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PROCESS OF PREPARING PYRIDINE AND 3-PICOLINE

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Our present invention, which is a continuation in part of our co-pending application Serial No. 198,231 filed November 29, 1950, now abandoned relates to a process of preparing pyridine and 3-picoline. More specifically, it relates to a process of preparing pyridine and 3-picoline by the interaction of acetylene, ammonia, and methanol.

Pyridine is obtained commercially as a by-product of the coal-tar industry. The manufacture of coal tar, coke, and related products starts with the placing of coal into a chamber and heating it out of contact with air. The coal is thereby decomposed into volatile products and into a non-volatile residue, coke. The volatile products, composed of condensable materials and non-condensable gases, are removed from the carbonization chamber and cooled, thereby condensing water and tar. These two substances, water and tar, constitute the bulk of the condensable materials evolved during the decomposition of the coal. After the complete removal of the water and tar, the remaining gas is passed through a preheater and then to a saturator. In the saturator the gas is contacted with dilute sulfuric acid. Ammonia and pyridine bases present in the gas are absorbed by the dilute sulfuric acid (about 6% H_2SO_4). The pyridine bases continue being absorbed until their concentration in the saturator bath becomes about 5% to 6%; ammonia is absorbed until all of the acid is neutralized. The saturator liquor is withdrawn when it becomes saturated with pyridine bases; the pyridines are recovered from this liquor by neutralizing it with ammonia gas from the ammonia still and separating the thus liberated crude pyridine bases from the ammonium sulfate solution.

The pyridine bases recovered from the coke oven gases contain a number of individual compounds. In commercial practice, the crude bases are fractionally distilled into four cuts:

	Boiling point, ° C.
Pyridine	115.8
2-picoline	129.5
3-picoline cut	143.6
Denaturing pyridine	Up to 165

The 3-picoline cut is composed of about equal parts of 3-picoline (B. P. 143.9° C.), 4-picoline (B. P. 144.9° C.), and 2,6-lutidine (B. P. 143.7° C.). Because the boiling points of these three methylpyridines are so close together, it is not possible to separate them from each other by fractional distillation. The patent literature is replete with processes for isolating one or more of these compounds from the 3-picoline cut; all are complicated processes and with one exception are not commercially practicable.

The amount of pyridines that is normally obtainable as a by-product of coal carbonization is limited. At the present time this insufficient amount is further curtailed because of economic considerations. The recovery of pyridine bases is incidental to the manufacture of ammonium sulfate. Unless there is a market for the ammonium sulfate, it is unprofitable to recover pyridine bases from coke oven gases. Today, some of the largest

producers of coal tar have discontinued recovering pyridine bases. The market for ammonium sulfate has gradually shrunk, until now it is difficult to sell more than a small amount of that which is potentially available. With the steady increase in the use of anhydrous ammonia as a fertilizer, it is expected that the demand for ammonium sulfate will continue to decline.

For a number of years the demand for pyridines has exceeded the supply. If this demand is to be satisfied, it is imperative that a new source of pyridine be found. Many attempts have been made to synthesize pyridine bases. Thus, for example, the U. S. Patent 1,882,158 dated October 11, 1932, describes a process of reacting acetylene with ammonia to prepare 2- and 4-methylpyridine as well as poly-methylated pyridines. This prior art patent also discloses a process of preparing quinaldine (which is 2-methylquinoline) by reacting aniline with acetylene.

In spite of the years of research that have been devoted to the study of pyridine synthesis, no one has heretofore developed a commercial process for the simultaneous preparation of pyridine and 3-picoline.

We have found we can react methanol, acetylene, and ammonia to form pyridine and 3-picoline. Furthermore, we have found that we can so control the reaction that practically no 2-picoline or 4-picoline is formed. In other words, we can make 3-picoline which is uncontaminated by 4-picoline.

By our process we can prepare pyridine and 3-picoline economically and in commercial quantities with very good yields. A commercial plant utilizing our process was put on stream this year.

In carrying out our invention we mix the vapors of methanol with acetylene and ammonia and pass the resultant mixture through a suitable reactor containing a catalyst. The temperature of the reactor is maintained preferably between about 400° C. and about 500° C. We prefer to carry out our process in a continuous manner although that is not necessary.

The reactor used may be of various types. We prefer the fluid catalyst type, similar to those normally used in carrying out cracking operations in the petroleum industry. Such reactors are of tubular form with suitable connections at entrance and exit. They are provided with means for supporting the fluid bed of catalyst, and are provided with any convenient means for heating them.

