

# Improvements in the Modeling of the Self-ignition of Tetrafluoroethylene

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**Abstract:** In order to prevent incidents in the industrial production of Teflon® from Tetrafluoroethylene (TFE), the safety related aspects of the self-heating process of TFE must be taken into account. Simulations of this self heating process were performed with COMSOL Reaction Engineering Lab® and COMSOL® COMSOL Multiphysics®. A complex reaction net was employed, resulting in a model allows for a good agreement with experimentally achieved results.

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

## 1. Introduction

Tetrafluoroethylene (TFE) is the monomer of the widely used polytetrafluoroethylene (PTFE), also known as Teflon®.

In addition to its high flammability, TFE belongs to the small group of decomposable gases. These gases are capable of exothermic reactions without the need of an oxidant.

Under specific conditions, which can even occur in the production process, an exothermic dimerization of TFE can start, leading to a self heating of the gas phase.



$$\Delta H_R = -83 \text{ kJ} - 105 \text{ kJ mol}^{-1} \quad (\text{Dimerization})$$

In some cases this can initiate an explosive exothermic decomposition reaction of the TFE, forming tetrafluoromethane and carbon black.

By reaching local temperatures of more than 1000 K a thermal ignition is likely to be happening.

In the past years a number of incidents in PTFE-producing plants all over the world were caused by this self-ignition of TFE. The decomposition reaction produces tetrafluoromethane and carbon black, according to the following reaction.



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

## 2. Theory

In a previous paper the self heating of TFE in a closed vessel using a simple reversible reaction was described [3].

The reaction rate of a chemical reaction is 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. By increasing the wall temperature, the heat release by the reaction would inevitably lead to a runaway resulting in a so called thermal explosion.

For the oxidation process of 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 takes place. The regarding wall temperature is called the *Minimum Ignition Temperature (MIT)*. Beside this MIT decomposable gases can also react without an oxidant when heated. To determine an analogue safety related property for decomposable gases another method is required to avoid the contact with other reactants, such as the oxygen in the air. Several decomposable gases can decompose only above a specific pressure, the so called limiting stability pressure. Therefore a closed pressure resistant vessel is used. With an adequate setup, tests at even elevated conditions can be carried out. The minimum temperature leading to an explosive decomposition in a closed vessel is then called the *Minimum Ignition Temperature of Decomposition (MITD)*.

## 3. Motivation

This study originally started by the initiation of a research project subsidized by an industrial association, PlasticsEurope, to improve the safety in PTFE producing factories.

The aim of the study was to determine the MITD for TFE at elevated condition and to create a numerical model which is capable of simulating the self heating process of TFE. 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. Parallel to the numerical work the model is continually validated by experiments.

#### 4. Numerical model

In order to transfer the results to real scale geometries used in industry, COMSOL Reaction Engineering Lab® and COMSOL® Multiphysics® were employed to model the problem.

For the simulations with COMSOL Reaction Engineering Lab®, a heat and mass balance in a batch reactor was considered. Up to 11 chemical reactions were coupled to describe the self heating process. Furthermore, a heat transfer coefficient gas to wall was calculated for each time step, based on the Grashoff, Peclet and Nusselt numbers.

Regarding the COMSOL Multiphysics® 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. As there is no phase change during the dimerization reaction and the analyzed system is closed, the total gas density stays constant and the *non-isothermal application mode* could be used wherein the gas density only depends on the temperature. However there is a predicament regarding the pressure that is generated in this application mode. This is because the pressure calculated with this module depends on the temperature only and not on the number of molecules, but during the dimerization the number of molecules decreases. However, the total density remains unchanged, because there is no phase change during the reactions, as mentioned.

The *convection and conduction mode (chcc)* is used to model the heat transfer resulting from the extended reaction net. Beside the exothermic dimerization reaction [Eq. 1] and the endothermic back reaction [Eq. 3], four

additional reactions are considered, as shown in Figure 1.



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

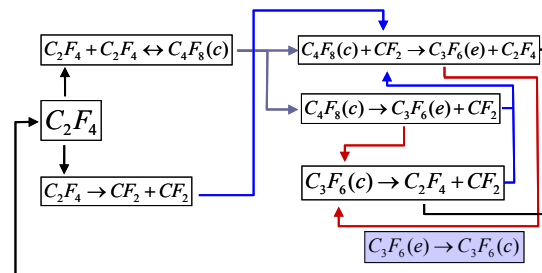


Figure 1: extended reaction net [2].

