Effect of Temperature on the Upper Flammable Limit of Methane, Ammonia, and Air Mixtures

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THE ANDRUSSOW process for hydrogen cyanide manufacture involves the reaction of a mixture of ammonia, methane, and air over a platinum catalyst at 1000° to 1100° C. If the composition of the feed gases is within the flammable region, a flash back will occur from the hot catalyst bed. Because the feed gases entering hydrogen cyanide reactors are heated by radiation from the hot catalyst bed and the flammable limits of the gases are broadened by increasing temperature, a research program was carried out to determine the upper (or fuel-rich) flammable limit of hydrogen cyanide synthesis gas as a function of temperature.

EXPERIMENTAL

Apparatus. TEST CHAMBER AND PREHEATER. The tests were carried out in a stainless steel pipe 2 inches in diameter and 4-1/2 feet long, which was mounted in a vertical position. The preheater consisted of a stainless steel pipe 1 inch in diameter, 41 inches long packed with 1/4-inch Berl saddles. The preheater was fastened by means of a flange directly below the test chamber. Both the preheater and test chamber were heated electrically by Nichrome resistance wire wound around the pipe and insulated from the pipe with asbestos paper. The whole apparatus was covered with a 2-inch thickness of asbestos insulation. The gases being tested entered at the bottom of the preheater and left through a pipe coupling near the top of the test chamber. The ignition source was located near the bottom of the test chamber with the flame detector located 2 feet above, so that it measured flame propagated in the same direction as the gas flow. The test chamber was equipped with two iron-constantan thermocouples located 2 inches above the ignition source and detector, respectively. A sample tap and a pressure gage were also located on the test chamber. A 100-p.s.i.g. rupture disk covered the top end of the pipe. The pressure on the test chamber was maintained at 15 p.s.i.g. by a pressure control value which was controlled by a controller (Foxboro M/52 Consotrol). The maximum pressure which could be applied to the pressure-sensing inlet on the controller without damaging the instrument was 20 p.s.i.g. To protect the controller from pressure surges during flame propagations, the pressure-sensing line from the test chamber went to a relay (Moore Products 61F). Twenty pounds of air pressure were supplied through this relay to the pressure-sensing inlet on the controller. This air pressure was the maximum pressure which could be supplied to this instrument, even when the test chamber pressure exceeded the 20 p.s.i.g. On the other hand, when the test chamber pressure was less than 20 p.s.i.g., the pressure was transmitted directly through the relay to the controller.

METERING SYSTEM. The desired gas compositions were obtained by metering the individual gases through predictability flowmeters (Emil Greiner Co., New York). To assure constant flow through the rotameters, product flow controllers (Moore Products Models 63BD and 63SD) installed for a constant downstream pressure, were placed upstream from the rotameters. The temperatures of the individual gases were measured with iron-constantan thermocouples. A pressure gage measured the outlet pressure of the rotameters. The individual gases from the rotameters were mixed in a manifold and then passed into the bottom of the preheater.

IGNITION SOURCE. The gases being tested were ignited by introducing a small flame into the test chamber. This flame consisted of an oxygen-hydrogen explosion which was produced by passing a mixture of oxygen and hydrogen through a spark.

The ignition system consisted of a rectangular stainless steel block with a 1/4-inch bore drilled through its length. One end of the bore opened directly into the test chamber. A spark plug extended through the block and into the bore near this end. At the other end of the block, two solenoid valves (Skinner X5M2500) opened into the bore. Each solenoid valve was connected through a pipe nipple to another solenoid valve, which in turn was connected to an oxygen or hydrogen cylinder. The high voltage for the spark plug was supplied by a Model T spark coil connected to a 6-volt battery. When the coil was activated, the spark fired continuously. A relay switch was placed in the circuit of the two solenoid valves adjacent to the ignition block and the battery–spark coil circuit so that closing this switch simultaneously opened the valves and fired the spark.

To operate the ignition source, the pipe nipples between the solenoid valves were pressured with their respective gases and all the solenoid valves were closed. The relay switch was then closed, which allowed the oxygen and hydrogen to flow into the bore while the spark was firing. The resulting explosion forced the flame out of the open end of the bore into the test chamber.

