

Combustion properties of ammonia

Misconception among operators is further removed as study shows ammonia has combustion properties similar to hydrocarbons. Observations indicate ignition is difficult and flame propagation in air mixtures is slow.

COMBUSTION OF AMMONIA HAS BEEN of interest for a long period of time, however available combustion properties have been inadequate to explain fully the anomalous behavior of ammonia or to permit satisfactory evaluation of the potential hazards of industrial operations. These limitations of the existing data prompted this study of a number of combustion properties.

Historically, the flammable limits of ammonia in oxygen were first published in 1809 (4), and are apparently the oldest recorded for any combustible. Nevertheless, it has been reported (1) that German investigators about a century later postulated decomposition mechanisms to explain explosions in refrigeration equipment because they did not know that ammonia could explode. By 1914, the

German work had led to the establishment of definite flammable limits for ammonia in air. A compilation of flammable-limit data (3) cites seven additional published studies of ammonia flammability during the period 1922 to 1949; and the pressures developed by ammonia-air explosions were measured in 1923 (5). In spite of this evidence, as late as 1951 ammonia was indicated to be noncombustible and experiments were cited (2) as "rough proof that ammonia does not support combustion or burn." This misconception is fairly widespread today—even among people associated with ammonia operations.

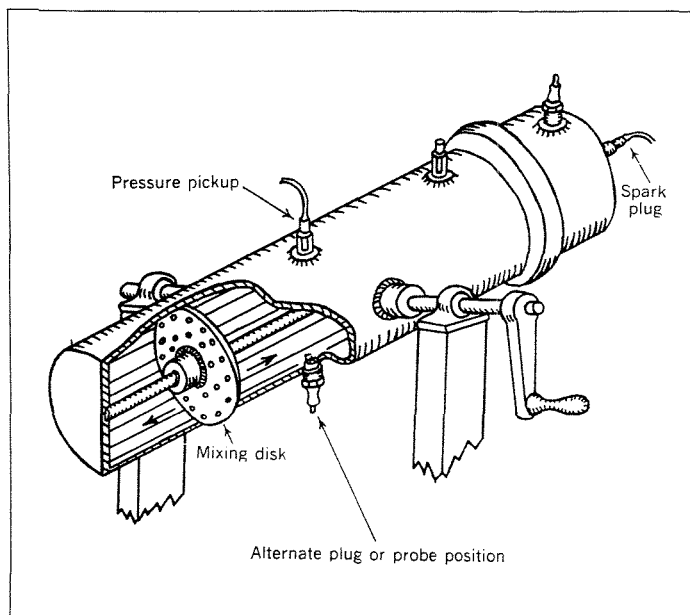
Although, these studies have shown ammonia to be flammable when mixed with air or oxygen in proper proportions and to be capable of generating

an explosive pressure, the historical incidence of fires or explosions attributable to ammonia is low. This fact may be explained in part by the observed difficulty of igniting ammonia (1) and by the low speed of flame propagation in ammonia-air mixtures (1, 5).

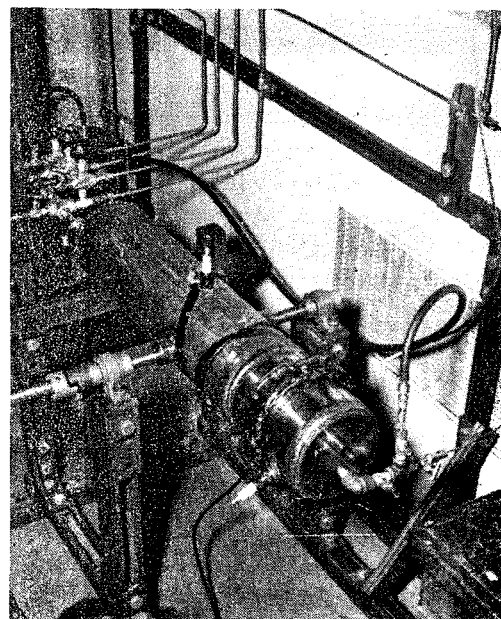
Studies were undertaken to determine the characteristics of diffusion flames, flammable-limit diagrams for mixtures with air and diluent nitrogen at several pressures and temperatures, explosion pressures within the flammable region, detonation characteristics, and ignition energies.

