Detonations in capillary tubes with nitrous oxide as an oxidizer

Thomas Meye*)
Elisabeth Brandes*)
Ulrich Krause**)
*)Physikalisch-Technische Bundesanstalt
Braunschweig, Germany
**)Otto von Guericke Universität
Magdeburg, Germany

1 Introduction

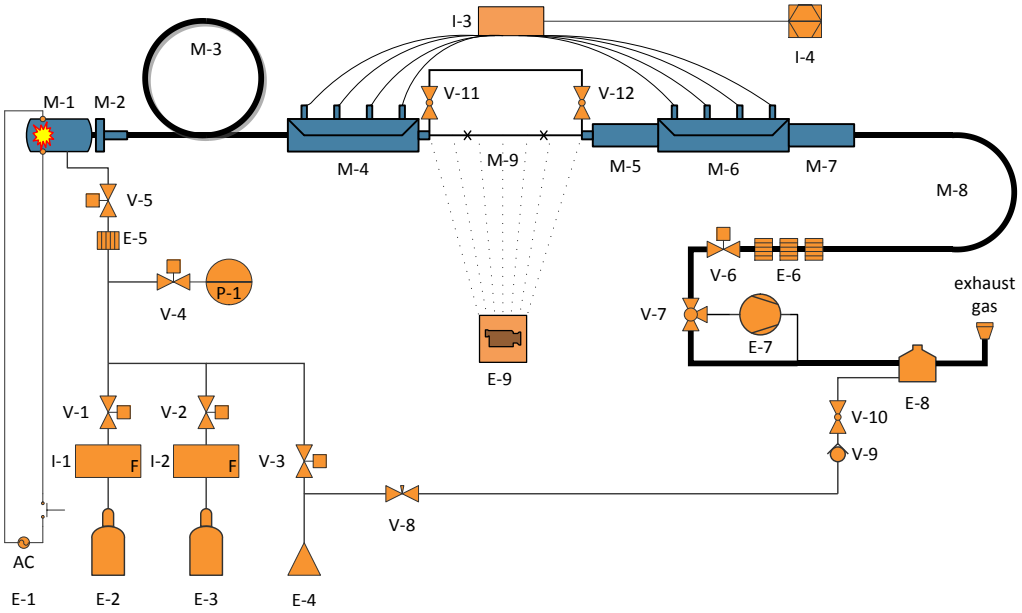
Microstructured process equipment is increasingly being used in chemical process engineering. The advantages of such arrangements which use capillary tubes with an internal diameter of less than 1 mm are the better control of the chemical reactions – i.e. their process parameters can be influenced more easily. For example, a more effective chemical synthesis can be expected which leads to purer reaction products and, thus, may contribute to an increased yield. In addition, it is assumed that the continuous reaction processes, the reduced temporal use of substances associated with them, and the small-scale reaction areas of a microreactor (in which the wall distances may be smaller than 1 mm) will reduce the safety risk. The question, however, is: Which microstructured process design allows the suppression of the propagation of a detonation when gaseous detonative mixtures of substances are used or created during the chemical process? An experimental test arrangement designed to generate stable detonations and to investigate their propagation behavior in capillaries was used to answer this question by drawing conclusions for the diameter of a capillary which is safe due to quenching detonations. Based on theoretical considerations, a detonation should be able to pass through a tube of diameter d only if the following correlation between the detonation cell width λ and d is valid: $d \geq \lambda/\pi \approx \lambda/3$ [2]. This theoretical consideration was proven in former investigations for flammable gas/oxygen mixtures [1]. The investigations reported here have been performed for nitrous oxide as an oxidizer. Nitrous oxide is regarded as an oxidizer with an oxidation potential between air and oxygen. From the safety engineering point of view, it does not reach the risk potential of oxygen while it has, at the same time, an enhanced oxidizing potential compared to air.

2 Experimental procedure

The investigations – determination of the detonation velocity, detonation pressure, detonation cell width - were performed using the experimental set-up shown in Figure 1 for detonative mixtures of ethane/nitrous oxide and propane/nitrous oxide. The (detonative) mixture is ignited by an electrical spark (14 kV) in module M-1. M-3 which is a circular tube (approx. 6 meters in length, diameter: 10 millimeters, circular tube diameter: 1000 millimeters) serves to stabilize the detonation. In step 1, the substance mixture composition which is optimal (lowest detonation cell width) for the propagation of a detonation through narrow tubes (10 millimeters) is determined using a modified (removing module M-9 so that module M-4 connects directly to module M-5) set-up. In the modules M-4 (circular cross-

Correspondence to: thomas.meye@ptb.de

section) and M-6 (square cross-section), the velocity of the detonation is measured by the use of four pressure transducers with each module and the time interval of the respective signal.



