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Investigations of Deflagration in a Four-Litre-Autoclave under Atmospheric and Non-Atmospheric Conditions

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A four-litre-autoclave was used to perform deflagration tests in a closed vessel. The aim was to investigate the suitability of this autoclave and to evaluate different parameters influencing the deflagration.

The validation of test results showed that the autoclave is suited for the performance of deflagration tests.

In comparison to tests performed in an open system according to VDI 2263-1 the results are in good agreement. In the closed vessel same characteristics as in the open test were determined. In addition, pressure rise and rate of pressure rise have been determined and used to characterise deflagrations.

The influence of sample weight, tube diameter, bulk density, initial pressure and temperature was investigated. Furthermore, the emerging gas amount and the rate of gas evolution were determined and compared with pressure curves. The use of a four-litre-autoclave for performing deflagration tests offers several advantages in comparison to an open test.

1. Introduction

Deflagrations are recurring causes for safety relevant occurrences in chemical industry. They often lead to injuries and destruction of buildings, and therefore losses of millions. That is why the deflagration capability of chemicals is an important feature that has to be considered in terms of chemical safety engineering.

According to TRAS 410 (Kommission für Anlagensicherheit, 2012), deflagration is a reaction of a given amount of substance, which can be started locally and which is propagating from this point on its own through the whole substance in shape of a reaction front. The propagating velocity of this front is smaller than the velocity of sound in the substance. High amounts of gases can be released, which may be burnable. The deflagration velocity rises with temperature and often also with pressure (Kommission für Anlagensicherheit, 2012). A special characteristic of deflagration is, that it can propagate without the presence of oxygen (Zwahlen, 1988). That leads to problems concerning the design of protective measures. For example inerting, a widely applied safety function, is ineffective in order to prevent a deflagration (Steinbach, 1995).

That is why the capability of deflagration has to be considered accurately during the performance of safety appraisals. For evaluation of deflagration capability, some test methods (C.1- and C.2-Test) are described in the UN manual of tests and criteria (United Nations, 2009) and in VDI 2263-1, part 1.6 “Deflagration” (Verein Deutscher Ingenieure, 1990).

Besides this kind of standard methods, some more methods are described in literature. Klais and Niemitz (1996) worked with autoclaves of 0.2 L to 0.75 L volume where the ignition is initiated with a melting wire. Badly igniting substances are covered with a 1:1 mixture of silicon and lead dioxide to be ignited. The authors suggest to describe the deflagration velocity q as a function of pressure p. This equation is known from rocket science, where deflagrating substances are used as a propellant.

$$q = a \cdot p^n + b \tag{1}$$

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Being b negligible and n is a positive real number, the deflagration velocity rises exponentially with increasing pressure. Antelmann (2001) examined the relation between weighted sample and maximum pressure, respectively maximum of pressure rise. She states that a higher initial weight leads to higher maximum pressure, respectively maximum of pressure rise, but it is not clear yet if the relationship is linear or potential.

This paper presents a new test method with an autoclave and a similar set up like in VDI 2263-1. First results are shown and compared with results obtained from VDI-test.

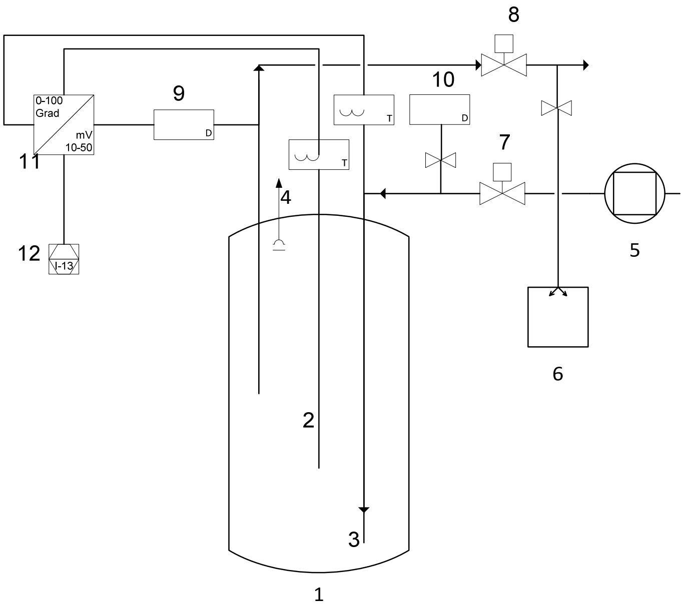
The investigation of deflagrations in closed systems has several advantages in comparison to open systems. First of all, the possibility of pressure measurement delivers additional characteristics like the maximum pressure and the maximum/averaged rate of pressure rise, which can be used to describe the velocity and the consequences of a deflagration (regarding pressure rise). Using a closed vessel and a gas meter one can also determine the emerged gas amount and the rate of gas emerging. Furthermore, an autoclave can easily be used to work with different gas atmospheres. Testing under higher or reduced initial pressure or in an atmosphere of nitrogen or oxygen is possible. Lastly, an autoclave is suited for the investigation of practical conditions. Production scale problems can be evaluated in lab scale using an autoclave.

