formed by thermal decomposition of nitrate, up to 40 mol %.

Acknowledgment

I acknowledge the assistance of K. E. Geis in fabricating the experimental apparatus and D. C. Macmillan in designing and programming the microprocessor.

Literature Cited

(1) Nissen, D. A. "A Single Apparatus for the Precise Measurement of the Physical Properties of Liquids at Elevated Temperature and Pressure," SAND80-8034; Sandia Laboratories: Livermore, CA, Oct 1980.
(2) Solomons, C.; White, M. S. *Trans. Faraday Soc.* **1969**, *65*, 309.
(3) Nissen, D. A.; Meeker, D. E. "Analytical Method for Nitrate Melts", in press.
(4) Nissen, D. A. "The Chemistry of the Binary $NaNO_3$-KNO_3 System", SAND81-8007; Sandia Laboratories: Livermore, CA, June 1981.
(5) Janz, G. J.; Krebs, U.; Siegenthaler, H. E.; Tomkins, R. P. T. *J. Phys. Chem. Ref. Data* **1972**, *1*, 587.
(6) Krivovyazov, E. L.; Sokolova, I. D.; Voskresenkaya, H. K. *J. Appl. Chem. USSR (Engl. Transl.)* **1963**, *36*, 2458.
(7) Ejima, T.; Nakamura, E. *J. Jpn. Inst. Metl. Sendai* **1975**, *39*, 680.
(8) Janz, G. J. *J. Phys. Chem. Ref. Data* **1980**, *9*, 909.
(9) Bloom, H.; Davis, F. G.; James, D. W. *Trans. Faraday Soc.* **1960**, *56*, 1179.

Received for review October 9, 1981. Accepted March 15, 1982.

Flammability Properties of Acrylonitrile and Acetonitrile

Silvio De Micheli* and Vittorio Tartari

Montedipe S.p.A., Research Center, 20020 Bollate (Milan), Italy

Flammability limits were determined for ternary mixtures of acrylonitrile–air–nitrogen, acetonitrile–air–nitrogen, and acetonitrile/water (azeotropic ratio)–air–nitrogen. For the acrylonitrile–air system, slightly wider limits than those reported before were found. Maximum safe values for oxygen contents are also reported.

Introduction

In order to define the potential "plant hazard", flammability data are necessary for the pure compounds and the mixtures involved in every chemical process. Lower and upper flammability limits (LFL and UFL, respectively) in air, flammability limit curves vs. added inert concentration, and minimum oxygen content are usually required at the pressure and temperature levels occurring in the plant.

If literature data are missing, or incomplete, or obtained by means of an improper experimental apparatus, new experimentation is needed, since methods have not yet been developed for calculating flammability limits theoretically.

Although acrylonitrile (AN) and acetonitrile (AcN) are very common chemicals, only the upper and lower limits for the former were measured (*1*). These data are inadequate to solve all safety problems in propylene ammoxidation plants, where both chemicals are produced and stored.

In this work we have defined the flammability fields for the pure compounds and for the AcN/water azeotrope in air–nitrogen mixtures.

Experimental Section

The apparatus used for the flammability limits determination is shown in Figure 1. Gaseous streams were taken from cylinders or from the laboratory supply and metered through flowmeters. The liquid phase was fed to a vaporizer by means of a reciprocating pump and dosed by a buret. Punched plates were inserted along the feeding lines to improve the turbulence.

The global stream was carefully mixed into a mixer. Feeding lines were kept to such a temperature level that vapor condensation could be avoided.

The test vessel consists of a stainless-steel tube 5-cm i.d. and 150 cm long so thick that it could withstand the mechanical and thermic solicitations resulting from flammability tests. The size of our vessel is analogous to those reported elsewhere (*1*). The influence exerted on flammability limits by inner diameters smaller than 5 cm is well-known (*1*).

A rupture disk is mounted at the bottom of the vessel to allow the rapid discharge of possible overpressures. During the discharge time the vessel can be bypassed without influencing the gaseous stream composition: this procedure allows one to carry out many tests with the same mixture.

If necessary the vessel can be heated electrically. The state of the temperature inside the vessel was monitored by the thermocouples shown in Figure 1.

The pressure was kept to a constant level by means of a volumetric valve situated at the top of the vessel.

