Auto-ignition hazard of mixtures of ammonia, hydrogen, methane and air in a urea plant

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Abstract

The auto-ignition of $NH_3/CH_4/H_2$/air mixtures constitutes a hazard that is of much concern in urea plants. In this study, the auto-ignition behaviour of $NH_3/CH_4/H_2$/air mixtures is investigated experimentally for pressures up to 7500 kPa. The experiments were carried out in a closed spherical vessel with a volume of 8 dm^3. The concentration and the pressure dependence of the auto-ignition temperature (AIT) were determined for four types of mixtures: NH_3/air, NH_3/CH_4/air, NH_3/H_2/air and $NH_3/CH_4/H_2$/air. The most ignitable NH_3/air mixtures were situated between stoichiometry and the upper flammability limit. Small amounts of methane and hydrogen decrease the AIT of NH_3/air mixtures to a large extent. The pressure dependence of the AIT could be correlated by a Semenov relationship. For the multi-fuel mixtures, a distinct deviation from the Semenov correlation was observed at the lowest temperatures. With respect to the explosion hazard in urea plants, the experimental results were used to assess realistic AIT values in the pool reactor and the ammonia scrubber, operating at a pressure of 15 000 kPa. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In many chemical processes, combustible gases and vapours at high pressures and high temperatures are present. In order to evaluate the auto-ignition hazard involved and to ensure the safe and optimal operation of these processes, it is important to know the auto-ignition temperature (AIT) of the gas mixtures. The AIT values found in literature are usually determined according to standard test methods in small vessels and at atmospheric pressure

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(e.g. DIN 51795, ASTM-E 659-75 or BS 4056) [1,2]. However, since the AIT is not a constant but decreases with increasing pressures and increasing volumes, these AIT values are often not applicable to industrial environments [3–6]. Furthermore, most available AIT data refer to single-component fuels, while information on multi-component fuels is scarce [7–9].

In this study, attention is focused on the auto-ignition hazard inside a urea plant. In the ammonia scrubber and the pool reactor of the plant, mixtures of ammonia, methane, hydrogen and air are exposed to a temperature of 150 °C and a pressure of 15 000 kPa. The maximum methane and hydrogen concentrations have been calculated to be 10 and 20 mol%, respectively. In order to evaluate these mixtures as to their auto-ignition characteristics, the AIT of NH_3/air mixtures is determined experimentally for pressures up to 7500 kPa and for concentrations ranging from 20 to 80 mol%. The effects of limited methane and hydrogen additions are also investigated. Simple scaling rules are used to estimate AIT values for the existing mixtures inside the urea plant.

2. Experimental apparatus and procedure

The experimental apparatus, illustrated in Fig. 1, consists of four major parts. The first part is the mixture preparation system, which is used to produce homogeneous mixtures of a desired composition. To do this, two different filling methods have been used, i.e. the constant flow method and the partial filling method. Homogeneous mixtures of two components, e.g. NH_3/air mixtures, are produced with the constant flow method. The flow rates of air and ammonia are controlled by a thermal mass flow controller and by a volumetric membrane pump, respectively. In the evaporator, the separate flows are mixed to obtain a homogeneous gas mixture. Downstream the evaporator, the total system is kept at a constant temperature of 150 °C to avoid condensation of ammonia. Homogeneous gas mixtures of
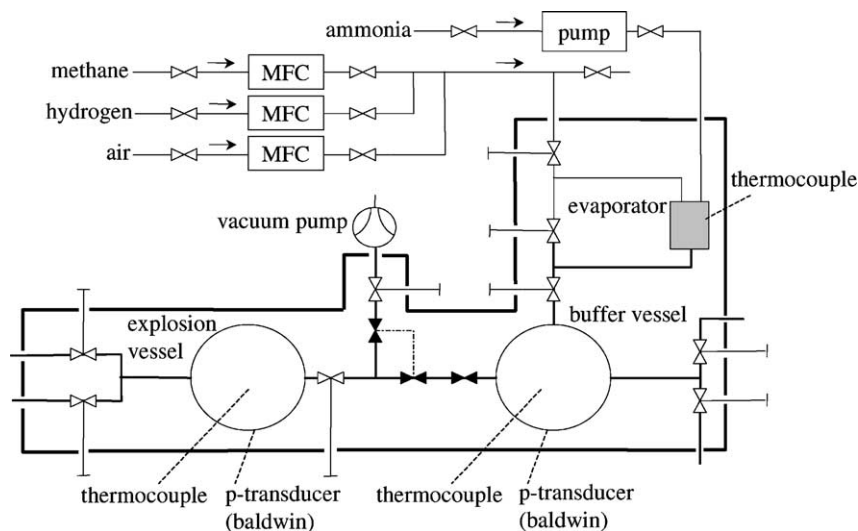

Fig. 1. Experimental apparatus.

