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Evaluation of Deflagration Behaviour Using Different Sized Autoclaves

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Deflagration tests were conducted with two kinds of autoclaves. Parameter studies were carried out concerning the gas atmosphere and substances used. Deflagration tests were performed in different pressure regions. Furthermore, deflagration test results of different substances were compared to the corresponding DSC results. Previous findings concerning vacuum conditions could be approved for a greater range of substances. In addition, investigations in nitrogen atmosphere were performed in order to investigate the deflagration behaviour. Experiments up to 161 bar could be utilized. An acceleration of deflagration velocity with increasing pressure was observed in a large pressure interval.

1. Introduction

The importance of deflagration testing was already outlined before, see Salg et al. (2015a,b) where a new test method utilizing a four-litre-autoclave was described based on the standard method described in the German industry guideline VDI 2263-1, part 1.6 Deflagration (Verein Deutscher Ingenieure, 1990). The advantages using an autoclave for deflagration testing were pointed out and the results were compared to standard test methods in open atmospheres.

In this present contribution the deflagration of some solid bulk materials in different sized autoclaves under different gas atmospheres, vacuum conditions as well as elevated pressures were investigated. Additionally DSC-results were compared to deflagration results.

2. Experimental set up

Two kinds of autoclaves were used for this study. A four-litre-autoclave, described by Salg et al. (2015a) with three thermocouples, a pressure sensor and a glow plug as ignition source was used. Additionally a smaller autoclave with a volume of 200 mL is used. In this case, a heating plate serves as ignition source. We installed two thermocouples and a pressure sensor. One thermocouple is positioned inside of the substance, the second one is positioned above the substance in the upper part of the autoclave. To perform an experiment a weighted amount of substance is filled into the autoclave, in contrast to the 4-L-autoclave without additional tube. Figure 1 shows the experimental set up of the 200-mL-autoclave.

Experiments were performed with Azodicarboxamide (ADCA), Azobiscyanovalericacid (ACVA), a substance here named substance X, Ammonium nitrate (NH_4NO_3) and mixtures of these substances with SiO_2 or $CaSO_4$ as inert filler. In addition to that we used ADCA mixed with a copolymer. ADCA and ACVA are azo-compounds used in polymer industry as blowing agents respectively as free radical initiators. NH_4NO_3 is an often used basis compound in fertilizers and in explosives.

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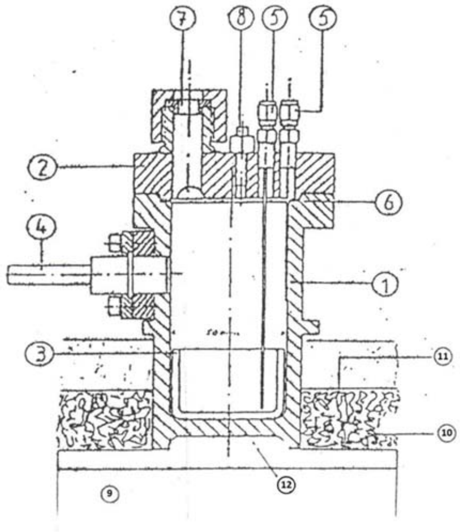

1) Vessel
2) Lid
3) Sample holder
4) Pressure sensor
5) Thermocouples
6) Sealing ring
7) Bursting disc
8) Pressure relief valve
9) Heating plate
10) Insulation
11) Aluminium sheet
12) Heat conduction plate (aluminium)

Figure 1: Experimental set up of 200-mL-autoclave

3. Results

3.1 Test results in 200-mL-autoclave and comparison to experiments in 4-L-autoclave

First of all, results from the new 200-mL-autoclave are compared with results available from the 4-L-autoclave. Therefore we consider the pressure values obtained in these autoclaves in Table 1, using ADCA as a sample with different weights.

