

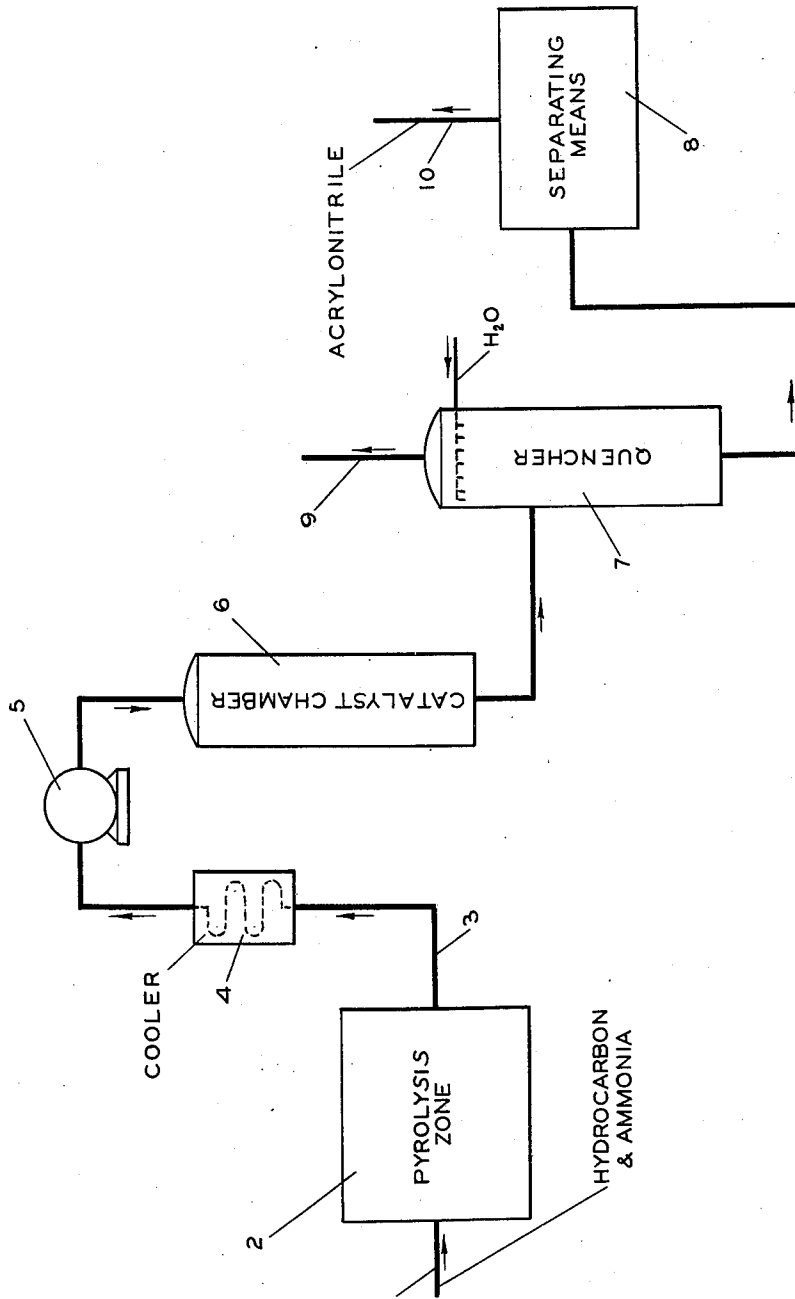
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2,370,849

PRODUCTION OF ACRYLONITRILE

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PRODUCTION OF ACRYLONITRILE

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4 Claims. (Cl. 260-464)

This invention relates to the production of acrylonitrile from gaseous petroleum hydrocarbons and ammonia. More specifically, it relates to the pyrolysis of hydrocarbons such as methane or ethane in the presence of ammonia, and to the catalytic treatment of the pyrolysis effluents to form acrylonitrile.

Acrylonitrile (vinyl cyanide), $\text{CH}_2=\text{CH}-\text{CN}$, is an important ingredient in the manufacture of certain types of synthetic rubber, and it has other valuable chemical uses as well. None of the methods hitherto proposed for its manufacture are entirely suitable for large scale commercial production, as they require materials which are relatively expensive and in some instances difficult and dangerous to handle.

It is an object of my invention to provide a continuous process for the manufacture of acrylonitrile from petroleum hydrocarbons and ammonia.

Another object of my invention is to provide a process in which acrylonitrile is formed by catalytic treatment of the effluents from a hydrocarbon pyrolysis carried out in the presence of ammonia.

A further object is to provide a process in which the production of hydrogen cyanide and acetylene by pyrolysis of petroleum hydrocarbons with ammonia is combined in a novel and advantageous manner with the catalytic reaction of hydrogen cyanide and acetylene to form acrylonitrile.