more than two components are produced with the partial filling method. The partial pressures for the different components are calculated for each desired composition and pressure. In succession, the different components are led through the evaporator and flow into the buffer vessel, which is the second part of the apparatus. The buffer vessel is used to maintain the premixed reactants at a high pressure (up to 15 000 kPa) and at a temperature of 150 °C. It has a volume of 8 dm^3 and can withstand pressures up to 350 MPa. When the partial filling method is applied, the buffer vessel is provided with a special filling lance to ensure the homogeneity of the mixture. The explosion vessel is the third and most important part of the apparatus. This spherical vessel has a volume of 8 dm^3 and is designed to withstand explosion pressures up to 25 000 kPa at temperatures up to 550 °C. The vessel is kept at the desired temperature by three electric heating units equipped with automatic temperature control. The explosion vessel is connected to the buffer vessel by means of a valved supply line. The last part of the apparatus consists of a data acquisition system. The pressures in both vessels are measured with Baldwin 5000 psi strain gauges, while the temperature rises during the tests are measured with Cr/Al thermocouples placed in the centre of the vessel. All signals are analysed and recorded on a computer.

To determine the auto-ignition limits, the following test procedure has been used. At the beginning of a test series, the temperature of the explosion vessel is set at the desired value. A homogeneous mixture of a desired composition and pressure is produced in the buffer vessel. After the explosion vessel has been evacuated, the gas mixture is transferred from the buffer vessel to the explosion vessel till the required pressure is reached. The pressure and temperature variations in the explosion vessel are monitored during maximum 15 min. Finally, the explosion vessel is evacuated and another test is conducted at a different pressure. For each test series, a gas sample is taken from the buffer vessel and is analysed in a gas chromatograph (relative error 1%). The occurrence of an auto-ignition is judged from the pressure and temperature histories (e.g. Fig. 2). When the temperature rise is smaller than 50 °C and no pressure increase is observed, the attempt is considered unsuccessful. A temperature rise larger than 50 °C accompanied with a pressure increase is classified as an auto-ignition.
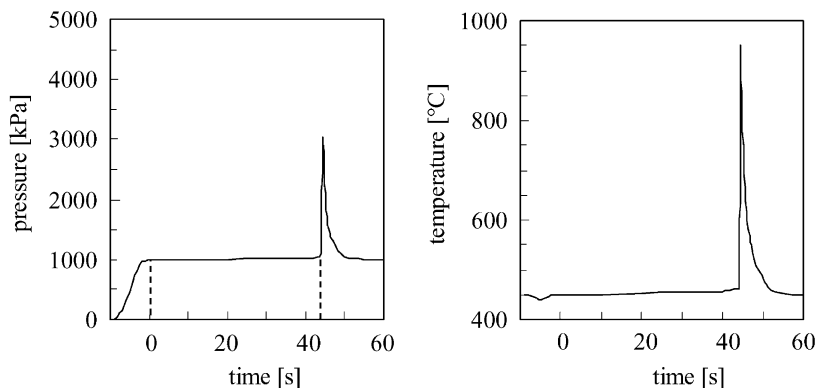

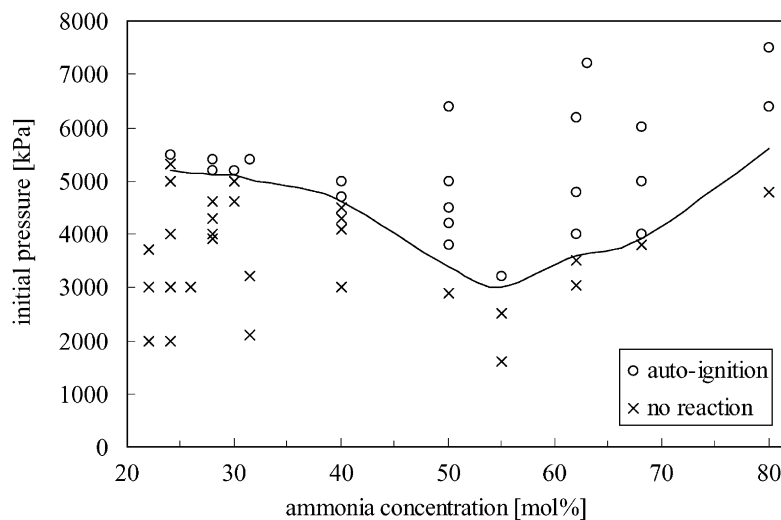Fig. 2. Recorded pressure (a) and temperature (b) histories in the explosion vessel.

Fig. 3. The auto-ignition region of NH_3/air mixtures at 550 °C.

3. Experimental results

3.1. NH_3/air mixtures

A first series of experiments aimed at identifying the mixture composition which is most sensitive to auto-ignition. To do this, the auto-ignition limit of NH_3/air mixtures was measured at a constant temperature of 550 °C, being the maximum temperature of the apparatus. The results are summarised in Fig. 3. The solid line in Fig. 3 represents the pressure limit beyond which auto-ignition occurs. The most ignitable mixture composition is found to be about 50 mol% ammonia in air. This observation is in good agreement with the results of previous studies, which show that the AIT for many compounds is found at concentrations 2–3 times the stoichiometric value [3,10].