The difference in the autoclaves is, of course, their volume. In general, we want to obtain pressure values up to 200 bar in order to evaluate the behaviour of substances under conditions they are possibly handled. In addition to that, according to Klais and Niemitz (1996), deflagration reactions accelerate with rising pressure. Using the four-litre-autoclave, this behaviour can be seen in a small pressure interval between 1 bar and 4 bar, but the maximum pressure rise is comparably small. We do not want to use higher sample amounts in order to get a high pressure value in the four-litre-autoclave. For ecologic, economic, health and safety reasons it is better to reduce the volume of the autoclave and spend less sample amounts when performing deflagration tests. Using a 200-mL-autoclave we obtained pressures up to 161 bar. Consequently we observe an increasing rate of pressure rise with increasing pressure across a large pressure interval. Figure 2 shows the rate of pressure rise at different pressure values in both autoclaves and with different sample weights. All experiments show increasing rates of pressure rise when pressure is increasing. After reaching the maximum rate of pressure rise, curves are decreasing until zero, when the maximum pressure is reached. The graphs differ in the values which are higher the smaller the autoclave and the larger the sample weight. They show the acceleration of the reaction with rising pressure. This is important to consider for deflagrations which start at elevated pressures. The dimension of pressure relief equipment must be higher then, as deflagrations not only start but also propagate faster.

Table 1: Autoclave sizes, fill levels and pressure values for ADCA

Size of autoclave [mL]	Sample weight [g]	Fill level [%]	Max. pressure [bar]	Max. rate of pressure rise [bar/s]	Averaged rate of pressure rise [bar/s]
200 mL	5	9.8	18	9	3
	15	29.5	73	90	72
	30	58,9	161	341	240
4000 mL	42.5	2.0	9	2	1
	85	4.1	19	5	4