Still another object is to prevent polymerization of hydrogen cyanide and acetylene during the catalytic process.

Another object is to provide a process in which the heat requirements of the catalytic step are supplied by the heat contained in the pyrolysis effluents.

I have now found that acrylonitrile may be produced in a highly improved manner by pyrolyzing a mixture of hydrocarbon and ammonia to form an effluent containing hydrogen cyanide and acetylene, and subjecting the effluent directly to catalytic treatment at a lower temperature, thereby causing the hydrogen cyanide and acetylene to combine to form acrylonitrile.

More specifically, in accordance with the invention, acrylonitrile is formed from low molecular weight hydrocarbons, e. g. methane or natural gas, and ammonia, by a two-stage process in which the hydrocarbons and ammonia are subjected to pyrolysis at temperatures of from 1000 to 1500° C. and sub-atmospheric pressure, followed by a catalytic treatment of the effluents at a temperature of 400 to 500° C. and atmospheric or higher pressure.

The hydrocarbon used in the feed to the pyrolysis step may be any hydrocarbon which yields acetylene upon pyrolysis. The hydrocarbon is usually a lower aliphatic hydrocarbon up to and

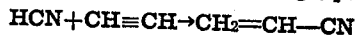
including C_4 hydrocarbons, namely methane, ethane, propane, normal butane, isobutane, ethylene, propylene, butene-1, butene-2 and isobutylene. Methane and natural gas are preferred because of their availability and cheapness.

The pyrolysis may be carried out in any convenient manner, the preferred conditions of operation being the following: The hydrocarbon feed should contain predominantly methane and/or ethane; the proportion of ammonia added may be varied over rather wide limits but the volume ratio of hydrocarbon to ammonia in the feed is usually between 10:1 and 5:1; the reactant gases should be substantially free of oxygen; the temperature should be at least 1000° C. and is preferably in the range 1300 to 1500° C. or even higher; the pressure is maintained at sub-atmospheric and preferably below 200 mm. of mercury; the contact time should be less than 0.10 second and is preferably 0.05 second or even less; the effluents are quickly cooled to a temperature in the range 400-500° C.

The heating may be done in non-porous refractory tubes contained in an electric furnace or oven, or the tubes may be heated by hot gases.

The catalytic treatment of the effluents from the pyrolysis step is carried out at the temperature to which the gases are cooled immediately after leaving the furnace, i. e. 400-500° C. Thus, a major portion of the heat required in the catalyst chamber is supplied by the gases themselves and preheating of the feed to the catalyst chamber is not required. In effect, a double use is made of a portion of the heat energy supplied for the pyrolysis reaction.

The feature of leading the pyrolysis effluents directly into the catalyst chamber (after cooling to the proper temperature) results in another important advantage. The reaction to be carried out in this second step of the process is, of course, the direct combination of hydrogen cyanide with acetylene according to the following equation:



It would be expected, on the basis of chemical theory, that a maximum yield of acrylonitrile would be obtained from a reactant mixture containing only hydrogen cyanide and acetylene, and that any inert diluent gases present (such as the hydrogen, methane, and nitrogen resulting from my pyrolysis reaction) would seriously lower the yield of acrylonitrile obtained. I have found, however, that such is not the case. Presumably because of the very pronounced tendency of hydrogen cyanide, acetylene, and acrylonitrile to polymerize, the yield of acrylonitrile obtained from mixtures containing nothing but hydrogen cyanide and acetylene is only about 10% of the theoretical. In my process, on the other hand, the inert diluents present serve to retard polymerization to such an extent that the ultimate

yield of acrylonitrile is much improved. In other words, the increase in yield by the prevention of the several types of polymerization reactions more than compensates for any slight decrease in yield due to the diluent effect upon the single desired reaction.

Still another advantage of my process results from the fact that the effluents from the pyrolysis step are used as the feed to the catalyst chamber. In prior art processes for making acrylonitrile from hydrogen cyanide and acetylene these materials are supplied separately to the reaction zone, thus necessitating storage and handling of poisonous hydrogen cyanide and explosive acetylene. In my process all dangers attendant to the handling of these materials are eliminated by using them in the second step of the process as fast as they are formed in the first.

The catalytic combination of hydrogen cyanide and acetylene may be carried out in any conventional catalyst chamber in which gaseous reactants may be contacted with solid catalysts at temperatures within the specified range, i. e. 400-500° C. Preferred catalysts are the cyanides of the alkali and alkaline earth metals, particularly sodium cyanide. They may be supported on porous materials such as silica gel, alumina, bauxite, and the like. The contact time may vary over rather wide limits, depending upon the composition of the pyrolysis effluent stream and upon the catalyst temperature, but is generally in the range 0.5 to 2 seconds. Unchanged hydrogen cyanide and/or acetylene may, of course, be recovered from the final products by known methods and recycled to the catalyst chamber. Any tendency of either reactant to "build up" in this part of the process may be compensated for by varying the proportion of ammonia introduced into the pyrolysis reaction. Reducing the proportion of ammonia, for example, results in an excess of acetylene over hydrogen cyanide in the pyrolysis effluents, while an increase in the proportion of ammonia in the feed effects the reverse result. The relative proportions of hydrocarbon and ammonia in the feed to the pyrolysis step may be such that the pyrolysis effluent contains approximately equimolar amounts of hydrogen cyanide and acetylene.

