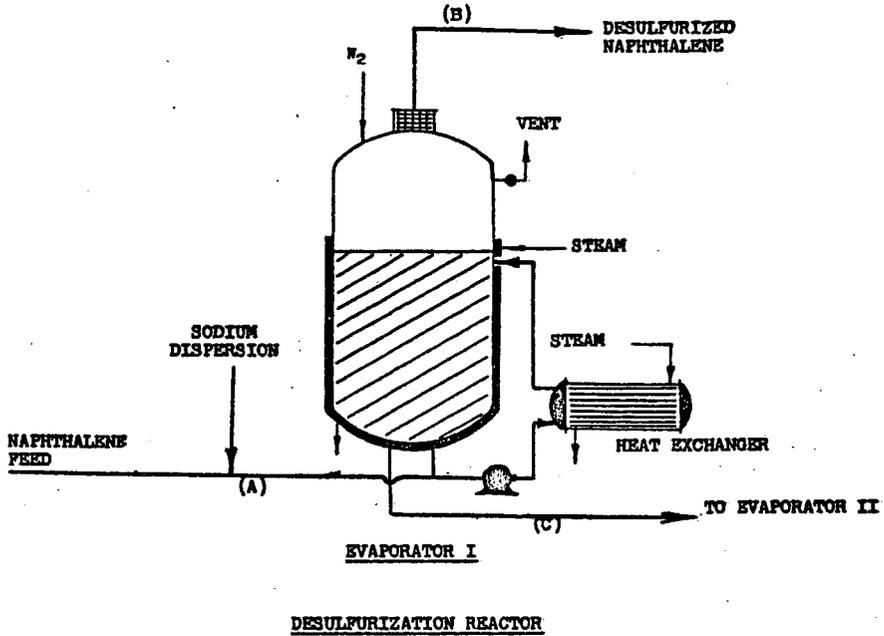
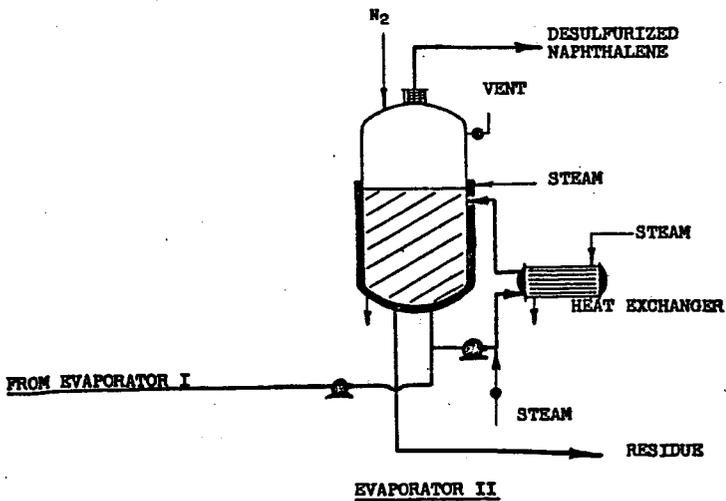


FIGURE 8



NAPHTHALENE RECOVERY AND RESIDUE SEPARATION

CHEMICALS FROM CARBAZOLE BY REDUCTIVE PROCESSES

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Introduction: Carbazole was discovered in coal tar in 1872 (1). Synonyms for carbazole are dibenzopyrrole and diphenyleneimine. The numbering system used by Chemical Abstracts for the carbazole ring is shown in Figure 1.

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(1) Graebe and Glaser, Ber., 5, 12 (1872).

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Carbazole melts at 245.5°C. and sublimes readily. Its boiling point is 354°C./760 mm. It is sparingly soluble in most common solvents with the exception of acetone and pyridine. While most of the ring-substituted carbazole derivatives are also high melting, many N-substituted carbazole compounds melt below 100°C. Of course, all carbazole derivatives are high boilers.

The N-atom of carbazole is very weakly basic. Actually, the imino hydrogen is replaceable by alkali metals. Nevertheless, in aromatic substitution reactions the NH group exerts the same o, p-directing influence as in diphenylamine. Thus, in electrophilic substitution reactions, the 3- and 6- (i.e. p-) positions react primarily, with some o-substitution in the 1- or 8- positions.

In addition to being found in coal tar several good syntheses for making carbazole are also available. For example, the method of Tauber (2) involves the heating of 2,2'-diaminodiphenyl with a strong mineral acid to give excellent yields of carbazole (Figure 2).

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(2) Tauber, Ber., 24, 197 (1891)

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However, while synthesis will deliver a product of highest purity, it is believed that coal tar carbazole of 97% or better purity will always be cheaper than the synthetic product.

It is not intended to elaborate here on the methods of extracting carbazole from coal tar, but a brief general review may be useful. Dry coal tar contains 1-2% of carbazole. Of this amount, about 35% is industrially recoverable (3). Thus, the po-

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(3) Lowry, ed., "Chemistry of Coal Utilization", J. Wiley & Sons, N. Y. 1945

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tential U. S. capacity for coal tar carbazole is in excess of 50,000,000 lbs./yr. Generally, carbazole is recovered from coal tar by distillation and extraction. A coal tar distillate boiling at about 320-60°C., is allowed to cool whereupon crystalline solids deposit. These solids are recovered by centrifugation and contain 30-40% of anthracene, 20-25% of carbazole, and 10-40% of phenanthrene, their homologs, and impurities such as methyl fluorenes. Carbazole, anthracene, and phenanthrene can be isolated from this cake by fractional crystallization and/or extraction.

The commercial uses of carbazole have been mostly European developments. They include dyes such as Hydron Blue, pesticides, and vinylcarbazole polymers. In the U. S., the latter two have apparently never progressed beyond the pilot plant stage.

As a part of a wide-ranging utilization research program for the high boiling components of coal tar, the chemistry of carbazole was surveyed. These studies included reduction, oxidation, nitration-reduction, chlorination, alkylation, carboxylation, sulfonation, acetylation, pyridylethylation, and dye chemistry.

Scientifically and in their commercial prospects, the studies of the reduction of carbazole were perhaps the most fruitful. The present paper deals, for these reasons, with this aspect of carbazole chemistry.

In the past, the reduction of the carbazole nucleus by chemical agents or by catalytic hydrogenation has been difficult. Thus, compared with aromatics and certain other nitrogen heterocyclics such as acridine, indole, and phenylpyrrole, carbazole is much more resistant to catalytic hydrogenation. The first report (4) of the catalytic hydrogenation of carbazole claimed the formation of 2,3-diethylindole as the main product. However, none of the subsequent investigators were able to substantiate this claim. von Braun and Ritter (5) were actually unable to hydrogenate purified carbazole in the presence of a nickel catalyst at 260°C. and 450 psig., and obtained only fair yields of 9-methyl-1,2,3,4-tetrahydrocarbazole and 1,2,3,4,5,6,7,8-octahydro-9-methylcarbazole from 9-methylcarbazole. The perhydrogenation of carbazole in an organic solvent at 160-220°C. and 590-1200 psig., using a nickel catalyst, was reported

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(4) Padoa and Chiaves, *Atti R. Accad. Lincei*, 16, 762 (1908); *Gazz. chim. ital.* 38, 236 (1903).

(5) v. Braun and Ritter, *Ber.*, 55, 3792 (1922).

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in a 1930 German patent (6). The best data were obtained by Adkins and Coonradt (7) who hydrogenated carbazole in the presence of Raney nickel at 230°C. to obtain an 87%

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(6) German pat. 514,822 (1930).

(7) Adkins and Coonradt, *J. Am. Chem. Soc.*, 63, 1563 (1941).

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yield of dodecahydrocarbazole; when they used a copper chromite catalyst under these conditions, a 72% yield of 1,2,3,4-tetrahydrocarbazole was obtained. However, this procedure required rather high pressures (of 3600-4400 psig.) and highly purified materials.

