Study of a Self Heating Process of Tetrafluoroethylene by the Exothermic Dimerization Reaction to Octafluorocyclobutane

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Abstract: The self heating process of Tetrafluoroethylene caused by an exothermic dimerization reaction was studied. The heat of reaction can lead to a thermal explosion by the decomposition of the Tetrafluoroethylene which caused several incidents in industrial PTFE-production plants. For the model three application modes in the Chemical Engineering Module were linked; non-isothermal-flow, conduction and convection and diffusion and convection. Different reaction kinetics, including multistep kinetics, were used to describe the mass balance. The model was validated by experiments and yielded well correlating results. In future simulations real industrial vessels shall be modeled to prevent further incidents by determine hazardous conditions by analyzing the transient temperature field.

Keywords: self heating, free convection, reactive flow, gas reaction

1. Introduction

The self heating process of tetrafluoroethylene (TFE) by the exothermic dimerization reaction to octafluorocyclobutane can lead to critical conditions in production plants for polytetra-fluoroethylene (PTFE) or other fluoropolymers. PTFE is made by the polymerization of TFE resulting in a suspension of PTFE in water. The gaseous phase of TFE inside the polymerization vessels can dimerize.

$C_2F_4 \rightarrow 0.5\ c\text{-}C_4F_8$ [Eq. 1]

$\Delta H_R = -103$ kJ mol^{-1} (Dimerization)

This reaction can cause a thermal runaway by generating local temperatures of more than 1000 K, which results in an explosive decomposition reaction of TFE forming tetrafluoromethane and carbon black. This has already caused several accidents in PTFE producing plants all over the world during the last years. The specialty of tetrafluoroethylene is the capability of exothermic reactions, as dimerization and decomposition without the presence of an oxidizer or other reactants.

$C_2F_4 \rightarrow CF_4 + C$ [Eq. 2]

$\Delta H_R = -257$ kJ mol^{-1} (Decomposition)

2. Theory

The reaction rate of a chemical reaction is in most cases mainly depending on the temperature. If an exothermic reacting gas or mixture is enclosed in a vessel and surrounded by walls with a constant temperature then it is possible to define a specific wall temperature at which the heat loss through the walls is equal to the heat production by the reactions. Increasing the wall temperature would inevitably lead to a runaway reaction resulting in a so called thermal explosion. For flammable gases a special test procedure according to EN 14522 is used to determine the minimum temperature at atmospheric pressure when an ignition by hot walls occurs. The regarding wall temperature is called *minimum ignition temperature (MIT)*. For decomposable gases another method is required to avoid the contact with other reactants, such as the oxygen in the air. Therefore a closed vessel is used. With this setup also tests at elevated conditions can be carried out. The minimum temperature leading to an explosive decomposition is called the *minimum ignition temperature for decomposition (MITD)*.

3. Motivation

The aim of the study is to develop a model that is capable of simulating the self heating process in real process geometries in PTFE producing plants. It is expected that the research will also reveal the critical conditions that are responsible for the self ignition of TFE gas. If this can be achieved further accidents may be prevented. In a first step the COMSOL model has to be validated by experimental data.

4. Governing Equations and Methods

The multiphysics model consists of the incompressible Navier-Stokes equations from fluid dynamics which is linked to a heat transfer equation and a mass balance equation. There are seven unknown field variables depending on each other:

- The velocity field components, *u* and *v*
- The pressure, *p*
- The temperature, *T*
- The concentration of Tetrafluoroethylene, *c1* and the concentration of the Dimer (Octafluorocyclobutane), *c2*

In order to transfer the results to real scale geometries used in industry, the COMSOL software was employed to model the problem. For this purpose the geometries of different test vessels were transferred to 2D geometries with axial symmetry in COMSOL.
Regarding the COMSOL software, three application modes of the *Chemical Engineering Module* are linked. The *non-isothermal flow mode (chns)* is used to describe the free convection caused by the volume force generated by different densities due to the exothermic dimerization reaction. The *convection and conduction mode (chcc)* is used to model the heat transfer including the heat generated by the exothermic dimerization reaction (see Equation 1), the endothermic back reaction (see Equation 3) and the heat loss through the walls.

