VALIDATION OF THE BRICK CODE WITH DATA FROM PRESSURE RELIEF EXPERIMENTS IN CASE OF RUNAWAY REACTIONS

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1. Introduction

Usually batch or semi-batch reactors are used for exothermic reactions. Often the reaction systems and the process control change. For this reason they imply a high risc potential. The reliable design of the emergency pressure relief system is very important to guarantee the safe operation of such reactors.

For the one-dimensional transient simulation of pressure relief processes the new BRICK code was developed [1,2]. The code was verified by many test cases including comparisons with analytical solutions for special cases. Examples for the validation of the code by depressurization experiments with water/steam are given in [1,2]. But to apply the code to the design of pressure relief systems of batch reactors it has to be validated for realistic reaction systems. Up to now 3 different systems were used for the validation, which represent 3 different situations. The first reaction is the esterification of methanol and acetic anhydride. In this case the pressure is caused by the evaporation of the components. The second is the decomposition of ammonium peroxydisulphate, where the pressure mainly builds up from the release of oxygen and the third is the thermal decomposition of hydrogen peroxide. This is a so called hybrid system, what means, that the increase of pressure results from the production of gas as well as from the evaporation.

2. Experiments

Data of pressure relief experiments for the esterification of methanol and acetic anhydride as well as for the decomposition of ammonium peroxydisulphate were available by courtesy of Wilhelm-Jost-Institut Hamm. The reactor has a height 1 meter and a diameter of 0.6 meter. This corresponds to a volume of 280 litres. For both reaction systems the kinetics of the reactions were investigated by calorimeter experiments at the Inburex GmbH Hamm. The data are also kindly placed at our disposal.

The most important parameter for these experiments are listed in the tables 1 and 2. For the esterification an initial composition of 38,6 wt-% methanol and 61,4 wt-% acetic anhydride was used. The initial concentration of ammonium peroxydisulphate was 35 wt-%.

Table 1: Calorimeter experiments - Inburex GmbH Hamm

Parameter	Esterification	Decomposition
Volume of the test cell	110 ml	120 ml
Mass of reaction mixture	73 g	75 g
Filling	70 %	70 %

Table 2: Pressure relief experiments - Wilhelm-Jost-Institut Hamm

Parameter	Esterification	Decomposition
Diameter of the orifice	13 cm	10 cm
Filling	90 %	80%

Small scale experiments with the thermal decomposition of hydrogen peroxide were done at our institute [3]. A 1.95 litre vessel was filled with 1 litre of 5, 10, 15, 17.5 and 20 wt-% H_2O_2 solution. Discharge orifices of 0.7 mm, 1 mm and 2 mm were used. The decomposition was initiated by an external heating. Experiments were carried out with a complete decomposition before starting the relief as well as with a relief during the runaway.