Prior work on the chemical reduction of carbazole was limited to the sodium-alcohol system. In 1907, the preparation of 1,4-dihydrocarbazole from carbazole by this reagent was reported (8). Later it was shown that the product of this reaction is a mixture containing at least 50% of carbazole, tetrahydrocarbazole, plus unknowns (9). Surprisingly, a 1950 publication again claimed the isolation of 1,4-dihydrocarbazole from this mixture (10). 1,2,3,4-Tetrahydrocarbazole can indeed be prepared in fair yield by the reduction of carbazole with sodium and alcohol (11).

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- (8) Schmidt and Schall, Ber., 40, 3225 (1907).  
(9) Barclay, Campbell, and Gow, J. Chem. Soc., 1946, 997.  
(10) Sanna, Gazz. chim. ital., 80, 572 (1950).  
(11) Zanetti, Ber., 26, 2006 (1893).
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The present paper concerns (1) a reinvestigation of the catalytic hydrogenation of carbazole, (2) a study of the chemical reduction of carbazole and derivatives with lithium metal in amine, and (3) some new N-substituted derivatives of carbazole and its hydrogenation products.

### 1) The Hydrogenation of Carbazole

Rhodium catalysts are effective for the hydrogenation of aromatic compounds and heterocyclics like pyrrole and pyridine at room temperature and atmospheric pressure while ruthenium catalysts are useful for the reduction of aromatic compounds at elevated temperature and pressure (12). The use of these catalysts for the hydrogenation of condensed heterocyclic ring systems has apparently been little explored.

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- (12) Gilman and Cohn, in "Advances in Catalysis", IX, 733 (1957), Academic Press, Inc., New York, N. Y.
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An investigation of the hydrogenation of carbazole revealed that 5% Rh-C and 5% Ru-C were about equally effective, with reduction of the carbazole ring beginning at about 100°C. and 500 psig. of hydrogen. Purification of materials was unnecessary. The use of a 5% Pd-C catalyst under similar conditions gave only about one fourth of the rate of hydrogenation realized with the rhodium or ruthenium catalysts. The conditions for obtaining optimum yields of either tetrahydro- or dodecahydrocarbazole are summarized in Table I. Thus, in the decalin medium the reduction of carbazole with a 5% Ru-C catalyst at 250 psig. of hydrogen and 250°C., when stopped at the pressure drop calculated for tetrahydrocarbazole, gave a 53% yield of tetrahydrocarbazole plus a 15% recovery of carbazole, the remainder of the product being higher hydrogenation products. The reduction of carbazole in decalin solution at 500 psig. and 200°C. in the presence of 5% Ru-C gave an 81% yield of dodecahydrocarbazole. Surprisingly, carbazole could be reduced in water suspension (pH 5.5) at 1000 psig. (320 psig. hydrogen partial pressure) and 200°C., using a 5% Rh-C catalyst, to obtain a 93% yield of dodecahydro-

carbazole. Both U.O.P. prereduced and stabilized nickel-on-kieselguhr and sponge nickel catalysts worked equally well under these conditions, to give 88-90% yields of dodecahydrocarbazole. In all of these systems the yields of tetrahydrocarbazole were only fair when the hydrogenation of carbazole was stopped at the theoretical hydrogen uptake for tetrahydrocarbazole. When carbazole was hydrogenated in an aqueous suspension, adjusted to pH 12 with potassium hydroxide, at 1000 psig. (320 psig. hydrogen partial pressure) and 250°C., the hydrogen uptake practically stopped at the tetrahydro stage and an 87% yield of 1,2,3,4-tetrahydrocarbazole could be isolated. The same experiment carried out in a water medium adjusted to pH 10 gave only a 67% yield of tetrahydrocarbazole.

As expected, 9-alkylcarbazoles were also easily reducible. For example, 9-methylcarbazole could be hydrogenated in decalin solution at 500 psig. of hydrogen and 150-200°C., using a 5% Pd-C catalyst, to give an 88% yield of N-methyldodecahydrocarbazole.

The facile perhydrogenation of ring-substituted carbazoles was demonstrated by the example of 3-amino-9-methylcarbazole (I). The hydrogenation of 0.135 m. of this compound in water containing 0.27 m. of hydrochloric acid in the presence of 5% Rh-C catalyst at 50-100°C. and 800-350 psig. gave a 72% yield of 3-amino-9-methyldodecahydrocarbazole (II, fig. 3).

It is known that partial hydrogenation of ring-substituted carbazoles is difficult to stop at a specific stage of reduction. In addition, the ring containing the substituent and/or the unsubstituted ring may be exclusively or simultaneously hydrogenated. The only such example investigated by us was 3-amino-carbazole (III) which gave a 38% yield of unchanged starting material and an 11% yield of 3-amino-1,2,3,4-tetrahydrocarbazole (IV) as the only identified product. The latter compound is structurally similar to the indole derivative tryptamine. 3-Amino-1,2,3,4-tetrahydrocarbazole was tested for its ability to inhibit (serotonin) monoamine oxidase and found to be moderately active but not as effective as Marsilid, amphetamine hydrazine, harmine, and harmaline for this purpose\*.

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\* Private communication from Dr. Bernard Witkop, Chief, Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases.

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Tetrahydrocarbazole itself should be a versatile intermediate useful in fields such as dyes, pharmaceuticals, and plastics. For example, the monomer 9-vinyl-1,2,3,4-tetrahydrocarbazole is made in excellent yield by vinylating carbazole with acetylene (13).

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(13) W. Reppe, Ann., 601, 133 (1956).

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Dodecahydrocarbazole possesses antioxidant activity in gasoline and should have anticorrosive action. These combined properties may make dodecahydrocarbazole a useful low-cost additive to fuels and lubricants. Dodecahydrocarbazole should also be useful in dye chemistry as a component of certain dye salts.

## 2) The Reduction of Carbazole Compounds with Lithium in Amine

The chemical reduction of benzenoid rings to the tetrahydro (cyclohexene) and hexahydro (cyclohexane) stage by means of the lithium in amine reagent has been reported recently (14, 15). The reduction of carbazole compounds with this reagent was investigated (Figure 4). It was hoped that 1,4-dihydrocarbazole might be obtained by

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(14) Benkeser, Robinson, Sauve, and Thomas, J. Am. Chem. Soc., 77, 3230 (1955).

(15) Reggel, Fridel, and Wender, J. Org. Chem., 22, 891 (1957).

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1,4-addition of lithium to one of the benzenoid rings of carbazole. However, when carbazole dissolved in n-propylamine was reacted with 2 moles of lithium per mole of carbazole, a product of m.p. 137-45°C. was obtained which could not be purified by recrystallization. When 4 moles of lithium per mole of carbazole were employed for the reduction, a 90% yield of 1,2,3,4-tetrahydrocarbazole was obtained. The latter was resistant to further reduction by lithium in amine. This result was unexpected, since aromatic amines such as N-methylaniline have been readily reduced by this reagent (16).

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(16) Benkeser, Lambert, Ryan, and Stoffey, J. Am. Chem. Soc., 80, 6573 (1958).

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Presumably, tetrahydrocarbazole, which is more basic than carbazole, formed a N-lithium compound and was thus stabilized against further reduction. This presumption was strengthened by the reduction of 9-methylcarbazole to 9-methyl-1,2,3,4,10,11-cis-hexahydrocarbazole with 12 moles of lithium per mole of carbazole in n-propylamine in good yield. The intermediate 9-methyl-1,2,3,4-tetrahydrocarbazole no longer has a hydrogen atom on the nitrogen atom and was therefore reduced further. This is the first synthesis of a hexahydrocarbazole directly from carbazole. cis-Hexahydrocarbazole itself was also resistant to further reduction by lithium in amine, yielding an 82% recovery of hexahydrocarbazole.

The reduction of ring-substituted carbazoles was briefly investigated and proved to be more complex. Thus, the reduction of 3-aminocarbazole with lithium metal in ethylene diamine gave a 27% recovery of starting material as the only identified product. A similar reduction of carbazole-3-carboxylic acid gave a 24% yield of a product tentatively identified as 1,4-dihydrocarbazole-3-carboxylic acid plus a 35% yield of an unidentified nonacidic product.