A highly satisfactory way of carrying out our invention is described more fully by means of the following specific examples:

Example 1

We prepared a gaseous mixture composed of two parts of acetylene, four and one-half parts of ammonia, and one part of methanol (the parts are by volume). We passed the mixture of vapors through a suitable reactor containing a fluidized catalytic bed of activated alumina (Alorco H—41 which had been impregnated with 10% zinc fluoride, the catalyst was finely divided, and all of it passes through 65 mesh. The reactor was maintained at a temperature between about 470°—480° C. As the mixture of acetylene, ammonia, and methanol passed through the reactor, a reaction occurred whereby pyridine, 2-picoline, and 4-picoline were produced. The vapors of the unchanged reactants and the reaction products were condensed as they emerged from the reactor, and the condensate was collected in a suitable receiver. The pyridine and the picolines were isolated from the condensate by fractional distillation. The pyridine obtained amounted to about 0.2 pound for each pound of acetylene passed through the reactor.

Example 2

The process of Example 1 was repeated with the exception that the gaseous mixture passed through the reactor was composed of three moles of ammonia and two moles of acetylene. The condensate (reaction product) was subjected to fractional distillation through the same fractionating column used in Example 1. No pyridine was recovered. 2-picoline was recovered in an amount corresponding to 34.0% of the reaction product. 4-picoline was recovered in an amount corresponding to 23% of the reaction product; as obtained from the fractionating column, the 4-picoline had a purity of more than 97% clearly indicating that no 3-picoline was formed.

Example 3

We prepared a gaseous mixture composed of one mole of acetylene, one mole of ammonia, and three moles of methanol. We passed the mixture of vapors through a fluid catalyst type of reactor 10 inches in diameter and 20 feet high containing 300 pounds of a fluidized catalytic bed of activated alumina (Alorco H—41) which had been impregnated with 10% zinc fluoride. The temperature of the reactor was maintained at about 425° C. The gaseous mixture of acetylene, ammonia, and methanol was passed through at a superficial velocity of 1.25 feet per second. As this mixture of acetylene, ammonia, and methanol passed through the reactor, a reaction occurred whereby pyridine and 3-picoline were produced. The vapors of the unchanged reactants and the reaction products were condensed as they emerged from the reactor, and the condensate was collected in a suitable receiver.

The condensate was composed of pyridine compounds and non-basic or neutral compounds. In order to separate these two groups of compounds, the condensate was acidified to a pH of 1 with sulfuric acid. The pyridine base compounds present dissolved in the dilute sulfuric acid solution. The non-basic compounds were insoluble and formed a layer on top of the sulfuric acid solution. These were separated by decantation. The last traces of non-basic compounds were removed by steaming the sulfuric acid solution. The sulfuric acid solution freed of non-basic contaminants was made strongly alkaline (pH 12.0) by the addition of sodium hydroxide. Pyridine bases separated from this strongly alkaline solution. They were removed by decantation. Any small amount of pyridines remaining in the alkaline solution were recovered by steam distillation and combined with the previously separated bases. After drying with flake caustic soda, the pyridine bases were fractionated through a two-inch diameter, 46-foot long fractionating column to recover pyridine and 3-picoline. The pyridine recovered amounted to 16.5%. The 3-picoline amounted to 24.5%; as obtained from the fractionating column, the 3-picoline had a purity of more than 95%, clearly indicating that no 4-picoline was formed. 2-picoline was also recovered, but only in an amount of 2.5%.

Example 4

The process of Example 3 was repeated with the exception that the gaseous mixture passed through the reactor consisted of one mole of acetylene, one mole of ammonia, and two moles of methanol. The pyridine bases obtained were subjected to fractional distillation through the same fractionating column used in Example 3. The pyridine recovered amounted to 14.5% of the reaction product. The 3-picoline recovered amounted to 22.5%; as obtained from the fractionating column, the 3-picoline had a purity of more than 95%, clearly indicating that no 4-picoline was formed. 2-picoline was recovered in an amount of 4.5%.

Example 5

The process of Example 3 was repeated with the exception that the gaseous mixture passed through the reactor was composed of one mole of acetylene, one mole of ammonia, and one mole of methanol. The pyridine bases recovered were subjected to fractional distillation through the same fractionating column used in Example 3. The pyridine recovered amounted to 21%. The 3-picoline amounted to 18%; as obtained from the fractionating column, the 3-picoline had a purity of about 85% indicating that 4-picoline was formed to some extent. 2-picoline was recovered in an amount of 9.5%.

Example 6

The process of Example 3 was repeated with the exception that the gaseous mixture passed through the reactor was composed of one mole of acetylene and one mole of ammonia; no methanol was used. The pyridine bases obtained were subjected to fractional distillation through the same fractionating column used in Example 3. No pyridine was recovered. 2-picoline was recovered in an amount of 32.0%. 4-picoline was recovered in an amount of 28.0%; the 4-picoline had a purity of 93%, clearly indicating that no 3-picoline was formed.

