***p*-Nitrotoluene.** The optimum sulfuric acid weight per 200-gram batch of *p*-nitrotoluene was the same as that with the ortho derivative—300 to 350 grams (Figure 3).

The optimum reaction temperature was from 65° to 70° C. as shown in Figure 4. A slight decrease in both yield and purity of product occurred at lower and higher temperatures, using the optimum initial sulfuric acid concentration of 90%.

The effect of initial sulfuric acid concentration on the yield at various temperatures (Figure 5) is highest at 90% H_2SO_4 from 50° to 90° C.

Summary

The quantity of sulfuric acid required for maximum yield of mononitration was found to be practically the same for both *o*- and *p*-nitrotoluene. However, there appeared to be a broader range in the *o*-nitrotoluene. For a 200-gram batch of mononitrotoluene, 350 grams of sulfuric acid is optimum when using the theoretical weight of nitric acid.

The optimum reaction temperature was practically the same for both isomers, about 65° to 70° C. At these temperatures and above, the reaction rate was essentially instantaneous.

The concentration of sulfuric acid required for optimum yield was similar for both *o*- and *p*-nitrotoluene. The minimum strength of sulfuric acid required for a maximum yield is about 90%. It appeared to make no difference whether the sulfuric acid was added to the nitric acid feed, placed with the mononitrotoluene, or mixed between the two.

Both isomers gave nearly quantitative yields under optimum conditions—98% for the *p*-nitrotoluene isomer and 100% for the *o*-nitrotoluene. An infrared study indicated no unreacted material in a reaction mixture of the ortho isomer.

The reaction conditions that gave the maximum yield of dinitrotoluene (based on a 200-gram charge of mononitrotoluene) are:

Variable	*o*-Nitrotoluene	*p*-Nitrotoluene
Wt. H_2SO_4, grams	250–350	350
Concn. H_2SO_4, grams	90	90
Temp., ° C.	50	65
Reaction time, min.	15 + 20	15 + 20

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Synthesis of Pyridines

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The vapor phase reaction of formaldehyde (40%), acetaldehyde, and ammonia at conditions of 360° C., 319% excess ammonia, and a total feed rate of 1.18 grams per hour per gram of catalyst produced a 48.6% optimum yield of pyridine and picolines. Thermodynamic and kinetic data are given for process design, and a preliminary flow sheet is presented.

NEW chemical products have recently created a demand for pyridine and its homologs as raw materials therefor. This is greater than the production capacity by classical methods, and an economical method is desired for their synthesis independent of coke oven operations. Three vapor phase reactions have been reported to yield pyridinic materials:

1. Between acetylene and ammonia over various catalysts with low yields and many side reactions (*13–16, 43*).
2. Between ammonia and methyl, ethyl, *n*-propyl, *n*-butyl, and allyl alcohols (*3, 20, 35*) over catalysts of the dehydrogenating-dehydrating type. The dehydrogenation may give an aldehyde which reacts with ammonia to give a maximum pyridinic yield of 7 mole %.
3. Between aliphatic aldehydes and ammonia over dehydrating catalysts, as the second step of (b) (*5–7, 8, 14, 22, 24, 27, 29, 30, 34, 40, 42*). The reaction between acetaldehyde and ammonia produces a maximum total yield from 30 to 50 mole % of pyridines and picolines (*14, 30, 40*), whereas acrolein and ammonia (*22, 24, 42*) produce a maximum total pyridine and picoline yield as high as 55 mole %.

Several other reactions with ammonia are reported—e.g., butadiene (*14, 47*) and ethylene oxide (*31*)—but in no case are the yields as promising as for the aldehyde-ammonia reaction. This was chosen as the basis for an attempted synthesis, although quantities of resins are known to be formed by side reactions. These resins are deposited on and rapidly poison the catalyst, especially when acrolein is used. In order to diminish the troublesome resin formation, a process was used to form the reacting aldehyde in situ (*2*). There would be continuous formation of the aldehyde in the reaction zone, and if its reaction with ammonia was at the same rate, the instantaneous aldehyde concentration would be very low, and resin formation would be minimized.

The equipment (Figure 1) was constructed mainly of glass. A cylinder of anhydrous liquid ammonia supplied ammonia va-

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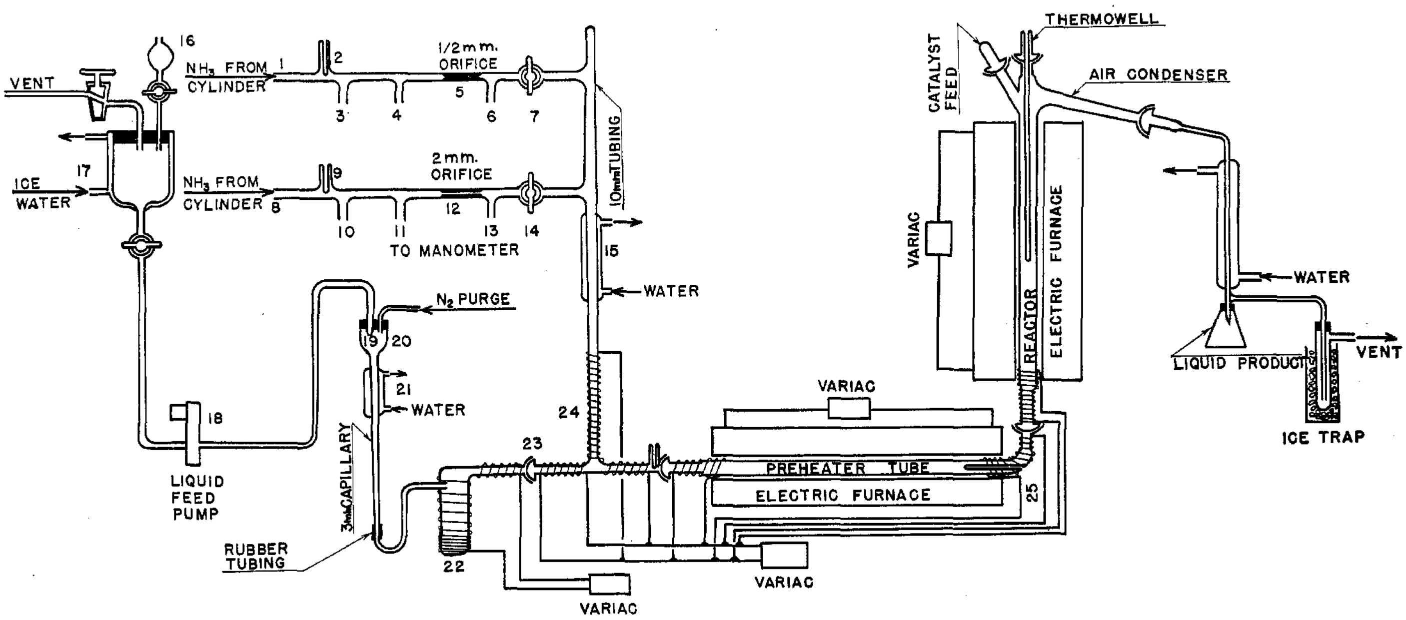