## 3) Some New N-Substituted Carbazole Derivatives

The noncatalytic reaction of 2- and 4-vinylpyridines with nucleophilic reagents such as sodiomalonic ester, piperidine, diethylamine, and sodium bisulfite was first recognized by Doering and Weil (17). Subsequently, this reaction, using alkali metal or acid catalysts, was applied to aromatic amines such as N-methylaniline (18),

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(17) Doering and Weil, J. Am. Chem. Soc., 69, 2461 (1947).

(18) Reich and Levine, J. Am. Chem. Soc., 77, 4913 (1955).

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and nitrogen heterocyclics such as pyrrole (18) and indole (19). The literature mentions that diphenylamine, which is structurally similar to carbazole, could not be pyridylethylated (18).

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(18) Reich and Levine, J. Am. Chem. Soc., 77, 4913 (1955).

(19) Gray and Archer, *ibid.*, 72, 3554 (1957).

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Carbazole and the hydrocarbazoles, which had not been pyridylethylated before, have now been reacted with 2- and/or 4-vinylpyridine to give excellent to fair yields of the corresponding N-pyridylethylation products (Fig. 5 shows an example) as listed in Table II. Carbazole itself and 1,2,3,4-tetrahydrocarbazole, which are very weak bases, were reacted in pyridine solution with vinylpyridine in the presence of alkali metal catalysts. 1,2,3,4,10,11-cis-Hexahydrocarbazole and dodecahydrocarbazole, which are relatively strong bases, were pyridylethylated using acid catalysts. Pyridylethylated carbazole has fungicidal properties which will be reported in detail elsewhere.

Although dodecahydrocarbazole has been known for more than 30 years, only a few derivatives have been prepared from it. A survey of the reactions of dodecahydrocarbazole revealed that it undergoes, as expected, all the usual transformations of a secondary cycloaliphatic amine. The melting points of the solid derivatives were not too sharp which was not surprising since the dodecahydrocarbazole was a mixture of stereoisomers. The new derivatives of dodecahydrocarbazole are tabulated in Table III.

The potential uses of these derivatives lie in the areas of corrosion inhibitors, fungicides, solvents, antioxidants, plasticizers, textile chemicals, resin curing agents and catalysts, and ore flotation agents. For example, the nitrous salt of dodecahydrocarbazole was found to be a good vapor phase corrosion inhibitor; and 9-dodecoyldodecahydrocarbazole might find application as a plasticizer with mild antioxidant properties.

Acknowledgements: The authors wish to thank Dr. J. O'Brochta for continued guidance and Messrs. J. Martini and H. Hampson for their experimental assistance.

#### Experimental

All melting and boiling points are uncorrected.

Dodecahydrocarbazole. - A 1-gal. stainless steel autoclave (stirring-type) was charged with 167 g. (1.0 m.) of 97% carbazole, 85 g. of a prereduced, stabilized nickel-on-kieselguhr catalyst (55% Ni), and 1000 ml. of water. The autoclave was sealed, the mixture was stirred and heated to 200°C., at which temperature the autogeneous pressure was 630 psig. The autoclave was pressured to 1000 psig with hydrogen, and repressured to 1000 psig. whenever the pressure fell to 700 psig. After 6 hrs., no further pressure drop occurred. The catalyate

was filtered. The insolubles were extracted with 500 ml. of benzene. The benzene extract was then used to extract the filtrate. The organic phase was distilled through a 4-in. Vigreux column to give 157 g. (88% yield) of dodecahydrocarbazole, b.p. 124-5°C./10 mm. (20).

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(20) Adkins and Coonradt, J. Am. Chem. Soc., 63, 1563 (1941), report b.p. 124-125°C./10 mm.

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The other perhydrogenations of carbazole were carried out similarly. The amount of catalyst used in the case of 5% rhodium-on-carbon or 5% ruthenium-on-carbon was 2-5% by wt. of the carbazole charge.

1,2,3,4-Tetrahydrocarbazole by the Hydrogenation of Carbazole. - A 1-gal. autoclave, charged with 167 g. (1.0 m.) of carbazole, 1000 ml. of water adjusted to pH 12 with dilute potassium hydroxide, and 85 g. of a prereduced nickel-on-kieselguhr catalyst, was stirred and heated to 250°C. A pressure of 680 psig. was reached. The autoclave was then pressured to 1000 psig. with hydrogen. A fast reaction ensued. The autoclave was repressured to 1000 psig. with hydrogen when the pressure fell to 800 psig. In 60 min., the hydrogen absorption had practically stopped. The mixture was allowed to cool, the autoclave was vented, and the catalyzate was filtered. The insolubles were extracted with a 500-ml. and a 200-ml. portion of benzene. The combined benzene extract was shaken with three 200-ml. portions of 30% hydrochloric acid, in which carbazole is insoluble. Dilution of the combined acid extracts with water to give a 15% hydrochloric acid concentration precipitated tetrahydrocarbazole. The precipitate was filtered off, washed with water, a little ammonia, and again with water, then dried to give 134 g. (87% yield) of 1,2,3,4-tetrahydrocarbazole, m.p. 115-8°C.; after one recrystallization from 95% ethanol, m.p. 118-9°C. (21).

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(21) Adkins and Coonradt, loc. cit., report m.p. 115-115.5°C.

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3-Amino-9-methyldodecahydrocarbazole. A 1-gal. stirring autoclave was charged with 26.0 g. (0.135 m.) of 3-amino-9-methylcarbazole, 1.0 l. of water, 23.8 g. (0.27 m.) of concentrated hydrochloric acid, and 4.0 g. of 5% Rh-C catalyst. The mixture was hydrogenated at 50-100°C. at 800-350 psig. of hydrogen pressure during 4 hrs. after which time no further pressure drop was observed. The catalyzate was filtered through a Celite filter. The clear filtrate was boiled for a short time and filtered again to remove solids which had formed. The filtrate was concentrated to 160 ml. volume, made alkaline with 28% ammonium hydroxide, and extracted with two 100-ml. portions of ether. The extract was dried over anhydrous sodium sulfate, concentrated, and the residual oil was distilled through a 4-in. Vigreux column to give 20.0 g. (72% yield) of a colorless mobile liquid, b.p. 115-25°C./3 mm. Redistillation gave a heart cut of b.p. 115-9°C./3.5 mm.

Anal. Calcd. for  $C_{13}H_{24}N_2$ : Neutral equiv., 104; N, 13.4  
Found: Neutral equiv., 108; N, 12.8

1,2,3,4-Tetrahydrocarbazole by Reduction of Carbazole with the Lithium in Amine Reagent. - To a solution of 8.35 g. (0.05 m.) of carbazole in 100 ml. of n-propylamine was added 1.46 g. (0.21 m.) of lithium ribbon in small pieces during 5 hrs. The mixture was stirred at room temperature overnight. Thereafter, 17 g. (0.32 m.) of ammonium chloride was added to the solution, the mixture was evaporated to dryness under vacuum, and the solid residue was taken up in 100 ml. of water. The resultant slurry was extracted with two 100-ml. portions of ether. The extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of the ethereal filtrate to dryness gave 8.6 g. (100% yield) of solids, m.p. 115-19°C. One gram of this product was recrystallized from 5 ml. of cyclohexane to give 0.9 g. (90% yield) of tetrahydrocarbazole, m.p. 119-20°C.

A similar reduction of carbazole in ethylenediamine at 85-100° with lithium gave a 87% yield of tetrahydrocarbazole.