3. Esterification of methanol and acetic anhydride

In a first step, calculations for the calorimeter experiment were done. In this experiment the reaction is completed without pressure relief. After the completed reaction there is a slight decrease of temperature and pressure because of the loss of heat. Using a heat-transfer coefficient of 6 W/(m^2 K), the temperature decrease of the calculation agres with the experiment. This is the only parameter adapted for the calculation. A very good agreement of the time dependent temperature and pressure curves was achieved. This means the modules for chemical
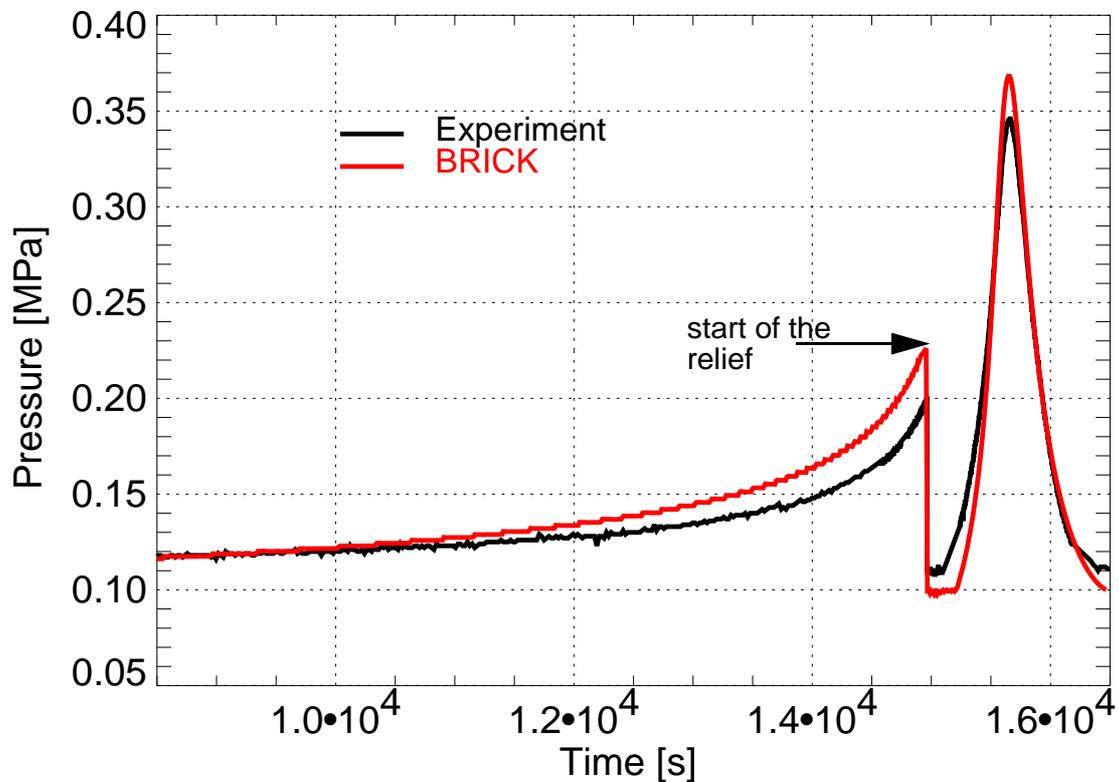

Fig. 1: Comparison of measured and calculated pressure in case of the 280 litre pressure relief experiment with the runaway esterification of methanol and acetic anhydride

reaction, phase transfer as well as for the calculation of material properties work well for this case.

Fig. 1 shows a comparison of the experimental and calculated pressure for the 280 litre pressure relief experiments. The pressure relief was started in the calculation, when the experimental starting temperature of the experiment was achieved. After starting the relief the pressure decreases rapidly to ambient pressure. However the cooling caused by evaporation is not sufficient to stop the reaction. For this reason the temperature even increases after the relief. The pressure peak caused by the runaway reaction is higher than the opening pressure. This is reflected very well by the calculation. The increase of pressure before starting the relief was mainly caused by the expansion of the liquid phase and the corresponding compression of the non-condensible gas. Since here the pressure is only a function of the temperature, material properties and the amount of the non-condensible gas (assumption of an ideal gas), it can be calculated analytically. Also other parameters like the location of the top level of the liquid phase were compared with analytical calculations. The agreement of all these analytically calculated values and the values obtained by the BRICK code confirm the right implementation of the model in the code. Differences between experiment and calculation may be caused by non-ideal behaviour of the fluid.

