

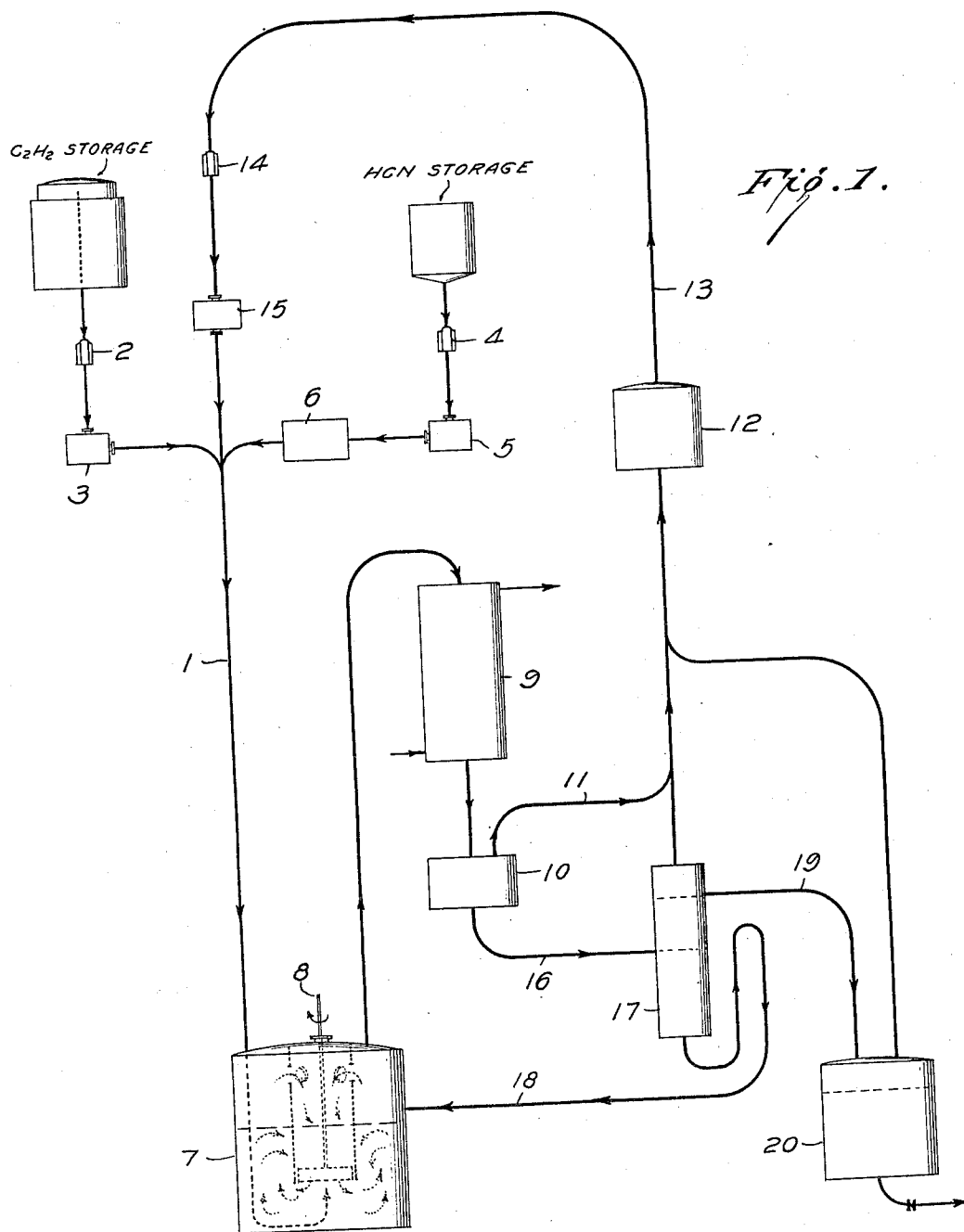
Sept. 25, 1945.

