Bundesanstalt für Materialforschung und -prüfung

TEST REPORT

Determination of the explosion region of ethane-HFO1234yf-air mixtures

BAM reference	II-2318/2009
Copy	1st copy of 2 copies
Customer	Umweltbundesamt Wörlitzer Platz 1 06844 Dessau-Roßlau
Order date	2009-10-08
Reference	54353-5/1 (Förderkennzeichen: 363 01 262)
Receipt of order	2009-10-12
Test samples	• Ethane, purity > 99.5, supplied by Air Liquide Germany GmbH • HFO1234yf (2,3,3,3-Tetrafluoropropylene) • Compressed air, free of moisture and oil, supplied by BAM
Receipt of samples	2009-09-07
Test date	Begin: 2009-10-12 End: 2009-10-30
Test location	BAM, Unter den Eichen 87, 12205 Berlin Building 40, Room 413
Test procedure according to	DIN 51649 "Determination of explosion limits of gases and vapours"

This test report consists of page 1 to 10.

TEST REPORT

1 Subject of the tests

BAM was commissioned to determine the explosion region of the ternary gas system ethane-HFO1234yf-air. The results should be compared to literature values also determined in the past by BAM for the ternary system ethane-R134a-air. Differences especially regarding the influence of the refrigerants on the explosion range of ethane-air respectively air shall be shown.

The tests shall be carried out according to the former German standard DIN 51649 "Determination of explosion limits of gases and vapours" in a glass tube. Although this standard was replaced by the European standard EN 1839 the former German standard was applied due to comparability to the literature values.

2 Safety characteristics, terms and definitions

The safety characteristics and terms used in this report are defined as follows:

Lower and upper explosion (flammability) limit (LEL, UEL)
Lower and upper limiting value of the flammable gas concentration in a gaseous fuel/air mixture, at which just no more flame propagation (explosion) takes place after an ignition.

Explosion range
The concentration range between LEL and UEL is called the explosion range. Fuel/air mixtures within the explosion range can be ignited by an ignition source.

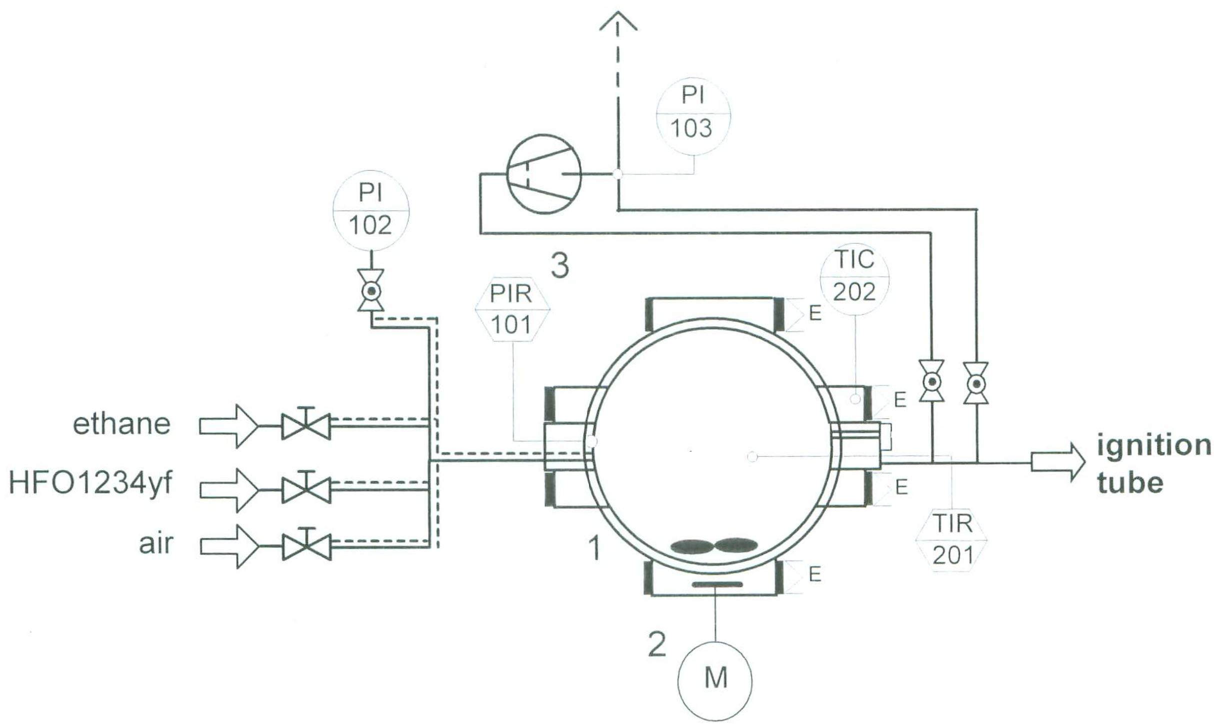
Explosion region
For a ternary gas mixture consisting of ethane, refrigerant and air the course of the LEL and UEL enclose the explosion region. For each refrigerant concentration one explosion range with LEL and UEL exists. The sum of all explosion ranges forms the explosion region.