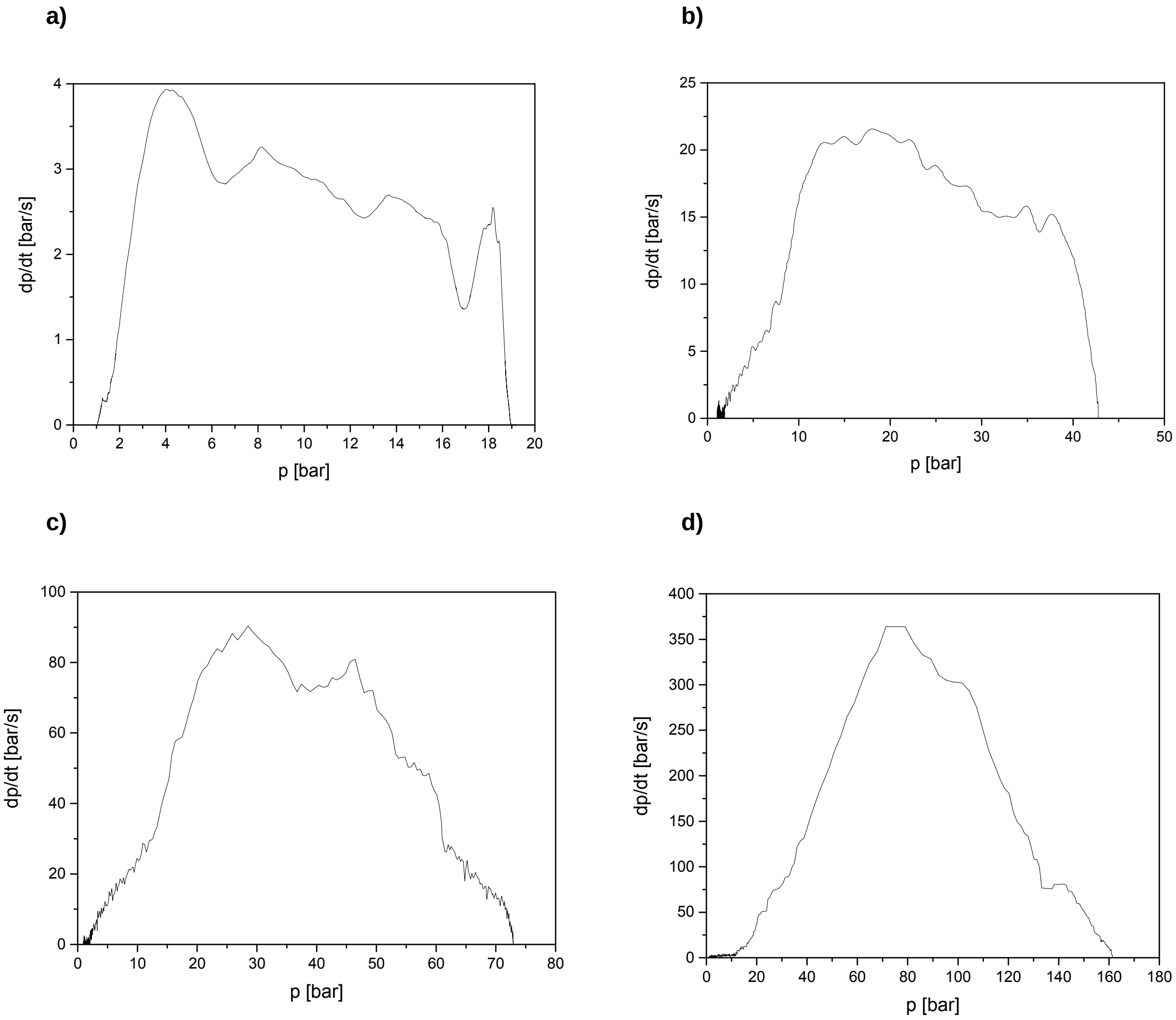

Figure 2: Rate of pressure rise as a function of pressure, experiments with ADCA. a) 4-L-autoclave, w = 85 g, b) 200-mL-autoclave, w = 10 g c) 200-mL-autoclave, w = 15 g, d) 200-mL-autoclave, w = 30 g

3.2 Tests in different atmospheres

As Salg et al. (2015a) pointed out, the deflagration of ADCA is less likely to occur under vacuum conditions. At elevated pressure, induction times are further decreasing and rates of temperature rise are increasing. We performed additional experiments with ADCA-SiO_2- and ADCA-$CaSO_4$-mixtures in the four-litre-autoclave, which confirm these findings. In Figure 3 it can be seen that the induction time for ADCA and ADCA-mixtures with SiO_2 and $CaSO_4$ is exponentially decreasing in the pressure region below 1 bar. Furthermore, the induction time of pure ADCA is the shortest in the region above 0.6 bar. In the region below 0.6 bar however, the induction time of an ADCA-$CaSO_4$-mixture (32/68 w%) is shorter than the one of pure ADCA.

These statements are also true using ACVA. An ACVA/SiO_2-mixture (50/50 w%) also shows higher induction times in vacuum and induction time seems to follow an exponential dependency on initial pressure. The induction time for high concentrated ACVA-mixtures is shorter than for corresponding ADCA-mixtures. For the 30/70-ACVA- respectively ADCA-mixtures, however, the opposite was observed.

Table 2 shows the details. Substance X shows the same behaviour like ADCA and ACVA: decreasing induction times and increasing rates of temperature rise with increasing pressure.