Diffusion flames

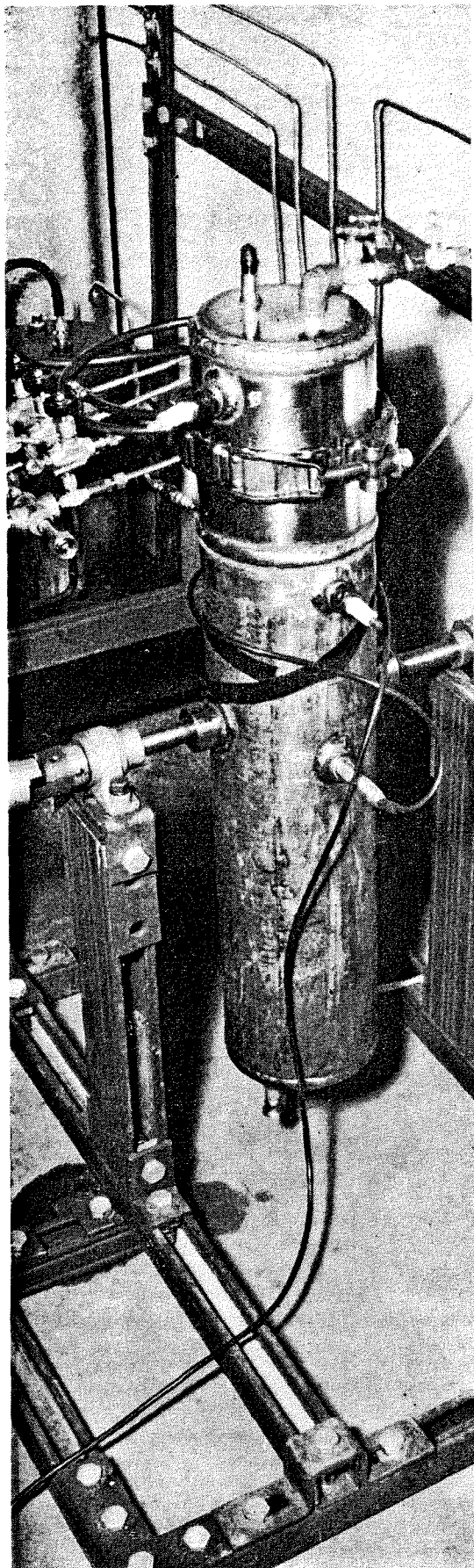
Combustion of ammonia was studied initially by observation of its visible diffusion flame. Anhydrous ammonia vapor was supplied through a 0.25-in.



Construction detail of explosion-pressure apparatus used in studying combustion of ammonia.



Explosion pressure apparatus in horizontal position connected to filling manifold.



Apparatus in vertical position connected to filling manifold.

diameter tube into an atmosphere of oxygen or air with an electrically heated wire helix as an igniter.

In oxygen, ignition occurred readily and the resulting stable flame burned as a greenish-white cone surrounded by a pale mantle streaked with orange and yellow. In air, however, the flame was not stable. Ignition occurred readily, but a flame-stabilizing hot surface was necessary to maintain the flame. The unenergized igniter was adequate for stabilization, and ammonia burned under these conditions with a pale yellow flame. Flame stability increased when the burner tube was pointed downward so the flame folded back on itself; however, stabilization by the igniter helix was still necessary.

The ready blowout of unstabilized ammonia flames in air is explained in part by the slow flame speed. The difficulty of maintaining a diffusion flame in air may have contributed to the belief that ammonia is noncombustible.