3 Experimental set-up and test procedure

3.1 Test apparatus

The test equipment is schematically shown in Fig. 1. The test mixtures were prepared separately in a 14-dm^3-sphere with a mixing device inside. After the preparation the gas mixture was filled to the ignition tube according to DIN 51649 (Fig. 2). Main part of the ignition tube was a vertical glass tube with an inner diameter of 60 mm and a height of 300 mm. This glass tube is a so called open system due to the non-fixed lid at the top. In case of strong reactions the overpressure is released by lifting the lid.

Prior to each ignition attempt, the tube was purged with the test mixture. The purging volume was at least ten times the volume of the tube. Subsequently the test mixture by-passes the glass tube and was supplied into the exhaust system; the inlet to the test vessel was sealed.



Legend:

1 14-dm^3-spherical vessel

2 mixing device

3 piezoresistive pressure sensor for the determination of the partial pressures of the mixture components and the final pressure of the mixture (measurement range 0 bara to 2 bara)

Fig. 1: Scheme of the used apparatus for the determination of the explosion limits of different specified gas mixtures at different initial conditions.

Fig. 2: Ignition tube according to DIN 51649: vertical glass tube (300 mm length, 60 mm inner diameter) and a high voltage spark ignition device 60 mm above the bottom of the tube

3.2 Ignition system

A series of induction sparks between two electrodes was used as the ignition source. Two electrodes made from stainless steel were positioned 60 mm above the bottom of the glass tube. A high voltage transformer, with a root mean square of 13 kV to 16 kV and a short circuit current of 20 mA to 30 mA, was used for producing the ignition spark. The primary winding of the high voltage transformer was connected to the mains via a timer set to the required discharge time. The spark discharge time was adjusted to 0,2 s. The power of the spark depends on the gas mixture. In air at atmospheric conditions according to calorimetric and electric measurements such a source gives a spark with a power of approximately 10 J.

3.2 Ignition criterion

The operator observed optically whether there was a flame detachment (Fig. 3) from the ignition source or not. This criterion was an optical one and was very sensitive to determine explosion limits.

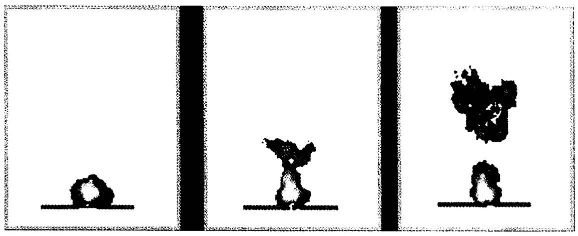


Fig. 3: Flame detachment as ignition criterion according to DIN 51649

3.3 Pressure and temperature equipment

One piezoresistive pressure transducer, type KELLER PAA-10, was installed to the mixing vessel in order to determine precisely the partial pressures of each component filled to the vessel. The transducer had a measuring range of 0 bara to 2 bara and was calibrated by an digital pressure controller, type DPI 515, GE Sensing GmbH. The error of these pressure transducers was better than 0.5 % FS.

