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MANUFACTURE OF HYDROCYANIC ACID

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This invention relates to the production of hydrocyanic acid from mixtures of saturated aliphatic hydrocarbons, oxides of nitrogen and nitrogen, and more particularly is concerned with the preparation of hydrocyanic acid from mixtures of paraffine hydrocarbons, such as natural gas, in the presence of oxides of nitrogen and nitrogen at an elevated temperature, preferably at about 1200° C. and higher.

I have discovered that relatively high yields of hydrocyanic acid can be obtained from aliphatic hydrocarbons of the formula C_nH_{2n+2}, individually or in admixture with each other or diluted with other compounds, in the vapor phase without substantial deposition of carbon, by conducting the thermal treatment of the paraffine hydrocarbons or their mixtures in the presence of an oxide of nitrogen, the nitrogen being present in relatively substantial amounts.

The process is preferably carried out in the absence of hydrogen and/or substantial amounts of water vapor since both substances unfavorably influence the reaction, thereby decreasing the possible yield of hydrocyanic acid. It is therefore desirable to avoid the extraneous introduction of these substances into the reacting mixture.

The output of hydrocyanic acid increases with an increase in the percentage of nitrogen in a mixture of nitrogen, oxides of nitrogen and saturated aliphatic hydrocarbon. A desirable ratio is one wherein N:NO is greater than about 3.5:1, preferably about 4:1 to 8:1 or higher. On the other hand, excellent results are obtained using a mixture wherein the ratio of hydrocarbon to nitric oxide is substantially 3.5:1 or greater. Operating with methane or natural gas, the following approximate proportions have been found excellent: CH_4 (or natural gas) 4: nitric oxide 1: nitrogen 8.

In lieu of natural gas, there may be utilized industrial gases containing paraffine hydrocarbons, such as coal gas, coke oven gas, gas from oil cracking plants, gas from destructive hydrogenation plants and the like. Free hydrogen may be removed from any of these mixtures prior to the thermolytic treatment, the removal or extraction step being carried out by any conventional method such as diffusion, absorption, etc.

The process can be carried out in the absence or presence of a catalytic agent amongst which may be described, active carbon, carborundum, sillimanite, Al_2O_3, silica, charcoal, quartz. If carried out in a heated tube, the reaction chamber therein may be unobstructed or may be packed with or may contain one or more of the catalytic substances. For the sake of steady operation, packing is preferably employed.

The yield of hydrocyanic acid increases rapidly with a rise in temperature of operation and after a practical optimum temperature increases but slowly. For example, working with a mixture containing natural gas or methane at about atmospheric pressure, the yield of hydrocyanic acid rapidly increases up to 1200° C. and then slowly increases up to about 1400° C. where the declining rate of increase no longer becomes of practical interest due to heat consumption and other uneconomical factors. With ethane, propane, isobutane, butane and the higher homologues of methane and their mixtures, higher yields are obtained at temperatures lower than 1200° C. than with natural gas.

Working with similar mixtures of CH_4, NO, and N_2 under identical conditions, other than temperatures, the following conversions of NO to HCN were noted:

	Degree C.
45% conversion at	1100
83% conversion at	1200
84.6% conversion at	1400

The time of residence of the reaction mixture in the reaction space has a great influence on the yield of hydrocyanic acid, which, for a given mixture of reactants, temperature, and catalyst, passes through a maximum as the time of residence in the reaction space is increased. I have found a period of from 1 to 2 seconds entirely satisfactory, although it is understood that at relatively high temperatures, shorter periods may be resorted to while at lower temperatures or at higher temperatures with large amounts of inert diluents, longer periods may be resorted to. Shorter periods may also be experienced with certain of the catalysts as will be apparent hereinafter.

An excess of the hydrocarbon increases the yield of hydrocyanic acid, but the advantage above 4—5 fold is small. The presence of free oxygen, in at least small amounts, does not appear to decrease the yield of hydrocyanic acid appreciably.

In lieu of nitric oxide, there may be employed nitrogen peroxide, nitrous anhydride, nitrogen tetroxide, nitrogen pentoxide and nitrous oxide. All these compounds yield nitric oxide upon heating, which is very stable and yet readily active.

The following examples are cited for illustra-

tive purposes only, and to disclose the influence or effect of the variable factors as temperature, time of heating, rate of cooling, excess hydrocarbon, diluent, etc.

EXAMPLE I

Catalyst: silica

Temperature °C.	Natural gas: NO:N_2	Time of contact, sec.	Yield on NO, percent
1200	2:1:2	1.66	50.0
1200	4:1:4	1.32	70.0
1200	8:1:8	1.7	73.0
1200	4:1:8	1.6	78.0
1400	4:1:8	0.58	84.6

EXAMPLE II

Natural gas: NO:N_2=4:1:4

Temperature, 1200° C.

Catalyst: silica

Time of heating, sec.	Yield on NO, percent
0.83	61.3
1.32	69.4
1.7	71.0
2.6	64.1
5.2	50.6

EXAMPLE III

Temperature 1200° C.

Natural gas: NO:N_2=4:1:4

Time of heating 1.66 to 1.67 sec.

Catalyst: silica

Yield on NO, percent	Reaction tube diameter	Exit tube diameter
	Inches	
57.7	¾	⅜ in.
75.0	1	6 mm.
80.0	1½	6 mm.

As shown by Example III, the yield is increased by rapid cooling of the reaction products after they have left the reaction space.

EXAMPLE IV

Temperature 1200° C.