D. J. SALLEY
PRODUCTION OF ACRYLONITRILE

2,385,469

Filed Jan. 14, 1942

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

ACRYLONITRILE PRODUCED, mol./hr.

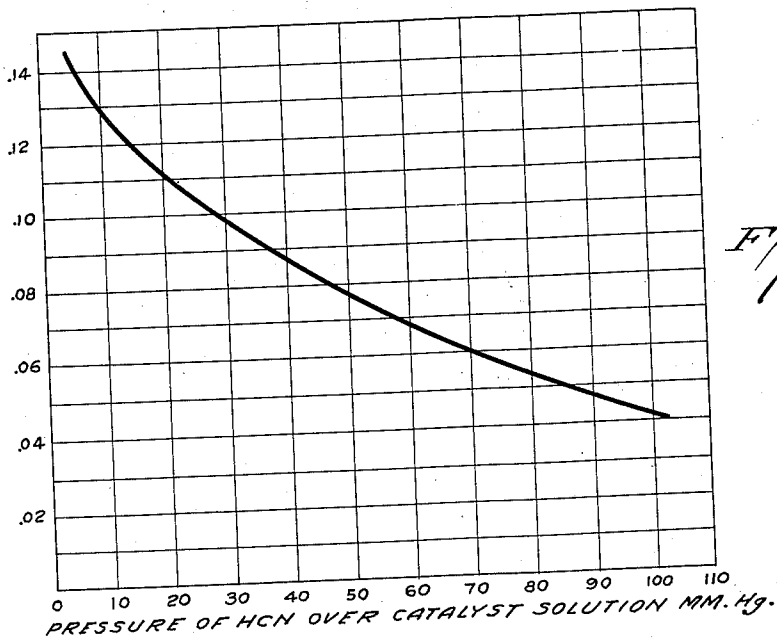


Fig. 2.

% YIELD OF ACRYLONITRILE
(HCN consumed basis)

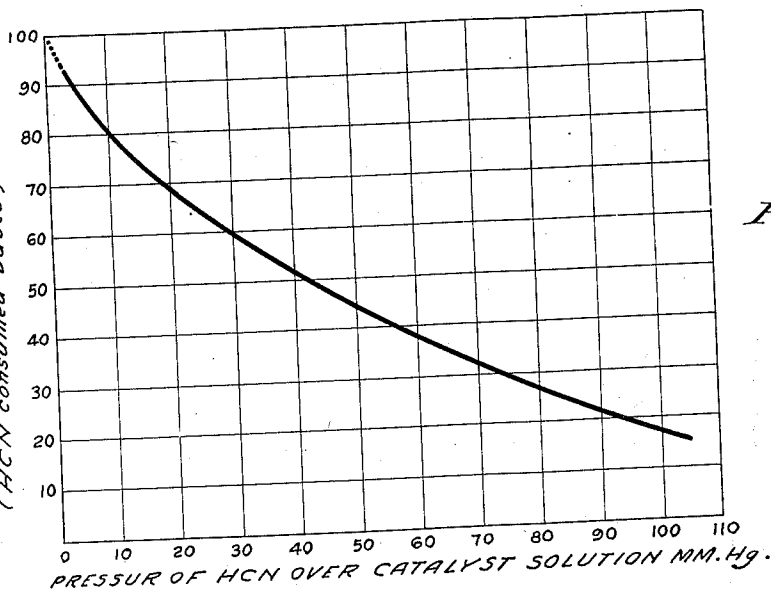


Fig. 3.

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UNITED STATES PATENT OFFICE

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PRODUCTION OF ACRYLONITRILE

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Application January 14, 1942, Serial No. 426,683

7 Claims. (Cl. 260-464)

The present invention relates to the production of acrylonitrile, and more particularly to an improved method for the catalytic production of acrylonitrile from hydrocyanic acid and acetylene.