As a next step, the pressure dependence of the AIT was determined for the mixture composition most sensitive to auto-ignition. Due to pressure limitations of the apparatus, the auto-ignition limit could only be measured at 525 and 550 °C. Fig. 4 shows the measured auto-ignition limit at these two temperatures together with the AIT value at atmospheric pressure [11]. As can be seen from Fig. 4, the pressure limit for auto-ignition increases with decreasing initial temperatures. This also implies that high pressures lead to lower AIT values. However, the effect of the pressure on the AIT is rather small, e.g. the AIT decreases with only 25 °C when the pressure is raised from 3400 to 7200 kPa.

3.2. NH_3/CH_4/air mixtures

The influence of methane on the auto-ignition limit of NH_3/air mixtures was studied for methane concentrations up to 10 mol%. Preliminary experiments already indicated that

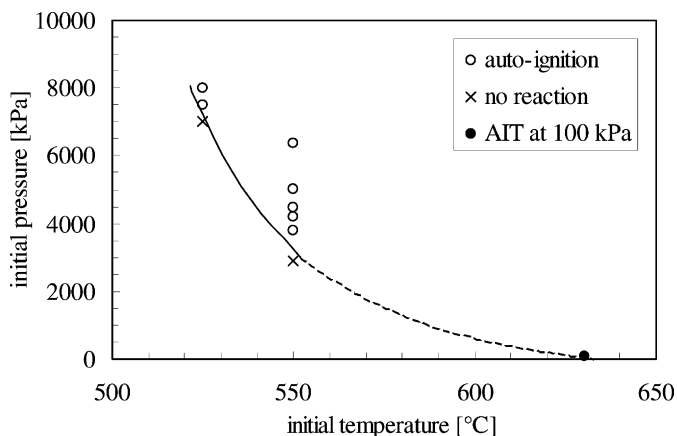Fig. 4. The auto-ignition limit of NH_3/air mixtures as a function of the initial temperature, determined for 50 mol% ammonia in air.

small fractions of methane in ammonia lower the AIT with more than 100 °C. First the auto-ignition limit of NH_3/air mixtures with 5 mol% methane was measured at an initial temperature of 450 °C. In contrast with the results of pure NH_3/air mixtures, the auto-ignition limit exhibits a minimum in the lean fuel range, as shown in Fig. 5. A mixture with an ammonia concentration of 5 mol% is the most ignitable. It has a minimum ignition pressure of 250 kPa. In a second set of experiments, the dependence of the auto-ignition limit on the methane concentration was investigated. The auto-ignition limits of NH_3/air mixtures with 2.5, 5 and 10 mol% methane are compared in Fig. 6. It is found that the auto-ignition limit decreases with increasing methane concentrations. In the investigated range, the mixture composition most sensitive to auto-ignition was found to be 5 mol% ammonia and 10 mol% methane in air.
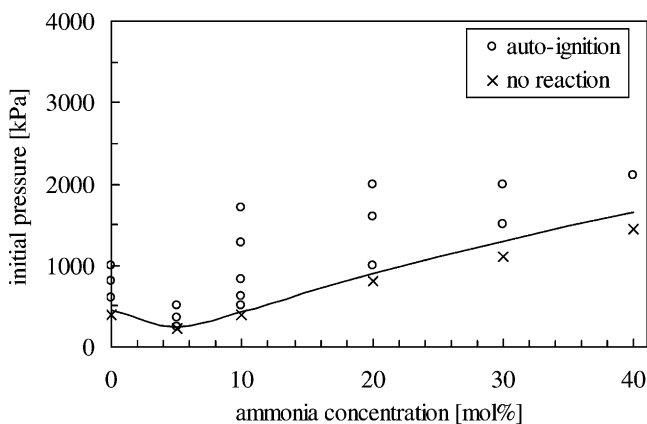

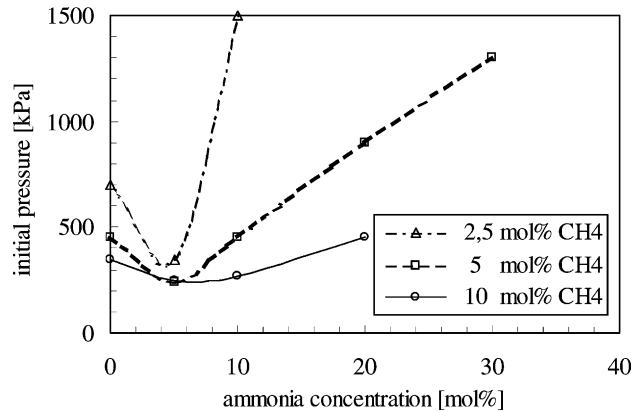Fig. 5. The auto-ignition region of NH_3/air mixtures with 5 mol% methane at 450 °C.

Fig. 6. The auto-ignition limits of NH_3/air mixtures with different methane fractions, determined at an initial temperature of 450 °C.