3-Amino-1,2,3,4-Tetrahydrocarbazole. - A solution of 36.4 g. (0.2 m.) of 3-aminocarbazole in 200 ml. (0.2 m.) of 1 N hydrochloric acid and 800 ml. of water was hydrogenated in a 1-gal. stirring autoclave in the presence of 3.0 g. of 5% Ru-C catalyst at 100°C. and 820 psig. of hydrogen for 12 hrs. The catalyze was then filtered to remove 17 g. of insolubles, i.e. a 38% recovery of 3-aminocarbazole (corrected for catalyst wt.) was made. Extraction of the insolubles with ethanol and concentration of the extract gave 3-aminocarbazole, m.p. 238-41°C. The aqueous filtrate was alkaline (pH 8) due to the formation of higher hydrogenated carbazoles. It was concentrated to 200 ml. volume, made strongly alkaline with ammonium hydroxide, and extracted with ether. The extract was evaporated to dryness to give 4.2 g. (11% yield) of solids, m.p. 116-70°C. After recrystallization from ethanol, m.p. 170-2°C. A sample was titrated in acetic acid with perchloric acid. The calculated neutralization equivalent for the title compound is based on the fact that tetrahydrocarbazole was found to be too weakly basic to be titratable.

Anal. Calcd for  $C_{12}H_{14}N_2$ : N. E. 186; Found, N. E. 184.

Since hexahydrocarbazole was titratable, the alternate structure, 3-amino-hexahydrocarbazole  $C_{12}H_{16}N_2$ , would have a neutralization equivalent of 94. 6-Amino-tetrahydrocarbazole is eliminated on the basis of its m.p. 152°. The ultraviolet spectrum of the product was similar to that of tetrahydrocarbazole but different from that of hexahydrocarbazole (Table IV).

9-Methyl-1,2,3,4,10,11-cis-hexahydrocarbazole. - A solution of 9.1 g. (0.05 m.) of 9-methylcarbazole in 200 ml. of n-propylamine was treated with 4.3g. (0.62 m.) of lithium ribbon in small pieces during 5 hrs. at 25°C. After stirring for an additional 1.5 hrs., some unreacted lithium pieces were removed with forceps. Finally, 33.2 g. (0.62 m.) of ammonium chloride was added to the solution. The solvent was evaporated. The residue was taken up in water and extracted with two 100-ml. portions of ether. The extract was dried over Drierite, filtered, and the filtrate was evaporated to give 9.8 g. of residue. This crude product was distilled through a semimicro Vigreux column to give 6.5 g. (71% yield) of 9-methylhexahydrocarbazole, b.p. 125-35°C./1 mm., 98 mole % pure by nonaqueous titration with perchloric acid in acetic acid. An authentic sample of 9-methyl-1,2,3,4-tetrahydrocarbazole was too weakly basic to be titrated by this method.

Anal. Calcd. for  $C_{13}H_{17}N$ : Neutral. equiv., 187  
Found: Neutral. equiv., 190

The ultraviolet spectrum of the product was similar to that of 1,2,3,4,10,11-cis-hexahydrocarbazole itself except that the absorption maxima were shifted to slightly higher wavelengths. This corroborates the proposed structure of the product further, since a similar slight shift to higher wavelength was observed in the ultraviolet spectra of 9-methyl-1,2,3,4,-tetrahydrocarbazole vs. 1,2,3,4-tetrahydrocarbazole. The comparative spectral data are given in Table IV.

Reduction of Carbazole-3-carboxylic Acid with Lithium in Amine. -

To a solution of 3.4 g. (0.016 m.) of carbazole-3-carboxylic acid in 100 g. of ethylamine was added at 25°C. during 40 min. 0.78 g. (0.112 m.) of lithium ribbon in small pieces. After stirring for 2 additional hrs. at 25°C., 5.95 g. (0.112 m.) of ammonium chloride was added. The mixture was evaporated to dryness under vacuum. The residue was digested in water and the mixture was extracted with ether. The extract was evaporated to dryness to give 1.8 g. of a nonacidic solid. This solid was distilled through a Bantamware column to give 1.2 g. (35 wt. % yield) of low-melting yellow solids, b.p. 220-70°C. (bath)/2 mm., which were not further investigated. The alkaline aqueous solution obtained above was acidified and extracted with ether. The ether extract was evaporated to dryness to give 0.8 g. (24 wt. % yield) of solids, m.p. 215-9°C; after vacuum sublimation, m.p. 220-1°C., colorless crystals. While carbazole-3-carboxylic acid has a -CO-absorption peak at 1660  $\text{cm}^{-1}$ , the product showed -CO-absorption at 1685  $\text{cm}^{-1}$ . This indicated that the carboxyl group of the product was in conjugation with a double bond (22) and that the product was probably 1,4-dihydrocarbazole-3-carboxylic acid.

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(22) L. J. Ballamy, "The Infra-red Spectra of Complex Molecules", 2nd Ed., John Wiley & Sons, New York 1958, p. 168

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Pyridylethylation of Carbazole and 1,2,3,4-Tetrahydrocarbazole. - A stirred mixture of 167 g. (1.0 m.) of carbazole, 115 g. (1.1 m.) of 2-vinylpyridine, 2.0 g. (0.05 m.) of small pieces of metallic potassium, and 1000 ml. of pyridine was refluxed for 3 hrs., then cooled to 60°C., and stirred for 0.5 hr. with 15 ml. of absolute ethanol. The solution was concentrated to ca. 250 ml. volume and poured into 2 l. of ice-water. An oil separated which solidified quickly. The solid was filtered off, washed with water, and air-dried to give 265 g. (98% yield) of crude product, m.p. 73-5°C. After recrystallization from 95% ethanol, m.p. 77-8°C., 99 mole % pure by nonaqueous titration with perchloric acid in acetic acid (only the pyridine N is basic enough to be picked up by this method).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2$ : Neutral. equiv., 272  
Found: Neutral. equiv., 275

The infrared spectrum of the product showed no NH absorption peak, indicating the formation of a 9-substituted carbazole.

The reactions of carbazole with 4-vinyl pyridine and of 1,2,3,4-tetrahydrocarbazole with 2- and 4-vinylpyridine were carried out in similar fashion.

Pyridylethylation of 1,2,3,4,10,11-cis-Hexahydro- and Dodecahydrocarbazole. - A mixture of 17.3 g. (0.1 m.) of cis-hexahydrocarbazole, 10.5 g. (0.1 m.) of 2-vinylpyridine, 6.0 ml. (0.1 m.) of glacial acetic acid, and 50 ml. of methanol was stirred and refluxed for 8 hrs. The alcohol was then stripped off and the concentrate was poured over 500 g. of crushed ice. A sticky gum formed. The mixture was made alkaline by the addition of 100 ml. of 10% sodium hydroxide and extracted with two 250-ml. portions of ether. The combined extracts were dried over Drierite, filtered, and concentrated. The residue (27.0 g., 97% yield) was distilled through a 4-in. Vigreux column to give 22.4 g. (80% yield) of a fraction of b.p. 175-80°C./1 mm., 98 mole % pure 9-[omega-(2-pyridyl) ethyl] - 1,2,3,4,10,11-cis-hexahydrocarbazole by nonaqueous titration with perchloric acid in acetic acid (both nitrogen atoms are basic enough to be picked up by this method).

Anal. Calcd. for  $C_{19}H_{23}N_2$ : Neutral. equiv., 139.5  
Found: Neutral. equiv., 142.4

Dodecahydrocarbazole was reacted with 4-vinylpyridine in the same manner, except that no solvent methanol was used.

Table I  
Catalytic Hydrogenation of Carbazole

<u>Catalyst</u> <sup>a)</sup>	<u>Medium</u>	<u>Total Pressure (psig.)</u>	<u>Hydrogen Partial Pressure (Psig.)</u>	<u>Temp. °C.</u>	<u>Main Product</u> <sup>b)</sup>
5% Ru-C	Decalin	250	250	250	53% THC
5% Ru-C	"	500	500	200	81% DHC
5% Rh-C	Water (pH 5.5)	1000	380	200	93% DHC
U.O.P.-Ni	"	"	"	"	86% DHC
Sponge-Ni	"	"	"	"	90% DHC
U.O.P.-Ni	Water (pH 12)	"	320	250	87% THC
U.O.P.-Ni	Water (pH 10)	"	"	"	67% THC

a) Ru-C = Ruthenium on carbon; Rh-C = rhodium on carbon; Universal Oil Products Ni catalyst = Prerduced and stabilized nickel on kieselguhr (55% Ni).

b) THC = 1,2,3,4-tetrahydrocarbazole; DHC = dodecahydrocarbazole.

