THE EXPLOSIVENESS OF GAS-PHASE METHANOL–AIR MIXTURES IN FLOW SYSTEMS

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Methanol is being used as starting material in numerous industrial syntheses. It attracted my attention when I studied the technology of formaldehyde production [1], because several explosions have occurred in the tube portion between the methanol evaporator and the formaldehyde reactor. No data could be found in the literature referring to the explosiveness of gas-phase methanol–air mixtures in flow systems [2]. I therefore carried out a series of experiments.

Experimental

An evaporating apparatus conform to commercial scale conditions, was used fitted with electric heating and temperature control and operated in the temperature range between 40 and 46 °C. The flow rate of the mixture varied between linear velocity values of 0.8 to 3.2 m/s. The experiments aimed mainly at the determination of the flammability limits and the explosion range of methanol–air mixtures of various ratios. A 12 V d.c. spark was used for ignition.

Objectives

The experiments referred to the following safety relationships:

(i) dependence of the flammability range on flow rate,

(ii) effect of the temperature of the evaporating system on the flammability range,

(iii) dependence of explosion limits on flow rate at different temperatures,

(iv) effect of water vapour and nitrogen on the flammability and explosion ranges, respectively.

Changes in the flammability range as a function of flow rate

The experiments were carried out at an evaporator temperature of 40 ± 1 °C. All flammability experiments were repeated twice, so that the data in the tables represent arithmetical means of three measurements. The results are listed in Table I. The flammability range is characterized by the lower and upper limit of methanol concentration. The results indicate that with increasing flow rate, the upper flammability limit increases by about 5 to 10% (its average value is 36.6%) by vol., whereas the lower limit (whose average is 4.4% by vol. does not change significantly.

Table I

Effect of flow rate on flammability

Linear flow rate m/s	Methanol concentration, % by vol.	
	lower limit	upper limit
0.8	4.4	34.3
1.0	4.3	36.8
1.2	4.8	34.9
1.5	4.2	36.1
1.7	3.9	36.3
2.0	4.7	37.9
2.2	4.1	36.1
2.6	4.6	38.8
2.9	3.7	36.4
3.2	5.2	38.6

Dependence of the flammability range on the temperature of the evaporating system

The temperature of the evaporator was set to 40 ± 1 °C, 43 ± 1 °C and 46 ± 1 °C, resp. The linear velocity of the gas stream was studied within the range characteristic for commercial scale plants, namely 1.2 m/s, 2.2 m/s and 3.2 m/s. The results are shown in Table II.

The lower limit of the flammability range slightly increased with temperature, depending on the linear velocity. The same result was found for the upper limit. If the industrial evaporating system's temperature can be kept within the temperature range of 40 to 46 °C, the average value of the lower limit of the flammability range is 5.3% by vol., the upper limit is 37.1% by vol. These values differ — though only slightly — from the flammability range of a static methanol–air mixture: data in the literature, referring to 20 °C and a pressure of 760 torr are 5.5 and 36.5% by vol. resp. [3, 4].

Table II

Effect of temperature on flammability

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	4.8	34.9
1.2	43	5.9	36.8
1.2	46	5.5	37.4
2.2	40	4.1	36.1
2.2	43	4.3	36.9
2.2	46	4.8	38.3
3.2	40	5.2	38.6
3.2	43	6.3	37.8
3.2	46	6.8	36.9

Determination of the explosion range

Gas flow rates and temperatures applied were the same as those in the experiments on flammability, since explosion is possible only within the flammability range. The results are listed in Table III.

The results indicate that the lower and upper limits of the explosion range depend on temperature and on the flow rate of the gas mixture. The average lower limit of the explosion range is 6.3% by vol., this value exceeding by 0.8% by vol., the lowest methanol concentration at which explosion can take place in a static system. It is remarkable from the technological viewpoint that the upper explosion limit for evaporator temperatures within 40 to 46 °C is 29.6% by vol., exceeding the highest explosive methanol concentration in a static system by 3.1% by vol.

Changes in the flammability range due to the presence of oxygen

Experimental conditions were the same as in the previous experiments with the only difference that 5% by vol. oxygen were added from an oxygen flask to the methanol–air mixture. The results are shown in Table IV.

In the presence of oxygen, the lower limit of the flammability range increased slightly with increasing temperature, as well as the upper limit. The lowest average concentration of methanol in the flammable gas mixture was 3.8% by vol., the highest 39.9% by vol., *i.e.* the flammability range widens by about 10—15% in the presence of oxygen.