It is known that acrylonitrile may be obtained by passing a mixture of hydrocyanic acid and acetylene over such materials as activated carbon, silica gel and metal cyanides heated at temperatures ranging from 400 to 500° C. Although these substances definitely catalyze the reaction, considerable side reactions occur and the rate of production of acrylonitrile is relatively slow. Consequently, the yield and quality of the nitrile produced under these conditions are not conducive to commercial operation.

The principal object of this invention is to devise a method wherein acrylonitrile may be readily and cheaply obtained. Another object resides in a method for the production of acrylonitrile requiring only simple equipment with high efficiencies. A further object is the provision of an improved method for catalytically producing acrylonitrile from hydrocyanic acid and acetylene. Other objects will appear hereinafter.

It has been found that the above objects may be accomplished by establishing a cycle of operation involving the steps of continuously charging a catalyst containing an aqueous solution of a cuprous salt maintained at a temperature not greater than 110° C., and preferably within the range of 60 to 90° C., with hydrocyanic acid and acetylene, said materials being introduced in such a state that the concentration, or in other terms, the partial pressure, of the acetylene always substantially exceeds that of the hydrocyanic acid in the catalytic chamber. Vapors of acrylonitrile, water, unreacted acetylene and the by-product gases (mainly vinyl acetylene and acetaldehyde) may be removed, the vapors of acrylonitrile and water condensed, the unreacted acetylene separated from the by-product gases and returned to the cycle, the condensate of acrylonitrile and water allowed to stratify into two layers, the lower or water layer returned to the catalytic chamber, and the upper layer of acrylonitrile recovered.

The operation may, for example, be accomplished in the apparatus shown in Figure 1 of the accompanying drawings in which acetylene and hydrocyanic acid are introduced from storage into feed-line 1, the former through meter 2 and pump 3, and the latter through meter 4, pump 5 and vaporizer 6. The gases then pass from feed-line 1 into chamber 7 containing the

catalyst. The catalytic chamber is heated to the desired temperature by a suitable heating device not shown. Agitator 8 provides thorough contact of the acetylene and hydrocyanic acid with the catalyst. The emerging vapors of acrylonitrile and water and the unreacted acetylene and by-product gases pass into the condenser and separator 9 wherein the acrylonitrile and water are condensed. Undesirable by-products such as vinyl acetylene are removed from the unreacted acetylene gas to a considerable extent by solution in the condensate. From the receiving vessel 10 the unreacted acetylene and remaining by-product gases pass through line 11 to absorption vessel 12 wherein the by-product gases are entrapped and the unreacted acetylene is returned through line 13, meter 14 and pump 15 to the cycle. Vessel 12 is preferably provided in duplicate with means for alternately directing the gas flow through one vessel or the other. When the absorbent in the vessel through which the gas is flowing loses its capacity to effectively absorb the by-products, the gas flow is directed through the other vessel and the exhausted adsorbent regenerated, e. g. by steaming. The condensate of acrylonitrile and water passes from receiving vessel 10 through line 16 to tank 17 wherein it stratifies into two layers. The lower or water layer is returned through line 18 to the catalytic chamber and the upper or acrylonitrile layer containing a portion of the by-products passes through line 19 to receiving tank 20 from whence it may be withdrawn and purified, as for example, by fractional distillation.

Absorbents which may be utilized for the removal of by-product gases from the excess acetylene are solids such as activated charcoal, fuller's earth and calcined bauxite. Liquids may also be used, preferably in continuous counter-current absorption, such as for example, higher alcohols, glycerol, glycol, dibutyl phthalate and refined paraffin base mineral oil.

As a catalyst for the reaction of acetylene with hydrocyanic acid to form acrylonitrile, this invention utilizes an acid solution of a cuprous salt (e. g. cuprous chloride, bromide, iodide, cyanide, formate, acetate, etc.). A soluble salt of ammonium, an amine or an alkali metal is added for the purpose of holding the otherwise relatively insoluble cuprous salt in solution, probably by combining with it to form a soluble complex salt. The advantage of the acidic nature of the catalyst is that it prevents the formation of potentially explosive acetylides.