Table II

Pyridylethylation of Carbazole and Hydrocarbazoles

<u>Nucleophile<sup>a)</sup></u>	<u>Vinylpyridine (VP)</u>	<u>Catalyst</u>	<u>Solvent</u>	<u>% Yield of Adduct</u>	<u>Melting or Boiling Point, °C.</u>
Carbazole	2-VP	K	Pyridine	98	m. 77-8
"	4-VP	Na	"	97	m. 173-4
THC	2-VP	"	"	29	b. 194-201/3 mm.
"	4-VP	"	"	55	m. 83-4
HHC	2-VP	Acetic Acid	Methanol	80	b. 175-80/1 mm.
DHC	4-VP	"	None	65	b. 174-82/2 mm.

a) THC = 1,2,3,4-tetrahydrocarbazole; HHC = 1,2,3,4,10,11-cis-hexahydrocarbazole;  
DHC = dodecahydrocarbazole

Table III

## Derivatives of Dodecahydrocarbazole

Dodecahydrocarbazole Reacted With	Product <sup>a</sup> (% Yield)	Physical Properties
Lauroyl Chloride	9-Dodecoyl DHC (87)	pale yellow oil, b.p. 247-52°C./3 mm.
KCN	DHC-9-carboxamide (74)	colorless crystals; m.p. 167-70°C. (f. EtOH)
Urea	" (88)	m.p. 180-2°C. (f. dil. EtOH)
CS <sub>2</sub>	N,N-(Perhydro-o,o'-biphenylene) dithiocarbamate (100)	almost colorless solid; m.p. 184-91°C. (f. EtOH)
HCOOCH <sub>3</sub>	8-Formyldodecahydrocarbazole (90)	colorless liquid, b.p. 157-9°C./4 mm.
CH <sub>2</sub> = CH <sub>2</sub> CN	9-(2-Cyanoethyl) DHC (89)	colorless oil, b.p. 157-61°C./2 mm.
Cyclohexanone	9-(1-Cyclohexenyl) DHC (62)	pale yellow oil, b.p. 155-60°C./1 mm.
CH <sub>2</sub> O + alpha-methylstyrene	1-(9-dodecahydrocarbazolyl)-3-phenyl-butene-3 (12)	colorless liquid, b.p. 169-80°C./1 mm.
Succinic Anhydride	9-(3-Carboxypropionyl) DHC (68)	colorless liquid, m.p. 111-5°C.
Phthalic Anhydride	9-(2-Carboxybenzoyl) DHC (74)	colorless solid, m.p. 182-7°C.
Maleic Anhydride	9-(omega-Carboxyacrylyl) DHC (65)	colorless solid, m.p. 124-9°C.
HNO <sub>2</sub>	Nitrous salt of DHC (68)	colorless solid, m.p. 150-5°C.
CH <sub>3</sub> COOH	Acetate of DHC (96)	colorless solid, m.p. 148-53°C.
BF <sub>3</sub>	BF <sub>3</sub> Adduct of DHC (89)	colorless solid, m.p. 212-4°C.

a) DHC = dodecahydrocarbazole

Table IV  
Comparative Ultraviolet Spectral Data

<u>Compound</u>	<u><math>\lambda</math> max (EtOH)</u>	<u>log E</u>
1,2,3,4-Tetrahydrocarbazole	227.5, 283, 291	4.5, 3.9, 3.8
9-Methyl-1,2,3,4-tetrahydrocarbazole	230, 287, 293.4	4.6, 3.8, 3.8
3-Amino-1,2,3,4-tetrahydrocarbazole	225, 283	4.5, 3.8
1,2,3,4,10,11-cis-Hexahydrocarbazole	241, 292	3.9, 3.4
9-Methyl-1,2,3,4,10,11-cis-hexahydrocarbazole	244, 294-5	3.8, 3.3