The ratio of oxygen to hydrogen in the bore was determined by the flow rates of the gases through the valve orifices, which in turn was determined by the density of the gas and the upstream pressure. This pressure was adjusted so that the relative flow rates were stoichiometric (2 hydrogen to 1 oxygen). The oxygen pressure was 75 p.s.i.a. and the hydrogen pressure was 45 p.s.i.a. Only the amount of gas contained in the pipe nipples between the valves was released into the bore. The pipe nipple volume was adjusted so that the total amount of each gas released was stoichiometric. The oxygen nipple was 1-1/2 inches long and 1/4 inch in internal diameter and the hydrogen nipple was 6 inches long and 1/4 inch in internal diameter.

FLAME DETECTOR. The propagation of a flame was detected by observing a rise in the gas temperature with a Chromel-Alumel thermocouple. The temperature rise was detected by the deflection of the galvanometer in a portable potentiometer (Leeds & Northrup). A temperature rise of about 30° C. was considered a flame propagation. The ignition source alone or a flame which traveled part way up the flame chamber was not sufficient to cause so great a temperature rise. The thermocouple extended into the flame chamber so that the bare junction was in contact with the gases.

Procedure. A point on the flammable limit was determined by testing a series of gas compositions in the vicinity of the flammable limit. To set up a series, it was first necessary to estimate the position of the flammable limits by several trial and error firings. The gas flows were then set so that the gas composition was at the estimated flammable limit. All the flow rates except one were held at these settings.

The one flow rate, either methane or ammonia, was then varied to give gas compositions both above and below the flammable limit. Five test firings were made for each methane or ammonia setting. The order of these test firings was made at random over the entire series. Total gas flow rates varied over a range from about 2.8 to 3.7 standard cubic feet per minute (measured at 70° F. 14.7 p.s.i.a.), the rate at any given test point being restricted by the capacity of the rotameters. For a given composition of gas, the flammable limits were found to be the same when the flow was varied from 1.9 to 3.4 standard cubic feet per minute (s.c.f.m.). All data were taken at a pressure of 15 p.s.i.g.

The percentage of flame propagation in the five firings for each composition was plotted against the percentage of methane or ammonia in the gas mixture. A straight line was then drawn through the approximate slope of these points. The point where the straight line intersected with 0% propagations was taken as the flammable limit (Figure 1). This procedure was then repeated with other series until several points along the flammable limit were defined. These points were plotted on ternary graphs and the curved line drawn through them was the upper flammable limit.

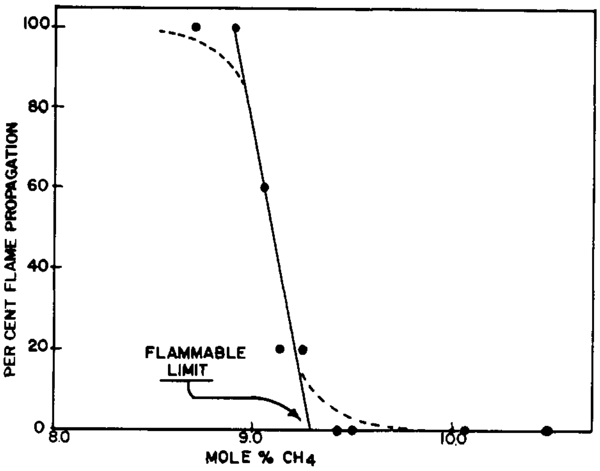

Figure 1. Flammable limit determination

Results. The upper flammable limits of ammonia, methane, and air at 25°, 100°, 200°, and 300° C. are shown in Figure 2. The composition of the gas at the flammable limit varied as a linear function of the gas temperature. This is illustrated in Figure 3 for the ammonia-air and methane-air binaries.