The most important element of uncertainty in the calculation is the modelling of heat transfer to the outside of the vessel. The influence of the heat transfer is shown in fig. 2. Here only the pressure peak after starting the relief is shown (compare time scales of fig 1 and 2). The red curve shows the pressure without any heat removal from the liquid. In case of the green curve,
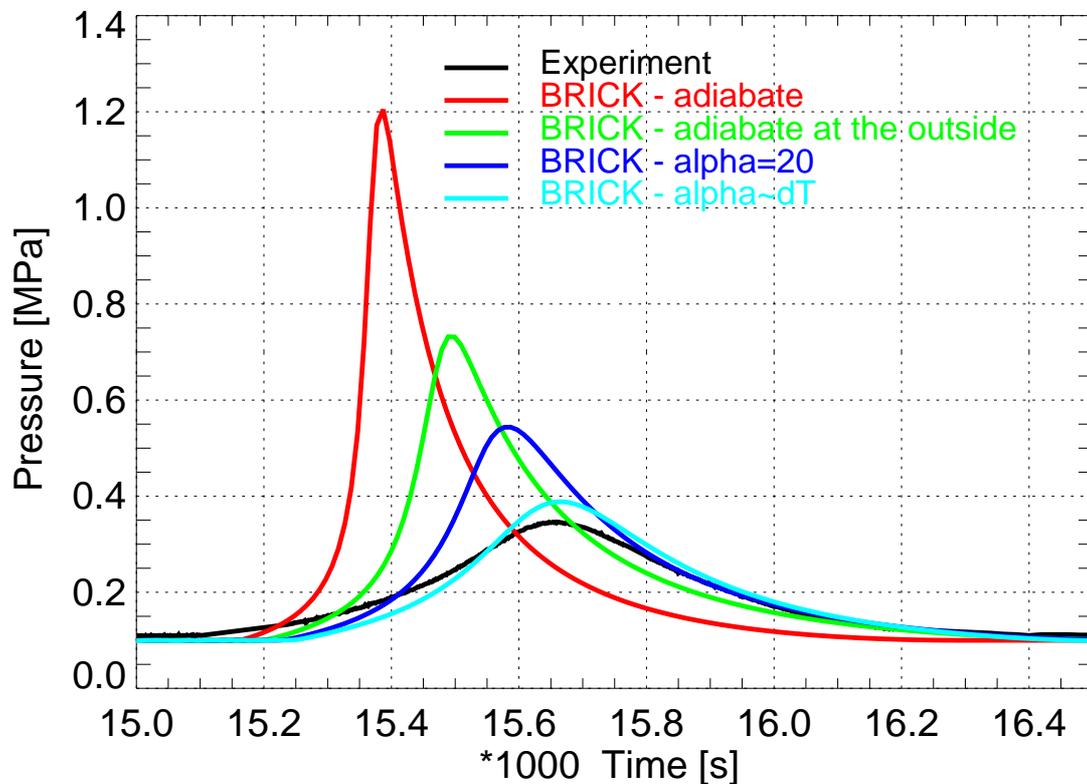

Fig. 2:   Case studies for the influence of the heat transfer for the 280 litre pressure relief experiment with the runaway esterification of methanol and acetic anhydride

the vessel wall is considered, but no heat transfer to the outside of the vessel is assumed. The assumption of a constant heat transfer coefficient to the outside is more realistic. The best agreement between experimental and calculational results was achieved with a heat transfer coefficient, which is proportional to the difference of the temperatures of the outside vessel wall and the environment. That indicates a non-linear behaviour of the heat transfer. However a physically based modelling was not possible, because the conditions of the outside cooling of the vessel are not well known. For the calculations only one node was considered. That means, a point model is used for the balance of energy, but the phase distribution is considered in the calculation over the vessel height.

4. Decomposition of ammonium peroxydisulphate

Due to the lack of material data for ammonium peroxydisulphate the calculations were done using data for hydrogen peroxide. According to the calorimeter experiments, an initial mass fraction of 7% hydrogen peroxide was used in the calculation, what means approximately the same mole fraction as in the case of a 35 wt-% ammonium peroxydisulphate solution. With this assumption an ideal agreement of the experimental and calculated time dependent pressure and temperature curves was achieved for the calorimeter experiments.

Fig. 3 shows a comparison of the measured and calculated pressure curve for the 280 litre pressure relief experiment. The pressure peak caused by the runaway does not reach the opening pressure in this case. There is a significant difference in the pressure increase before the relief.
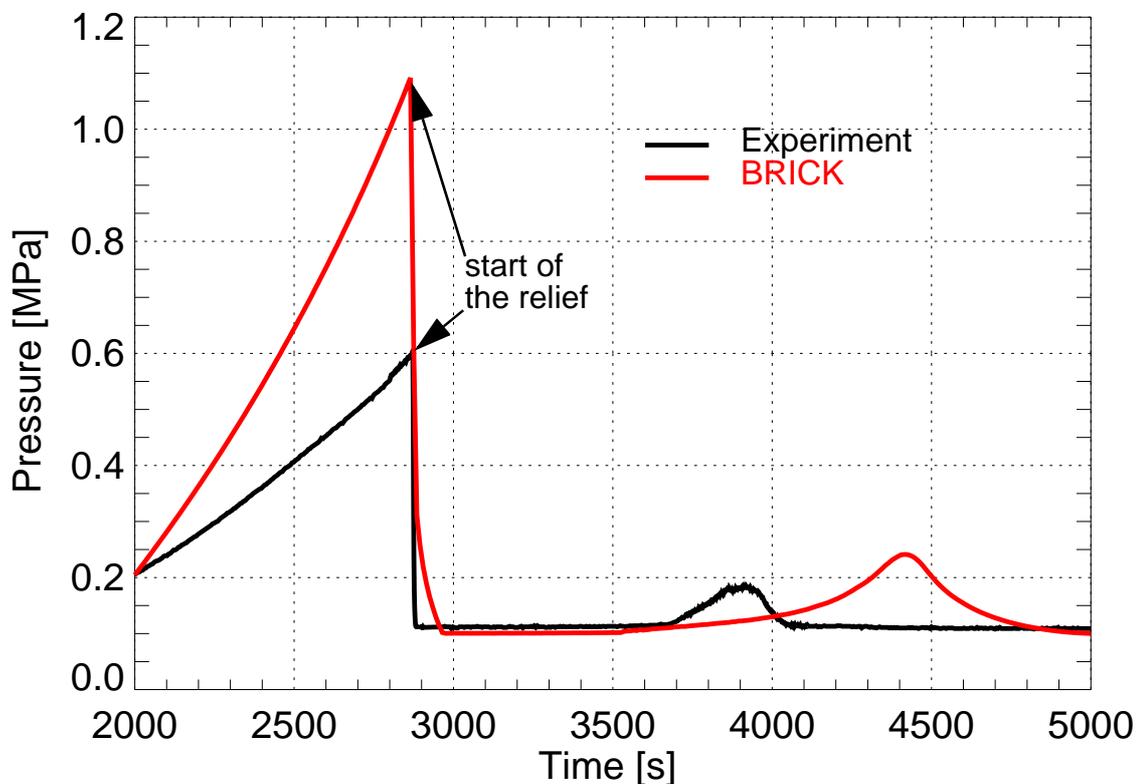