A typical example of the catalyst composition

(parts being by weight) is as follows: 272.5 parts of cuprous chloride, 147 parts of ammonium chloride, 3.5 parts of concentrated hydrochloric acid (37%) and 300 parts of water. In preparing the catalyst solution the preceding proportions need not be adhered to rigidly. However, it is preferable that the aqueous solution be highly concentrated with respect to the cuprous chloride. The amount of acid added is such that when the solution reaches its clear yellow state it is acid to Congo red paper and shows a pH of 2 to 4 on standard alkacid paper.

It is believed that in the operation of the catalyst, the acetylene and hydrocyanic acid dissolve in the catalyst solution to form complexes of varying composition with the catalyst, and that the concentrations of these complexes depend on the concentration of the dissolved molecules which in turn depends on the equilibrium partial pressures of the gases (C_2H_2 and HCN). It is further believed that these complexes react among themselves to produce acrylonitrile.

In accordance with the above, it has been found that the rate of formation and the percent yield of acrylonitrile on the basis of the hydrocyanic acid consumed, decrease in a non-linear manner with increase in the partial pressure of the hydrocyanic acid in the ingoing gas mixture.

The data given in Table 1 below illustrate the effect of change in pressure of hydrocyanic acid on the rate of formation and the percent yield of acrylonitrile, operating under the following conditions:

Acetylene flow rate, 50 liters per hour (measured at 25° C. and 760 mm.)

Initial catalyst composition, 272.5 g. CuCl, 147 g. NH_4Cl , 300 g. H_2O , 3.5 g. conc. HCl.

Catalyst volume, 500 cc. (at reaction temperature)

Temperature of catalyst solution, $86^\circ \pm 0.5^\circ$ C.

Stirring rate of catalyst solution, 960 R. P. M.

Total pressure in apparatus, approximately one atmosphere.

Table 1

Pressure of HCN input mm. Hg	Pressure of HCN over catalyst solution mm. Hg	HCN consumed mol/hr.	HCN consumed, per cent	Acrylonitrile produced, mol/hr.	Per cent yield of acrylonitrile on basis of HCN consumed
60.0	2.3	0.160	92	0.150	93.8
58.7	3.1	0.152	90	0.145	95.5
59.4	3.8	0.150	88	0.140	93.3
59.6	4.0	0.149	87	0.142	95.3
78.4	15.7	0.141	61	0.107	76.0
105.3	21.1	0.199	62	0.120	60.5
151.0	52.7	0.150	29	0.075	50.0
152.0	50.5	0.174	34	0.078	43.0
153.0	57.1	0.127	24	0.076	59.0
154.0	57.8	0.123	24	0.071	57.0
265.0	102.8	0.297	27	0.040	14.0

Thus it will be seen that high yields of acrylonitrile are obtained when the partial pressure of the hydrocyanic acid over the catalyst solution is minute, for example, in the range of 2.3 to 15.7 mm. Even though the partial pressure of the hydrocyanic acid is maintained at 102.8 mm., a yield of 14% acrylonitrile is obtained which is higher than that heretofore attained by known methods.

The partial pressures of hydrocyanic acid over the catalyst solution, as listed in column 2 of the above table, are values calculated by means of the following formula:

$$^pHCN = (P - ^pH_2O) \frac{^mHCN}{M}$$

wherein P is the atmospheric pressure, ^mHCN is the mols of HCN recovered per hour, and M is the sum of the mols of all the components recovered per hour. In order to obtain these results, it will be readily seen that it was necessary in each operation to determine the amount of each component recovered per hour from the effluent gases.