To close the equation system, the *convection and diffusion mode (chcd)* is used to model the mass balance by linking the reaction kinetics.

When considering, the complex reaction net, there are nine unknown field variables depending on each other:

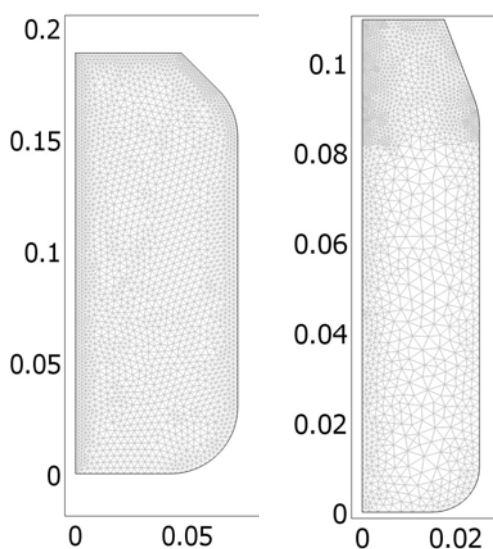
- The velocity field components,  $u$  and  $v$ ;
- The pressure,  $p$ ;
- The temperature,  $T$ ;
- The concentration of Tetrafluoroethylene ( $C_2F_4$ ),  $c1$ ;
- The concentration of the dimer ( $C_4F_8$ ),  $c2$ ;
- The concentration of  $C_3F_6$ ;  $c3$ ;
- The concentration of  $CF_2$ ;  $c4$ .

The geometry and the corresponding mesh used in the calculations are shown in Figure 2. Due to the symmetry of the problem a 2D geometry using the axial symmetry modus was used.

Table 1 shows the mesh statistics for the used geometries in the Multiphysics model. The used mesh had always a quality higher than 0.6.

Table 1: Mesh statistics for different vessel sizes

Mesh parameter	0.2-dm <sup>3</sup> -vessel	3-dm <sup>3</sup> -vessel
Number of elements	3078	4752
Degrees of freedom	13208	71012
Element aria ratio	0.0103	0.0664



**Figure 2:** Geometry and mesh used in the calculations, left: 3-dm<sup>3</sup>-vessel, right: 0.2-dm<sup>3</sup>-vessel

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.

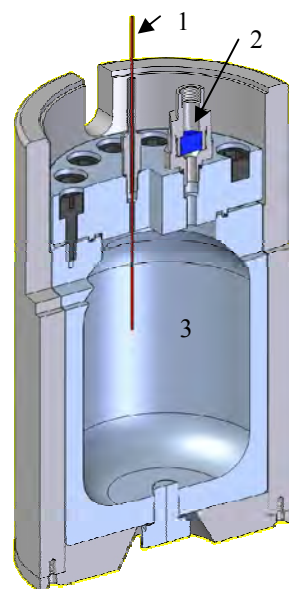
## 5. Experimental work

The dimerization reaction was studied experimentally in several test series in closed vessels with volumes ranging from 0.2 dm<sup>3</sup> to 3 dm<sup>3</sup>. Figure 3 shows a schematic view of the 3 dm<sup>3</sup> autoclave, where the employed measuring devices are detailed. The internal pressure and internal temperature of the vessel were measured during the tests.

Before each experiment the vessel was evacuated and then heated to the desired initial temperature. Then, TFE was filled to the defined initial pressure. The inlet was closed and pressure and temperature inside the vessel were recorded. If a peak in the pressure and temperature curves was observed, this was defined as an ignition. Tests were repeated for each initial pressure, where the temperature was varied in steps of  $\pm 10$  K, until the lowest temperature leading to an ignition was detected. This temperature is the MITD for the specific initial pressure and vessel volume.

Furthermore, 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 measuring inside the autoclave [7] using a method described by Matula [6].