Table III

Dependence of the explosion range on flow rate and temperature of evaporator

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	6.7	27.7
1.2	43	5.6	31.4
1.2	46	6.3	33.1
2.2	40	6.8	27.5
2.2	43	5.7	30.8
2.2	46	6.9	28.9
3.2	40	5.6	26.3
3.2	43	6.9	28.9
3.2	46	7.4	32.1

Table IV

Changes in the flammability range in the presence of oxygen

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	3.9	36.3
1.2	43	3.4	39.6
1.2	46	4.6	41.4
2.2	40	5.4	38.1
2.2	43	3.8	41.4
2.2	46	4.9	42.3
3.2	40	6.3	37.9
3.2	43	7.1	41.5
3.2	46	4.2	42.1

Changes in the explosion range due to the presence of oxygen

The objective of the experiments was to state the effect of 5% by vol. oxygen on the lower and upper limit of the explosion range at different temperatures and flow rates. The results are presented in Table V.

These results show that the explosion range is somewhat narrower than the flammability range (cf. Table IV). The average values of the lower and upper limits are 5.4 and 29.4% by vol., respectively.

Table V

Changes in the explosion range in the presence of oxygen

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	4.3	29.1
1.2	43	4.9	31.3
1.2	46	6.1	28.3
2.2	40	5.3	32.1
2.2	43	4.9	30.3
2.2	46	5.8	27.1
3.2	40	6.3	26.9
3.2	43	5.9	29.8
3.2	46	4.8	30.9

Changes in the flammability range due to the presence of nitrogen

The objective of these experiments was to determine to what extent the flammability range could be reduced by the presence of nitrogen. 5% by vol. nitrogen were added from a flask to the evaporator. The results are shown in Table VI.

These results demonstrate that in the presence of nitrogen, the lower limit of the flammability range changes proportionally with temperature. This is, however, not the case for the upper flammability limit.

Table VI

Flammability range changes in the presence of nitrogen

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	5.8	33.2
1.2	43	7.4	31.1
1.2	46	7.9	34.3
2.2	40	6.1	30.8
2.2	43	7.2	33.6
2.2	46	7.9	35.8
3.2	40	6.3	32.3
3.2	43	5.8	34.1
3.2	46	7.9	31.6

The experiments also indicated that the presence of 5% by vol. nitrogen leads to a narrowing of the flammability range: the average lower and upper limits are 6.9 and 32.9% by volume, respectively.

Changes in the explosion range due to the presence of nitrogen

Experimental conditions were identical with those of the previous experiments, with the difference that a 12 V d.c. spark was used for ignition. The results are presented in Table VII.

The results show that the addition of 5% by vol. nitrogen significantly contributes to safety, since it results in an important narrowing of the explosion range: the average lower and upper limits are 9.1 and 26.7% by vol., respectively.

Table VII

Explosion range changes in the presence of nitrogen

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	9.3	26.8
1.2	43	8.4	24.3
1.2	46	8.8	28.2
2.2	40	10.3	25.7
2.2	43	9.1	30.1
2.2	46	7.8	26.9
3.2	40	8.9	28.3
3.2	43	11.1	25.7
3.2	46	8.3	24.5

Effect of water vapour on the flammability of methanol–air mixtures

The inhibiting effect of water vapour being well known, it appeared of interest to study its efficiency in the present case. The results obtained in the presence of 5% by vol. water vapour introduced into the evaporator system are presented in Table VIII.

The data indicate that in the presence of 5% by vol., water vapour the lower and upper flammability limits average at 9.1 and 29.2% by vol., respectively. This is equivalent to a reduction of the upper flammability limit by 10 to 15%.

Table VIII

Flammability range changes in the presence of water vapour

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	7.9	29.1
1.2	43	8.4	31.2
1.2	46	9.6	32.8
2.2	40	10.1	27.4
2.2	43	7.3	32.1
2.2	46	9.7	30.3
3.2	40	11.2	28.1
3.2	43	8.7	26.3
3.2	46	9.7	25.6

Effect of water vapour on the explosion range

Experimental conditions were similar to that in the previous experiments with the difference that 5% by vol. water vapour was added to the preheated air and introduced in this form into the evaporator system. A 16 V d.c. spark was used for ignition. Experimental results are listed in Table IX.

The results demonstrated that in the presence of 5% by vol. water vapour, the average lower and upper limits of the explosion range are 8.9 and 24.9% by vol., respectively.

Table IX

Explosion range changes in the presence of water vapour

Linear flow rate m/s	Temperature of evaporator, °C	Methanol concentration, % by vol.	
		lower limit	upper limit
1.2	40	8.2	24.1
1.2	43	9.3	26.3
1.2	46	8.9	28.2
2.2	40	7.3	23.6
2.2	43	9.8	27.1
2.2	46	6.4	22.6
3.2	40	10.3	26.7
3.2	43	9.1	23.8
3.2	46	11.2	21.9

Summary

The experimental results obtained allowed to state that the safety of the evaporator system could substantially be increased by providing for the temperature being kept at 43 ± 1°C. The upper limits of the flammability and explosion ranges, particularly in starting-up, breakdown and standstill periods, can substantially be reduced by adding 5 to 8 % by vol. nitrogen to the gas mixture.

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