V-1 to V-7	pneumatic valve, remote-controlled
V-8	needle valve
V-9	non-return valve
V-10	spherical valve, manual
V-11	spherical valve (bypass in), manual
V-12	spherical valve (bypass out), manual
P-1	pressure transducer 10 bar, piezoresistive
I-1 and I-2	mass flowmeter
I-3	charge amplifier
I-4	processor
E-1	high voltage source, 14 kV, 20 mA
E-2	flammable gas
E-3	oxidizer
E-4	compressed-air
E-5	flame trap, 0.25 mm
E-6	flame trap, triple, 0.25 mm
E-7	vacuum pump
E-8	washing tower, NaOH
E-9	high-speed camera
M-1	ignition vessel, electric spark ignition
M-2	insulating module, ceramic
M-3	stainless steel tube, helix, 6000 mm
M-4	measuring section (circular cross-section) with pressure transducers, piezoelectric
M-5	adaper, circular-to-square cross-section
M-6	measuring section (square cross-section) with pressure transducers, piezoelectric
M-7	adapter, square-to-circular cross-section
M-8	stainless steel tube, 3000 mm
M-9	capillary tube

Figure 1: Schematic construction

In addition, the detonation cell pattern of the detonation is recorded with the covers of modules M-4 and M-6 which are coated with a soot layer. This allows the detonation cell width to be determined. Only detonation cells fulfilling the following requirements are chosen: The detonation cell must have one or more immediate neighbor detonation cells connected with a permanent triple-point track or the detonation cell must have nearly a typical form (rhomb) with complete circumferential triple-point

track. In step 2 the validity of the equation $d \geq \lambda/\pi$ is investigated with module M-9 installed. This 'capillary tests' are performed with three different capillary materials to check the influence of the material on the detonation transmission: tempered steel, cold-drawn steel and KPG. KPG is a calibrated precision borosilicate glass. The length of the capillaries was 1000 mm. A detonation transmission is documented by pressure signals of at least one pressure transducer in module M-6. The detonation tests with the KPG capillaries are, in addition, documented with a high-speed camera. Thus, the penetration depth of the detonation inside the capillary in case no detonation transmission has occurred (no pressure signal with module M-6) can be recorded. For this 'capillary tests' till now only mixture compositions which in step 1 gave the smallest detonation cell width are investigated. As shown by [1] for flammable substances/oxygen mixtures, it is assumed also for substances/nitrous oxide mixtures that the composition of the mixtures found in step 1 as optimal, is also optimal to propagate as a detonation through capillaries. That means a detonation through a capillary whose diameter is smaller than the determined safe diameter should not be possible in the case of other concentrations of the fuel/oxidizer mixture.

3 Results

The maximum detonation velocities are found for ethane (see Figure 2) and propane at 1.5 times the stoichiometric flammable substance concentration and they lie, depending on the starting pressure, in the range between 2250 m/s and 2350 m/s. Compared to ethane, no difference worth mentioning was detected for propane as regards the detonation velocities of the two substances. One characteristic of a stable gas detonation is the formation of relatively uniform detonation cells [4]. As an example, Figure 3 shows the measured detonation cell widths of ethane. The smallest detonation cell widths occur at 1.2 times the stoichiometric flammable substance concentration more or less independent of the starting pressure. In the case of reduced starting pressures and in the substoichiometric range, only very irregular detonation cell patterns occur, whereas regular detonation cell patterns can be found in the case of atmospheric and elevated starting pressures and in the case of slightly hyperstoichiometric fuel concentrations (Figure 4).

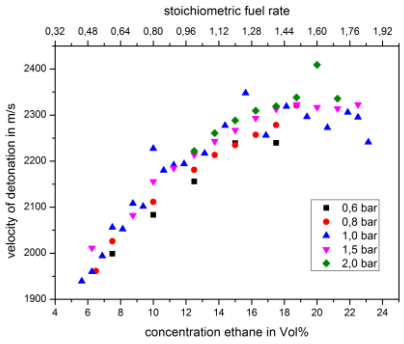


Figure 2: Velocity of the detonation

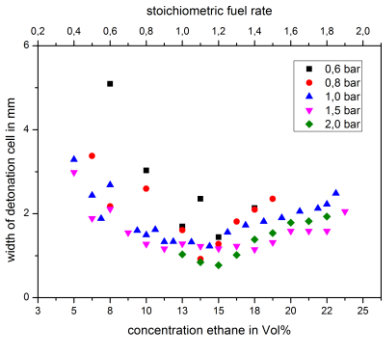


Figure 3: Width of a detonation cell

According to the theoretical consideration, it is assumed that the inner circumference of a tube limits the propagation of a detonation inside it as soon as the detonation cell width λ is larger than the available inner circumference of the tube (so-called 'λ/3 rule' ($\pi \approx 3$)) [2]. Thus, the following correlation should be valid for the limiting capillary diameter:

$$\lambda = \pi * d_{lim}$$

Hereby, d_{lim} is regarded as the capillary diameter which quenches the detonation.