Figure 1. Experimental vapor phase reaction equipment

1, 8.	Ammonia inlet lines
2, 9.	Ammonia stream thermowells
3, 10.	Ammonia stream pressure taps
4, 6, 11, 13.	Manometer taps
5, 12.	Ammonia orifices
7, 14.	Stopcocks
15, 21.	Coolers
16.	Liquid feed inlet
17.	Liquid feed storage
18.	Zenith pump
19, 20.	Dropper assembly
22.	Vaporizer, nichrome wound
23.	Metal-glass transition joint
24.	Ammonia transfer line
25.	Preheater tube thermowell

por; the ammonia feed line containing the $^1/_2$-mm. capillary orifice, 5, was used for low flow rates (25 ml. to 400 ml./min.), while the line containing the 2-mm. orifice, 12, was used for higher flow rates (400 ml. to 3000 ml./min.). The volume flow rate, temperature, and pressure of the gaseous ammonia feed was measured, and the weight of ammonia was calculated within the average deviation of the orifice calibrations of ±0.5%.

Liquid feed of aldehydes was introduced by a Zenith metering pump giving 0.297 ml. per revolution. Electrical control of the motor and a gear train provided a wide range of pump speeds and outputs to give any predetermined flow rate between 0.0564 and 11.7 ml. per minute with a maximum deviation of ±0.3% at the low flow rates and much lower deviations at higher rates. The liquid feed entered a silver brazed copper vaporizer, 22, with a neck having a female 28/15 connection to a mating glass ball joint to the rest of the apparatus. Exposed transfer lines were electrically heated and insulated with $^1/_2$-inch thickness of asbestos.

The horizontal preheater and vertical reactor tubes were fabricated of 19-mm. heavy wall glass combustion tube and were heated by enclosing electric furnaces. The 12-inch heated section of each was variac controlled. Identical preheater and reactor tubes were of high temperature–resistant glass for work above 450° C. The preheater and reactor temperatures were controlled within 15° C. of the preselected value during a 3-hour run. They were measured within ±0.6° F. by iron-constantan thermocouples using a Wheelco portable indicating potentiometer. An air-cooled and an ice water–cooled condenser followed, and the condensates were combined. Off gas from the ice trap was vented unless a material balance was being established.

Table I. Test of Experimental Equipment

Run	α-Picoline, Mole %	γ-Picoline, Mole %	High Boiling Pyridines, Mole %
Mahan (*30*)	9.5	10.6	9.0
4	11.1	10.1	8.7
5	10.7	10.2	8.0
6	9.9	11.2	8.0

In order to test the performance of the equipment, part of the work of Mahan (*30*) on the reaction between acetaldehyde and ammonia was repeated, and the results are given in Table I.

Analysis of Reaction Products

The combined liquid product of a run contained, besides pyridines: water, unreacted ammonia and aldehydes, and minor amounts of products of side reactions. It was extracted four times with 50-ml. portions of ethyl ether. The extracts were combined, dried over calcium chloride, and the ether was distilled off, first at atmospheric pressure, then under vacuum. Benzene was also used as a solvent but was more difficult to separate because it boils closer to the pyridines.

A Todd distillation column (*45*) was used to analyze the extract. Solid derivatives, usually picrates and methiodides, were prepared from each distillation fraction obtained. Melting points and mixed melting points were taken to identify each fraction and compared with Heilbron (*23*).

In order to test the analytical method, six known synthetic mixtures were fractionated after an ether extraction, and the maximum error as determined was 2%.

The pyridine used in these synthetic mixtures was of reagent grade; the α-picoline was fractionated in a distillation column equivalent to 30 theoretical plates. A heart cut was made, boiling at 129.4° to 129.5° C., from an α-picoline sample of over 90% purity obtained from the Koppers Coke Co. The β-picoline was the best grade, at least 98%, obtainable from Eastman Kodak Co. This was further purified by the method of Riethof, Richards, Savitt, and Othmer (*36*). Reagent grade 2,4-lutidine boiling at 158° to 159° C. was also used to make up the test mixtures, since high boiling pyridines were expected to be present. The determined densities, refractive indices, boiling points, melting points of the corresponding picrates, and the melting points of the methiodides all agreed closely with those of Heilbron (*23*).