The temperature of the gas mixture inside the mixing vessel as well as inside the ignition tube were measured by using 1,5 mm thermocouples type "K" (NiCr/NiAl).

3.4 Preparation of the test mixtures

The test mixtures containing ethane, HFO1234yf and air were prepared according to the partial pressure procedure in a mixing vessel at final pressures of 2 bara. The following procedure was carried out:

- Evacuation of the mixing vessel and all pipes,
- Filling of ethane to the vessel up to the partial pressure,
- Filling of HFO1234yf up to its partial pressure,
- Filling of air up to its partial pressure (final mixing pressure).
- Homogenization of the mixture by means of a mixing device.

3.5 Performing the explosion tests

After purging the ignition tube with the test mixture the gas flow was stopped. Then an ignition was attempted with the induction spark when test mixture is quiescent (about 15 s after gas flow was stopped), and it is observed whether a flame detaches from the ignition source or not.

If an ignition is observed, the amount of ethane respectively HFO1234yf in the test mixture was iteratively varied until no further flame detachment follows. The step size for the variation was fixed to 0.2 mol-%. The test mixture with which a further flame detachment just failed was used to carry out another four tests. The determination was terminated when all five tests have taken place without flame detachment. If this was not the case, the ethane content was varied again, i.e. for the determination of the LEL the ethane content was reduced by one step size; for the UEL, it was increased by one step size.

This procedure was carried out for different fixed amounts of HFO1234yf respectively ethane in order to determine the course of the lower and the upper explosion limits and therefore the complete explosion region of the ternary gas system.

4 Results

In whole together 96 ignitions 12 explosion limits have been determined. In Tab. 1 to Tab. 12 the ignition tests are presented. the five ignition tests for each explosion limit validation are marked with a grey background.

Tab. 1: Ignition tests for the determination of the LEL of ethane-air (atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%		flame detachment yes / no
	ethane	air	
1	2.4	97.6	no
2	3.0	97.0	yes
3	2.6	97.4	yes
4	2.4	97.6	no
5	2.4	97.6	no
6	2.4	97.6	no
7	2.4	97.6	no

Tab. 2: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (3.0 mol % HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
8	1.2	3.0	95.8	yes
9	0.8	3.0	96.2	no
10	1.0	3.0	96.0	yes
11	0.8	3.0	96.2	no
12	0.8	3.0	96.2	no
13	0.8	3.0	96.2	no
14	0.8	3.0	96.2	no

Tab. 3: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (0 mol-% ethane = LEL of HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%		flame detachment yes / no
	HFO1234yf	air	
15	6.4	93.6	yes
16	6.2	93.8	no
17	6.2	93.8	no
18	6.2	93.8	no
19	6.2	93.8	no
20	6.2	93.8	no

Tab. 4: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (0 mol-% ethane = UEL of HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%		flame detachment yes / no
	HFO1234yf	air	
21	14.2	95.8	yes
22	14.4	95.6	no
23	14.4	95.6	no
24	14.4	95.6	no
25	14.4	95.6	no
26	14.4	95.6	no

Tab. 5: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (15.0 mol-% HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
27	1.5	15.0	83.5	yes
28	1.2	15.0	83.8	yes
29	0.8	15.0	84.2	yes
30	0.6	15.0	84.4	yes
31	0.4	15.0	84.6	no
32	0.4	15.0	84.6	no
33	0.4	15.0	84.6	no
34	0.4	15.0	84.6	no
35	0.4	15.0	84.6	no

Tab. 6: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (1.0 mol % ethane; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
36	1.0	15.2	83.8	yes
37	1.0	15.4	83.6	no
38	1.0	15.4	83.6	no
39	1.0	15.4	83.6	no
40	1.0	15.4	83.6	no
41	1.0	15.4	83.6	no