2. Experimental

The aim in constructing the autoclave was, to have a comparable set up to the open test from VDI 2263-1. That means a tube with closed bottom is used, where the test substance is filled in. During measurement the tube is hanging at the lid of the vessel. A glow plug is used for ignition. The experimental set up of the four-litre-autoclave is shown in Figure 1.

A cylindrical autoclave with an inner volume of four litres is used, which can withstand a maximum pressure of 400 bar. It is installed on a vertically adjustable table fixed at a carriage, so that it can be moved easily. The lid is fixed at a holder which is installed at the upper end of the carriage. It is never moved so that sensors and pipes can remain in the same position at every experiment. To close the autoclave, the vessel is moved upwards and connected with the lid.

At the lid the gas in- and outlets, thermocouples, the construction for ignition and a rupture disc are placed. ¼''-pipes with Swagelok-fittings are used to lead gases into the autoclave and out of it. The remote controlled valves are located at the end of the pipes. At the gas outlet-pipe, a piezoresistive pressure sensor (Keller AG) is placed, which has a range between 0 bar and 200 bar, an exactness of 0.1 bar and a responding time of 10 ms. The signal is registered with a piezoresistive amplifier (Kistler Instrumente AG).



1) Autoclave with heating jacket
2) Thermocouples T1, T2, T3 (inside the tube)
3) Thermocouple outside the tube (T autoclave)
4) Rupture disc
5) Compressor
6) Vacuum pump
7) Remote controlled valve in
8) Remote controlled valve out
9) Pressure sensor
10) Vacuum Manometer
11) A/D converter
12) Computer

Figure 1: Experimental set up of 4-L-autoclave

To perform an experiment, the tube is filled with a weighted amount of substance and it is hung up at the lid of the autoclave. During hanging the tube up, three thermocouples are put inside the tube and placed centric at varying elevations. The first thermocouple (T1) measures the temperature at a height of 4.5 cm, the second one (T2) at a height of 6.5 cm and the third one (T3) at a height of 8.5 cm, determined from the bottom of the tube. Another thermocouple is installed to measure the temperature inside the autoclave but outside the tube. The position of all thermocouples is fix and not varied between experiments.

The signals of the thermocouples and of the pressure sensor are registered with a computer after A/D conversion.

For analyzing the experiments, five characteristics are determined. These are the induction time what is the time from switching on the glow plug until the start of the reaction. Therefore the temperature curve of T1 is considered and the point of the first temperature rise is defined by Eq(2).

$$\text{s(point of 1st temperature rise)}=\frac{1}{2}\left[\text{s(basis line)}+\text{s(maximum)}\right] \tag{2}$$

It is the point at which the slope s of the tangent equals half times the sum of the slope of the basis line and the maximum slope. In order to check if the rise of temperature is really reflecting a starting and self propagating reaction, it has to be made sure that there is also a pressure rise within the same time interval. The second characteristic is the maximum pressure that is determined directly from measured data. Thirdly, the deflagration velocity is determined from the staggered temperature signals. Finally, the rates of pressure and temperature rise are determined by evaluating the slope of the pressure and temperature curves. For determining the maximum rates, the maximum slope of the curves is considered and for determining the average slope, a linear slope is considered from 20 % to 80 % of the maximum value of pressure or temperature.

3. Results

3.1 Validation

The reproducibility in the closed vessel is tested by performing 20 measurements with identical parameters. 85 g of Azodicarboxamide (ADCA) is used and filled into the tube up to a height of 9 cm for all experiments. In this way, a bulk density of 0.52 g/cm³ is obtained. The values of mean and standard deviation for every characteristic in the closed test are shown in Table 1.