The effect of the initial pressure on the AIT of NH_3/CH_4/air mixtures was determined for the most ignitable mixture composition. Fig. 7 shows the auto-ignition limit measured at various initial temperatures between 395 and 450 °C. Again, the AIT decreases with increasing pressure, but tends to level off at about 1000 kPa. This could suggest that for these mixtures, auto-ignition is governed by a high-temperature branch at pressures below 1000 kPa, whereas at pressures above 1000 kPa it is governed by a low-temperature branch [4,5,12].

3.3. NH_3/H_2/air mixtures

The influence of hydrogen on the auto-ignition limit of NH_3/air mixtures was investigated for hydrogen concentrations up to 20 mol%. Also here preliminary experiments indicated

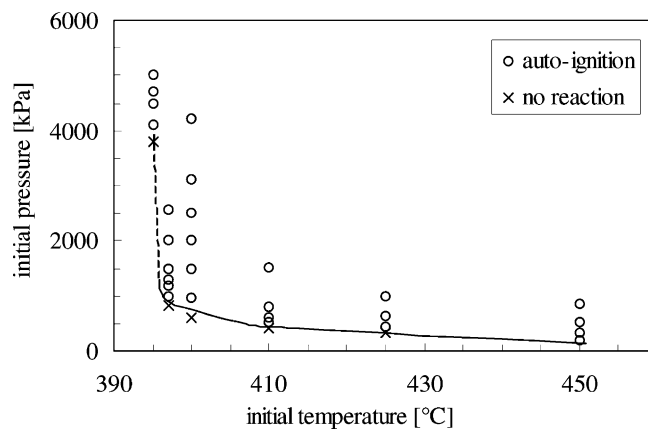Fig. 7. The auto-ignition limit of NH_3/CH_4/air mixtures as a function of the initial temperature, determined for 5 mol% ammonia and 10 mol% methane in air.

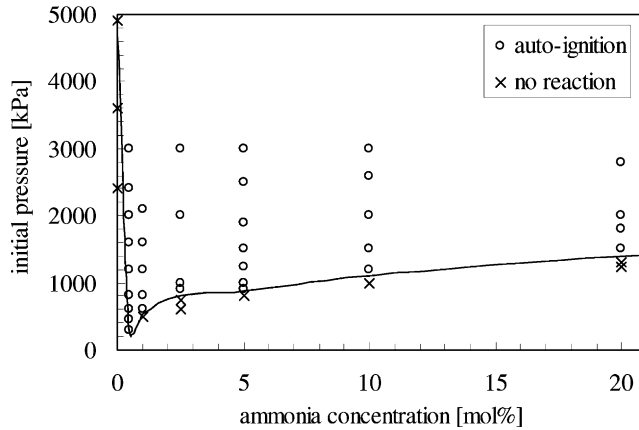Fig. 8. The auto-ignition limit of NH$_3$/air mixtures with 5 mol% hydrogen at 450 °C.

that small fractions of hydrogen in ammonia lower the AIT with more than 100 °C. First the auto-ignition limit of NH$_3$/air mixtures with 5 mol% hydrogen was measured at an initial temperature of 450 °C. The results are presented in Fig. 8. They are similar to those of NH$_3$/CH$_4$/air mixtures, i.e. the auto-ignition limit exhibits a minimum in the lean fuel range. A mixture with an ammonia concentration of only 1 mol% is the most ignitable. A second set of experiments was conducted to determine the influence of the hydrogen concentration on the auto-ignition limit. The auto-ignition limits of NH$_3$/air mixtures with 2.5, 5, 10 and 20 mol% hydrogen are compared in Fig. 9(a) and (b). The auto-ignition limit of mixtures with 20 mol% hydrogen could not be measured accurately at 450 °C and was therefore determined at 425 °C. It can be seen from Fig. 9(a) and (b) that the auto-ignition limit decreases with increasing hydrogen concentrations. Mixtures with a
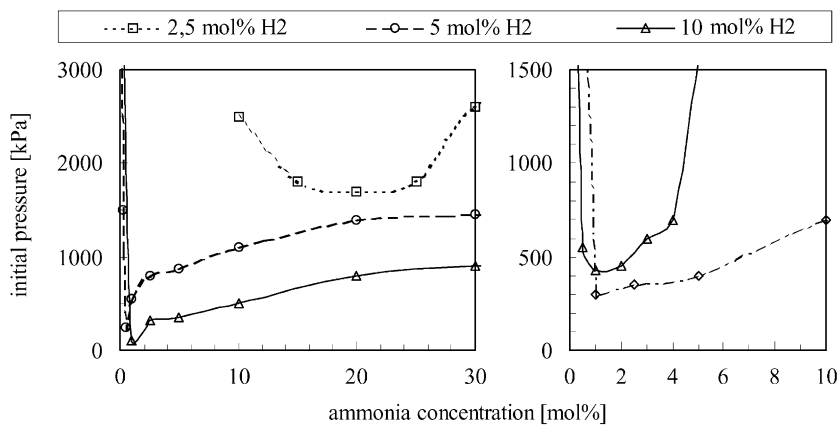
Fig. 9. The auto-ignition limits of NH$_3$/air mixtures with different hydrogen fractions, determined at (a) 450 °C and (b) 425 °C.
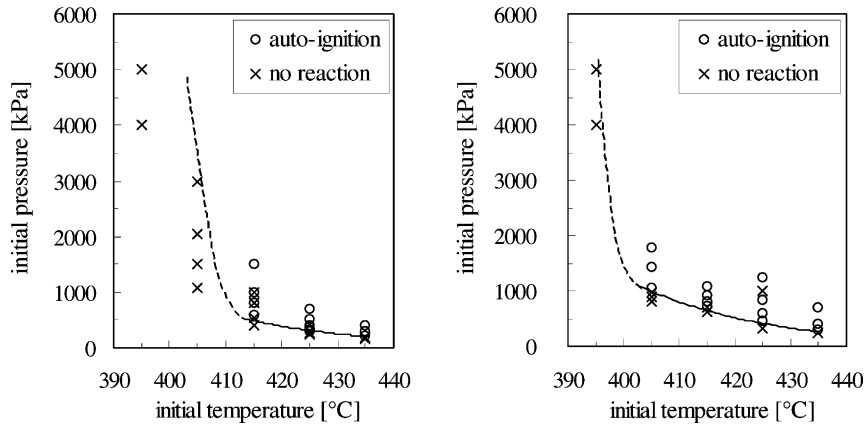
Fig. 10. The auto-ignition limit of NH_3/H_2/air mixtures as a function of the initial temperature, determined for (a) 1 mol% NH_3 and 20 mol% H_2 in air, and (b) 5 mol% NH_3 and 20 mol% H_2 in air.