Flammable limits

A mixture of a combustible gas or vapor with a supporter of combustion is flammable if ignition at one point induces self-propagation of flame through the mixture. Flammable limits are the borderline flammable concentrations of a combustible in a specific supporter of combustion. Most commonly, the limits are determined with air to provide the familiar upper and lower flammable limits tabulated in handbooks. However, mixtures are encountered in which the oxygen-nitrogen ratio differs from that of air. In this case, the flammable limits become a continuous curve defining a region within which mixtures of the three components are flammable.

Although extensive data covering the effects of temperature, direction of flame propagation, and other variables on the flammability of ammonia in air are available (3), no complete flammable limit curves for mixtures with air and diluent nitrogen have been reported. Such curves were determined experimentally in a stainless-steel tube having an internal diameter of 1.5 in. and a length of 10.5 in. with mixtures prepared by proportioning the gases by pressure. The gases were distributed uniformly by being added through a small-diameter perforated inlet tube extending through the length of the combustion tube. Mixture composition was verified by analysis for ammonia and oxygen with a modified Orsat gas analyzer. Temperature within the tube was controlled by an electrically heated jacket. The ignition source was a spark plug at the bottom of the tube.

Table 1. Detonation data for ammonia.

Mixture, Vol. %	Detonation Induction Distance		Pressure Factor, Stable Detonation
	2-in. Pipe	4-in. Pipe	
55 NH ₃ , 45 O ₂	8 ft.	15 ft.	19
50 NH ₃ , 40 O ₂ , 10 N ₂	10 ft.	17 ft.	19
42 NH ₃ , 35 O ₂ , 23 N ₂	16 ft.	19 ft.	21

Flame propagation was detected by a thermocouple near the top of the tube, and the signal was recorded by a high-speed millivolt recorder.

The flammable-limit data obtained at 75°F and an initial pressure of 15 lb./sq. in. gauge are shown in Figure 1. This curve defines the boundary between flammable and nonflammable mixtures of ammonia, oxygen, and nitrogen. Volume percentages of the first two of these components are shown directly, nitrogen concentration is obtained by difference. The diagonal dotted line designates the composition of mixtures of ammonia with air. Hence, the intersections of the flammable-limit curve with this line are the lower and upper limits in air: 15.3 and 25.7%, respectively. These values are in reasonable agreement with the generally accepted limits of 15 and 28% in air at atmospheric conditions. (3). The difference presumably results from the smaller diameter of the tube used in the present study. The lowest point on the curve is the oxygen minimum—a limiting oxygen concentration below which no mixture is flammable regardless of the concentration of ammonia. The value of 14.3% for this minimum is high compared with most combustibles; hydrocarbons, for example, usually have oxygen minima of 11 to 12%. This high minimum value may be an additional indication of the low combustibility of ammonia.

The influence of temperature and pressure is shown in Figure 2. The flammable region is enlarged by increases in temperature or pressure. In this respect, ammonia is similar to most common combustibles. The numerical change in the limits in air between 75°F and 300°F is very close to the reported values (3) for the same temperature change at atmospheric pressure.

Explosion pressures

Explosion pressures have been reported only for ammonia-air mixtures (1, 5); no data are published for mixtures with nitrogen as a diluent. In order that hazards can be evaluated

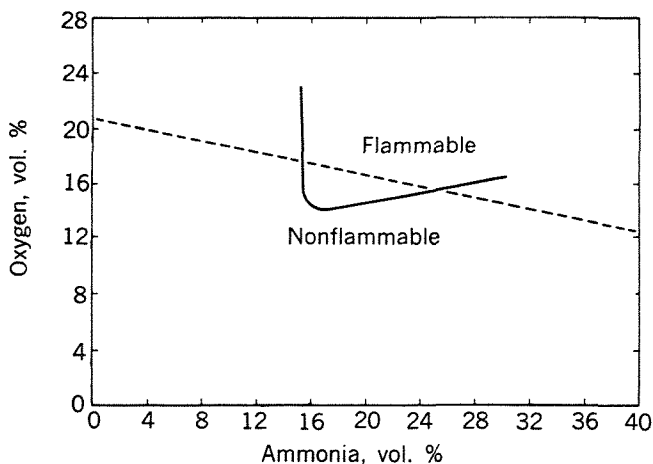


Figure 1. Flammability of ammonia-oxygen-nitrogen mixtures at 75°F and 15 lb./sq. in. gauge.