It is evident from the data of Table 1 that the partial pressures of hydrocyanic acid in the outgoing gases increase as those of the ingoing hydrocyanic acid are increased. It is believed that the pressure of the hydrocyanic acid over the catalyst solution is substantially in equilibrium with the hydrocyanic acid dissolved in the catalyst, and that these values offer a true basis for the evaluation of the effect of hydrocyanic acid pressure on the reaction. Furthermore, they show clearly that the rate of production of acrylonitrile and the yield on the basis of the hydrocyanic acid consumed decrease as the partial pressure of the hydrocyanic acid over the catalyst solution increases. Thus, for example, at 2.3 mm. HCN, the rate was 0.15 mol per hour and the yield 93.8%, whereas at 102.8 mm. HCN, the rate and yield dropped to 0.04 and 14%, respectively.

The curves of Figures 2 and 3 of the accompanying drawings further illustrate the influence of hydrocyanic acid pressure upon the reaction. The curve of Figure 2 shows clearly how very low the outgoing pressure of HCN is to be maintained in order to obtain the maximum reaction rate. Obviously, this curve will turn toward the origin, for instance in the region below 1 mm. pressure, for at zero partial pressure of HCN over the catalyst solution the rate of reaction is limited by the rate of supply of HCN. On the other hand, the curve of Figure 3, which shows the remarkable increase in yield of acrylonitrile with decrease in pressure of HCN over the catalyst solution, may be extrapolated to zero pressure of HCN where it indicates a 100% yield.

Theoretically, this implies that if HCN was introduced into the catalyst solution in infinitesimal amounts so that no HCN pressure was established in the effluent gases, all of the HCN would react to produce only acrylonitrile. However, if hydrocyanic acid is completely absent from the catalytic chamber during the operation the main reaction which takes place is the formation of acetylene polymers. The presence of even small concentrations of hydrocyanic acid inhibits the reaction of acetylene polymerization.

Furthermore, it has been found that the catalyst maintains its activity over extended periods when operating at low pressure of HCN over the catalyst solution. The data of Table 2 illustrate

the effect of elapsed time on the rate of acrylonitrile formation, operating under the same conditions as given for Table 1.

Table 2

Elapsed time, hr.	Acrylonitrile produced, g./hr.
pHCN = 2 to 4 mm.	
7.34.....	7.61
20.52.....	7.96
24.62.....	7.69
26.62.....	7.55
pHCN = 50 to 52 mm.	
2.22.....	5.23
4.92.....	4.01
13.85.....	3.74
24.70.....	1.92

The acrylonitrile appears to be stable in the reaction chamber which is confirmed by the fact that when added to the catalyst solution and heated under reflux for several hours, it remains unchanged. However, during continuous operation it is advisable not to allow the acrylonitrile to build up in the catalytic chamber to a concentration substantially greater than 2% by weight of the catalyst solution, otherwise its rate of formation decreases rapidly.

It is further believed that an increase of total pressure would permit the use of higher equilibrium partial pressures of hydrocyanic acid and cause a more rapid reaction rate since the solubility of the hydrocyanic acid and acetylene in the catalyst solution depends on their pressures.

However, due to the explosive nature of acetylene at higher pressures, two atmospheres is considered to be the upper practicable limit.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims.

I claim:

1. The method of producing acrylonitrile which includes the steps of continuously reacting together hydrocyanic acid and acetylene in a heated solution of an acid reacting cuprous salt as a catalyst, in the presence of a solubilizer for the catalyst while maintaining the partial pressure of the acetylene greater than that of the hydrocyanic acid over the catalyst solution.
2. Method of claim 1 wherein the catalyst is heated at a temperature within the range of 60 to 110° C.
3. Method of claim 1, further characterized in that the catalyst comprises an acid reacting aqueous cuprous chloride solution.
4. Method of claim 1, in which the solubilizer includes ammonium chloride.
5. Method of claim 1, further characterized in that the reaction is carried out under a pressure not greater than substantially two atmospheres.
6. Method of claim 1, further characterized in that the partial pressure of the hydrocyanic acid over the catalyst solution is maintained within the range of 2.3 to 15.7 mm.
7. The method of claim 1, in which the solubilizer is chosen from a compound of the class consisting of ammonium, amine and alkali metal salts.

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