**Figure 3:** Sectional view of a 3 dm<sup>3</sup> vessel used for the experiments to determine the MITD for TFE; 1 – thermocouple, 2 – pressure transducer, 3 – internal vessel volume (cylindrical reaction chamber)

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, according to the following equation.

$$p(t) = \frac{1}{2} \left( \frac{1}{\frac{k_2(T) \cdot t}{RT} + \frac{1}{p_{C_2F_4}(t_0)}} + p_{C_2F_4}(t_0) \right) \quad [\text{Eq. 4}]$$

In this equation the rate constant  $k_2$  also depends on the temperature. By choosing relatively low temperatures for the walls the temperature increase by the exothermic reaction could be nearly neutralized in the experiments. Then the temperature in [Eq. 4] stays constant and for each wall temperature a rate constant could be determined.

According to the performed experiments, an Arrhenius second order reaction rate forward reaction [Eq. 1] was observed, in agreement with previous results [Matula, 1968; Buravtsev *et al.*, 1985; Babenko *et al.*, 1998]. The following expression represents the reaction rate:

$$k_f = 82800 \left[ \frac{\text{m}^3}{\text{mol s}} \right] e^{\left( \frac{-105200 [\text{J/mol}]}{RT} \right)} \quad [\text{Eq. 5}]$$

The previous equation is valid for low temperatures. In fact, 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 [Eq. 3] which is not negligible above temperatures of 550 K was taken from several authors found in the NIST kinetics data base, and is expressed as follows:

$$k_b = 2,1 \times 10^{16} \left[ \frac{\text{m}^3}{\text{mol s}} \right] e^{\left( \frac{-310961 [\text{J/mol}]}{RT} \right)} \quad [\text{Eq. 6}]$$

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. In fact, in preliminary calculations performed, the model did not converge for temperatures above 700 K. Therefore, different kinetics were introduced for the higher temperature range, which led to a further improvement of the model. Here a 2-stage-kinetics for the forward reaction was introduced.

Generally, the source term for the heat production results from the reaction enthalpy of the dimerization process. Since this is a second order reaction the equation is the following.

$$\dot{q}_{Dim} = V \cdot \Delta H_R \cdot c_{TFE}^2 \cdot A_{pF} \cdot e^{\frac{-E_a}{RT}} \quad [\text{Eq. 7}]$$

The corresponding heat source term is:

$$Q = R_{cl} \cdot \Delta H_{Rf} \quad [\text{Eq. 8}]$$

where:

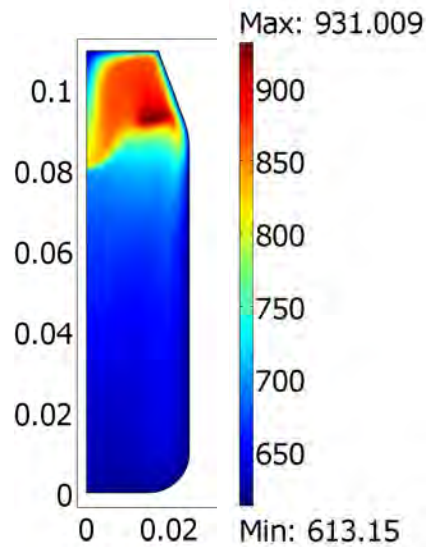
$$R_{cl} = r_{f,C_2F_4} + r_{b,C_2F_4} = -2 \cdot k_f c_1^2 + 2 \cdot k_b c_2 \quad [\text{Eq. 9}]$$

$R_{cl}$  is the complete reaction rate for TFE including forward and backward reaction.  $\Delta H_{Rf}$  is the reaction enthalpy for the forward reaction forming the dimer.

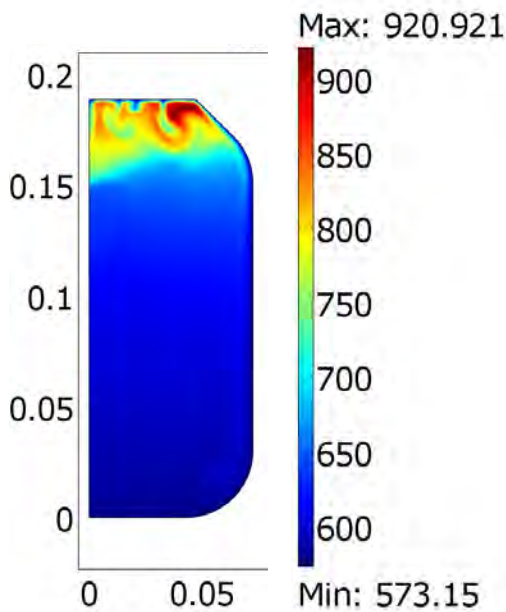
As mentioned previously, a complex net of reaction was finally used in the simulations presented in this paper (Figure 1). Accordingly, to the heat source presented by [Eq. 8] further endothermic or exothermic terms are considered, which take into account for the side reactions.