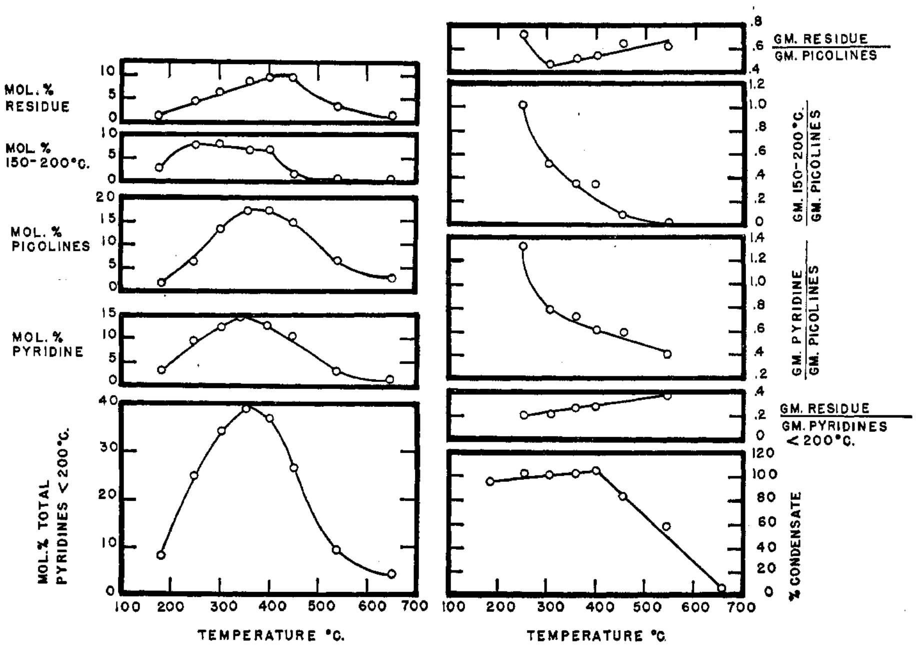


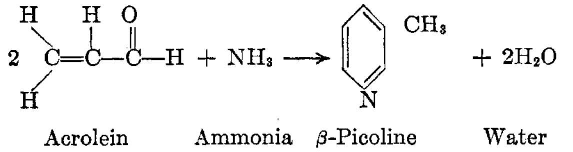
Figure 2. Effect of temperature on product yield

Preliminary Experiments

Two reactions that would produce aldehydes in the reaction zone were studied at a speed to give a concentration sufficiently low to minimize resin formation. The first was the method of Church and Joshi (*10*) for dehydrogenating ethanol to acetaldehyde. Ammonia was added to react the acetaldehyde as fast as it formed. Poor yields of pyridines resulted. Next, formaldehyde (40%) and acetaldehyde were reacted to form acrolein which then reacted with ammonia added to form pyridine and β-picoline, as in run 16, Table IV. Encouraging results were obtained with 22.2 mole % yield of total pyridines, and further studies were made of the reaction.

Thermodynamic Considerations

Acetaldehyde and formaldehyde convert almost completely to acrolein (*18, 19, 37, 38, 46*). As the total yield of pyridine and picolines obtained in preliminary experiments was only 12.6 mole %, it seemed advisable to determine the equilibrium yield of pyridines from the reaction of ammonia, acetaldehyde, and formaldehyde. If, for practical purposes, acetaldehyde and formaldehyde are assumed to yield a complete equilibrium conversion to acrolein, the controlling action is between acrolein and ammonia giving principally pyridine and β-picoline. Pyridine is probably formed by the secondary decomposition of β-picoline (*42*); hence the first reaction is



(1)

The data necessary for the thermodynamic calculations are given below. Where experimental data were lacking, two independent methods of estimation were used when possible. Data are for the gaseous state at 25° C. and one atmosphere, unless otherwise noted.

Acrolein. $C_p = 5.02 + 42.96(10^{-3})T - 15.86(10^{-6})T^2$ was calculated by the group contribution method of Andersen, Beyer, and Watson (*1*). As an independent check, the Dobratz method (*12*) yielded results that agreed within 7% between 300° and 1000° K. $\Delta H_f^\circ = -20.50$ kcal./g. mole and $\Delta G_f^\circ = -15.57$ kcal./g. mole from experimental measurements (*4*).

Ammonia. $C_p = 6.189 + 7.887(10^{-3})T - 7.28(10^{-7})T^2$ as determined by Spencer and Flannagan (*39*) from the experimental data of Thompson (*44*). $\Delta H_f^\circ = -11.04$ kcal./g. mole from experimental measurements (*32*). ΔG_f° was calculated as -3.88 kcal./g. mole from the relationship $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$, where $\Delta S_f^\circ = S^\circ_{NH_3} - {}^1/_2\, S^\circ_{N_2} - 3/2\, S^\circ_{H_2}$; the standard entropies for ammonia, nitrogen, and hydrogen are available (*32*) from experimental data.