hydrogen concentration of 20 mol% and an ammonia concentration between 1 and 5 mol% show the highest ignitability in the investigated range.

The effect of the initial pressure on the AIT of NH_3/H_2/air mixtures was determined for two mixture compositions: 1 mol% NH_3 and 20 mol% H_2 in air (a) and 5 mol% NH_3 and 20 mol% H_2 in air (b). Fig. 10(a) and (b) show the auto-ignition limits of both mixtures, measured at various initial temperatures between 395 and 435 °C. For a mixture with 5 mol% NH_3 and 20 mol% H_2 in air (Fig. 10(b)), the AIT decreases with increasing pressure, but again tends to level off at about 1000 kPa. For a mixture with 1 mol% NH_3 and 20 mol% H_2 in air (Fig. 10(a)), the AIT levels off at an even lower pressure.

3.4. $NH_3/CH_4/H_2$/air mixtures

Finally, the combined influence of both methane and hydrogen on the auto-ignition limit of NH_3/air mixtures was investigated. To reduce the number of experiments, only two
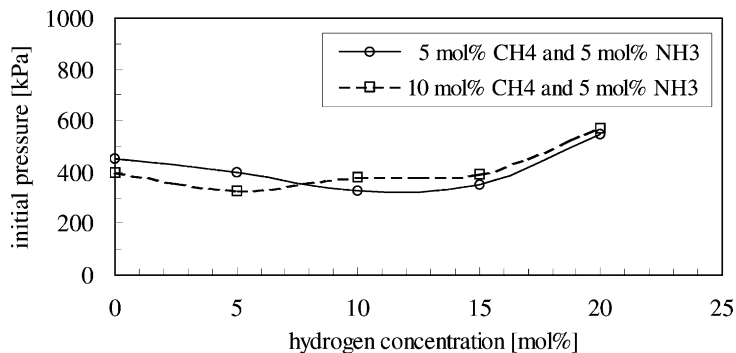

Fig. 11. The auto-ignition limits of $NH_3/CH_4/H_2$/air mixtures as a function of the hydrogen concentration, determined at 425 °C.
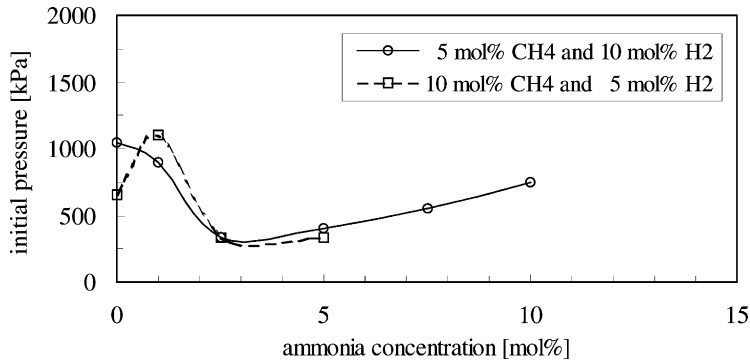
Fig. 12. The auto-ignition limits of $NH_3/CH_4/H_2$/air mixtures as a function of the ammonia concentration, determined at 425 °C.