## 6. Discussion

The temperature distribution in the gas phase calculated some seconds after the filling of TFE is presented in Figure 4 and Figure 5, for a 0.2 dm<sup>3</sup> and a 3 dm<sup>3</sup> vessel, respectively, calculated by COMSOL Multiphysics®.



**Figure 4:** Temperature field in K in a 0.2-dm<sup>3</sup>-vessel after 6 s at an initial pressure of 0.5 MPa absolute (2D-axial symmetry) and a constant wall temperature of 340°C [Calculation with COMSOL Multiphysics®]

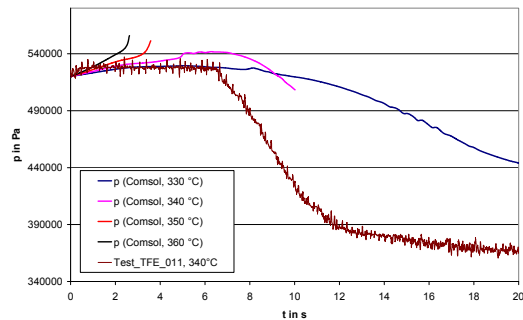


**Figure 5:** Temperature field in K in a 3-dm<sup>3</sup>-vessel after 21 s at an initial pressure of 0.5 MPa absolute (2D-axial symmetry) and a constant wall temperature of 300°C [Calculation with COMSOL Multiphysics®]

Both figures show a hot zone in the upper part of the vessels. This is due to the buoyancy effect which is generated by the local temperature differences due to the heat generation by the dimerization reaction. There are several small downward streams which are formed at the top and move to the walls where they disappear. This is due to the cooling effect of the walls and produces a lot of turbulences in the gas leading to continuous supply of non reacted TFE from the lower part of the vessel into the hot upper reaction area.

The effect of temperature layering could be verified by experiments with several small thermocouples in a 0.2-dm<sup>3</sup>-vessel.

In Figure 6 the validation of the developed model is done by comparing the experimentally measured pressure with the pressure generated by COMSOL Multiphysics®. The experimental initial pressure in the test was 0.5 MPa absolute and the initial wall temperature amounted to 340 °C. If these conditions are set in the model, a good agreement with the experimental data is observed.



**Figure 6:** Comparison of simulated pressure and experimental data for a 340 °C wall temperature and an initial pressure of 0.5 MPa absolute in a 3 dm<sup>3</sup> vessel [Calculation with COMSOL Multiphysics®]

In Figure 6 it is also shown, that if the wall temperature in the model is increased to 350 °C, a steep pressure increase would be observed. This means, that the heat loss through the wall can not compensate the heat generated by the dimerization reaction. Therefore, the reaction rate increases according to [Eq. 5] 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:

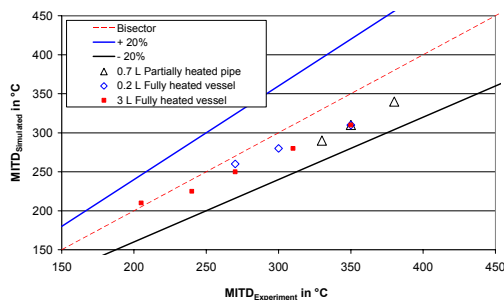
$$p = \frac{RT}{V} \quad \text{with } V = \text{const.} \quad p \sim T \quad [\text{Eq. 10}]$$

For the specific case presented in Figure 6, the MITD predicted by the model would be 350 °C, since this is the first temperature value in a range  $\pm 10$  K, where an ignition is observed.