Figure 1

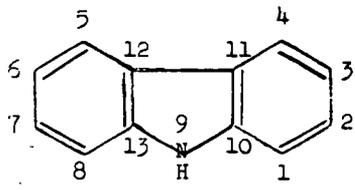


Figure 2

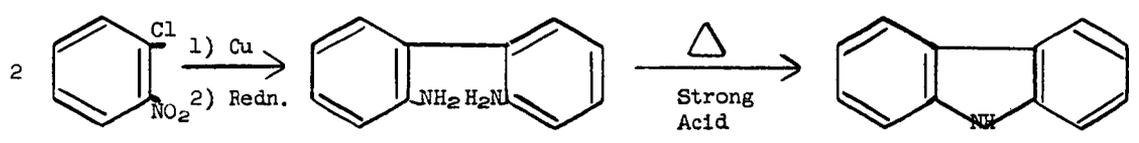


Figure 2

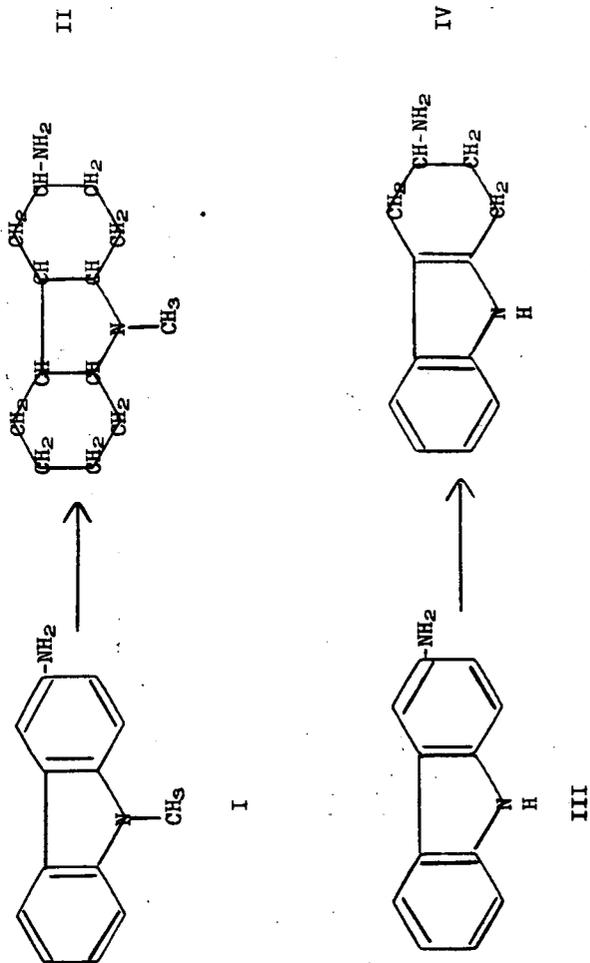


Figure 4

Lithium in Amine Reductions

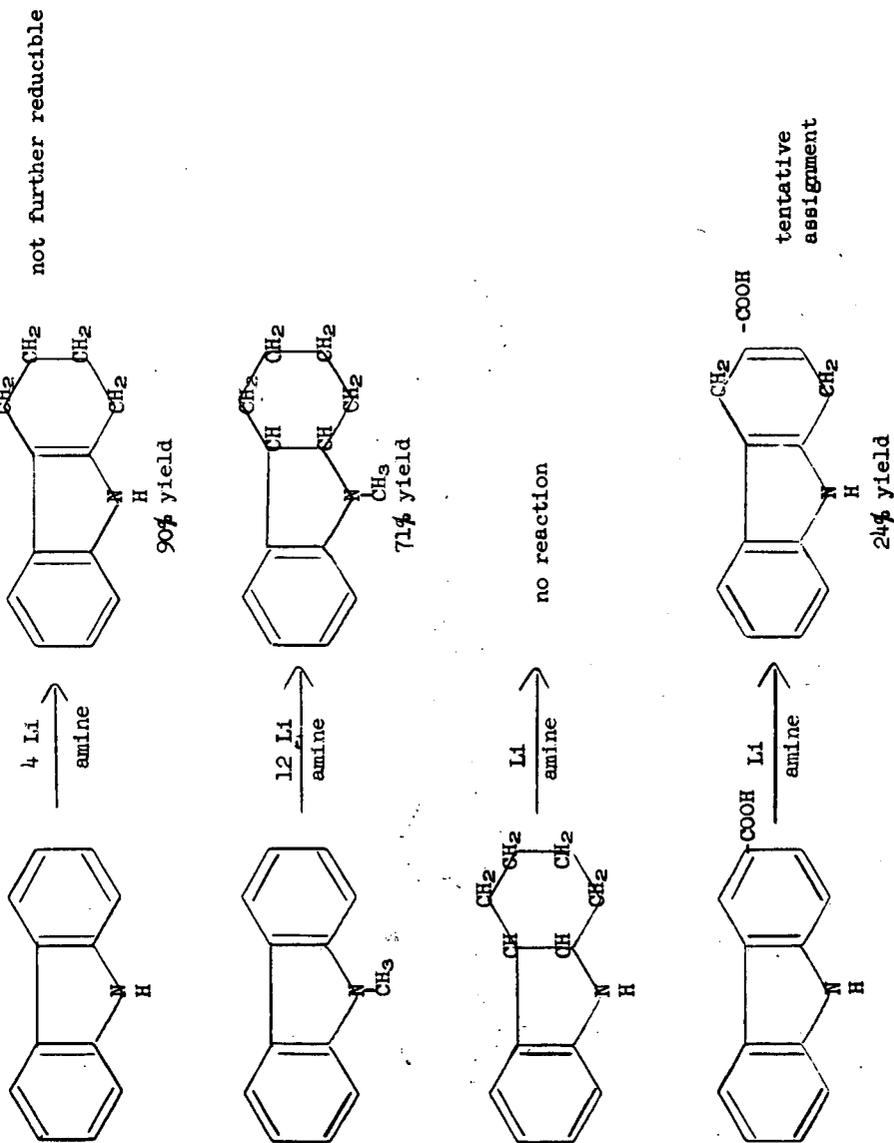
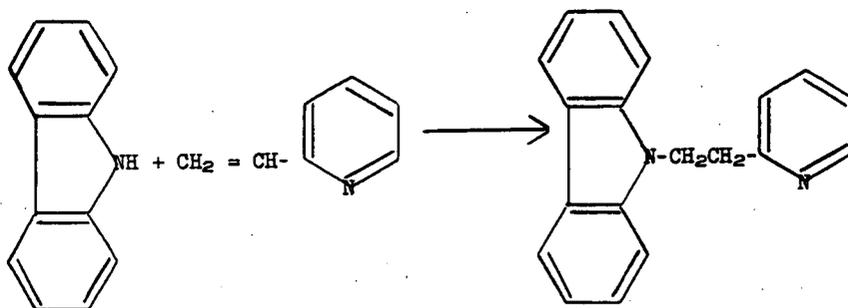


Figure 5



THE GAS-CHROMATOGRAPHIC ANALYSIS OF COKE-OVEN  
BENZENE-TOLUENE-XYLENE (BTX),  
BENZENE-TOLUENE (BT), AND BENZENE  
FOR MINOR COMPONENTS

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Introduction

Rapid methods for analyzing coke-oven benzene-toluene-xylene (BTX), benzene-toluene (BT) and benzene fractions for minor components are necessary to supplement purification processes for improving the quality of the benzene, toluene, and xylene fractions of light oil. During the investigation of methods for removing sulfur-containing compounds and other impurities from BTX and BT fractions, it was suspected that catalyst poisoning and the formation of undesirable resins were caused at least in part by cyclopentadiene, which occurs in such fractions when they are first collected. Since cyclopentadiene dimerizes easily, a method of analyzing for both the monomer and the dimer was desired. Along with the investigation of purification processes, one of the recurring analytical problems in our laboratory is the determination of trace impurities in refined light-oil products. The cyclohexene, cyclohexane, and methylcyclohexane contents of benzene were of particular interest.

Colorimetric methods for detecting and determining cyclopentadiene (1,10,13) and dicyclopentadiene (6,13) have been reported. Methods in which a maleic anhydride reaction (3,9) is utilized have been published. The condensation reaction between cyclopentadiene and aldehydes or ketones to form highly colored fulvenes has been used for the quantitative determination of cyclopentadiene and dicyclopentadiene in hydrocarbon mixtures (7). Techniques that involve saponification (2) and bromination (5,12) have been investigated. Infrared (11) and ultraviolet (8,14) spectrophotometric techniques have been published for determining cyclopentadiene and dicyclopentadiene in hydrocarbon mixtures. Various procedures, including mass spectrometry and infrared spectroscopy, can be used to determine the paraffin content of aromatic hydrocarbons. The total paraffin content of benzene is obtained by the ASTM sulfonation procedure D851-47.

Most of these methods are complicated by difficulties associated with interfering compounds, lengthy analysis times and, in some instances, poor sensitivity. The ASTM method for paraffins is not applicable to the analysis of specific paraffins. Mass-spectrometric and infrared spectrophotometric methods are much too difficult, if not impossible, for use in the hydrocarbon concentration ranges of particular interest in this investigation.

The purpose of this paper is to describe the apparatus and materials used in developing gas-liquid chromatographic methods of analysis for determining (1) cyclopentadiene and dicyclopentadiene in BTX and BT fractions, and (2) cyclohexene, cyclohexane, and methylcyclohexane in benzene.

## Experimental

### Apparatus

The instrument used was the Perkin-Elmer Corporation Model 154-B Vapor Fractometer. A 0-10 millivolt recorder (Leeds-Northrup Co.) was used for the cyclopentadiene and dicyclopentadiene methods. For the cyclohexene, cyclohexane, and methylcyclohexane method, the same instrument was converted to a 0-1 millivolt recorder. Samples were introduced into the instrument through the liquid sample-handling valve by means of uncalibrated Perkin-Elmer capillary pipettes. Helium was used as the carrier gas. The columns and standard operating conditions for each method are listed in Table I.

### Materials

The following reagents were used as standards. Phillips Petroleum Company Research Grade benzene was used in developing the methods for the analysis of cyclopentadiene and dicyclopentadiene in BTX and BT. A commercial benzene, containing a negligible amount of cyclohexane and methylcyclohexane as the only non-aromatic impurities, was used in developing the method for trace amounts of cyclohexene, cyclohexane, and methylcyclohexane in benzene. The dicyclopentadiene (95.6 wt % pure) was obtained from the Matheson Company. The cyclopentadiene was prepared by depolymerizing a portion of Matheson dicyclopentadiene, fractionating the depolymerized product, and recovering the cyclopentadiene fraction. The cyclopentadiene obtained by this method was 89.2 mole per cent pure, as determined by gas-liquid chromatography and mass spectrometry. The cyclohexene, cyclohexane, and methylcyclohexane were Phillips Petroleum Company Research Grade.

### Procedure

Synthetic mixtures containing 0-2 weight per cent cyclopentadiene in benzene, 0-0.7 weight per cent dicyclopentadiene in benzene, and 0-0.5 weight per cent each of cyclohexene, cyclohexane, and methylcyclohexane in benzene were prepared. In the latter mixtures, the concentrations of the three components were varied independently, and dilutions of these mixtures were made, to provide solutions in which the concentrations of each component covered the three concentration ranges, 50-500, 5-50, and 0-5 parts per million (ppm).

All mixtures were chromatographed under the standard operating conditions. The gas-chromatographic data were corrected for purity of the standards, and calibration curves were prepared in which peak heights were related to concentration. The calibration curves were linear for all compounds in all concentration ranges investigated. In measuring the height of a peak, both in synthetic mixtures and in samples analyzed, the net height above the base line was always used.