The induction time and the maximum pressure are sufficiently reproducible. Standard deviations of 4 s respectively 1 bar are precisely enough to describe deflagrations of different substances that usually vary in a range of several minutes and bar.

Other characteristics, especially the deflagration velocity and the rate of pressure rise, are afflicted with a high standard deviation. During decomposition the emerging gases build coincidental channels and bubbles inside the packed bed causing variations regarding deflagration velocity and rate of pressure/temperature rise.

This problem concerning rising gases also occurs in tests according to VDI 2263-1. Generally it occurs when the substance is ignited from below and therefore emerging gases flow through the packed bed. It does not occur when the sample is ignited from above, because released gases rise upwards without flowing through the substance. That is why experiments ignited from above show better reproducibility in general. Nonetheless there is a great interest in igniting from below because hot gases are warming up the sample and therefore it is more likely that there will be a deflagration. Furthermore this case is rather typical for deflagrations that occur under practical conditions. (Grewer, 1994)

Table 1: Comparison of test results with ADCA obtained in closed and open test

	Closed			**Open**		
Characteristic	Mean	Standard deviation	Relative variation from mean [%]	Mean	Standard deviation	Relative variation from mean [%]
Induction time [s]	22	4	20	28	2	8
Deflagration velocity [mm/s]	13	8	58	12	7	62
Maximum pressure [bar]	18	1	6			
Maximum rate of pressure rise [bar/s]	5	3	66			
Averaged rate of pressure rise [bar/s]	4	3	79			
Maximum rate of temperature rise [°C/s]	48	16	33	24	7	29
Averaged rate of temperature rise [°C/s]	37	11	31	16	6	38

3.2 Comparison with open test according to VDI 2263-1

After having tested the reproducibility of the experiments in the closed vessel, the test results obtained in closed (four-litre-autoclave) and open (VDI 2263-1) apparatus are compared to each other. Therefore these results are also included in Table 1. There are similarities and differences looking at the characteristics. The induction time lies in the same range for both tests, whereby in the open test, it is about 6 s longer than in the closed one. This might be because of differences in heat transfer. The autoclave is a closed system where there is possibly no convection inside. Therefore heat losses from the tube will be smaller than in an open system where free convection is present. But there could also be other factors influencing the induction time. It has to be taken into account that a difference of 6 s is not high regarding the standard deviation obtained from the tests and regarding the margin of uncertainty that is usually reached in deflagration tests. One can see that the percental error is similar in both, closed and open test.

Looking at the rate of temperature rise, it can be found that mean values obtained in the closed test are higher than the ones obtained in the open test. This can be well explained because the temperature is significantly influenced by hot gases arising in the packed bed. If they flow quickly through the tube, the measured temperature difference will be lower and vice versa. In the closed system one can assume that gases need more time to leave the tube because there is a barrier at the top. Because there is only 1 cm space between top of the tube and closing lid of the vessel gases will accumulate inside the tube. Gas accumulation causes heat accumulation and therefore higher variation in temperature inside the tube per time unit.

Standard deviation however is higher in the closed test. The diffusion and spreading of gases is a product of coincidence as it depends on the packing of the substance in the tube which differs in every case. In fact the preparation of the filling is standardised, but there are still coincidental factors affecting its formation that cannot be eliminated. Gases being longer present inside the tube, like in the closed test, have a higher potential to cause coincidence.

The mean and standard deviation of deflagration velocity are almost the same in the open and closed test. The evaluation of pressure curves also shows that an acceleration of deflagration cannot be seen in the four-litre-autoclave with the used sample weights. Pressure curves measured in the four-litre-autoclave normally have a linear shape and no increase in slope with progressing time. This is explained by relatively small pressures obtained in the four-litre-autoclave when a sample weight between 10 g and 127 g is used. One could use greater sample weights to obtain higher pressures in that autoclave. But firstly a modified test setup would be needed because a larger sample mass does not fit into the tube. And secondly high substance consumption would be the consequence. It is better to reduce the volume of the autoclave if kinetic studies under rising pressure shall be performed. It is known that autoclaves with a volume of 200 mL are sufficient for the evaluation of deflagration capability (Klais and Niemitz, 1996).