Fig. 3:   Comparison of measured and calculated pressure in case of the 280 litre pressure
relief experiment with the runaway decomposition of ammonium peroxydisulphate
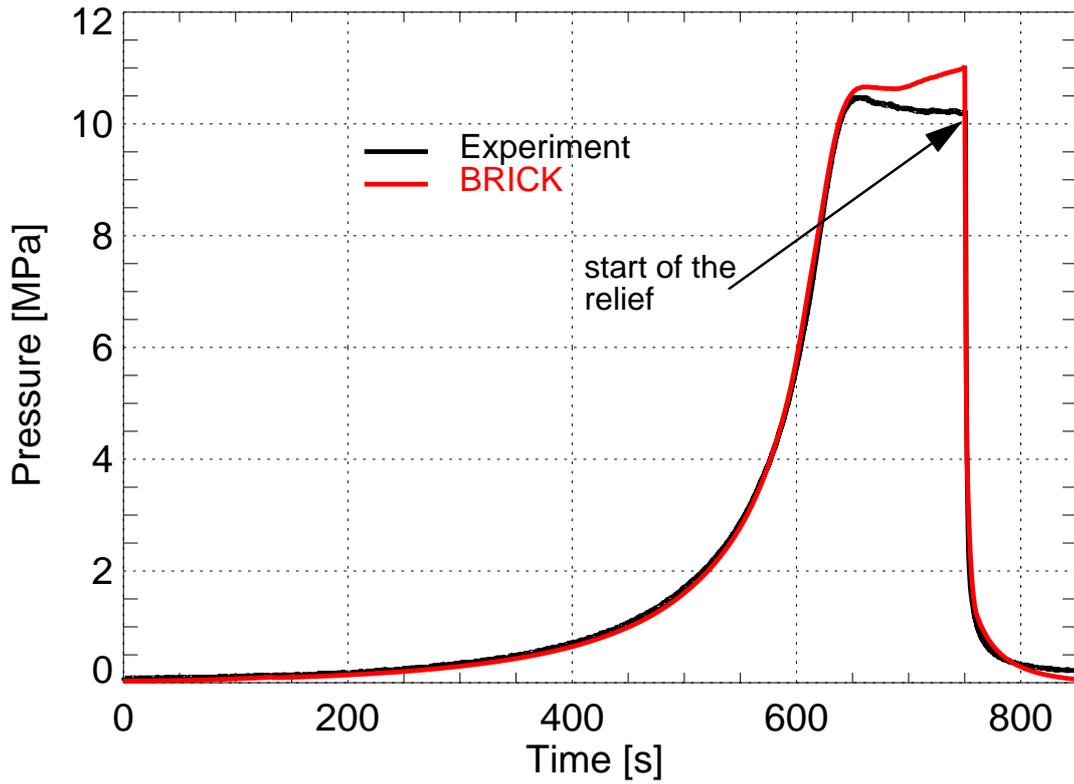
Fig. 4: Comparison of measured and calculated pressure in case of the 1.95 litre pressure relief experiment with the runaway decompostion of hydrogen peroxide (complete reaction)
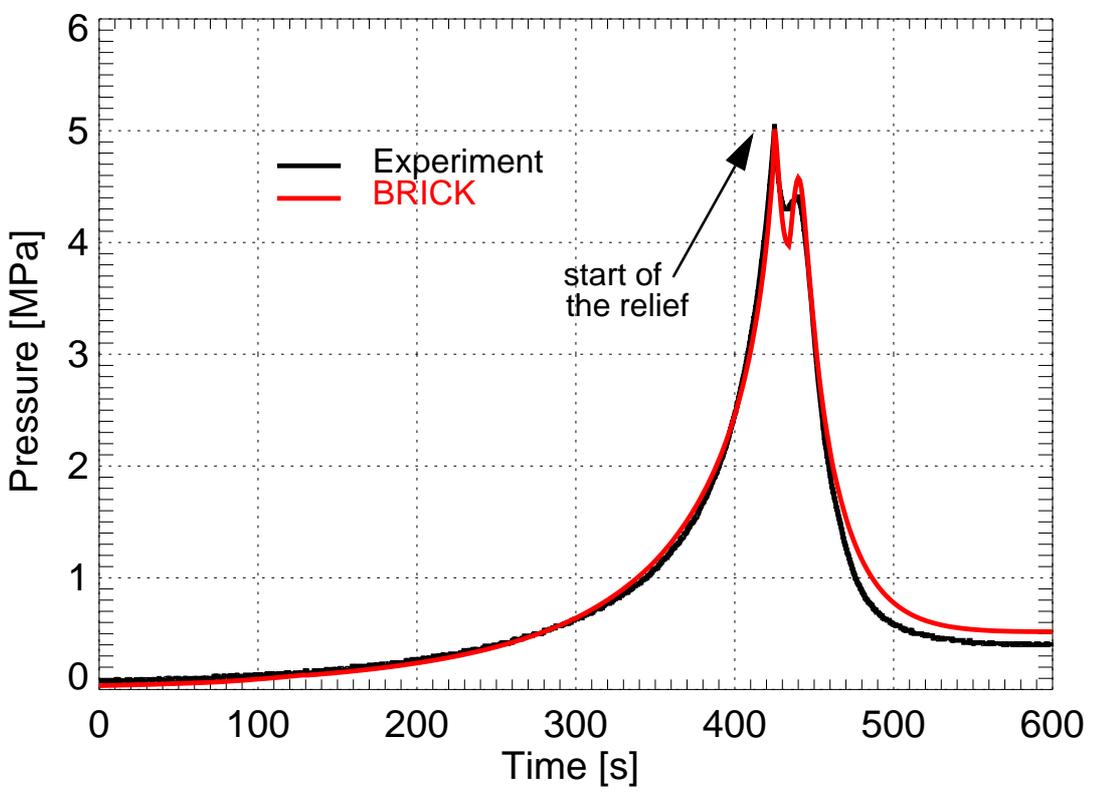