Water. $C_p = 7.219 + 2.374(10^{-3})T + 2.67(10^{-7})T^2$ as correlated by Spencer and Flannagan (*39*) from experimental

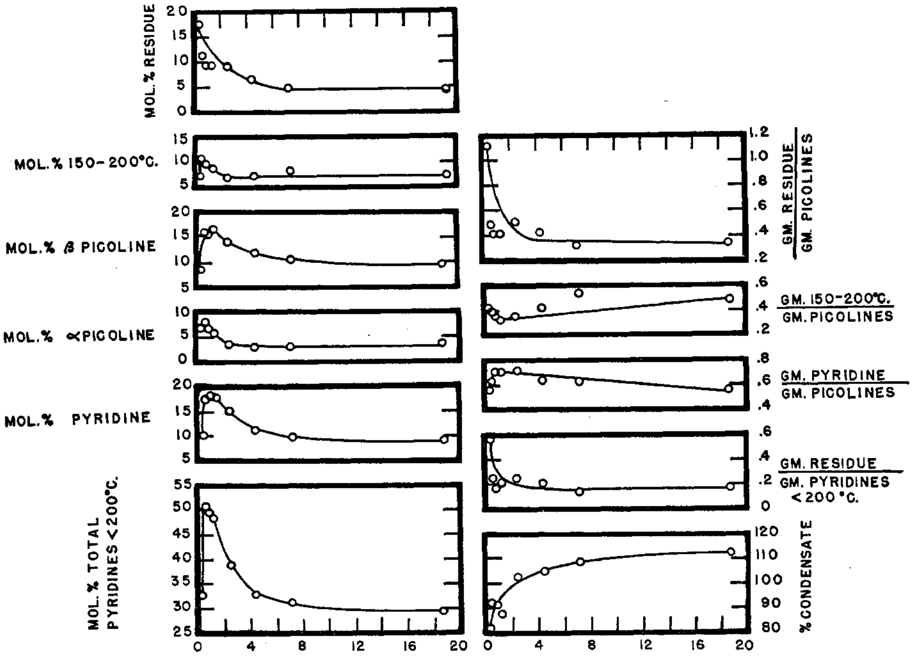


Figure 3. Effect of space velocity on product yield

data (*21, 41, 48*). $\Delta H_f^\circ = -57.7979$ kcal./g. mole was from experimental data (*32*). ΔG_f° was calculated as -54.6351 kcal./g. mole in the same manner as calculated for ammonia. The standard entropies for water, hydrogen, and oxygen were taken from experimental data (*32*).

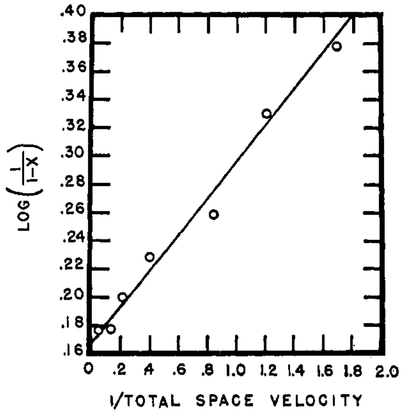


Figure 4. Test for pseudo first order reaction

β-Picoline. Necessary thermodynamic data are unavailable, although corresponding data are available for pyridine. The needed data were estimated from the available data for pyridine by adding the contribution of the CH_3 side chain. This method has been satisfactorily used for benzene homologs (*1*), and it seemed reasonable here because of the nearly identical chemical behavior of the two rings (*17, 26*) as well as their structural similarity (*33*).

For β-picoline the equation $C_p = -2.656 + 105.733(10^{-3})T - 44.545(10^{-6})T^2$ was derived from heat capacity data for pyridine (*28*) using the group contribution method (*1*) for the CH_3 group.

The heat of formation of β-picoline has been calculated as $\Delta H_f^\circ = 27.16$ kcal./g. mole from experimentally determined heat of combustion data (*11*).

The entropy of gaseous pyridine is available from experimental measurements (*27*). The effect of the CH_3 group was calculated (*1*). Using this calculated value and the experimental entropies for hydrogen, nitrogen, and graphite (*32*), ΔS_f° was calculated; $\Delta G_f^\circ = 45.09$ kcal./g. mole was then calculated for β-picoline using the relationship $\Delta G_f^\circ = \Delta H_f^\circ - T\,\Delta S_f^\circ$. For Reaction 1 $\Delta G_f^\circ = -29.2$ kcal./g. mole which was calculated using the relation

$$\Delta G_f^\circ = \Sigma n_i\, \Delta G_{f\,i(\text{products})}^\circ - \Sigma n_i\, \Delta G_{f\,i(\text{reactants})}^\circ \quad (2)$$

and $\Delta H_f^\circ = -36.48$ kcal./g. mole which was calculated using the relation

$$\Delta H_f^\circ = \Sigma n_i\, \Delta H_{f\,i(\text{products})}^\circ - \Sigma n_i\, \Delta H_{f\,i(\text{reactants})}^\circ \quad (3)$$

Equations for heat of formation and free energy of formation as functions of temperature were computed using published procedures (*25*).

$$\Delta H_f^\circ = -35{,}834 - 4.45T + 8.34(10^{-3})T^2 - 2.252(10^{-6})T^3 \quad (4)$$

$$\Delta G_f^\circ = -35{,}834 + 10.23T \log T - 8.34(10^{-3})T^2 + 1.126(10^{-6})T^3 - 0.658T \quad (5)$$

The equilibrium constant, K, was then calculated as a function of temperature using the relation (*25*) $\log K = -(\Delta G_f^\circ/4.576\text{T})_T$. Values of ΔH_f°, ΔG_f°, and log K are given in Table II for the temperature range of interest. For this reaction, assuming the fugacity coefficients of reactants and products are all equal to unity:

$$\left[\frac{N_{C_6H_7N} \times N_{H_2O}^2}{N_{C_2H_4O}^2 \times N_{NH_3}}\right] = K \quad (6)$$

Table II. Thermodynamic Study

Temp., ° K.	ΔH_f°	ΔG_f°	log K
298	−36,480	−29,200	21.40
400	−36,420	−26,710	14.63
500	−36,260	−24,300	10.62
600	−35,990	−21,940	7.96
700	−35,640	−19,620	6.14
800	−35,215	−17,360	4.74
900	−34,730	−15,160	3.69
1000	−34,200	−13,020	2.85