3.3 Tests under varying initial pressure

Besides tests under atmospheric pressure, we carried out experiments with reduced initial pressure. We chose different initial pressures smaller 1 bar. Measurements with ADCA show, that under vacuum (10 mbar) a deflagration starts eight times later and propagates more slowly. Figure 2 shows that the dependency of induction time from initial pressure can be described by an exponential function in the sector below 1,000 mbar.

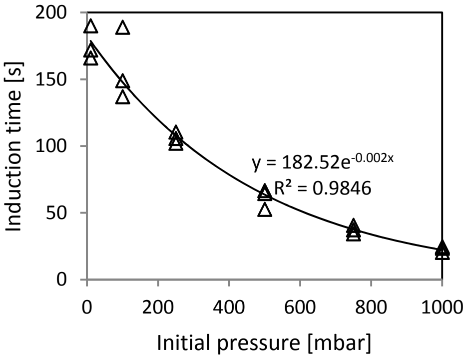


Figure 2: Dependency of induction time from initial pressure

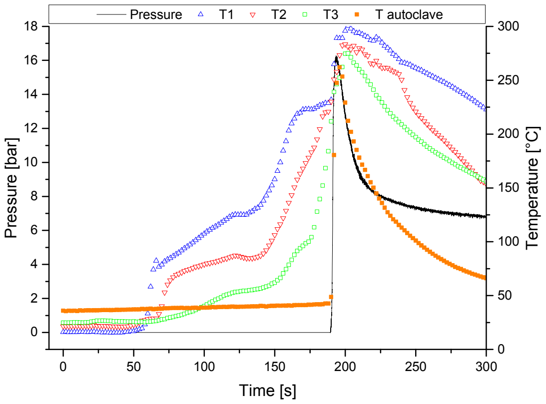


Figure 3: Test result, ADCA with initial pressure of 10 mbar

Experiments with ADCA at higher initial pressure (up to 4 bar overpressure) show that this exponential dependency is not valid in the sector above 1,000 mbar. However rates of temperature rise are up to three times higher when comparing experiments with 1 bar and 5 bar initial pressure. That shows the important role of gas accumulation concerning heat transfer that has already been mentioned when discussing rates of temperature rise. Heat transfer in a packed bed is very low under vacuum. Firstly, there is almost no heat conduction within the gas phase. Remaining heat conduction results from contact points of solid particles. Secondly, convection cannot take place as long as there is no fluid that moves through the packed bed. Thirdly, thermal radiation has, compared to conduction or convection, a small impact on heat transfer in a packed bed, independent on pressure (Schlünder and Tsotsas, 1988). So at the beginning of a vacuum experiment, heat transfer from glow plug through the sample runs very slowly. After a certain time, i. e. in the experiment shown in Figure 3 after 50 s, a local ignition is detected which extinguishes again. This produces a small amount of gases and energy. These processes could occur at different positions and lead to gas liberation and energy release, additionally to the energy brought in by the glow plug. Gas liberation leads to larger conductive and convective heat transfer, energy release leads to higher sample temperature. This again leads to new local ignitions that release gases and energy. These single steps go on and on, so the process is accelerating by itself. In summation, this leads to the start and propagation of the decomposition reaction, in our example shown in Figure 3 after 190 s.

With this theoretical model, smaller induction times at overpressures can be explained as well. If there is a higher gas amount inside the packed bed, heat conduction and convection is getting larger that means the sample locally reaches ignition temperature faster.

3.4 Other test results

Additional parameters were investigated with the four-litre-autoclave. These are the influence of sample weight or filling height, tube diameter, initial temperature and bulk density. The results are shown in Table 2. Standard experiments are carried out with a filling height of 9 cm and 85 g of ADCA. Experiments with about 3/4, 1/2 and 1/3 of standard filling height and weight show, that a variation in filling level does not influence the induction time. The maximum pressure however is in fact influenced by the sample weight. A linear dependency of maximum pressure from sample weight was found. Rates of pressure and temperature rise are higher when using higher weights or filling heights. But it is not clear if there is a characteristic dependency like linearity for example.