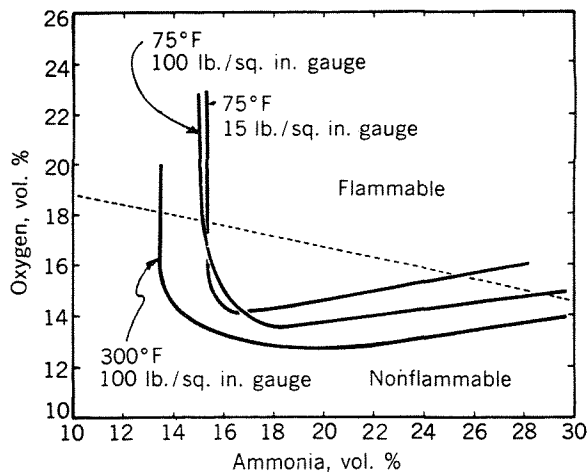


Figure 2. Flammability of ammonia-oxygen-nitrogen mixtures at different temperatures and pressures.

properly, potential explosion pressure throughout the flammable region should be known. These pressures were measured in a 25-in. length of 5-in. stainless-steel pipe with associated apparatus as shown in Figure 3. Mixtures were prepared by proportioning the gases by pressure measured with a 60-in. precision mercury manometer. Thorough mixing was accomplished by an internal perforated disk, which slid from end to end along a guide rod as the pipe was rocked. After mixing, composition was checked by analysis. Explosion pressure was measured by a calibrated crystal pick-up feeding an oscilloscope through a bridge circuit. The oscilloscope trace was photographed to provide a permanent record. Several locations of sparkplug igniter and pressure-sensing crystal provided various combinations of flame-propagation direction and geometry.

The resulting maximum explosion pressures are plotted in Figure 4 in terms of pressure factors; *i.e.*, the absolute explosion pressure divided by the absolute initial pressure. These explo-

sion pressures were found to depend upon the direction of flame propagation and the relative position of spark and pressure pick-up, as well as the mixture composition. Figure 4 shows only the maximum pressures obtained with the several geometric configurations used. Inasmuch as previous studies with other combustibles have shown pressure multiplication to be almost independent of initial pressure, Figure 4 is applicable to a wide range of initial conditions.

As expected, the highest explosion pressure is obtained with mixtures near stoichiometric composition. However, it is unexpected to find a several-fold pressure multiplication with mixtures immediately within the boundary of the flammable region. Thus, any flammable composition is a potential explosion hazard, though magnitude of the hazard does increase with a reduction of nitrogen diluent at a constant ammonia-oxygen ratio. The magnitude of the pressure ratios observed for ammonia is roughly three quarters that found for common hydrocarbon fuels under similar conditions.

Detonation characteristics

Gaseous detonation is the outgrowth of an explosion where geometric configuration permits acceleration of the flame front. As the flame-front speed becomes supersonic, pressure increases to a value several-fold greater than in an explosion and provides a sharp discontinuity at the shock front. The slow-burning character of ammonia does not prevent establishment of this supersonic detonation shock front; it only delays the process by increasing the induction distance. This characteristic of ammonia detonations has been shown experimentally. Flammable mixtures were ignited in both 2-in. and 4-in. diameter pipes with pressure measured by probes indicating on an oscilloscope.