Example 7

The process of Example 3 was repeated with the exception that the gaseous mixture passed through the reactor was composed of two moles acetylene, two moles ammonia, and one mole of methanol. The pyridine bases recovered were subjected to fractional distillation through the same fractionating column used in Example 3. The pyridine recovered amounted to 14.5%. The 3-picoline amounted to 17.5%; the 3-picoline as obtained from the fractionating column had a purity of about 50% indicating that as much 4-picoline was formed as there was of 3-picoline. The 2-picoline recovered amounted to 16%.

Example 8

The process of Example 3 was repeated with the exception that the gaseous mixture passed through the reactor was composed of four moles acetylene, four moles ammonia, and one mole of methanol. The pyridine bases recovered were subjected to fractional distillation through the same fractionating column used in Example 3. The pyridine recovered amounted to 11%. The 3-picoline amounted to 17%; as obtained from the fractionating column, the 3-picoline had a purity of about 50%, indicating that 4-picoline was formed in an amount equal to the 3-picoline formed. 2-picoline was recovered in an amount of 24.5%.

Example 9

A zinc zeolite catalyst was prepared in the following manner. A four-inch diameter porcelain tube eight feet long was mounted vertically and filled with distilled water. Then 21.75 pounds of "Decalso Permutit" was slowly added to form an ion exchange bed approximately 90 inches long. A zinc chloride solution (3.5 pounds of zinc chloride and 100 pounds of water) was flowed downward over the Permutit in order to replace zeolitic sodium by zinc ion. The zeolite was washed with 20 pounds of distilled water, drained, and placed in a drying oven. The zinc zeolite was dried for about 72 hours at 85° C. It was then ground to 65 mesh and finer. (Decalso Permutit is a synthetic sodium-alumino-silicate used for water softening.)

The process of Example 1 was repeated with the following exceptions. The zinc zeolite catalyst prepared above was used. The temperature of the reactor was maintained at 425° C. The gaseous mixture passed through the reactor was composed of two moles of acetylene, two moles of ammonia, and one mole of methanol. The pyridine content of the water-free reaction product was about 29%. The 3-picoline amounted to 24%; as

obtained from the fractionating column, the 3-picoline had a purity of about 50% indicating that 4-picoline was also formed.

Example 10

A gaseous mixture composed of one mole of acetylene, one mole of ammonia, and three moles of methanol was passed through a suitable reactor containing a fluidized catalytic bed of activated alumina which had been impregnated with 10% cadmium fluoride, the catalyst was finely divided, and all of it passed through 65 mesh. The reactor was maintained at a temperature of about 425°–435° C. As the mixture of reactants passed through the reactor, a reaction occurred producing pyridine and 3-picoline. The vapors of the unchanged reactants and the reaction products were condensed as they emerged from the reactor; the condensate was collected in a suitable receiver. The pyridine and the picolines were isolated from the condensate by fractional distillation. The pyridine content of the reaction product was about 20.9%. The 3-picoline amounted to about 15%; it was about 95% pure.

Example 11

The process of Example 10 was repeated with the exception that the catalyst used was a silica-magnesia catalyst impregnated with 10% zinc fluoride. The pyridine in the reaction product amounted to 19%. The yield of reaction product was about 0.50 to 0.60 pound per pound of acetylene passed through the reactor.

Example 12

A zinc Filtrol catalyst was prepared as follows: 2,500 grams of "Filtrol 58" (which is a grade of montmorillonite clay having an amorphous or gel structure) was placed in a five-gallon glass container and a zinc chloride solution (227 grams of anhydrous zinc chloride was dissolved in 17 pounds of distilled water) was poured over the Filtrol. After this solution was poured over the Filtrol, a slurry was made by stirring for about one hour. The solids were removed from the slurry by filtration. The residue was removed from the filter and returned to the glass container. It was treated again with a zinc chloride solution prepared as mentioned above. The resulting slurry was filtered again. This process of slurrying the Filtrol and removing the aqueous solution was repeated fifteen times. Finally, the zinc Filtrol was thoroughly washed with distilled water. It was then dried in an oven and ground. Analyses of the thus-prepared catalyst showed it to contain about 2.5% zinc.

The process of Example 10 was repeated with the exception that the above prepared zinc Filtrol was used as catalyst. The condensate obtained was subjected to fractional distillation through an efficient fractionating column to recover pyridine and 3-picoline. The pyridine recovered amounted to about 7.9%. The 3-picoline recovered amounted to about 11%; as recovered from the fractionating column, the purity of the 3-picoline was more than 95%.

Example 13

The process of Example 9 was repeated with the exception that the catalyst used was alumina impregnated with 10% cupric chloride. The pyridine content of the condensate was about 14.8%. The condensate amounted to about 0.35 to 0.40 pound per pound of acetylene used.