It is remarkable that the induction time is decreasing with increasing tube diameter. In smaller tubes, higher heat losses to the outside are occurring. This means that tubes smaller than 48 mm should be insulated to avoid heat losses and therefore longer induction periods. Deflagration velocity is decreasing with increasing tube diameter. It can be assumed that a deflagration is propagating faster in smaller tubes, because there is less space for a radial spread and therefore the deflagration front is moving faster upwards. Simultaneously, rates of pressure and temperature rise are increasing with increasing tube diameter. Comparing deflagrations with same velocity in different tube diameters, it is obvious that in larger tubes there is a larger mass conversion per time because of the larger diameter. In the small tube, we have 0.16 g ADCA per volume profile over the cross section with 1 mm height. In the medium tube, we have 0.42 g per volume profile and in the large tube we have 0.94 g.

Table 2: Test results – investigation of different parameters

Parameters investigated	Chosen conditions	Induction time [s]	Deflagration velocity [mm/s]	Maximum pressure [bar]	Max. rate of pressure rise [bar/s]	Max. temperature [°C]	Max. rate of temperature rise [°C/s]
Filling height | Weight	9.0 cm | 85 g	22	13	18	5	317	48
	6.8 cm | 65 g	24	*	13	3	308	32
	4.5 cm | 41 g	21	*	6	1	282	33
	3.0 cm | 25 g	21	*	3	0.1	261	28
Tube diameter | Weight	4.8 cm | 85 g	22	13	18	5	317	48
	3.2 cm | 30 g	32	17	3	1	256	41
	2.0 cm | 12 g	33	24	1	0.1	191	32
Initial temperature	20 °C	22	13	18	5	317	48
	80 °C	17	*	21	8	319	35
Bulk density | Weight	0.52 g/mL | 85 g	22	13	18	5	317	48
	0.63 g/mL |102 g	19	8	21	6	321	71
	0.73 g/mL |119 g	17	9	23	5	321	68
	0.78 g/mL |127 g	21	10	27	6	324	67

*not detected

So both results, decreasing deflagration velocity and increasing rate of pressure rise with increasing tube diameter can be explained. Taking the measured deflagration velocities into account, there is a mass conversion of 3 g/s in the small tube, 6 g/s in the medium tube and 12 g/s in the large tube.
Tests at higher initial temperature (80 °C) show that a deflagration starts and propagates faster. The rate of temperature rise however is smaller at higher initial temperature as the maximum temperature is the same taking 20 °C or 80 °C as initial temperature.
There is no real variation in experiments with different bulk densities, besides effects on maximum pressure and maximum rate of temperature rise due to mass differences. For denser packed beds, a higher sample weight is used so that all experiments are performed with the same filling height of 9 cm.
Finally, the determined gas amount during a deflagration of 85 g ADCA is 20 L. Comparing this value to an out of the maximum pressure calculated volume value, good agreement can be found. The maximum rate of gas evolution is smaller (1.9 L/s) than time dependent volume values calculated out of the pressure curves (14.7 L/s). This discrepancy is caused by limitations in dimensioning of experimental set up (Salg, 2013). Further investigations have to be done to estimate the gas evolution curves based on the pressure curves and to find better agreement concerning this point.

4. Conclusion

The four-litre-autoclave is suited to carry out deflagration tests under confined conditions. Testing in a closed vessel provides the advantage of pressure measurement and therefore the investigation of additional characteristics like pressure and rate of pressure rise. The validation of test results shows that some characteristics are sufficiently reproducible and others are afflicted with a certain grade of uncertainty which is common for this kind of deflagration test described in VDI 2263-1. Test results show good agreement with results obtained in the open test. Induction time and deflagration velocity are comparable in both test methods. Differences in rates of temperature rise were explained by gas accumulation inside the tube in the closed vessel. The maximum pressure obtained in the four-litre-autoclave is 27 bar using a sample weight of 127 g. In order to obtain higher pressures with the same sample amount, further investigations will be done using smaller autoclaves. Given the fact that vacuum conditions can delay the occurrence of a deflagration of ADCA, one can think about using this as a safety function by processing substances able of deflagration under reduced pressure. Offering the advantages of testing in a closed system, the use of a four-litre-autoclave for evaluation of deflagration behaviour is a good supplement to the test methods currently used. One can benefit from additional characteristics and one has the possibility to perform experiments under different atmospheric conditions. In this way real operating conditions can be simulated in lab scale. That is why the experimental set up will be used and improved further on.

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