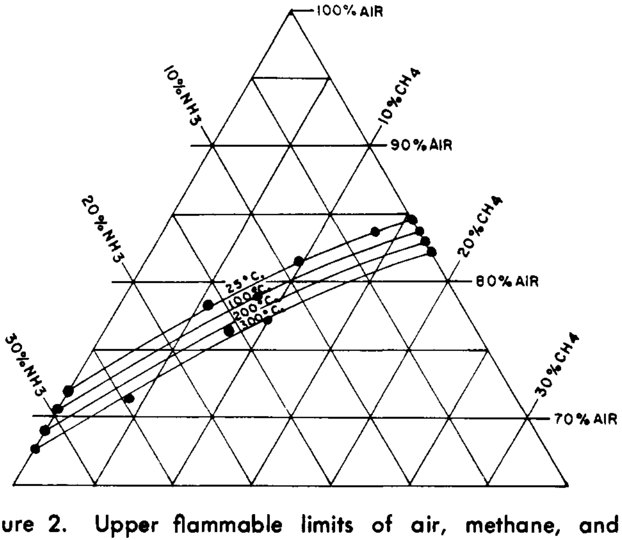

Figure 2. Upper flammable limits of air, methane, and ammonia mixtures as volume per cent at various temperatures

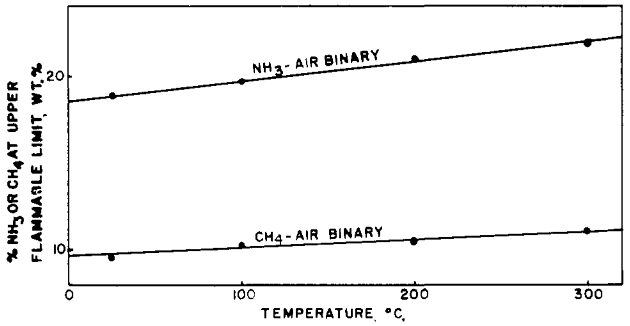

Figure 3. Linear relationship between temperature and upper flammable limit of ammonia-air and methane-air binaries

DISCUSSION

A flammable mixture of gases is any mixture which is capable of propagating a flame. Any flammable mixture can be diluted with one of its components until it is no longer flammable. In other words, the zone of gas compositions which will propagate a flame has a definite upper and lower limit above and below which no flame propagation can occur. The lower limit contains the minimum amount of fuel and the upper level the maximum amount of fuel which is flammable. The upper limit, rich in fuel, is the subject of this study.

There are many variables which influence the flammable limits of combustible gases. This has been the cause of considerable contradiction among the data reported in the literature. In interpreting the results of any flammability study it is necessary to consider all of these variables and to know what effect each has on the limits of flammability.

The direction of flame propagation, whether upward, downward, or horizontal, will affect the flammable limits. Upward propagation gives the broadest limits, because of convection currents and favorable buoyancy conditions introduced by the hot flame front. The fact that no dependence of flammable limits on flow rate was observed in this study indicates that the flow rate was sufficiently high to make convection and buoyancy effects negligible. A flame front moving in the same direction as the gas flow is favored over one moving against the gas flow. This study was carried out under the most favorable conditions for flame propagation—namely, upward and with the gas flow.

The ignition source must contain enough energy to assure ignition of the gas and at the same time not affect the propagation of the flame through the gas. Weak sources may fail to ignite borderline mixtures which if ignited would propagate a flame, while strong sources may cause flame "caps" in nonflammable mixtures which give the false appearance of flame propagations. The important factor in the ignition source is the total amount of energy available and not the temperature of the source. For this reason a flame which covers a large area may be more satisfactory than a spark.

A spark was initially used as the ignition source, but was too weak. The results were not reproducible in the ternary mixtures and the spark would not ignite the ammonia-air binaries at all. The introduction of a continuously firing spark was an improvement, but the reproducibility was still poor. An exploding wire was next used as the ignition source and gave good results. Unfortunately, it required entering the test chamber after each firing to replace the wire. This was too time-consuming. The oxygen-hydrogen flame had sufficient energy to give reliable ignitions and could be fired repeatedly without entering the test chamber.

The only drawback to the use of a thermocouple for flame detection was that it required an arbitrary definition of the temperature rise produced by a flame. It was necessary to know whether the flame actually came in contact with the thermocouple. In most cases this was obvious. However, in a few cases intermediate temperature rises resulted from flames which traveled part way up the pipe and were then quenched. In these cases it was necessary to define arbitrarily the amount of temperature rise caused by a flame propagation. The effect of this arbitrariness on the flammable limits was small.