different methane concentrations were considered, i.e. 5 and 10 mol%. A first series of experiments was conducted at an initial temperature of 425 °C and aimed at identifying the most ignitable mixture composition. This was done in two steps. First, the auto-ignition limit of $NH_3/CH_4/H_2$/air mixtures was determined as a function of the hydrogen concentration, assuming a constant ammonia concentration (5 mol%) and a constant methane concentration (5 or 10 mol%). As can be seen in Fig. 11, the auto-ignition limit is little dependent on the hydrogen concentration. For mixtures with 5 mol% methane and 5 mol% ammonia, the lowest ignition pressure is obtained for a hydrogen concentration of 10 mol%. Whereas for mixtures with 10 mol% methane and 5 mol% ammonia, the lowest ignition pressure is found for a hydrogen concentration of 5 mol%. As a next step, the influence of the ammonia concentration on the auto-ignition limit of $NH_3/CH_4/H_2$/air mixtures was determined, keeping the methane and the hydrogen concentration constant. The results are presented

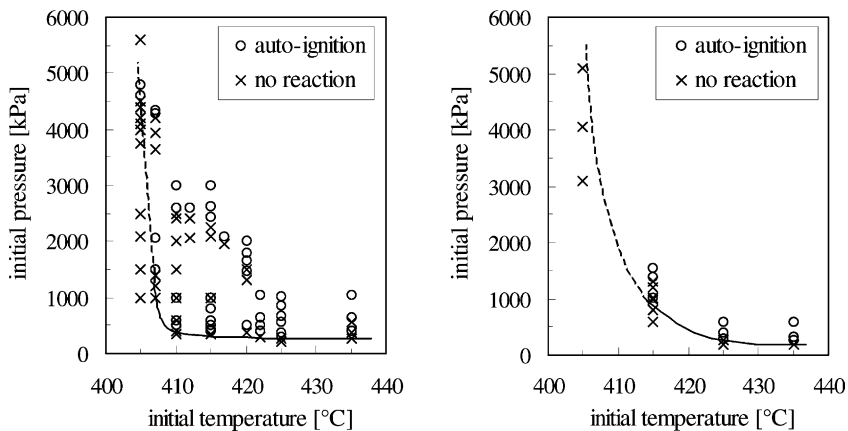Fig. 13. The auto-ignition limit of $NH_3/CH_4/H_2$/air mixtures as a function of the initial temperature, determined for (a) 2.5 mol% NH_3, 5 mol% CH_4 and 10 mol% H_2 in air, and (b) 2.5 mol% NH_3, 10 mol% CH_4 and 5 mol% H_2 in air.

in Fig. 12. A minimum ignition pressure of 330 kPa is obtained for an ammonia concentration of 2.5 mol%. At an initial temperature of 425 °C, two mixture compositions show the highest ignitability in the investigated concentration range: 5 mol% CH_4, 10 mol% H_2, 2.5 mol% NH_3 in air (a) and 10 mol% CH_4, 5 mol% H_2, 2.5 mol% NH_3 in air (b).

In a second set of experiments, the pressure dependence of the AIT was determined for the most ignitable mixture compositions. Fig. 13 shows the auto-ignition limit as a function of the initial temperature for a mixture with 5 mol% CH_4, 10 mol% H_2 and 2.5 mol% NH_3 in air (a) and for a mixture with 10 mol% CH_4, 5 mol% H_2 and 2.5 mol% NH_3 in air (b). In the investigated temperature range, it is demonstrated that the auto-ignition limit of Fig. 13(a) is lower than the auto-ignition limit of Fig. 13(b). Again, the AIT decreases with increasing pressures, and tends to level off at a pressure of about 1000 kPa.

4. Extrapolation to plant conditions

Due to practical considerations, the AIT values could only be obtained for limited pressures in a vessel with a volume of 8 dm^3. In order to apply the measured AIT data to full-scale urea plants, extrapolation is needed.

4.1. Extrapolation to plant pressures

The pressure dependence of the AIT could only be established for pressures up to 7500 kPa. The experimental results can be extrapolated to plant pressures by means of the so-called Semenov correlation [5,13]. Based on the thermal ignition theory, Semenov derived the following relationship between the AIT and the initial pressure:

$$\ln\left(\frac{p}{T}\right) = A\frac{1}{T} + B \tag{1}$$

where p is the initial pressure (Pa) and T the AIT (K).

Eq. (1) can be plotted as a straight line in a $\ln(p/T)$ versus $1/T$ diagram. The Semenov plots of the investigated mixtures are presented in Fig. 14. The linearity of the plots confirms the validity of the Semenov correlation. The plots of the multi-fuel mixtures show a distinct deviation from the linear behaviour at the low-temperature end of the experimental range. A possible explanation can be found in the transition from high-temperature branch to low-temperature branch at these specific conditions. The constants A and B of Eq. (1) were determined by the method of the least-squares for the linear section of the plots and are listed in Table 1. Eq. (1) was used to estimate AIT values at pressures above 7500 kPa. Calculated AIT values are listed in Table 2 for pressures up to 16 500 kPa, being the maximum pressure that can arise in a urea plant during abnormal operation.