$c\text{-}\ C_4F_8 \rightarrow 2\ C_2F_4$ [Eq. 3]

$\Delta H_R = 206$ kJ mol^{-1} (Decay of Dimer)

The *convection and diffusion mode (chcd)* is used to model the mass balance by linking two or more reaction kinetics.

5. Numerical Model

This model mainly consists of a gas domain that is surrounded by fixed walls (vessel) at a constant temperature. There is no inlet or outlet, because a prefilled closed vessel is modeled.

5.1 Model Evolution

In a first approach only the forward reaction [Eq. 1] into Octafluorocyclobutane (dimer) was considered. This yields results for gas temperatures up to 550 K only. For higher temperatures the introduction of the backward reaction from the dimer into TFE [Eq. 3] was necessary. This improved the results but simulations did not converge for temperatures above 700 K. Therefore a different kinetics was introduced for the higher temperature range which led to a further improvement of the model. In this case a 2-stage kinetics for the forward reaction was introduced. (see chapter 6)
The source term for the heat production results from the reaction enthalpy of the dimerization process. Since it is a second order reaction the equation is.

$$\dot{q}_{Dim} = V \cdot \Delta H_R \cdot c_{TFE}^2 \cdot A_{pF} \cdot e^{\frac{-E_a}{RT}} \qquad \text{[Eq. 4]}$$

The regarding term for the heat source in the *chcc (convection and conduction)* mode in COMSOL is:

$$Q = R_{c1} \cdot \Delta H_{Rf} \quad \text{[W/m³]} \qquad \text{[Eq. 5]}$$

with

$$R_{c1} = r_{f,C_2F_4} + r_{b,C_2F_4} = -2 \cdot k_f c_1^2 + 2 \cdot k_b c_2 \qquad \text{[Eq. 6]}$$

R_{c1} is the complete reaction rate for TFE including forward and backward reaction. ΔH_{Rf} is the reaction enthalpy for the forward reaction forming Dimer.

5.2 Non-Isothermal Flow

As there is no phase change during the dimerization reaction the gas density stays constant and the *non-isothermal application mode* could be used. However there is a predicament regarding the pressure that is generated in this application mode. This is because the pressure depends on the temperature only and not on the number of molecules, but during the dimerization the number of molecules decreases. However the density stays the same

because there is no phase change during the reactions.
In order to compare the experimentally measured pressure with the pressure calculated by the COMSOL model the concentrations of the *convection and diffusion application mode* were used. The *diffusion and convection mode* consists of the reversible dimerization reaction and calculated binary diffusion coefficients, which have a minor effect on the results. The applied kinetics were taken from several authors and partly from own experiments.

6. Experimental Results

The dimerization reaction was studied experimentally in several test series in closed vessels. The tests were carried out at constant wall temperatures at different initial pressures. The internal pressure and internal temperature of the vessel were measured during the tests. With every test the temperature was increased stepwise, until the exothermic reactions inside the vessel led to an explosive decomposition reaction. In a previous research project the kinetics of the dimerization reaction of TFE also for elevated conditions was studied in closed vessels via the pressure drop measured inside the autoclave.
Therefore two vessels with volumes of 0.2-dm³ and 3-dm³ were evacuated. Then the vessels were heated to a constant wall temperature and filled with TFE to the wanted initial pressure. The inlet was closed and pressure and temperature inside the vessel were recorded.
If the curves of the measured and the modeled pressure correspond to each other the temperature field generated by the numerical simulation can be analyzed to determine the critical temperatures. Those critical temperatures are regarded as an initiator of explosive decomposition reactions.
In reality the pressure in a closed vessel drops during the dimerization reaction because the number of molecules is reduced. This pressure decrease can be described by linking the ideal gas law, the reaction equation and the rate equation.

$$p\ (t) = \frac{1}{2}\left(\frac{1}{\frac{k_2(T)\cdot t}{RT} + \frac{1}{p_{C_2F_4}(t_0)}} + p_{C_2F_4}(t_0) \right) \qquad \text{[Eq. 7]}$$

In this equation the rate constant k_2 also depends on the temperature. By choosing temperatures below 500K constant wall temperature the temperature increase by the exothermic reaction could be nearly neutralized in the experiments. Then the temperature in equation 6 stays constant and for each wall temperature a rate constant could be determined.