In oxygen or oxygen-enriched air, ammonia detonated readily at atmospheric pressure, Table 1. With nitrogen increased to 40% and ammonia and oxygen in stoichiometric proportions, only one detonation was obtained in several trials at atmospheric pressure in the 2-in. pipe. However, at 35 lb./sq. in. gauge this mixture detonated readily within a distance of 84 ft.

Velocity of the detonation shock wave in the ammonia-oxygen mixture, measured at 90 ft. in the 2-in. pipe, was 7800 ft./sec. This speed is the same magnitude as detonation velocities reported for hydrogen or hydrocarbon-oxygen mixtures (6). However, a comparative test in 2-in. pipe showed the induction of detonation in propane-oxygen to occur in less than one-tenth the distance required for ammonia-oxygen.

Attempts to detonate ammonia-air mixtures were unsuccessful at pressures up to 60 lb./sq. in. gauge in the 105-ft. length of 2-in. pipe used in these studies. At atmospheric pressure, ignition was difficult in the horizontal

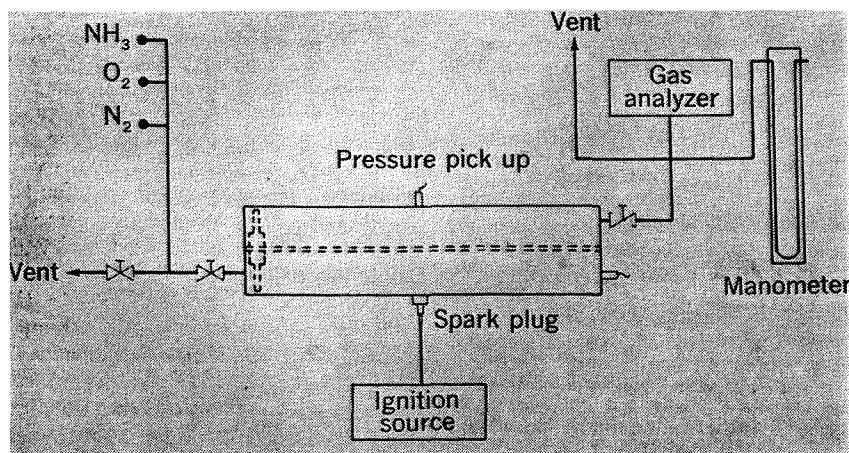


Figure 3. Explosion-pressure apparatus with associated equipment.

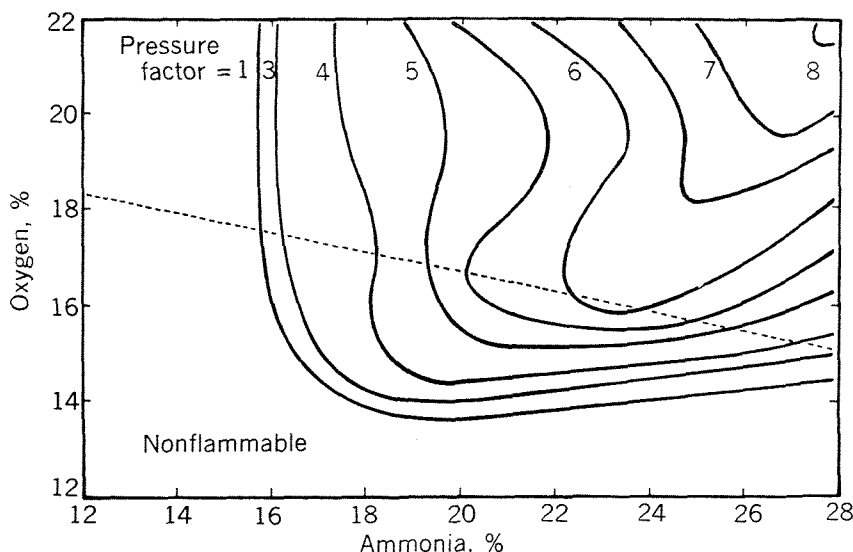


Figure 4. Maximum explosion pressures of ammonia-oxygen-nitrogen mixtures.

open pipe, and flame propagated about 1 ft./sec. with only small pressure indications. Even at 60 lb./sq. in. gauge, the flame speed did not increase measurably above the valve at atmospheric pressure. However, these results do not preclude acceleration and ultimate detonation if the pipe were considerably longer. By analogy with results obtained with propane in air and in oxygen, it is estimated that 500 to 600 ft. of 2-in. pipe would be required to establish a detonation in ammonia-air mixture.