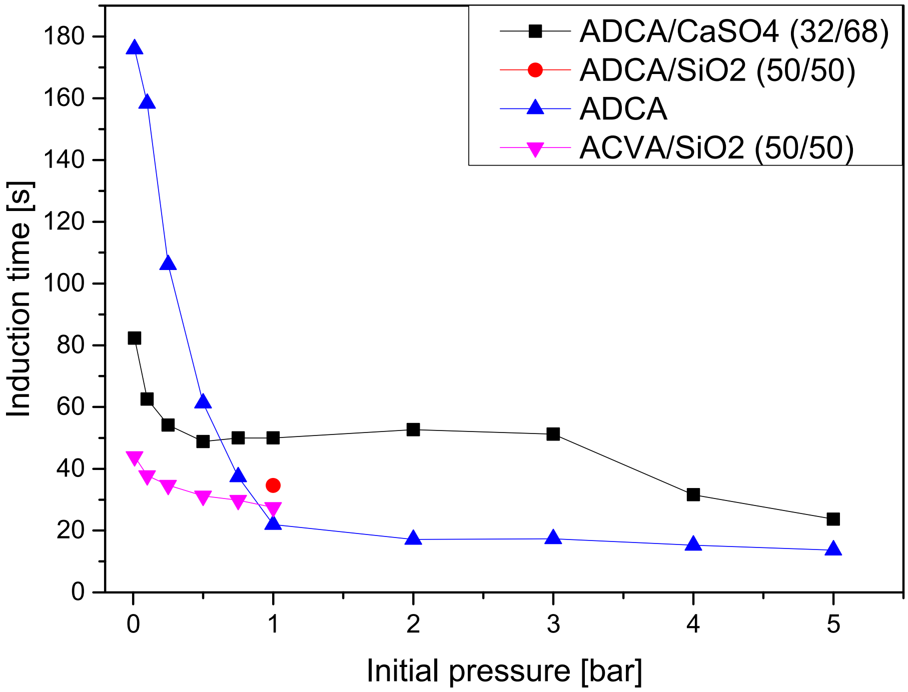

Figure3: Dependency of induction time of ADCA and ADCA-mixtures with SiO_2 and $CaSO_4$ on initial pressure

Besides varying initial pressure, we performed deflagration tests under nitrogen atmosphere. We carried out these experiments in order to examine, if the differing test results in vacuum are caused by the absence of oxygen or by the absence of gases in general. For this purpose we used the four-litre-autoclave. As an inert atmosphere, we chose nitrogen with 1 bar pressure. To ensure the complete absence of oxygen, we evacuated the closed vessel three times, pressurized the autoclave with nitrogen and after the third evacuation, we adjusted the initial pressure. For nitrogen experiments we used ADCA/SiO_2 (50/50), ADCA/$CaSO_4$ (32/68), pure ADCA and substance X.

Table 2: Test results for different substances and mixtures

Substance	Initial pressure [bar]	Induction time [s]	Deflagration velocity [mm/s]	Max. pressure [bar]	Max. rate of pressure rise [bar/s]
ADCA	1	22	12.7	19.0	5
ADCA/SiO_2 (50/50) in nitrogen	1	37	22.3	3.0	0.18
ADCA/SiO_2 (30/70)	1	91	1.3	1.1	0.01
ADCA/SiO_2 (30/70) in vacuum	0.01	321	1.1	0.3	0.004
ADCA/$CaSO_4$ (32/68), denser packed bed, w = 150.5 g	1	84	0.2	3.0	0.01
ADCA/$CaSO_4$ (32/68) in nitrogen	1	56	0.6	2.9	0.01
ACVA	1	9	25.0	1.3	0.23
ACVA/SiO_2 (50/50)	1	27	7.1	1.8	0.01
ACVA/SiO_2 (50/50) in vacuum	0.01	44	1.5	0.6	0.01
ACVA/SiO_2 (30/70)	1	122	0.3	1.6	0.02
Substance X (50/50)	1	85	1.26	1.3	0.001
Substance X (50/50) in vacuum	0.01	165	0.21	0.2	0.0005
Substance X (50/50) in nitrogen	1	88	0.56	1.3	0.01

As the results show, experiments in nitrogen atmosphere do not differ from experiments carried out in ambient air conditions. We detected no nameable differences in all characteristics usually evaluated for each experiment. As described in theory, oxygen is not necessary for the occurrence of deflagrations (Steinbach, 1995). Therefore, results in vacuum are definitely not different to results obtained under ambient conditions, because of the absence of oxygen, but because of the absence of gases in general and therefore reduced heat conduction.