Time of heating 1.7–2.0 seconds

Catalyst: silica

Natural gas:NO:N_2	Yield on NO, percent
Diameter of the reaction Tube 0.5 in.:	
2:1:2	50.0
4:1:4	71.0
8:1:8	73.0
Diameter of the reaction Tube 1.5 in.:	
2:1:8	71.8
4:1:8	83.5
4:1:4	83.0

The mixture of nitrogen and nitric oxide can be obtained by the oxidation of ammonia, the hydrocarbon or hydrocarbons being added to the oxidation mixture, from which water, preferably, has been removed. Sufficient natural gas or paraffine hydrocarbon should be added to make the ratio of C_nH_{2n+2} to nitric oxide, at least about 3.5 or 4 to 1. The ratio of NO to N in the oxidation mixture should be about 1:7.5 to 1:8.

The following table shows the influence of various catalysts on the time of heating:

Sillimanite and carborundum

Temperature 1200° C.

Gas: NO:N_2=4–1–8

Diameter of tube, 1.0 in.

Sillimanite		Carborundum		Silica		No catalyst	
Time of heating, sec.	Yield on NO, percent	Time of heating, sec.	Yield on NO, percent	Time of heating, sec.	Yield on NO, percent	Time of heating, sec.	Yield on NO, percent
0.25	73.3	0.29	56.5	0.73	73.7		
0.26	74.0	0.29	59.5	0.98	76.8		
0.64	81.0	0.42	66.0	1.25	77.7		
0.66	82.0	0.67	72.5	1.33	78.8		
0.80	82.0	0.75	73.0	1.40	79.0		
1.10	80.0	0.86	72.6	1.62	78.0		
1.50	74.0	1.03	66.8	2.12	71.7		
1.51	72.2	1.22	63.6	2.25	67.2		
1.75	70.8	1.47	61.4				
1.77	71.2	1.54	60.5				
2.15	69.5	2.40	57.5			2.2	83.7
		2.45	58.3			2.4	83.2

It will be noted that catalysis materially reduces the time of contact.

The concentration of hydrocyanic acid in the exit gas varies up to above 6% and the HCN may be recovered by any of the conventional modes. It may be recovered as an alkali cyanide and regenerated by means of a mineral acid or may be recovered per se by means of a scrubbing agent or solvent which is subsequently subjected to distillation or the like.

It is extremely desirable that iron or ferrous alloys be absent or out of contact with the materials undergoing reaction as iron is catalytically favorable to the deposition of carbon.

While I have in the foregoing described in some detail the preferred embodiment of my invention and some variants thereof, it will be understood that this is only for the purpose of making the invention more clear and that the invention is not to be regarded as limited to the details of

operation described, nor is it dependent upon the soundness or accuracy of the theories which I have advanced as to the reasons for the advantageous results attained. On the other hand, the invention is to be regarded as limited only by the terms of the accompanying claims, in which it is my intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

I claim as my invention:

1. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to a temperature not less than about 1200° C. in the presence of a substantial amount of nitrogen and an oxide of nitrogen in the substantial absence of water.

2. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to an elevated temperature in the presence of a substantial amount of nitrogen and nitric oxide for a period not substantially greater than two seconds in the substantial absence of water.

3. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to an elevated temperature in the presence of nitrogen and preformed nitric oxide wherein the ratio of hydrocarbon to nitric oxide is greater than 3.5:1 in the substantial absence of water.

4. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to an elevated temperature in the presence of nitrogen and preformed nitric oxide, in the proportion not less than 3.5:1, respectively in the substantial absence of water.

5. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to an elevated temperature in the presence of nitrogen and preformed nitric oxide, the ratio of hydrocarbon to nitric oxide being at least 3.5:1 and the ratio of nitrogen to nitric oxide being at least 3.5:1 in the substantial absence of water.

6. A process of producing hydrocyanic acid which comprises heating methane to at least 1200° C. in the presence of nitrogen and preformed nitric oxide in the substantial absence of water.

7. A process of producing hydrocyanic acid which comprises heating methane to at least 1200° C. in the presence of nitrogen and preformed nitric oxide, the methane being in excess of that amount capable of conversion under the conditions of operation in the substantial absence of water.

8. A process of producing hydrocyanic acid which comprises heating methane to at least about 1200° C. in the presence of nitrogen and preformed nitric oxide, the proportions of CH_4: NO:N being at least 4:1:4 in the substantial absence of water.

9. A process of producing hydrocyanic acid which comprises heating natural gas to at least about 1200° C. in the presence of nitrogen and preformed nitric oxide, the proportions of natural gas: NO:N being about 4:1:8 in the substantial absence of water.

10. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to at least about 1200° C. in the presence of nitrogen, preformed nitric oxide and a hydrocyanic acid forming catalyst in the substantial absence of water.

11. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to at least about 1200° C. in the presence of nitrogen, preformed nitric oxide and sillimanite in the substantial absence of water.

12. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to at least about 1200° C. in the presence of nitrogen, preformed nitric oxide and carborundum in the substantial absence of water.

13. A process of producing hydrocyanic acid which comprises heating a saturated aliphatic hydrocarbon to at least about 1200° C. in the presence of nitrogen, preformed nitric oxide and silicia in the substantial absence of water.

14. A process of producing hydrocyanic acid which comprises oxidizing ammonia with an amount of oxygen-containing gas so as to obtain a mixture of nitrogen and an oxide of nitrogen, substantially removing the water content thereof, subsequently adding thereto a saturated aliphatic hydrocarbon and heating the mixture to an elevated temperature until substantial conversion of hydrocarbon to hydrocyanic acid is attained.

15. A process of producing hydrocyanic acid which comprises oxidizing ammonia with an amount of oxygen-containing gas so as to obtain a mixture of nitrogen and an oxide of nitrogen, substantially removing the water content thereof, subsequently adding thereto natural gas and heating the mixture to an elevated temperature until substantial conversion of hydrocarbon to hydrocyanic acid is attained.

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