Table III. Catalysts Studied

Catalyst	Specifications and Analysis
A	Activated silica-alumina (15% alumina and 85% silica cast pellets, 1/8 inch); highly porous
B	Activated boron phosphate (16–32 mesh granules)
C	Gel type silica-alumina (90% silica, 9% alumina, 1% sulfate impurities, 16–32 mesh granules)
D	Crystalline type silica-alumina (87.5% silica, 12.5% alumina, 1/8-inch pellets)
E	Silica gel (8–14 mesh granules)
F	Activated alumina (1/8-inch pellets)

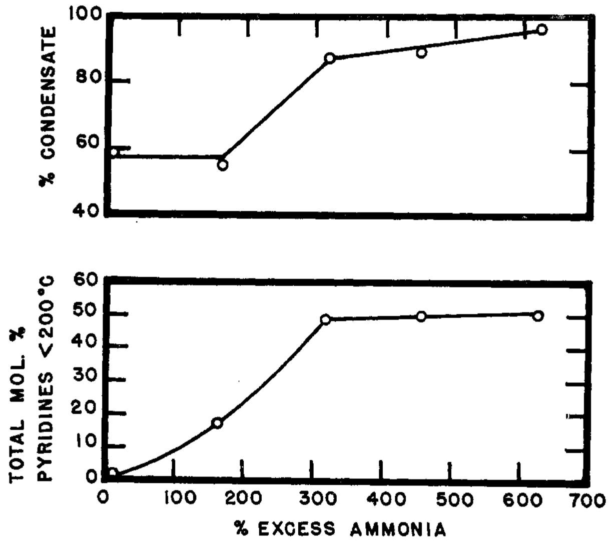


Figure 5. Effect of excess ammonia

The reaction of equilibrium was found from Equation 6 to proceed substantially to completion between 298° and 800° K. Since the total number of moles in Equation 1 remains unchanged, inert diluents will not affect the equilibrium. A great increase of pressure will improve only slightly the equilibrium conversion; this merely because of the effect of pressure on the fugacity coefficients. Thus thermodynamic considerations do not limit the desired reaction.

Effect of Different Catalysts

A set of identical runs, Table IV, was made for the reaction between acetaldehyde, 40% formaldehyde, and ammonia, using the catalysts of Table III. Runs 17, 19, and 20 gave about the same yields of pyridine and β-picoline, the desired products. Run 19 yielded considerably more high boiling material, and its catalyst was eliminated from further work. Of the two remaining choices, catalyst A was selected as the most advantageous because of its lower cost and because it is highly porous. Porosity

Table IV. Catalyst Search

Run	Catalyst	Feed Rate, G./Hr./G. Catalyst: Acetaldehyde	Formaldehyde	Water	Ammonia	Temp., ° C.	Yield (Mole %): Pyridine	β-Picoline	High boiling	Total
16	A	0.550	0.376	0.639	0.296	408	5.3	7.3	9.6	22.2
17	A	0.880	0.602	1.023	0.472	456	10.2	14.7	10.7	35.6
18	B	0.791	0.541	0.920	0.426	457	1.6[a]	2.3[a]	1.7[a]	5.6
19	C	0.801	0.547	0.931	0.431	449	10.1	12.5	15.6	38.2
20	D	0.770	0.526	0.894	0.414	444	10.9	13.1	10.5	34.5
21	E	0.733	0.502	0.852	0.395	455	4.2	6.0	4.3	14.3
22	F	0.787	0.538	0.911	0.420	448	3.9	5.9	5.1	14.9

[a] Insufficient sample for analytical distillation; same analysis was assumed as for run 17.

Table V. Effect of Temperature

Run	Temp., ° C.	Yield, Grams: Total liquids	Total pyridines	Yield (Mole %): Pyridine	α-Picoline	β-Picoline	150–200° C.	Residue boiling above 200° C.	Condensate, %	G. Residue/G. Pyridines Boiling below 200° C.	Pyridines Boiling below 200° C., Total Mole %	G. Pyridine/G. Picolines	G. 150–200° C./G. Picolines	G Residue/G. Picolines
25	183	175.6	5.82	3.2[a]	0[a]	2.0[a]	2.7[a]	1.5[a]	94.5	0.205[a]	7.9[a]	1.33[a]	1.143[a]	0.713[a]
24	252	183.8	17.48	9.7	0	6.2	8.1	4.6	102.0	0.205	24.0	1.33	1.143	0.713
27	307	182.9	24.64	12.2	2.5	10.7	7.9	6.3	101.0	0.200	33.3	0.782	0.517	0.460
23	361	184.1	29.76	14.9	3.3	13.8	6.9	9.0	102.5	0.246	38.9	0.713	0.349	0.509
29	401	186.3	28.84	12.4	3.1	14.1	6.8	9.5	104.5	0.273	36.4	0.615	0.343	0.535
17	456	162.8	22.84	10.2	0	14.7	1.2	9.7	82.5	0.385	26.1	0.592	0.071	0.640
26	545	136.5	8.32	3.0	0	6.3	0	3.4	58.0	0.367	9.3	0.400	0	0.625
28	658	79.8	3.97	1.4[b]	0[b]	3.0[b]	0[b]	1.6[b]	5.3	0.367[b]	4.4[b]	0.400[b]	0[b]	0.625[b]

[a] Insufficient sample for analysis; same analysis as run 24 is assumed.
[b] Insufficient sample for analysis; same analysis as run 26 is assumed.

was expected to be an asset during the reaction and also during catalyst regeneration.