Arrhenius equation for the forward reaction (TFE to octafluorocyclobutane):

$$2C_2F_4 \xrightarrow{f} c-C_4F_8 \qquad \text{[Eq. 8]}$$

with

$$k_f = 82800\left[\frac{\text{m}^3}{\text{mol s}}\right] \quad e^{\left(\frac{-105200[\text{J/mol}]}{RT}\right)}$$

(low temperature kinetics)

All experiments for the determination of the dimerization kinetics were done at temperatures below 550 K due to the necessity of a small reaction rate.
The necessary backward reaction which is not negligible above temperatures of 550 K was taken from several authors found in the NIST kinetics data base.

Arrhenius equation for the backward reaction (octafluorocyclobutane to TFE):

$$c-C_4F_8 \xrightarrow{b} 2C_2F_4 \qquad \text{[Eq. 9]}$$

with $k_b = 2{,}1\times10^{16}\left[\frac{\text{m}^3}{\text{mol s}}\right] \quad e^{\left(\frac{-310961[\text{J/mol}]}{RT}\right)}$

For the numerical modeling of hazardous condition often temperatures above 650 K are reached while the calculation. Therefore a more detailed literature study revealed a decreasing reaction rate above temperatures of 650 K.

7. Hitherto Results/Discussion

First simulations already show promising results. For the low temperature range up to 550 K the model is consistent with the "low temperature" kinetics.
The validation is done by comparing the experimentally measured pressure with the simulated pressure generated by COMSOL.
Since the first approach with a single kinetics for the forward reaction for a wide spread temperature range lead to not correlating results for gas temperatures above 550 K a more detailed kinetics was necessary. Therefore a detailed review of the available literature was done delivering only the known kinetics. Different authors described a decreasing rate constant above a specific temperature without analyzing this effect. Thereupon the kinetics for the temperature range above 550 K was experimentally determined resulting in a lower rate constant. This new "high temperature" kinetics for the forward dimerization reaction was introduced in the model. There a simple switch temperature is used to change the kinetic constants regarding to the calculated temperature.

For nearly constant gas temperatures the pressure drops down as in figure 2.1 regarding the above formula.

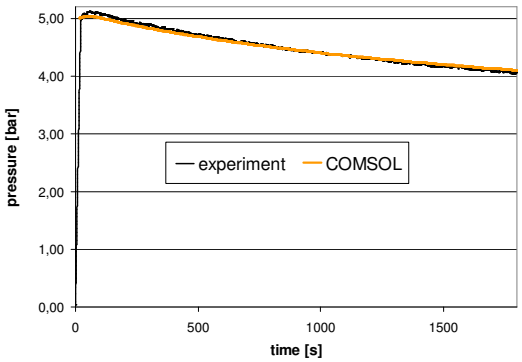

Figure 7.1: Comparison of simulated pressure and experimental data for 250 °C wall temperature and an initial pressure of 5 bar absolute in a 3-dm³ vessel

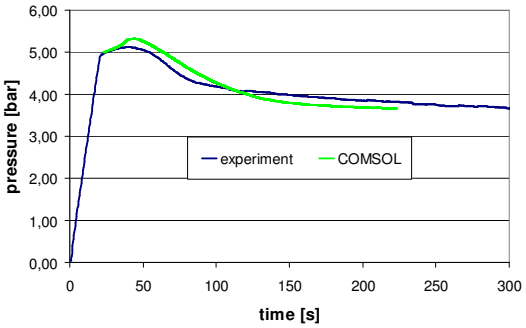

Figure 7.2: Comparison of simulated pressure and experimental data for 300 °C wall temperature and an initial pressure of 5 bar absolute in a 3-dm³ vessel

For higher initial wall temperatures the inner gas temperature increases, since the heat loss through the wall can not compensate the heat generated by the dimerization reaction. Therefore the reaction rate increases and the pressure primary rises according to the ideal gas law before dropping down by the reduction of mole numbers resulting in a thermal explosion.

$$p = \frac{RT}{V} \quad \text{with V = const.} \quad p \sim T$$

[Eq. 10]

Figure 2.2 shows the pressure drop in a vessel with a wall temperature 10 K below the self ignition temperature. The first linear pressure increase shows the filling process. The regarding temperature field is shown in figure 7.3.