Ignition energy

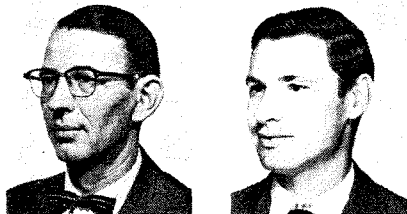
Ignition of a flammable mixture requires both adequate temperature and sufficient energy. Although ammonia has a high ignition temperature (1200°F) in air (7), such common ignition sources as sparks and flames provide adequate temperature. Therefore, the observed difficulty in igniting ammonia mixtures must result from its high ignition energy.

Ignition energies for ammonia and two hydrocarbons were determined by discharging a condenser of known capacitance, charged to predetermined voltages, through spark plugs or spark gaps formed from 0.125-in. wire. Mixtures of the combustible with air were varied through the flammable range to locate the minimum energy. Observed minimum ignition energies, in millijoules, were 680 for ammonia, 0.4 for *n*-hexane, and 0.3 for *n*-heptane. The results for hydrocarbons agree with values reported by other investigators (6). At first, the abnormally high value for ammonia was suspected to be caused by the quenching effect of the spark-plug geometry. However, similar values of ignition energy were also found with the wire spark gaps.

Hence, a very high ignition energy must be accepted as characteristic of ammonia. The value of 680 millijoules is at least ten times the spark energy used in automotive test engines and exceeds the energy available in many other ignition sources. In view of this energy requirement, the difficulty or failure of ignition experienced by some investigators is readily understood.

Conclusion

The combustion properties of ammonia are similar to those of such known hazardous materials as hydrocarbons. If flammable mixtures form, an explosion or detonation can occur with resultant damaging pressures. However, ammonia-air mixtures are difficult to ignite and they burn with little vigor. In the absence of oxygen



Bulkley

Husa

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enrichment, the risk of initiating accidental fire or explosion is low. #

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Questions and Answers

R. F. Schwab—Factory Insurance Association, Hartford, Conn.: In the particular chamber that you used, did you measure the rate of pressure rise of the explosion of ammonia-air?

Bulkley: We have curves showing pressure rise for each test run. We did not calculate rates of pressure rise, but these numbers can be derived from the curves. As you know, these values will be dependent upon the position of the tube and direction of flame propagation. The pressures reported are the maximum pressures obtained independent of the tube position.

W. A. Mason—The Dow Chemical Co., Midland, Mich.: An explosion was reported some time ago in which ammonia was suspected as the fuel. The report indicated that the ammonia in this system had been subjected to fairly high temperatures. This led to the conclusion that there may have been some decomposition of the ammonia into hydrogen and nitrogen. It was suspected that this hydrogen might have been the cause of the explosion. The ammonia which escaped caused some injury to the people involved.

Bulkley: About the time of the first World War, there was a considerable amount of work done in Germany on this point. There had been some refrigeration plant explosions, and decomposition was suspected as the source of the difficulty. As I recall the results, they found that there was not enough decomposition, even with prolonged heating, to account for the explosions. They eventually came to the conclusion that it was really an ammonia explosion.

There are a few incidents in the literature of explosions of ammonia. Considering the amount of ammonia that has been handled, the way some of it has been handled, and the fact that flammable mixtures undoubtedly have existed, the number of these accidents is relatively small. #