The products leaving the catalyst chamber contain, besides acrylonitrile, hydrogen, methane, nitrogen, and perhaps unchanged hydrogen cyanide or acetylene. This effluent is cooled down to a suitable temperature below the boiling point of acrylonitrile, for example to room temperature. It is preferred to cool these gases by a direct water quench as they leave the catalyst zone. Separation and recovery of the acrylonitrile and other components is then readily accomplished in conventional manner.

In the drawing a preferred embodiment of my process is illustrated in diagrammatic form. A preheated gaseous mixture of hydrocarbon and ammonia is introduced through line 1 into pyrolysis unit 2. This may consist of a plurality of non-porous refractory tubes of small diameter (e. g. 10 mm.) heated to a temperature of 1500° C. by means of hot gases. The effluents pass through line 3 to cooler 4 where the temperature is reduced to about 450° C., and thence to compressor 5. By means of this compressor the pressure in pyrolysis chamber 2 is maintained below 200 mm. of mercury while that in the catalyst chamber 6 is slightly above atmospheric. Suitable valves (not shown) are of course employed in conjunction with this control of pressure. The compressed

cooled effluents pass from compressor 5 into catalyst chamber 6.

The effluents from catalyst chamber 6 are quenched with water in quencher 7, from which they are passed to separating means 8. Here acrylonitrile is recovered in conventional manner for example by fractional distillation, the acrylonitrile being removed via line 10. Light gases such as hydrogen and nitrogen are removed from the top of quencher 7 through line 9.

Example

Ammonia and natural gas in the ratio 1:9 by volume were subjected to pyrolysis at 1500° C. and 100 mm. of mercury pressure. The rate of flow was adjusted so as to give a contact time of 0.05 second. The effluents were quickly cooled to 450° C. and passed over solid sodium cyanide at a pressure slightly above atmospheric and with a contact time of 1.5 seconds. The products were quenched with water and the acrylonitrile recovered by fractional distillation.

I claim:

1. The process for the production of acrylonitrile which comprises admixing a low-boiling paraffin hydrocarbon having one to two carbon atoms per molecule with ammonia in a gas volume ratio within the range of five to ten volumes of said hydrocarbon per volume of ammonia, subjecting said mixture to pyrolysis under conditions effecting the formation of hydrogen cyanide and acetylene, and passing the total effluent of said pyrolysis into contact with the cyanide of an alkali metal as catalyst under conditions effecting the conversion of hydrogen cyanide and acetylene to acrylonitrile.

2. The process for the production of acrylonitrile which comprises admixing a low-boiling hydrocarbon having one to two carbon atoms per molecule with ammonia in a gas volume ratio within the range of five to ten volumes of said hydrocarbon per volume of ammonia, subjecting said mixture to pyrolysis at a temperature within the range of 1000 to 1500° C. under conditions effecting formation of hydrogen cyanide and acetylene, cooling the total effluent of said pyrolysis to a temperature within the range of 400 to 500° C., and passing the total effluent at said temperature into contact with the cyanide of an alkali metal as catalyst under conditions effecting the conversion of hydrogen cyanide and acetylene in said effluent to acrylonitrile.

3. The process of claim 2 in which the paraffin hydrocarbon comprises chiefly methane and the catalyst is sodium cyanide.

4. The process for the production of acrylonitrile which comprises admixing methane with ammonia in a gas volume ratio within the range of five to ten volumes of methane per volume of ammonia, subjecting said mixture to pyrolysis at a temperature within the range of 1300 to 1500° C. and at a pressure within the range of 100 to 200 mm. of mercury for a period of time within the range of 0.05 to 0.10 seconds effecting formation of hydrogen cyanide and acetylene, cooling the total effluent of said pyrolysis to a temperature within the range of 400 to 500° C., and passing the total effluent at said temperature directly into contact with a sodium cyanide catalyst at substantially atmospheric pressure for a period of time within the range of 0.5 to 2 seconds effecting conversion of hydrogen cyanide and acetylene in said effluent to acrylonitrile.

HARRIS A. DUTCHER.

CERTIFICATE OF-CORRECTION.

Patent No. 2,370,849.

March 6, 1945.

HARRIS A. DUTCHER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 38, claim 2, after "low-boiling" insert "--paraffin--"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of June, A. D. 1945.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.