With the peak-height and concentration data obtained in the investigation of the synthetic mixtures of cyclohexene, cyclohexane, and methylcyclohexane in benzene, equations were derived by the method of least squares; these equations were used to calculate the concentrations of cyclohexene, cyclohexane, and methylcyclohexane in benzene.

## Results and Discussion

In the preliminary experimental work associated with the analysis of BTX and BT for cyclopentadiene, a 20-microliter sample of crude BTX was chromatographed under standard operating conditions. The resulting chromatogram, Figure 1,

in the range of interest (emergence time, 0 to 12 min), revealed one major peak and five minor peaks. When 20 microliters of a solution of approximately 0.5 weight per cent cyclopentadiene in benzene was chromatographed under identical conditions, the retention time for cyclopentadiene was very nearly equal to the retention time of peak number 1, Figure 1. The substance producing this peak in the chromatogram of the sample was tentatively identified as cyclopentadiene.

To confirm this tentative identification, the substance producing peak number 1, Figure 1, was trapped from the vent line of the gas chromatograph in a trap cooled in liquid nitrogen, and the material collected was analyzed by mass spectrometry. It was almost entirely cyclopentadiene. A very small concentration of an unidentified constituent was also detected. This impurity may have had a retention time similar to that of cyclopentadiene, but its concentration was so low that it could cause only negligible errors.

Not shown in Figure 1 is the remaining portion of the chromatogram (emergence time, 12 to 174 min), which revealed 11 additional peaks attributed to thiophene, toluene, the xylene isomers, dicyclopentadiene, and other unidentified constituents. These compounds were of no interest in the development of this method, except that they had to be removed from the column before another sample could be analyzed. Therefore, they were removed by back-flushing the column, a technique that reduces the time of analysis from 175 minutes (at standard operating conditions) to approximately 15 minutes. Only slight modifications of the flow system of the instrument and a few additional manipulations of controls are required.

Mass-spectrometric analysis of the cyclopentadiene used as a standard in this investigation indicated the presence of 10.1 mole per cent dicyclopentadiene. Because a pure cyclopentadiene standard was not available for comparison, it was not practicable to determine accurately the purity of the cyclopentadiene used. However, a reasonable estimate of the purity was deduced from the fact that the gas-liquid chromatogram of a 20-microliter sample of the cyclopentadiene standard revealed one major peak and eight minor peaks. None of the peaks represented the dicyclopentadiene in the sample because the retention time of this compound is much greater at the standard operating conditions than any constituent shown. No attempt was made to identify the minor peaks present in the chromatogram. However, if the thermal conductivities of the substances representing the minor peaks are assumed to be equal to that of cyclopentadiene, the combined unidentified impurities total 0.7 per cent. Consequently, the cyclopentadiene used as the standard for developing this method was assumed to be 89.2 mole per cent pure.

The average absolute error obtained in the analysis of a series of synthetic mixtures that contained 0 to 2 weight per cent cyclopentadiene was  $\pm 0.01$  weight per cent. The least detectable concentration of cyclopentadiene by the procedure described is 0.05 weight per cent.

In the preliminary experimental work associated with the analysis of BTX and BT for dicyclopentadiene, a 200-microliter portion of a silica-gel-treated BT was chromatographed under the standard operating conditions. The resulting chromatogram, Figure 2, revealed four major peaks and several minor peaks. Peak numbers 1, 2, 3, and 4 represent the benzene, toluene, xylenes, and unknown fractions of the sample. When a 200-microliter sample of a 1.4 weight per cent solution of dicyclopentadiene in benzene was chromatographed under the same conditions, the retention time for the dicyclopentadiene was very nearly equal to the retention

time of peak number 4, Figure 2. It appeared that this peak in the chromatogram of the sample was due, at least in part, to dicyclopentadiene.

This tentative identification was confirmed by the previously described gas-chromatographic mass-spectrometric analysis. The substance causing this peak in the chromatogram of the sample was mainly dicyclopentadiene with a very small proportion of a C<sub>9</sub> aromatic. The concentration of the C<sub>9</sub> aromatic was so small that any error it might cause would be negligible.

It was necessary to introduce a large quantity (200 microliters) of the sample into the instrument to obtain a measurable height for peak number 4. Although this peak appears to be relatively large in Figure 2, it was barely perceptible in the chromatogram of 200-microliter portions of several other BT samples examined.

The chromatogram of a 10-microliter sample of the Matheson dicyclopentadiene used as the standard in this determination displayed one major impurity peak. If the thermal conductivity of the substance causing this peak is assumed to be equal to that of the dicyclopentadiene, the Matheson dicyclopentadiene is 95.6 weight per cent pure. This value is based on the assumption that the major peak in the chromatogram is caused only by dicyclopentadiene. To confirm this assumption, this peak was trapped and analyzed by mass spectrometry. In addition to dicyclopentadiene, only traces of a C<sub>9</sub> aromatic were identified.

The method developed for determining dicyclopentadiene in BT was used to determine dicyclopentadiene in 18 samples in duplicate of crude BT or materials derived from it. The results of these analyses indicated that the average repeatability of the method is approximately 0.001 weight per cent over the range from 0 to 0.3 weight per cent dicyclopentadiene. The least detectable concentration of dicyclopentadiene by this method is 0.01 weight per cent. The time required for one measurement is approximately 10 minutes.

In the preliminary experimental work associated with the analysis of benzene for cyclohexene, cyclohexane, and methylcyclohexane, a 50-microliter portion of a sample of 1°-benzene was chromatographed under the standard operating conditions. The resulting chromatogram, Figure 3, revealed several peaks preceding the benzene peak. Tentative identification of the peaks was accomplished by chromatographing a portion of a synthetic blend of hydrocarbons in benzene and comparing the retention-time data of the synthetic blend with the retention-time data of the sample. Figure 4 illustrates the resolution of several hydrocarbons (Table II) obtained under the standard operating conditions.

To confirm the tentative identifications, the impurities of the sample of 1°-benzene were concentrated by progressive freezing, as described by Glick (4). This procedure was necessary because the impurities were in the ppm range. The concentrated impurities were chromatographed under the standard operating conditions, and the substances producing the unknown peaks were trapped as previously described and analyzed by mass spectrometry. By use of this technique, the major impurities were found to be n-heptane, cyclohexane, and methylcyclohexane (peaks no. 1, 2, and 3, respectively, of Figure 3). No cyclohexene was detected. The minor peaks shown in the chromatogram were attributed to small amounts of other hydrocarbon impurities.

Some difficulty was experienced in obtaining a paraffin-free benzene to be used as a standard in the preparation of synthetic mixtures. A commercial benzene was found that was almost completely paraffin-free. When a 500-microliter

portion of this benzene was chromatographed under operating conditions selected to give maximum sensitivity, the chromatogram, Figure 5, revealed two small peaks (peaks no. 1 and 2) preceding the benzene peak. These peaks were attributed to cyclohexane and methylcyclohexane, respectively, and their concentration was found to be approximately 2 ppm each.

The method developed for the determination of trace impurities in benzene was used to analyze several samples of benzene for cyclohexene, cyclohexane, and methylcyclohexane. The results of these analyses indicated that the average repeatability of the method is approximately 1 ppm over the range of 0 to 50 ppm and approximately 3 ppm over the range of 50 to 500 ppm for both cyclohexane and methylcyclohexane. No cyclohexene was detected in any samples analyzed. The lower limit of detection for each of the compounds was approximately 1 ppm. This value could probably be lowered by utilizing an amplifier to increase the signal from the detector. For the concentration ranges of 50-500, 5-50, and 0-5 ppm, the standard deviations for the respective compounds in the analysis of synthetic mixtures are shown in Table III.

#### Acknowledgements

The author wishes to thank C. F. Glick, who assisted in the development of the method for dicyclopentadiene in BTX and BT, and J. E. Friedline, who performed the mass-spectrometric analysis.