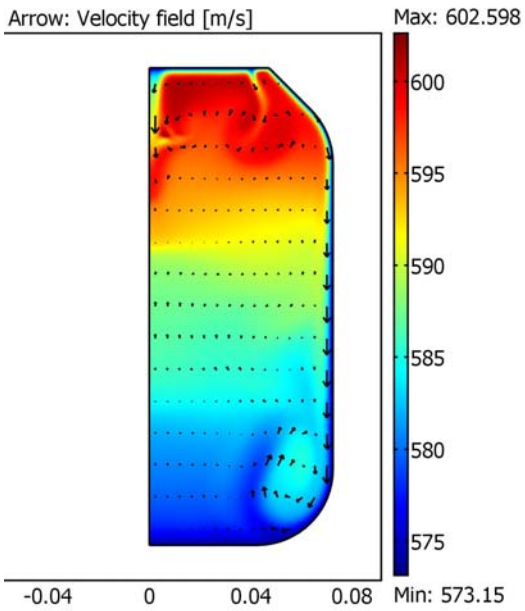

Figure 7.3: Temperature field in a 3-dm³ vessel after 95 s at an initial pressure of 5 bar absolute (2-D-axial symmetry) and a constant wall temperature of 300°C

The figure shows two main downward streams, at the wall and in the center at the axis of symmetry. This is due to the cooling effect of the walls and the lid. These streams stay quite constant for the whole modeled time period of 600 seconds. Moreover there are several small downward streams which are formed at the top and move to the walls where they disappear. This produces a lot of turbulences in the gas leading to continuous supply of non reacted TFE from the lower part of the vessel in the hot reaction area.

The transient modeling of the reactions, taking place inside the 0.2-dm³ autoclave, showed a significant temperature layering of more than 120 K even in small geometries with an inner height of about 120 mm. This effect was confirmed by own experiments. This indicates a possible increasing of the temperature in cavities finally resulting in a thermal explosion.

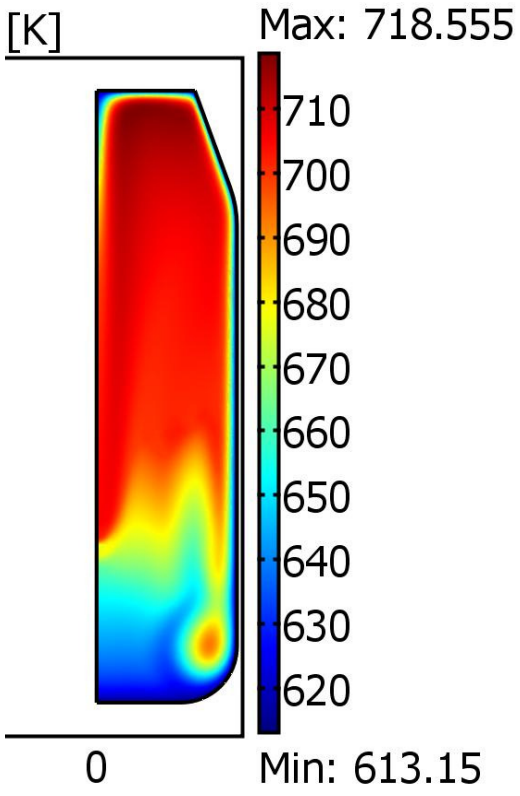

Figure 7.4: Temperature field in a 0.2-dm³ vessel after 10s at an initial pressure of 5 bar absolute (2-D-axial symmetry) and a constant wall temperature of 340°C

8. Expected Results

The velocity field showed downward streams with a velocity in the range of 0.13 m/s in a 3-dm³-vessel.
After a successful validation of the model other geometries like pipes with different diameters, different flow regimes and orientations as well as vessels with bigger volumes and internals will be modeled. Depending on the flow velocity of the TFE gas inside a supply pipe, the wall temperature could be higher as higher the gas velocity is before a significant self heating takes place. Moreover it might be possible to determine the maximum temperature of a hot surface inside such a vessel (now only a small part, not the complete wall) filled with TFE, which would induce the self heating process and finally initialize the explosive decomposition.