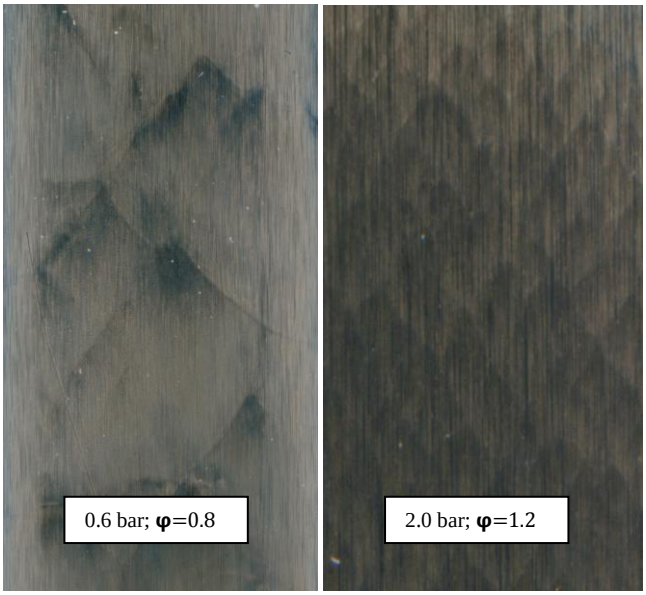


Figure 4: Detonation cell patterns of ethane at different initial pressures and different mixture compositions

With the capillary tests, the limiting capillary diameters calculated based on the lowest determined detonation cell widths are then investigated in a targeted way by selecting suitable capillary sizes. The capillary tests were carried out for that flammable substance concentration where the lowest detonation cell width was found (1.2 times the stoichiometric concentration) during the tests in step 1. In Table 1, the results of these investigations are summarized. For the two steel capillaries (tempered steel and cold-drawn steel), no differences as regards the suppression behavior in the case of a detonation could be detected. As mentioned above, the high-speed camera allows a more detailed statement about the interaction of the detonation propagation / transmission and the diameter of the KPG capillaries, because here – in contrast to the steel capillaries – quenching of the detonation inside the capillary can be observed.

Table 1: Detonation characteristics in different capillary tubes

flammable gas	initial pressure in bar	d_{lim} in mm	KPG-capillary tube in mm							tempered steel in mm			cold-drawn steel in mm		
			0.15	0.2	0.4	0.6	0.8	1	2	0.24	0.51	1	0.22	0.5	1
C_2H_6	0.6	0.46			1000	1000									
	0.8	0.41			1000										
	1	0.39			1000										
	1.5	0.37		100											
	2	0.25		100											
C_3H_8	0.5	0.37				1000									
	1	0.27			1000										
	2	0.24													

Safe Diameter (capillary tube test)
xxxx quenching in capillary tube after xxxx mm
detonation transmission

4 Conclusions

The determination of the mixture composition for which the maximum detonation velocity is found is not sufficient to draw conclusions with respect to the optimal substance composition for a detonation through a capillary, as the fuel fraction for optimal detonation transmission in a capillary tube is considerably lower. Former tests by the Physikalisch-Technische Bundesanstalt with flammable substances/oxygen mixtures show the mixture concentration around the maximum detonation velocity

is not the optimal concentration for the detonation transmission in capillary tubes. For the substance mixtures investigated, the smallest and most regular detonation cell patterns occur in the slightly rich range of the flammable substance concentration (at 1.2 times the stoichiometric concentration). The use of the different materials (KPG, tempered steel and cold-drawn steel) does not seem to have any influence on the detonation characteristics of the capillaries. The results of the capillary tube tests suggest that the detonation cell width can be regarded as a limiting indicator in capillary structures. The capillary diameters determined with the aid of the 'λ/3 rule' d_{lim} are very close to the experimentally found diameter where no detonation transmission was detected (no pressure signal recorded in module M-6). This fits the theoretical considerations well. The high speed records with KPG capillary tube tests, however, show that detonations are able to penetrate into a capillary and even pass through till the end of the capillary with a diameter close to d_{lim}. Taking the criterion 'penetration depth of the detonation < 50 mm' would be more on the safe side. That means for none of the determined detonation cell widths and the corresponding capillary diameters determined by the 'λ/3 rule', a detonation into the vessel arranged behind the capillaries occurs. To decide if the criterion 'no pressure signal recorded behind the capillary' is sufficiently safe or if a safety margin is necessary and possible, tests with additional flammable substance/nitrous oxide mixtures, more finely graduated capillary diameters and longer capillaries have to be carried out.

Reference

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