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Table I

STANDARD OPERATING CONDITIONS

<u>Condition</u>	<u>Determination</u>		
	<u>Cyclopentadiene in BTX and BT</u>	<u>Dicyclopentadiene in BTX and BT</u>	<u>Cyclohexene, Cyclo- hexane, and Methyl- cyclohexane in Benzene</u>
Column	6 ft x 0.375 in. of o- and p- Benzylbiphenyls, 24% on Fisher Column Packing	12 ft x 0.25 in. of Dow Corning Silicone Stopcock Grease, 25% on Burrell Inert Carrier	20 ft x 0.25 in. of Paraplex U-148, 25% on Burrell Kromat-FB, and 14 ft x 0.25 in. of Paraplex G-54, 20% on Burrell Kromat-FB
Temperature (°C)	60	140	100
Pressure (psig)	5	25	20
Flow (ml/min)	210	330	50
Detector Voltage (volts)	8	8	8
Sample Size (µl)	20 (nominal)	200 (nominal)	50 (nominal) 500 (nominal)
Recorder Range (mv)	0-10	0-10	0-1

Table II

ABBREVIATED NOMENCLATURE OF C<sub>5</sub> TO C<sub>8</sub> HYDROCARBONS USED IN THE SYNTHETIC  
BENZENE-PARAFFIN MIXTURE

<u>Compound</u>	<u>Abbreviated Nomenclature</u>
n-Pentane	n-P
2-Methylpentane	2-MP
n-Hexane	n-Hex
2,4-Dimethylpentane	2,4-DMP
Cyclopentane	CP
2-Methylhexane	2-MHex
3,3-Dimethylpentane	3,3-DMP
3-Methylhexane	3-MHex
Methylcyclopentane	MCP
2,3-Dimethylpentane	2,3-DMP
2,2,4-Trimethylpentane	2,2,4-TMP
3-Ethylpentane	3-EP
n-Heptane	n-Hep
1,1-Dimethylcyclopentane	1,1-DMCP
Cyclohexane	CHexane
2-Methylheptane	2-MHep
3-Methylheptane	3-MHep
Methylcyclohexane	MCH
n-Octane	n-Oct
Cyclohexene	CHexene

Table III

STANDARD DEVIATIONS OBTAINED IN THE ANALYSIS OF SYNTHETIC MIXTURES OF  
CYCLOHEXENE, CYCLOHEXANE, AND METHYLCYCLOHEXANE IN BENZENE

<u>Concentration Range, ppm</u>	<u>Standard Deviations, ppm</u>		
	<u>Cyclohexene</u>	<u>Cyclohexane</u>	<u>Methylcyclohexane</u>
50-500	4.6	7.7	5.5
5-50	0.7	0.4	0.5
0-5	0.1	0.2	0.3

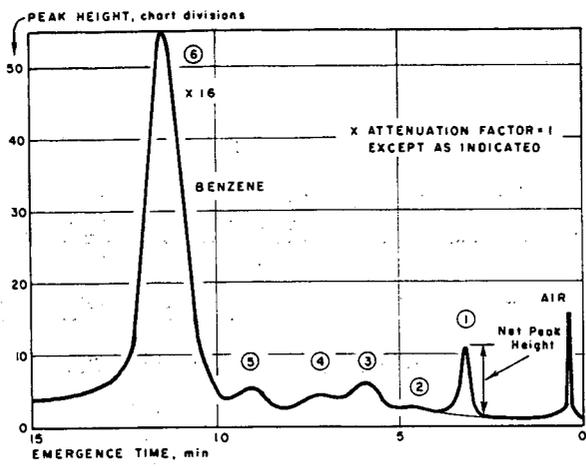


FIGURE 1

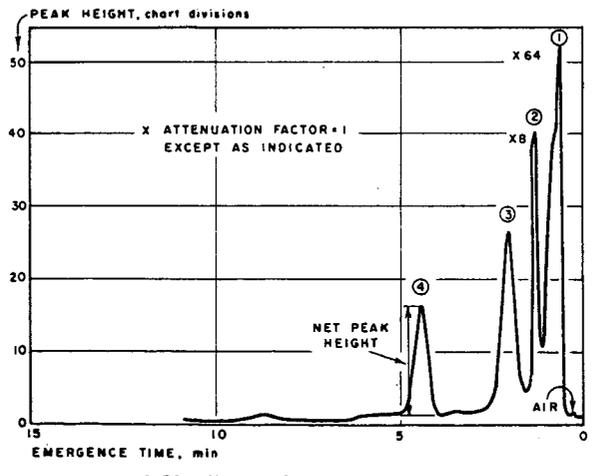
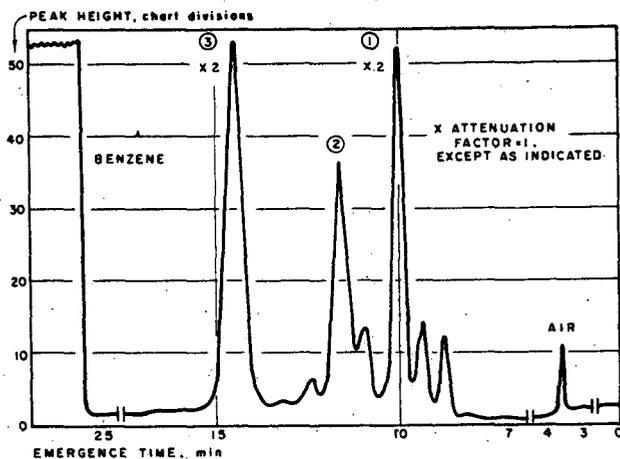
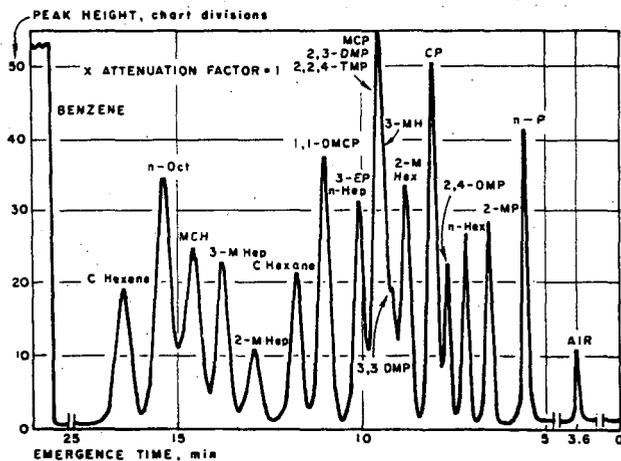


FIGURE 2



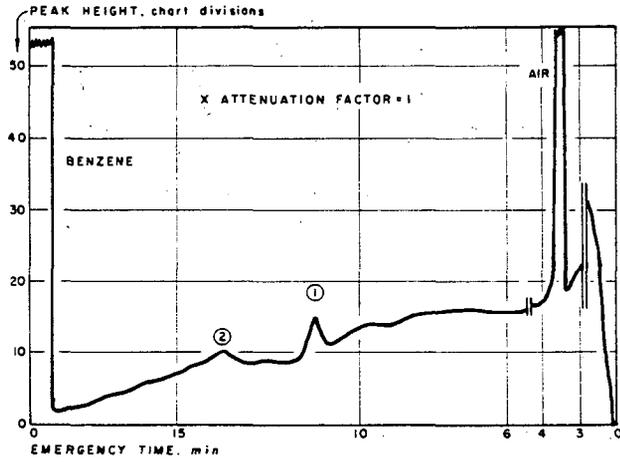
CHROMATOGRAM OF A 1° COKE-OVEN BENZENE

FIGURE 3



CHROMATOGRAM OF A SYNTHETIC MIXTURE OF HYDROCARBONS

FIGURE 4



CHROMATOGRAM OF 1° COKE-OVEN BENZENE USED AS A STANDARD  
FIGURE 5