3.3 Connection between deflagration test results and DSC-experiments

Additionally we compared deflagration test results and DSC-results. DSC being used as a screening tool for energy properties of unknown substances is a very convenient way to gain information about the thermal response. As for one DSC-experiment only some milligrams of the sample are needed, an estimation of deflagration behaviour could reduce the experimental efforts. To start our investigations we compare onset temperatures and decomposition energies measured with DSC to deflagration test results for each substance we used as shown in Table 3.

We observe similar onsets for ADCA and for different mixtures with ADCA except for ADCA/SiO_2 (30/70). The decomposition energies, however, are certainly different. Pure ADCA contains the highest decomposition energy. ADCA mixed with other substances has, depending on the grade of dilution, lower decomposition energies, as these substances act as inert filler materials which do not contribute to the reaction. Consequently, regarding the deflagration test results, pure ADCA gives the highest maximum pressure values and rates of pressure and temperature rise. It is remarkable that even ADCA/SiO_2 (30/70) shows a deflagration despite its low decomposition energy of 319 J/g. A commonly used criterion says, a deflagration of a substance with decomposition energy smaller 500 J/g is unlikely to occur.

The onset temperature of ACVA is approx. 100 °C lower than the one of ADCA, the decomposition energy is approx. half of the energy detected at ADCA. Comparing the deflagration test results of these two substances, we observe that the deflagration of ACVA is starting much faster due to the lower onset temperature. The relation between DSC decomposition energy and velocity of deflagration is not so clear so far. ACVA shows a fast deflagration, even faster than ADCA, despite the decomposition energy of ACVA is much less than the one of ADCA and close to the 500 J/g-criterion.

Ammonium nitrate has a very high decomposition energy but we obtain no deflagration because it couldn’t be ignited with the described test set up using a glow plug or a heating plate as ignition source. The high onset temperature is an indication that NH_4NO_3 is difficult to ignite.

These findings show that DSC-tests can be used as a screening tool to predict the likelihood of a deflagration. Together with other prediction tools, statements can become better and more reliable. Our next step is to get kinetic data out of DSC-experiments and in this way to make further predictions about the deflagration behaviour.

Table 3: DSC data of substances used, heating rate = 5 K/min (screening)

Substance name	Onset [°C]	Extrapolated onset [°C]	Decomposition energy [J/g]
ADCA	179	205	1198
ADCA/SiO_2 (30/70)	152	179	319
ADCA/SiO_2 (50/50)	179	208	699
ADCA/$CaSO_4$ (32/68)	187	207	407
ADCA with Copolymer 1	179	209	769
ADCA with Copolymer 2	183	209	611
ACVA	74	122	575
Substance X	145	155	621
NH_4NO_3	231	268	2368

4. Conclusion

Investigations of deflagration behaviour in autoclaves of different sizes have been performed. We observed the acceleration of deflagration velocity with increasing pressure. Using a 200-mL-autoclave, it was possible to obtain pressures up to 161 bar and to observe the deflagration rate dependency covering a large pressure region. The different deflagration behaviour under vacuum conditions was described for ADCA already but now determined for other substances also. It can be assumed that handling of deflagration able substances under vacuum can delay the start of a deflagration and therefore can reduce the risk of deflagrations in general. Different gas atmospheres do not influence the deflagration reactions. This was shown comparing experiments under nitrogen and oxygen atmosphere. The reason for later starting deflagrations in vacuum can be found in reduced heat conduction because of the absence of gases.

Comparing deflagration test results with DSC data showed that DSC-tests can be used as a screening tool to predict the likelihood of a deflagration. Although the data basis is comparably small, these findings are promising to continue these studies.

The goal of our work is to improve prediction methods in order to get reliable indicators out of small scale experiments, not only DSC-tests. In this way, laboratory tests could become needless in future what would be an advantage when only small amounts of substance are available or when consumption of high sample amounts is too expensive.

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