Tab. 7: Ignition tests for the determination of the LEL of ethane-HFO1234yf-air (2.0 mol % ethane; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
42	2.0	15.4	82.6	yes
43	2.0	15.6	82.4	yes
44	2.0	15.8	82.2	no
45	2.0	15.8	82.2	no
46	2.0	15.8	82.2	no
47	2.0	15.8	82.2	no
48	2.0	15.8	82.2	no

Tab. 8: Ignition tests for the determination of the UEL of ethane-HFO1234yf-air (3.0 mol % ethane; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
49	3.0	15.4	81.6	no
50	3.0	15.2	81.8	no
51	3.0	14.8	82.2	no
52	3.0	14.4	82.6	yes
53	3.0	14.6	82.4	no
54	3.0	14.6	82.4	no
55	3.0	14.6	82.4	no
56	3.0	14.6	82.4	no
57	3.0	14.6	82.4	no

Tab. 9: Ignition tests for the determination of the UEL of ethane-HFO1234yf-air (12.5 mol % HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
58	4.6	12.5	82.9	no
59	4.4	12.5	83.1	yes
60	4.6	12.5	82.9	no
61	4.6	12.5	82.9	no
62	4.6	12.5	82.9	yes
63	4.8	12.5	82.7	no
64	4.8	12.5	82.7	no
65	4.8	12.5	82.7	no
66	4.8	12.5	82.7	no
67	4.8	12.5	82.7	no

Tab. 10: Ignition tests for the determination of the UEL of ethane-HFO1234yf-air (10.0 mol-% HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
68	6.0	10.0	84.0	yes
69	7.0	10.0	83.0	no
70	6.6	10.0	83.4	no
71	6.4	10.0	83.6	yes
72	6.6	10.0	83.4	no
73	6.6	10.0	83.4	no
74	6.6	10.0	83.4	no
75	6.6	10.0	83.4	yes
76	6.8	10.0	83.2	no
77	6.8	10.0	83.2	no
78	6.8	10.0	83.2	no
79	6.8	10.0	83.2	no
80	6.8	10.0	83.2	no

Tab. 11: Ignition tests for the determination of the UEL of ethane-HFO1234yf-air (5.0 mol-% HFO1234yf; atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%			flame detachment yes / no
	ethane	HFO1234yf	air	
81	10.0	5.0	85.0	yes
82	11.0	5.0	84.0	yes
83	11.4	5.0	83.6	no
84	11.2	5.0	83.8	no
85	11.2	5.0	83.8	no
86	11.2	5.0	83.8	no
87	11.2	5.0	83.8	no
88	11.2	5.0	83.8	no

Tab. 12: Ignition tests for the determination of the UEL of ethane-air (atmospheric pressure; 25 °C)

Test-No.	mixture composition in mol-%		flame detachment yes / no
	ethane	air	
89	14.0	86.0	yes
90	14.4	85.6	yes
91	14.6	85.4	yes
92	14.8	85.2	no
93	14.8	85.2	no
94	14.8	85.2	no
95	14.8	85.2	no
96	14.8	85.2	no

5 Summary

The experimentally determined explosion limits of the ternary gas system ethane-HFO1234yf-air are summarized in Tab. 13.

Tab. 13: Ignition tests for the determination of the LEL of HFO1234yf-air (atmospheric pressure; 25 °C)

Explosion limit No.	mixture composition in mol-%		
	ethane	HFO1234yf	air
1	2.4	0	97.6
2	0.8	3.0	96.2
3	0	6.2	93.8
4	0	14.4	85.6
5	0.4	15.0	84.6
6	1.0	15.4	83.6
7	2.0	15.8	82.2
8	3.0	14.6	82.4
9	4.8	12.5	82.7
10	6.8	10.0	83.2
11	11.2	5.0	83.8
12	14.8	0	85.2

The resulting explosion region is shown in Fig. 4. Reason for the determination was the comparison to the explosion region of ethane-R134a-air already determined in the past according to DIN 51649 at the same initial conditions. The comparison is shown in Fig. 4 as well.