4.2. Extrapolation to plant volumes

Unfortunately, the effect of the vessel volume on the AIT could not be determined experimentally. Instead, calculations were made based on two existing correlations, i.e. the Beerbower correlation [14] and the Semenov correlation [5,13].
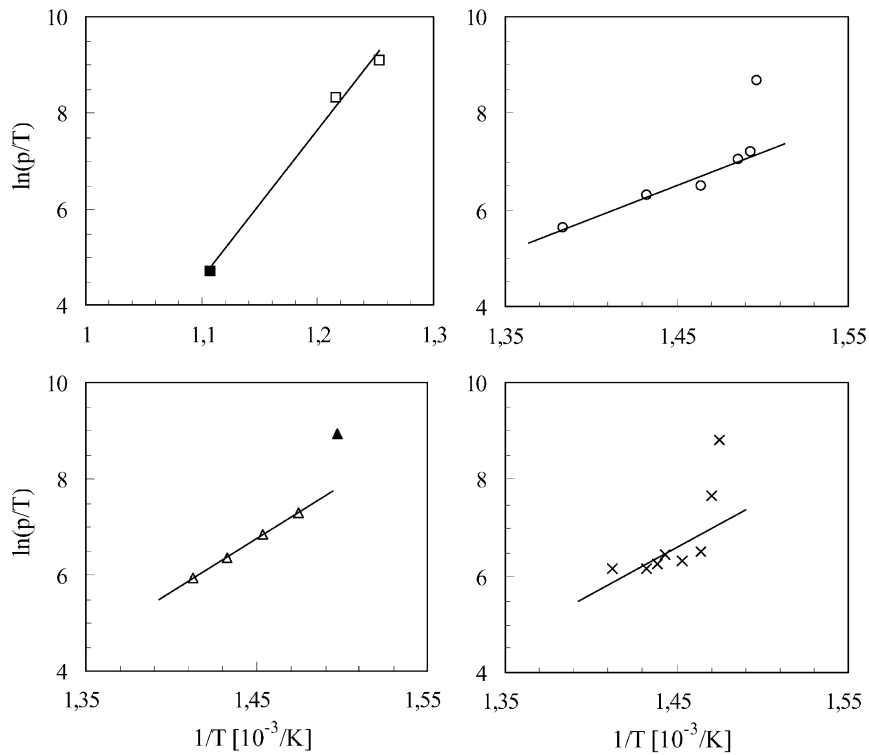
Fig. 14. Semenov plots for: (a) NH_3/air (50:50); (b) NH_3/CH_4/air (5:10:85); (c) NH_3/H_2/air (5:20:75); (d) NH_3/CH_4/H_2/air (2.5:5:10:82.5).

Table 1
Values for the constants *A* and *B* of Eq. (1)

	A	*B*
NH_3/air	30950	−29.5
NH_3/CH_4/air	13850	−13.6
NH_3/H_2/air	21900	−25.0
NH_3/CH_4/H_2/air	19400	−21.6

Table 2
Calculated AIT values (°C) at different initial pressures, based on the Semenov correlation

	AIT values (°C)			
	10 000 kPa	12 500 kPa	15 000 kPa	16 500 kPa
NH_3/air	522	517	513	511
NH_3/CH_4/air	321	315	310	308
NH_3/H_2/air	359	355	351	349
NH_3/CH_4/H_2/air	348	344	340	338

Table 3
Calculated AIT values (°C) at 16 500 kPa for different vessel volumes, based on the Beerbower correlation

	AIT values (°C)			
	$8\,dm^3$	$120\,dm^3$	$1.42\,m^3$	$7.1\,m^3$
NH_3/air	511	465	423	395
$NH_3/CH_4/air$	308	283	261	246
$NH_3/H_2/air$	349	320	293	276
$NH_3/CH_4/H_2/air$	338	310	285	268

The Beerbower correlation is a simple empirical correlation, which gives reasonably good AIT values that are on the safe side. Beerbower noticed that for a large number of fuels plots of the AIT versus the logarithm of the vessel volume tended to be straight lines, which converge to an AIT value of 75 °C in a volume of $10^{12}\,dm^3$. So the AIT values for different volumes can be calculated from a known AIT value according to Eq. (2). Table 3 gives the estimated AITs for different volumes of interest in a urea plant, i.e. $120\,dm^3$ (volume of the exhaust pipe of the scrubber), $1.42\,m^3$ (volume of one compartment of the pool reactor) and $7.1\,m^3$ (total volume of five compartments of the pool reactor):

$$T_2 = \frac{T_1 - 75}{\log V_1 - 12} \log V_2 + \left[75 - \frac{T_1 - 75}{\log V_1 - 12} \times 12\right] \tag{2}$$

where T_i is the AIT (°C) and V_i the vessel volume (dm^3).

A second correlation for the volume dependence of the AIT is based on the theory of thermal ignition. Semenov derived that AIT is a function of the surface to volume ratio of the vessel. For spherical vessels, it is a function of the vessel diameter only. The relation between the AIT and the vessel diameter is given by the following expression:

$$\ln\left(\frac{p}{T}\right) = A\frac{1}{T} + B' + \ln\left(\frac{1}{d}\right) \tag{3}$$

where p is the initial pressure (Pa), T the AIT (K) and d the vessel diameter (m).

The constants A and B' can be calculated from the constants of Eq. (1) and are listed in Table 4. Eq. (3) was used to estimate AIT values for different volumes of interest in a urea plant. The calculated values are summarised in Table 5.