Fig. 5: Comparison of measured and calculated pressure in case of the 1.95 litre pressure relief experiment with the runaway decompostion of hydrogen peroxide (Relief at 5 MPa)

The reason for this difference is not clear. Analytical estimations confirmed the calculated increase of pressure. The runaway happens a little bit later in the calculation than in the experiment. Again the uncertainty of the heat transfer may be a reason for that.

5. Decomposition of hydrogen peroxide

Fig. 4 and 5 show the pressure as a function of time for an experiment with a complete reaction before starting the relief and an experiment with a pressure relief, which was started at a pressure of 5 MPa. In the first case a 2 mm orifice and in the second case a 0.7 mm orifice was used. In both cases a good agreement was achieved. The pressure recovery after starting the relief was obtained in the experiment and also in the simulation with the BRICK code. The heating of the vessel was an additional element of uncertainty. The heating power of the vessel wall was adapted in the calculation.

6. Conclusions

Comparisons of the parameters calculated by the BRICK code with analytical solutions, which may be obtained for some simple cases, showed, that the code works correct. The agreement of the calculated and measured parameters as a function of time is satisfactory in most cases. The main uncertainty in the calculation is the modelling of the heat transfer from the vessel to the environment. Improvements are necessary. In addition, models for the axial heat transfer both in the fluid and in the wall should be implemented.

References

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