Effect of Temperature

The effect of temperature is shown in Table V and Figure 2. The feed was always preheated to the reaction temperature. Acetaldehyde and formaldehyde in stoichiometric amounts and a 319% excess of ammonia were used. All runs were made with a total of 63.8 grams of acetaldehyde, 43.6 grams of formaldehyde (anhydrous basis), 74.1 grams of water, 51.4 grams of ammonia, and 32.6 grams of catalyst. Time was 3 ± 0.08 hours, and total space velocity was 2.47 ± .08 g./hr./g. of catalyst.

Figure 2 shows a maximum yield of low boiling pyridines at 360° C. The maximum yield of each individual pyridinic product also occurred very close to 360° C. At temperatures above 400° C. the percentage of condensate drops sharply, indicating decomposition. A further advantage of operating at 360° C. is that the ratio of the residue to pyridines having boiling points below 200° C. is nearly at its minimum value (Figure 2). Accordingly, 360° C. appeared to be the optimum temperature and was used for all further experimental work.

Effect of Space Velocity

The space velocity was varied by changing the rate of feed of reactants, always in the same ratios. A constant 319% excess of ammonia was maintained, with 32.6 grams of catalyst and temperature of 360° C. In runs 23, 32, 31, and 33 (Table VI) the total feeds were 63.8 grams acetaldehyde, 43.6 grams formaldehyde, 74.1 grams water, and 51.4 grams ammonia. Exactly half of each of these amounts was used for the other four runs to reduce the elapsed time for a run.

Figure 3 shows that higher space velocities do not allow sufficient time for the desired reaction to take place, whereas space velocities below 0.59 g./hr./g. of catalyst give sufficient residence time in the reaction zone to produce considerable amounts of residue. The maximum yield for each of the desired products also occurs at or very near the same space velocity as the maximum for the total yield of low boiling pyridines. The maximum yield of desired products was obtained in run 35. However, run 34 at twice the throughput rate yielded only slightly less low boiling pyridines. Run 34 had a lower ratio of residue to low boiling pyridines, and its total space velocity of 1.18 g./hr./g. of catalyst was regarded as optimum.

Effect of Aldehyde-to-Ammonia Ratio

The effect of different amounts of excess ammonia was determined by a series of runs (Table VII). The total weight of feed was the same for each run. Temperature at 360° C. and space velocity at 1.18 g./hr./g. of catalyst were kept constant at these optimum values, previously established. All runs lasted 3 hours, using 32.8 grams of catalyst as before. The yields of pyridinic materials increased with an increase in the excess ammonia (Figure 4), but this effect lessened above 319% excess ammonia, which was selected as optimum for further work. Table VII shows excess ammonia to have almost no effect on the relative amounts of the pyridinic products.

Material Balance

A complete material balance was established by repeating the optimum run, run 34, and making a complete analysis of both gaseous and liquid products. The uncondensed gases discharging from the water-cooled condenser were dried over calcium chloride and then absorbed in a known amount of standard sulfuric acid, followed by a water absorber and a dry ice trap. The gain in weight of the drying tower indicated the water content of the gases. The contents of the acid absorber, water absorber, and dry ice trap were combined. An aliquot was titrated with standard sodium hydroxide, using phenolphthalein indicator, to determine the excess of sulfuric acid; and the ammonia absorbed was then calculated. The same aliquot was then used to determine acetaldehyde by the standard iodine method. Formaldehyde was then determined by subsequent treatment with Fehling's solution, and precipitation and ignition of copper oxides.

The liquid products were extracted with ether, and the pyridinic materials were determined as usual. The ether contained no

Table VI. Effect of Space Velocity

Run	Length of Run, Hr.	Yield, Grams		Yield, Mole %					Condensate, %	G. Residue/G. Pyridines Boiling below 200° C.	Pyridines Boiling below 200° C., Total Mole %	G. Pyridine/ G. Picolines	G. 150–200° C./G. Picolines	G. Residue/G. Picolines	Space Velocity, G./Hr. G. Catalyst			
		Total liquids	Total pyridines	Pyridine	α-Picoline	β-Picoline	150–200° C.	Residue boiling above 200° C.							Acetaldehyde	Formaldehyde	Total aldehydes	Total Feed
36	12.00	80.7	16.02	10.1	6.8	8.5	7.3	17.9	81.3	0.573	32.7	0.565	0.413	1.132	0.081	0.056	0.137	0.30
35	6.00	86.2	19.10	17.4	7.4	15.8	10.3	11.4	91.5	0.242	50.9	0.613	0.395	0.486	0.162	0.112	0.274	0.59
47	4.27	85.9	18.40	17.9	6.5	15.6	9.4	9.4	91.0	0.167	49.4	0.688	0.367	0.410	0.227	0.157	0.385	0.83
34	3.00	84.0	18.20	18.0	5.8	16.5	8.3	9.4	87.5	0.203	48.6	0.687	0.325	0.409	0.323	0.223	0.546	1.18
23	2.92	184.1	29.76	14.9	3.3	13.8	6.9	9.0	102.5	0.246	38.9	0.713	0.349	0.509	0.672	0.457	1.129	2.45
32	1.57	186.3	24.88	11.0	3.0	11.9	7.2	6.6	104.5	0.209	33.1	0.630	0.421	0.429	1.24	0.848	2.09	4.52
31	0.98	190.3	22.10	9.7	2.7	10.5	8.1	4.3	108.1	0.146	31.0	0.619	0.532	0.315	1.99	1.36	3.35	7.26
33	0.38	193.6	21.49	8.8	3.8	9.6	7.4	4.4	111.2	0.170	29.6	0.558	0.477	0.342	5.16	3.52	8.68	18.82