Table 4
Values for the constants A and B' of Eq. (3)

	A	B'
NH_3/air	30950	−30.9
$NH_3/CH_4/air$	13850	−15.0
$NH_3/H_2/air$	21900	−26.4
$NH_3/CH_4/H_2/air$	19400	−23.0

Table 5
Calculated AIT values (°C) at 16 500 kPa for different vessel volumes, based on the Semenov correlation

	AIT values (°C)			
	8 dm^3	120 dm^3	1.42 m^3	7.1 m^3
NH$_3$/air	511	493	478	468
NH$_3$/CH$_4$/air	308	286	267	255
NH$_3$/H$_2$/air	349	333	320	311
NH$_3$/CH$_4$/H$_2$/air	338	321	306	296

4.3. Discussion

As the AIT decreases when the pressure and the volume of the gas increases, the lowest and thereby most critical AIT values are found for a volume of 7.1 m^3 and a pressure of 16 500 kPa. These values are found in the last column of Tables 3 and 5.

Comparing these data shows that the estimated AIT values obtained from the Beerbower correlation (Table 3) are lower than the values obtained from the Semenov correlation (Table 5). Consequently, the lowest value in Table 3 (246 °C) corresponds with the most critical AIT value in a urea plant. Although this AIT value is obtained by means of a strong extrapolation, it can be considered as a conservative value, because of the following reasons:

- The extrapolation to plant pressures is based on the linear section of the Semenov plots, which corresponds with the low-pressure measurements (100–1000 kPa). However, the experiments with the multi-fuel mixtures show that the AIT tends to level of at higher pressures. The Semenov correlation based on the low-pressure measurements will therefore give underestimated AIT values.
- The AIT is determined in air, whereas the oxygen to nitrogen ratio in a urea plant is 19/81. Furthermore, the mixtures in a urea plant contain considerable fractions of water and carbon dioxide so that the oxygen to inert ratio is even lower than 19/81.
- The AIT is determined in a spherical vessel, which gives the lowest AIT value according to the Semenov theory. In vessels with a higher surface to volume ratio, e.g. the cylindrical pool reactor, the AIT value is expected to be higher.
- Auto-ignition will only appear in the vapour containing fraction of the pool reactor. As the pool reactor is mainly filled with liquid, the vapour containing fraction will be much smaller than the total volume of 7.1 m^3.

Finally, as the maximum temperature in a urea plant is 185 °C, which is lower than the calculated AIT, direct auto-ignition will most probably not occur in a urea plant.

5. Conclusion

In order to evaluate the auto-ignition hazard in urea plants, experiments were conducted to define the auto-ignition limits of NH$_3$/CH$_4$/H$_2$/air mixtures. The auto-ignition limits were measured for pressures up to 7500 kPa and temperatures up to 550 °C, using a 8 dm^3 spherical vessel. The experimental results were used to estimate AIT values in the pool

reactor and the ammonia scrubber of a urea plant. The estimated values were achieved by extrapolation using the Semenov correlation and the Beerbower relationship. The lowest AIT for the existing mixtures inside the urea plant is calculated to be 246 °C, which is higher than the maximum temperature in the plant. Based on these calculations, it was concluded that direct auto-ignition is unlikely to occur in urea plants.

References

[1] B.P. Mullins, Spontaneous Ignition of Liquid Fuels, Butterworths, London, 1955.
[2] BS 4056: Method of Test for Ignition Temperature of Gases and Vapours, British Standard Institution, 1966.
[3] M. Caron, M. Goethals, G. De Smedt, J. Berghmans, S. Vliegen, E. van 't Oost, A. van den Aarssen, J. Hazard. Mater. 65 (1999) 233.
[4] M.R. Chandraratna, J.F. Griffiths, Combust. Flame 99 (1994) 626.
[5] J.U. Steinle, E.U. Franck, Ber. Bunsenges. Phys. Chem. 99 (1995) 66.
[6] T.J. Snee, Loss Prev. Bull. 81 (1988) 25.
[7] D. Kong, R.K. Eckhoff, F. Alfert, J. Hazard. Mater. 40 (1995) 69.
[8] J.F. Griffiths, D. Coppersthwaite, C.H. Phillips, C.K. Westbrook, W.J. Pitz, In: Proceedings of the 23th International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1990, pp. 1745.
[9] C.F. Cullis, C.D. Foster, Combust. Flame 23 (1974) 347.
[10] N.P. Setchkin, J. Res. Nat. Bur. Stand. Res. Pap. 2516 53 (1954) 49.
[11] J. Bond, Sources of Ignition, Flammability Characteristics of Chemicals and Products, Butterworths–Heinemann, Oxford, 1991.
[12] G.M. Panchenkov, V.V. Malyshev, V.V. Makarenkov, et al., Russ. J. Phys. Chem. 46 (1972) 1303.
[13] I. Glassman, Combustion, 2nd Edition, Academic Press, Orlando, FL, 1987.
[14] R.D. Coffee, Chem. Eng. Prog. Loss Prev. 13 (1980) 74.