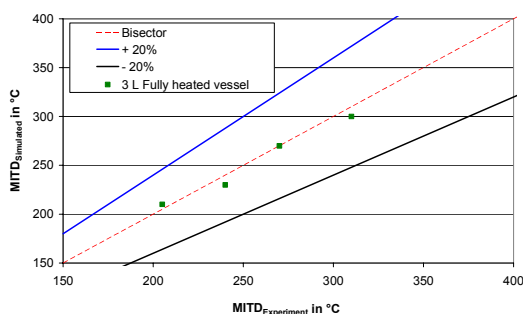
As mentioned, calculations with improved kinetics for the prediction of the MITD were performed both with COMSOL Reaction Engineering Lab® and COMSOL Multiphysics®. Good agreements with the experimental data have been obtained for both calculation methods, as shown in Figure 7 and Figure 8. Simulations performed with COMSOL Multiphysics® show the best agreement and allow for the observation of local hot spots. Furthermore, with this method the pressure evolution up to the ignition can be modeled with good accuracy.

By using the COMSOL Reaction Engineering Lab® to determine the MITD no significant influence of the side reactions could be found, unless the primary reversible dimerization reaction was included. The reason might be the missing local distribution of heat, as it was observed within the experiments. In fact, the

influence of the side reactions will not affect the calculation, because these reactions need higher temperatures to generate non negligible reaction rates. Nevertheless, nearly all results simulated with the COMSOL Reaction Engineering Lab® delivered lower values for the MITD compared to the experimental ones. Thus the results are on the safe side.



**Figure 7:** Accuracy of the MITD predictions with COMSOL Reaction Engineering Lab®



**Figure 8:** Accuracy of the MITD predictions with COMSOL Multiphysics®

By including the side reactions into the COMSOL Multiphysics® model a much better agreement of the simulated and the experimental values could be achieved. Here the side reactions influence the heat generation, due to high local temperatures where their reaction rates overcome the rate of the dimerization reaction.

### 7. Solver Problematic (COMSOL Multiphysics®)

For solving the model the UMFPACK solver was used first. 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 occurs, the highest velocities are found in its

proximity. Therefore, the element size had to be reduced. Otherwise even the UMFPACK solver ran into an error. For the autoclave interior the predefined mesh size was set to extra fine and for some boundaries a specific number of elements where set .

Since COMSOL Multiphysics® is capable of using more than one CPU, the PARDISO solver was used instead. Here all eight cores of the available workstation were used. Nevertheless the solving time could not be significantly reduced . In fact, the PARDISO solver did not work for the same initial mesh and solver parameters which were used for the UMFPACK solver. 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 the UMFPACK solver. These effects only occurred when linking the *non-isothermal flow mode (chns)* application mode to the *conduction and diffusion (chcd)* mode. Without the *non-isothermal flow mode (chns)* the PARDISO solver solved the model very fast and without presenting any error.

Moreover the non-isothermal flow calculation worked only fine by activating the stabilization method *isotropic diffusion* using a parameter of 0.1.

### 8. 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 the self heating of the system and finally to an explosive decomposition that may results in a massive destruction of plant equipment or even worse might lead to fatalities.

As to gain information on the self heating process of TFE, simulations were performed with COMSOL Reaction Engineering Lab® and COMSOL Multiphysics®. A complex reaction scheme was used to model the self-heating process, which includes not only the dimerization reaction but also the most important side reactions.

Good agreements with the experimentally determined MITDs have been obtained for both calculation methods. Simulations performed with COMSOL Multiphysics® show the best agreement and allow for the observation of local

hot spots. Furthermore, with this method the pressure evolution up to the runaway can be predicted with good accuracy.

## 9. Outlook

On the basis of the successful validation of the model presented, COMSOL Multiphysics® might be used to simulate other geometries like pipes with different diameters, different flow regimes and orientations as well as vessels with larger 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. In the simulations performed with a 3-dm<sup>3</sup>-vessel, the velocity field showed downward streams in the range of 0.13 m/s, but this might be strongly affected by the studied geometry.

Moreover, it might be possible to determine the maximum temperature of a local hot spot inside a vessel filled with TFE, which would induce the self heating process and finally initialize the explosive decomposition.

Especially for situations where a high buoyancy effect or forced convection occurs the Multiphysics model might give better predictions than the Reaction Engineering Lab model.

In a next step the presented models will be used to predict the MITD of TFE in a 100-dm<sup>3</sup>-vessel. In a final validation state tests in a large vessel with a volume of ~ 100 dm<sup>3</sup> will be carried out.

## Acknowledgement

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