9. Solver Problematic

Table 9.1 shows the mesh statistics for the used geometries.

Table 9.1: Mesh statistics for different vessels

Mesh parameter	**0.2-dm³-vessel**	**3-dm³-vessel**
Number of elements	2698	5756
DOF	29259	62094
Element aria ratio	0.0576	0.0267

For solving the model mainly the UMFPACK solver was used. This worked well only after a manual arrangement of the net point distribution at the walls. Due to the cooling effect of the walls while the exothermic dimerization reaction there are the highest velocities near the wall. Therefore the element size had to be reduced. Otherwise even the UMFPACK solver ran into an error. For the inner net the predefined mesh size was set to extra fine.
Since COMSOL is capable of using more than one CPU for solving the multiphysics model the PARDISO solver was also used. Here all eight cores of the workstation were used. Nevertheless the solving time could not be reduced for this model. There are two main points responsible as far as our simulation showed. PARDISO did not work for the same initial mesh and solver parameters which were used for UMFPACK. The mesh size had to be reduced and the relative and absolute tolerance had to be set to a tenth of the value used for UMFPACK. These effects only occurred when linking the Navier-Stokes application mode to the conduction and diffusion mode. Without Navier-Stokes PARDISO solved the model very fast and without any error.

10. Conclusions

The safety related considerations of the self heating process of TFE by the exothermic dimerization reaction to Octafluorocyclobutane is necessary to prevent incidents in PTFE-production plants. The released temperature due to the dimerization reaction can lead to an explosive decomposition that mainly results in a massive destruction of plant equipment or even worse might injures persons. Therefore COMSOL was used to determine a physical model which includes the application modes: *non-isothermal flow*, *convection and conduction* and *convection and diffusion* to describe the transient process of self heating. Different formal kinetics are used to improve the model accuracy. The results of the numerical simulation are validated by experimental data and show promising results including a reversible reaction where two species are involved. Especially for gas temperatures up to 550 K the existing models works very well when only a forward reaction is considered. For temperatures above 550 K and below 800 K the model was improved by a more detailed kinetics including a backward reaction and a 2-stage forward reaction kinetics approach. For temperatures above 800 K up to about 1000 K another kinetics approach is necessary including more reactions and probably also the decomposition kinetics of TFE, which is not known yet.

11. References

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12. Appendix

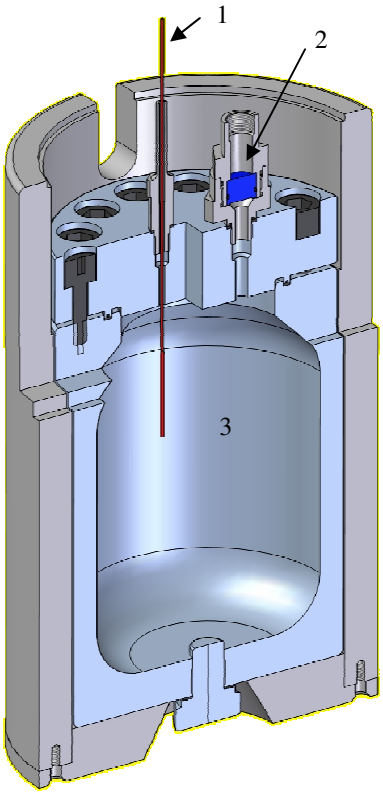

Figure 12.1: Sectional view of a 3-dm³ vessel used for the experiments to determine the MITD for TFE; 1 – thermocouple, 2 – pressure transducer, 3 – internal vessel volume (cylindrical reaction chamber)