The distance of 2 feet between the igniter and the detector was also arbitrary. This distance had to be great enough so that the detector was not influenced by the ignition source. Two feet appeared to be sufficient. As a flame travels through a tube, a certain amount of heat is transferred from the flame front to the vessel walls. In small tubes this heat loss narrows the flammable limits. As a general rule the effect is negligible if the vessel diameter is 5 cm. or greater (*1*), a condition satisfied by the present 2-inch internal diameter chamber.

A limited number of runs indicated that increasing the pressure in the flame chamber from atmospheric to 15 p.s.i.g. caused a change in the flammable limit of about 1% in the air-rich direction. Because Andrussow hydrogen cyanide reactors normally operate under a pressure of about 1 atm. gage, all determinations were carried out at 15 p.s.i.g. in order to eliminate pressure effect as a variable.

Mixtures of flammable gases in the vicinity of their flammable limits have a certain statistical probability of propagating a flame. The curve of per cent flame propagation *vs.* composition roughly represented these statistical probabilities. This curve is an S-shaped curve which asymptotically approaches 100 and 0% flame propagation. Because the curve never reaches the line of 0% propagation, it is necessary to define arbitrarily the point at which the mixture is no longer considered flammable. This was done in these tests by extending the slope of the inflection of the S curve until it intersected the line of 0% flame propagation (Figure 1). In most cases the intersection was at a composition which has less than a 5% probability of propagating a flame.

As a check on the rotameter calibrations, several gas mixtures were sampled and chemically analyzed for per cent ammonia. In every case the analyzed composition fell within ±0.5% (absolute) of the calculated composition.

Extrapolation of the data to the Andrussow catalyst temperature of 1000° to 1100° C. is probably not justified. It has been found unnecessary to do so, however, because results from a test reactor indicate that gas mixtures lying on the 500° C. flammability line (by extrapolation) will not flash back from the Andrussow catalyst at flow rates as low as 0.5 linear foot per second.

ACKNOWLEDGMENT

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Hydrogen Cyanide Stability and Heat of Polymerization

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SOME TIME ago a steam-traced, heavily insulated 5-gallon container which was being used as a partial vaporizer for hydrogen cyanide exploded in one of the company laboratories. Because this company manufactures hydrogen cyanide and stores it in quantity, it was necessary to find out what caused the explosion, what could be done to prevent similar explosions, and whether hydrogen cyanide was likely to decompose with explosive violence under ordinary conditions of storage and use.

A literature survey revealed only three reports of studies of the stability of hydrogen cyanide under various conditions. Walker and Eldred (*3*) investigated the stability of hydrogen cyanide at several pressures and temperatures in steel bombs heated by a gas flame. They also tested ammonia, sodium hydroxide, and sodium cyanide as polymerization initiators and sulfuric acid and copper as inhibitors. Wohler and Roth (*4*) showed that hydrogen cyanide is a powerful explosive that can denonate completely on very strong initiation. Sporzinsky and Salter (2) studied the effects of various oxalates as inhibitors at 100° C.

This investigation covered the effects of temperature, sodium hydroxide, water, hydrogen cyanide polymer, and "weathered" hydrogen cyanide on the length of time that hydrogen cyanide can be held without violent polymerization; and the effect of the relative amount of hydrogen cyanide in a container on the incubation time. The heat of polymerization of hydrogen cyanide at 25° C. has also been determined.

EXPERIMENTAL

Stability Studies. These studies were carried out in the explosion bomb shown in Figure 1. The bomb was constructed of super pressure tubing, 5/8 inch in inside diameter and 1-7/8 inches in outside diameter. It was equipped with a 10,000 p.s.i. rupture disk, strain gage, and thermocouple. The strain gage was connected to a recorder and the thermocouple to a recorder controller. The bomb was heated by two Nichrome ribbon heaters wrapped around an insulated copper sleeve which slipped over the body of the bomb.

A 1/4 replicate, 2^5 factorial experiment was used to evaluate the effects of temperature, sodium hydroxide concentration, weathering, water content, and hydrogen cyanide polymer content on the stability of hydrogen cyanide. The conditions for each run and the results are given in Table I.