Example 14

Instead of using acetylene, we can use the hydrated form of acetylene, i. e., acetaldehyde. We prepared a gaseous mixture of one mole of acetaldehyde, one mole of ammonia, and two moles of methanol. This mixture was reacted as was the mixture used in Example 4. The yields of pyridine, 3-picoline, and of 2-picoline were as indicated in Example 4.

In place of the activated alumina, the silica magnesia, the Filtrol, and the zeolite as catalyst supports, we may use other catalyst supports, such as fuller's earth, pumice, silica, and the like.

In place of the zinc fluoride, the cupric chloride, and the cadmium fluoride, we may utilize other catalysts, such as zinc chloride, cadmium chromate, cadmium molybdenate, lead chromate, zinc phosphate, and the like. As a matter of fact, we have caused acetylene, ammonia, and methanol to react by passing the mixture of the vapors over alumina itself; while the conversion to pyridine, 3-picoline, and other pyridines was not high, it was appreciable.

As is evident from the specific examples given above, the proportions of the reactants may be varied widely. It is important, however, to have all three reactants present if pyridine is to be formed in any appreciable amount.

The temperature at which the reaction is conducted may be varied widely. In general, we prefer to have the reaction temperature above about 400° C. and below about 500° C. It has been our experience that at temperatures below about 400° C., we have too large a proportion of the reactants passing through without reacting. At temperatures above about 500° C., we find that our catalyst becomes inactivated more rapidly and we obtain too many side reactions.

We claim as our invention:

1. The process of preparing pyridine and 3-picoline which comprises an interaction of acetylene, ammonia, and methanol in the presence of a catalyst useful in the preparation of picolines from acetylene and ammonia.

2. The process of preparing pyridine and 3-picoline which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst useful in the preparation of picolines from acetylene and ammonia maintained at an elevated temperature, and recovering pyridine and 3-picoline from the reaction product.

3. The process of preparing pyridine and 3-picoline which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst useful in the preparation of picolines from acetylene and ammonia maintained at a temperature between about 400° C. to about 500° C. and recovering pyridine and 3-picoline from the reaction product.

4. The process of preparing pyridine and 3-picoline which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst comprising zinc fluoride maintained at a temperature between about 400° C. to about 500° C., and recovering pyridine and 3-picoline from the reaction product.

5. The process of preparing pyridine which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst comprising an activated alumina impregnated with zinc fluoride maintained at a temperature between about 400° C. and about 500° C. and recovering pyridine from the reaction product.

6. The process of preparing pyridine which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst comprising activated alumina impregnated with 10% zinc fluoride maintained at a temperature between about 400° C. and about 500° C. and recovering pyridine from the reaction product.

7. The process of preparing pyridine which comprises mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst comprising activated alumina impregnated with 10% zinc fluoride maintained at a temperature between about 470° C. and 480° C., and recovering pyridine from the reaction product.

8. The process of preparing pyridine which comprises

mixing the vapors of acetylene, ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst comprising activated alumina impregnated with 10% zinc fluoride maintained at a temperature between about 415° C. and 425° C., and recovering pyridine from the reaction product.

9. The process of preparing pyridine which comprises preparing a gaseous mixture composed of about two parts of acetylene, of about four and one-half parts of ammonia, and of about one part of methanol, passing the resultant mixture through a reactor containing a catalyst comprising activated alumina impregnated with 10% zinc fluoride maintained at a temperature between about 470° C. and 480° C., and recovering pyridine from the reaction product.

10. The process of preparing pyridine which comprises preparing a gaseous mixture composed of about two parts of acetylene, of about four and one-half parts of ammonia, and of about one part of methanol, passing the resultant mixture through a reactor containing a catalyst comprising activated alumina impregnated with 10% zinc fluoride maintained at a temperature between about 415° C. and 425° C. and recovering pyridine from the reaction product.

11. The process of preparing pyridine and 3-picoline which comprises preparing a gaseous mixture composed of acetylene, ammonia, and methanol in a ratio of one mole of acetylene to one mole of ammonia to one mole of methanol passing the resultant mixture through a reactor containing a catalyst useful in the preparation of picolines from acetylene and ammonia maintained at an elevated temperature, and recovering pyridine and 3-picoline from the reaction product.

12. The process of claim 3 in which the gaseous mixture is composed of acetylene, ammonia, and methanol in molar ratios of 1:1:1.

13. The process of claim 3 in which the gaseous mixture is composed of acetylene, ammonia, and methanol in molar ratios of 1:1:3.

14. The process of preparing pyridine and 3-picoline which comprises mixing the vapors of acetaldehyde (hydrated acetylene), ammonia, and methanol, passing the resultant mixture through a reactor containing a catalyst useful in the preparation of picolines from acetylene and ammonia maintained at an elevated temperature, and recovering pyridine and 3-picoline from the reaction product.

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