Mixtures were ignited by an inductive spark located in the middle of the vessel. The igniter consists of two stainless-steel wire electrodes held by a tubular Teflon piece and spaced 2 mm apart. The wires are connected to a 50-cycles transformer, operating at 220-V input, 12 000-V output. An energy of 20 J was released during the discharge time, which was held constant at $\sim$50 ms. The mixture to be tested could be sampled at the inlet, at the middle, and at the outlet of the vessel, in order to control the homogeneity of the composition all along the vessel. The volumetric composition of the mixture was determined by using an on-line gas chromatograph.

The propagation of the flame was detected by two 0.1-mm gauge Pt–Rh 6%/Pt–Rh 30% thermocouples extending into the vessel to a point about 10 mm from the vertical axis of the vessel. These thermocouples have a very low time constant (0.07 s).

During these tests we considered only upward flame propagation. It is known that the limits measured under these conditions are wider than those determined under any other condition.

The rapid output generated by the thermocouples was stored on a variable-frequency transient recorder and afterward was replotted on a two-channel chart recorder. Start, duration, and power of the electrical discharge were monitored on the same recorder.

Owing to the low threshold limiting value (TLV) fixed for these compounds (TLV proposed for AN = 1–2 ppm), the vent line discharged into a torch and gases were burned carefully.

The equipment and the feeding pump were installed into a heavily constructed pressure box and were operated from outside, so that the operator was fully protected from any

0021-9568/82/1727-0273$01.25/0 © 1982 American Chemical Society

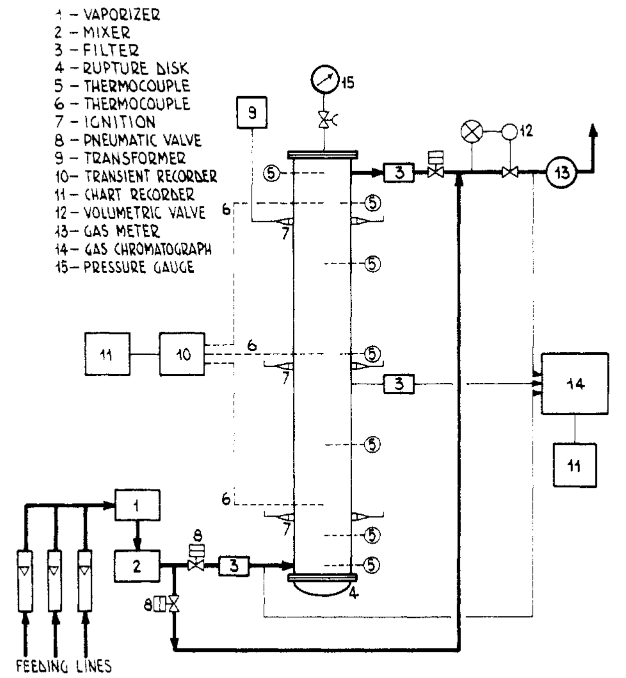

Figure 1. Experimental apparatus.

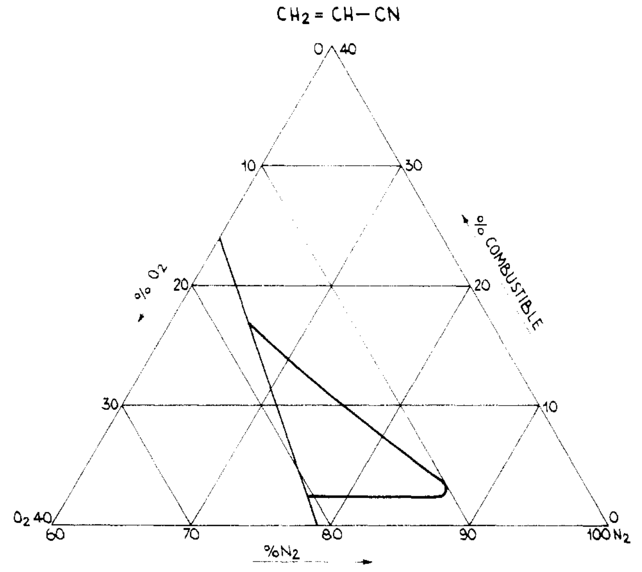

Figure 2. Flammability limits (vol %) for the system AN-air-N_2 at 40–45 °C and 140 kPa.

hazard connected with unexpected explosions and releases of chemicals.

Results and Discussion

The flammability limits determination is performed by detecting two nearly equal compositions of the gaseous mixture, the former of which is able to propagate the flame all along the tube and the latter is not. We define the second composition as the flammability limit.

Flammability Limits of AN-Air-N_2 Mixtures. Table I summarizes the results of our tests and Figure 2 shows the flammability field of AN-air-N_2 mixtures.