The explosion regions are finally comparable large considering the whole region. But there is an important difference which is caused by the flammability of HFO1234yf itself. Therefore the course of the lower explosion limit of ethane hits the x-axis at the LEL respectively the UEL of HFO1234yf. That leads to the fact that in case of HFO1234yf leakages the probability to produce explosive atmospheres in presence of hydrocarbons is larger compared to R134a.

The presence of hydrocarbons depends on the use of the refrigerant. In many cases there are hydrocarbons as an oil present. Mineral oil are hydrocarbons with long C-chains which can be cracked at hot surfaces. Smaller molecules are formed which can also react with the refrigerant. As a final crack product ethane can occur. Therefore the influence of ethane on the explosion region is shown in place of any possible hydrocarbons.

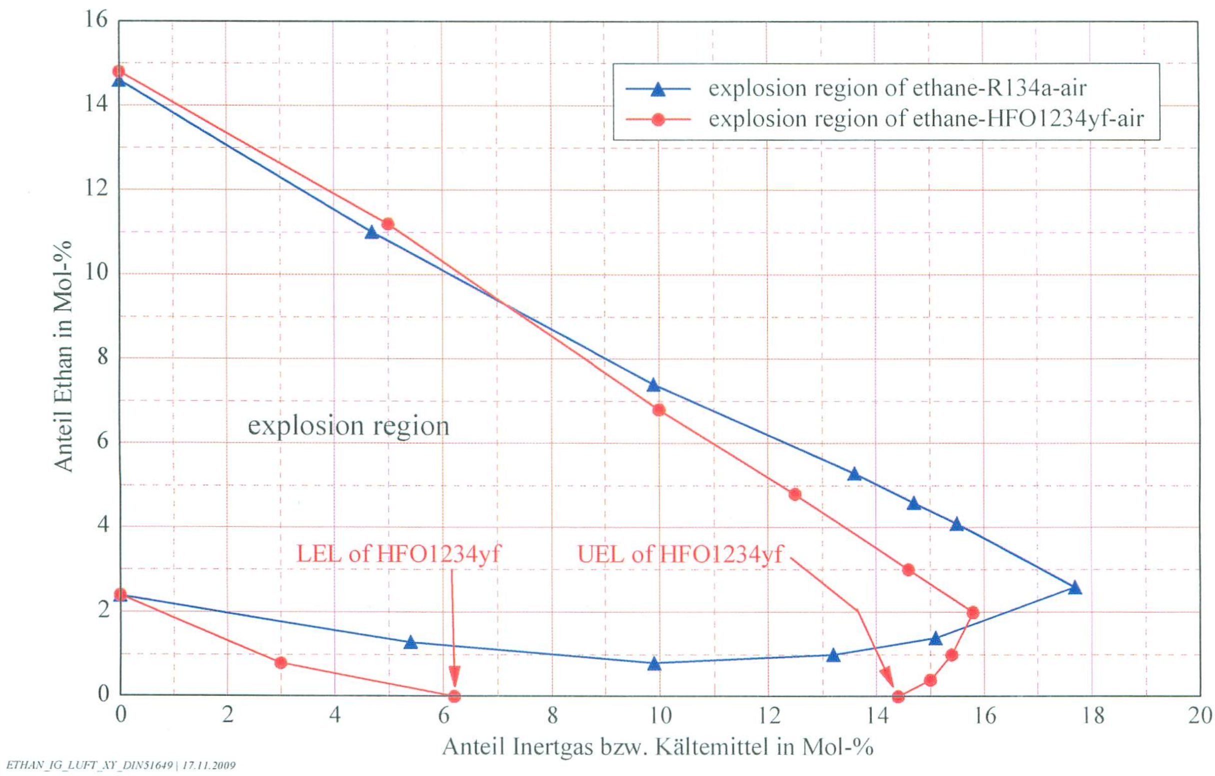


Fig. 4: Explosion regions of ethane-R134a-air and ethane-HFO1234yf-air, determined at atmospheric pressure and 25 °C according to DIN 51649

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