Table VII. Effect of Excess Ammonia

Run	Feed, Grams				Excess Ammonia, %	Yield, Grams		Pyridines Boiling below 200° C., Total Mole %	Condensate, %	Yield, Mole %					G. Residue/G. Pyridines Boiling below 200° C.	G. Pyridine/ G. Picolines	G. 150–200° C./G. Picolines	G. Residue/G. Picolines
	Acetaldehyde	Formaldehyde	Water	Ammonia		Total liquids	Total pyridines			Pyridine	α-Picoline	β-Picoline	150–200° C.	Residue boiling above 200° C.				
37	27.4	18.7	31.9	38.5	628	76.4	15.76	50.4	96.5	18.4	6.6	15.8	9.6	14.0	0.295	0.687	0.372	0.608
40	29.7	20.3	34.6	31.8	455	79.4	16.98	50.1	89.7	18.3	6.2	15.9	9.7	14.8	0.289	0.667	0.371	0.589
34	31.9	21.8	37.1	25.7	319	84.0	18.20	48.6	87.5	16.0	5.8	16.5	8.3	9.4	0.203	0.687	0.325	0.409
38	34.8	23.7	40.3	17.7	164	72.3	9.33	17.3	54.7	6.5	2.4	5.6	2.8	9.5	0.576	0.700	0.301	1.153
39	38.4	26.2	44.5	7.3	0	83.0	0	0	59.6	0	0	0	0	0	...	...	...	...

detectable aldehydes and only a minute trace of ammonia. A part of the residual water layer from the extractions was titrated with sulfuric acid. Acetaldehyde and formaldehyde were then determined as for the gas analysis.

Each analytical determination was made in triplicate, and the entire material balance was carried out twice. The two runs agreed within 1% in all cases. Balances showed that 98.3% of the ammonia, 92.9% of the acetaldehyde, and 94.9% of the formaldehyde were accounted for, as shown in Table VIII.

Catalyst Life

Fresh catalyst was used for each of the runs described. In order to study the catalyst life, run 34, the optimum run, was repeated and continued for an extensive time, without changing the catalyst. At the end of each 3 hours the liquid products were removed, and the refrigerated feed tank was refilled. No appreciable change in yield was noted during the first 21 hours, but thereafter the yields diminished. At the end of 27 hours the catalyst was regenerated; thereafter the yields showed that it had regained its initial activity. After another 21 hours, another decline in yield was noted; again regeneration restored the initial activity. The study was terminated after a total of 64 hours of operation with the same catalyst.

Catalyst regenerations were carried out at 360° C. using a mixture of 5% oxygen and 95% nitrogen to burn off the accumulated carbon. During regeneration the temperature tended to rise above 360° C., but in no case did it rise above 400° C. Regeneration was carried out until the off gas no longer gave a test for carbon dioxide with calcium hydroxide solution.

Order of Reaction

The reaction studied in this work is complex and known to proceed through several intermediate stages (*42*). Since the nature of these is uncertain and since stoichiometric equations for many of the side reactions cannot be written with certainty, the concept of pseudo-reaction orders was utilized.

An elementary section of a steady state catalytic flow system gives, by material balance

$$F\,dx = r\,dw$$

$$\int_0^W \frac{dw}{F} = \int_0^W \frac{dx}{r}$$

$$\frac{W}{F} = \int_0^x \frac{dx}{r} = \frac{1}{S_v} \tag{7}$$

for a reaction that goes substantially to 100% completion

$$r = k(1 - x)^n \tag{8}$$

combining Equations 7 and 8

$$\frac{1}{S_v} = \frac{1}{k}\int_0^x \frac{dx}{(1 - x)^n} \tag{9}$$

for pseudo first-order behavior, $n = 1$, and on integration of Equation 9

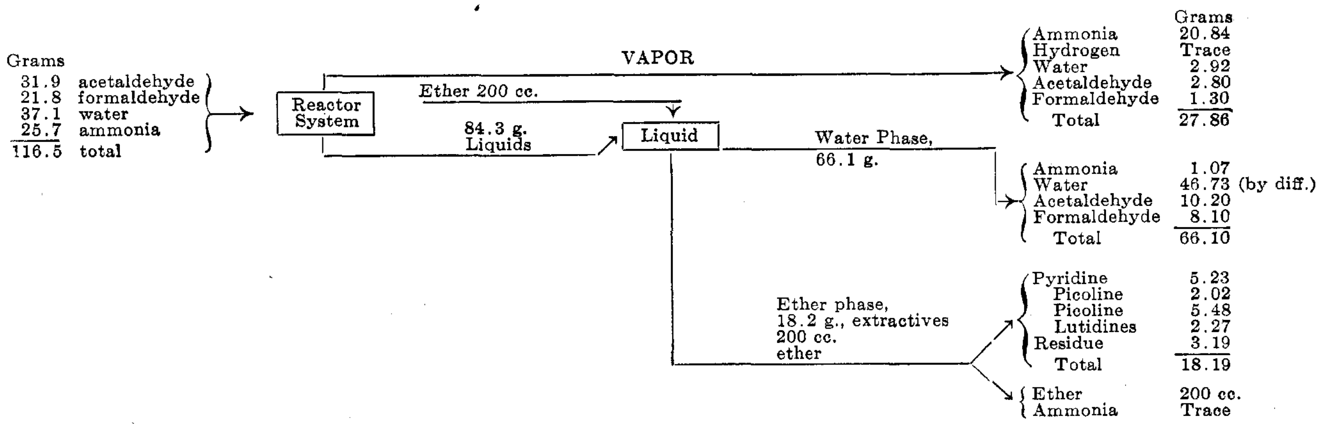
$$\frac{1}{S_v} = -\frac{1}{k}\ln(1 - x) = \frac{2.303}{k}\log\left(\frac{1}{1 - x}\right)$$

hence, a plot of $1/S_v$ versus $\log\left(\frac{1}{1 - x}\right)$ should be linear for a reaction of the pseudo first order. From Equation 9 if n is any value but 1, integration gives

$$\frac{1}{S_v} = \frac{1}{(n - 1)k}\,\frac{1}{(1 - x)^{n-1}}$$

Obviously, values for n can be selected to test the order of the assumed reaction by determining which plot of $1/S_v$ versus

Table VIII. Material Balance



Catalyst gain in weight 1.06 grams

$1/(1 - x)^{n-1}$ gives the closest fit. The data were tested assuming reactions of the pseudo first, second, third, one half, and one and one half order. The best fit was obtained for the assumption of a pseudo reaction of the first order, and is shown in Figure 5.