The determination was performed at the starting absolute pressure of 140 kPa, with constant volume and upward flame propagation. During the upper flammability limit determination, it was difficult to work at room temperature without falling into condensation phenomena whether in the feeding line or in the vessel. For that reason we performed all of the runs at a slightly higher temperature (40–45 °C).

Table I. AN-Air-N_2 Mixture Compositions[a]

AN	N_2	O_2	ignition propagation
2.35	77.25	20.40	no
2.64	77.02	20.34	yes
2.42	77.20	20.38	no
2.54	77.09	20.37	yes
2.23	85.05	12.72	no
2.70	85.18	12.12	yes
2.24	83.56	14.20	no
2.48	83.10	14.42	yes
2.42	80.88	16.70	no
2.74	81.42	15.84	yes
2.30	86.92	10.78	no
2.50	86.90	10.60	yes
2.40	86.98	10.62	no
2.58	87.07	10.35	yes
3.25	86.77	9.98	no
3.12	86.35	10.53	yes
4.42	85.48	10.10	no
4.54	84.78	10.68	yes
6.94	81.40	11.66	no
6.22	81.53	12.25	yes
7.25	81.05	11.70	no
6.40	81.33	12.27	yes
8.74	77.98	13.28	no
8.00	78.50	13.50	yes
11.30	74.00	14.70	no
11.00	73.77	15.23	yes
14.23	69.90	15.87	no
13.20	70.50	16.30	yes
14.25	70.23	15.52	no
13.30	70.90	15.80	yes
17.51	65.25	17.24	no
16.82	65.80	17.38	yes
17.34	65.39	17.27	no
17.25	65.45	17.30	yes

[a] Volume percent.

Table II. AcN-Air-N_2 Mixture Compositions[a]

AcN	N_2	O_2	ignition propagation
4.35	75.65	20.00	no
4.52	75.53	19.95	yes
5.37	79.94	14.69	no
5.33	79.89	14.78	yes
5.28	78.14	16.58	no
5.59	77.89	16.52	yes
5.39	81.21	13.40	no
5.61	80.93	13.46	yes
5.62	81.40	12.98	no
5.89	78.95	15.16	yes
5.80	81.20	13.00	no
5.88	80.38	13.74	yes
6.50	81.28	12.22	no
6.20	81.00	12.80	yes
6.84	80.44	12.72	no
6.40	80.40	13.20	yes
9.10	76.20	14.70	no
9.10	76.05	14.85	yes
11.30	72.85	15.85	no
11.40	72.40	16.20	yes
14.80	67.40	17.80	no
14.20	67.87	17.93	yes

[a] Volume percent.

The reported lower flammability limit was determined by using a 2-in. i.d. reactor opened at the bottom, considering upward flame propagation, while for the upper limit determination the reactor was 1-in. i.d. and opened at the top. The temperature in this experiment was 29.4 °C. The ignition power is unknown.

The differences between literature data (LFL = 3.05 vol %; UFL = 17.05 vol %) and our results (LFL = 2.42 vol %; UFL = 17.34 vol %) could be ascribed to the differences of ex-

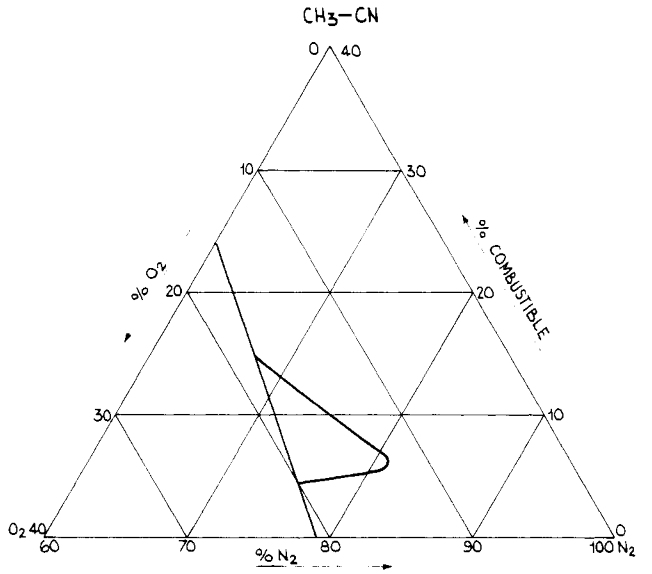

Figure 3. Flammability limits (vol %) for the system AcN-air-N_2 at 40–45 °C and 140 kPa.