Plant Flow Sheet

Figure 6 shows a process flow sheet for a plant based on the process described here. Material balances were obtained by ratioing the data shown in Table VIII. The total liquid products from the reactor are extracted with benzene in D-1, and the raffinate is batch distilled in D-3 to recover unreacted aldehydes. Distillation of the ternary mixture of formaldehyde-acetaldehyde-water yields 37% formaldehyde in the bottoms, which are recycled. The mixture of water and acetaldehyde goes overhead and is redistilled in D-3 to recover anhydrous acetaldehyde for recycle. The water is removed as bottoms.

The extract layer from D-1 is batch distilled in D-2; the benzene is recovered and recycled; and the various pyridinic fractions are collected. It was previously found that a desirable life for a catalyst is at least 21 hours, and, since 3 hours are required for regeneration, all units were sized on the basis of a full day's production in 21 hours. A preliminary cost estimate was made for a plant and its operation using data of Chilton (*9*) and other sources. Profitable operation is indicated.

Conclusions

A process has been developed for producing low boiling pyridines using as raw materials formaldehyde, aldehyde, and ammonia. These are inexpensive, plentiful, and independent of coking operations. Under optimum conditions, yields of nearly 50 mole % of the desired products are obtained, and the unreacted aldehydes and ammonia are recovered and recycled. The process has been shown to be economical, and patent protection is being secured.

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Thanks are due the Allied Chemical and Dye Corp. for the granting of a research fellowship to Sherman L. Levy, which helped to make this work possible. Thanks are also due Harriet Levy for help in the preparation of the manuscript.

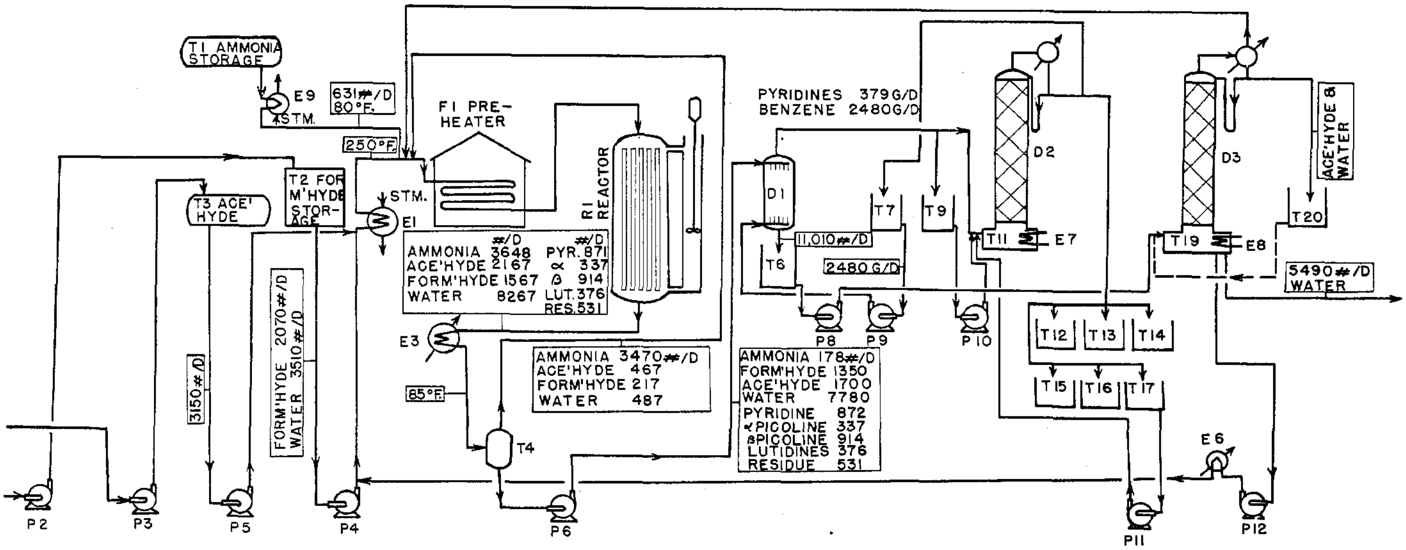

Figure 6. Process flow sheet for producing 1,000,000 pounds per year of total pyridines

Nomenclature

C_p = heat capacity at constant pressure cal./g. mole ° C.
T = temperature, ° K.
ΔH_f° = standard heat of formation kcal./g. mole
ΔG_f° = standard free energy of formation kcal./g. mole
ΔS_f° = standard entropy of formation cal./g. mole ° C.
S° = standard entropy cal./g. mole ° C.
N = number of moles
n = reaction order
F = feed rate
W = mass of catalyst
r = rate of reaction moles products/mass catalyst/unit of time
x = conversion moles of product/mole of feed
S_v = space velocity
k = apparent reaction velocity constant
K = equilibrium conversion constant

Subscripts

i = individual reactant or product

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