Table III. AcN/H_2O (Azeotropic Ratio)-Air-N_2 Mixture Compositions[a]

azeotrope	N_2	O_2	ignition propagation
7.05	73.52	19.43	no
7.41	73.24	19.35	yes
6.83	73.70	19.47	no
7.42	73.23	19.35	yes
7.36	76.12	16.52	no
7.42	76.06	16.52	yes
7.19	77.96	14.85	no
8.04	77.20	14.76	yes
7.63	78.29	14.08	no
8.10	77.64	14.26	yes
8.50	78.01	13.49	no
8.73	77.39	13.88	yes
9.69	76.77	13.54	no
9.50	76.36	14.14	yes
11.06	74.94	14.00	no
10.11	75.39	14.50	yes
14.80	69.85	15.35	no
13.94	70.55	15.51	yes
17.87	64.97	17.16	no
17.33	65.39	17.28	yes

[a] Volume percent.

perimental apparatuses and temperatures.

The maximum safe oxygen concentration is 9.98 vol % (see Figure 2).

Flammability Limits of AcN-Air-N_2 Mixtures. In spite of its wide use as a chemical and solvent, no data are available on flammability properties of AcN.

Table II shows the results obtained with the above mixtures. Experimental conditions were identical with those of AN mixtures. Figure 3 shows the complete field of flammability for ternary mixtures.

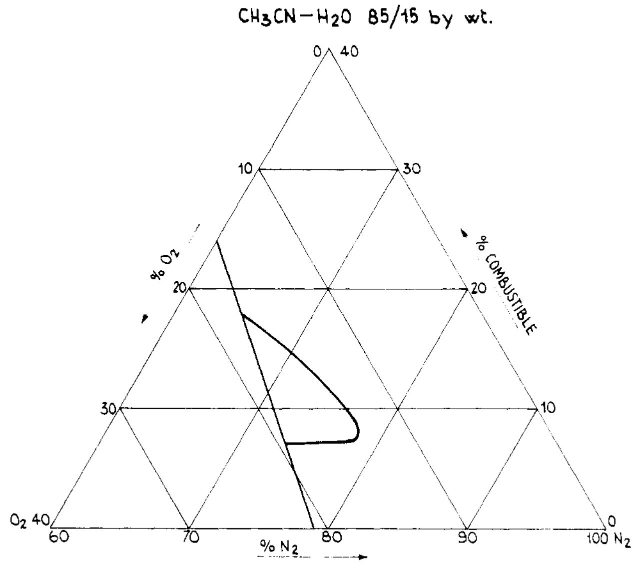

Figure 4. Flammability limits (vol %) for the system AcN/H_2O (azeotropic ratio)-air-N_2 at 40–45 °C and 140 kPa.

The percentage of AcN corresponding to the lower limit in air is 4.35 vol % and that corresponding to the upper limit in air is 14.80 vol %.

No mixture of AcN-air-N_2 can propagate the flame at the tested pressure and temperature level if it contains less than 12.22 vol % of oxygen.

Flammability Limits of the Azeotropic AcN/Water Mixture with Air and N_2. The composition of the above azeotropic mixture is reported in the literature by several authors (*2*, *3*), the percentage of water ranging from 14.2 to 17.0 wt % and from 27.4 to 31.8 vol %. For our purpose we tested a mixture containing 15 wt % of water.

The flammability limits are given in Table III for this azeotrope in all mixtures of air and nitrogen, with upward flame propagation, at 140-kPa absolute pressure and 40–45 °C. Figure 4 shows the derived flammable area.

The percentage of pure AcN corresponding to the lower limit of the azeotrope in air (7.05 vol %) is 5.03 vol %; the azeotropic upper limit (17.87 vol %) corresponds to 12.75 vol % of pure AcN.

The minimum oxygen content capable of sustaining flame propagation in azeotropic mixtures is 13.49 vol %.

Acknowledgment

Mr. Flavio Costantini's contribution in operating the experimental equipment is gratefully acknowledged.

Literature Cited

(1) Coward, H. F.; Jones, G. W. "Limits of Flammability of Gases and Vapors"; U.S. Government Printing Office: Washington, DC, 1952.
(2) Taramasso, M.; De Maldè, M. *Chim. Ind.* (*Milan*) **1967**, *49*, 820.
(3) Volpicelli, G. *Chim. Ind.* (*Milan*) **1967**, *49*, 720.

Received for review October 23, 1981. Accepted April 6, 1982.