# Modeling Helps Improve Safety in the Production of Teflon

One of the most useful plastics ever discovered, Teflon, involves a dangerous manufacturing process. COMSOL Multiphysics is helping researchers determine how to identify risky situations when designing production facilities.

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We know it as the non-stick coating Teflon, but chemists know it as PTFE (polytetrafluoroethylene). This now ubiquitous substance was discovered in 1938 by Dr. Roy J. Plunkett. This substance has since revolutionized the plastics industry and created a new branch with annual sales in the billions of dollars.

Because this substance is so non-toxic, biologically inert and has excellent resistance to chemicals, organic solvents, acids and alkalis, it is used for piping and valves for the processing of aggressive chemicals and substances.

## Dangerous in the Making

As useful as PTFE is, the polymerization process whereby TFE gas is converted into this solid can be dangerous. Not only is TFE highly flammable, it belongs to the small group of decomposable gases that are capable of exothermal reactions (those that generate heat) without the need of an oxidant. Under specific conditions that can even occur in the production process — generally when local temperatures reach the range of 500 K — an exothermic dimerization of TFE gas can start, leading to a self-heating of the gas phase. In some cases, this can in turn initiate an explosive decomposition reaction.

In an effort to help its member companies better understand how to improve safety in PTFE production facilities and prevent future accidents, for several years the industry organization PlasticsEurope has been subsidizing experimental research and the development of a mathematical model of the self heating of TFE at the BAM Federal Institute for Materials Research and Testing in Berlin, Germany. The resulting model, created with COMSOL Multiphysics, is to our knowledge the only CFD code used to study this particular phenomenon.

Until now, we have addressed this issue by conducting tests on small autoclaves where we would determine the Maximum Ignition Temperature of Decomposition (MITD). The MITD depends on the initial pressure and on the vessel geometry; Fig. 1 shows the drawing of a 3 $dm^3$ vessel. Therefore, we would perform test for a number of initial pressure-vessel volume conditions and could interpolate between them. However, we are unable to conduct such tests on very large autoclaves of the size used in industry because of the very high effort required to deal with the amount of gas and due to the extensive setup and necessary manpower.

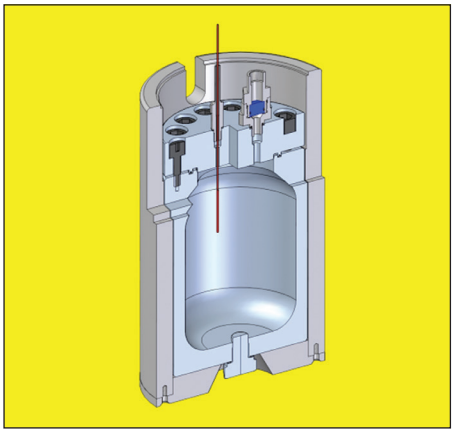

Fig. 1. Sectional view of a 3 $dm^3$ vessel used for the experiments to determine the Maximum Ignition Temperature of Decomposition for TFE.

These restrictions led to the desire for a mathematical model that could predict the behavior of the studied phenomenon in large autoclaves. The model was designed to simulate the self-heating process of TFE so as to determine the MITD for TFE at elevated pressures. This research will therefore help reveal the critical conditions responsible for the self-ignition of TFE.

## Identifying the Key Reactions

A particular challenge in developing this model was to identify a suitable chemical reaction mechanism. Until now, researchers have only concerned themselves with a single reaction, the dimerization reaction where two TFE molecules "bump" into each other to create a new bigger molecule; this is the main reaction which releases energy to the gas and can result in a runaway condition if the heat builds up to critical levels. We soon learned, however, that using this reaction alone resulted in a model with poor correlation to some of the experimental results. Before you can model this decomposition reaction, you must also consider the many other reactions that begin parallel to dimerization.

Only after extensive study and research were we able to identify many reactions that took place in the heated gas phase, but we didn't know which ones were important for the self-heating that leads to the point of the explosion. This is where we first turned to COMSOL, specifically to the Chemical Reaction Engineering Module. In this software, which was very easy to set up, we included all of the dozen or more reactions we had identified as possibly being important. With the aid of the software we were able to find the six reactions that were needed for an accurate model and have confidence that we could omit the others for this particular study because they take place at temperatures above the self-ignition temperature, meaning they start only if the system is already experiencing a runaway.

However, this first simulation assumed that the reaction was taking place in a controlled environment with a perfectly mixed system and didn't account for local distributions. The results were lower values for the MITD compared to experimental ones, meaning that the results were on the conservative side. Furthermore, in this setup, no significant influence of the side reactions could be found unless the primary reversible dimerization reaction was included.

## A More Complex Model

Thus, we started to also include the effects of fluid flow and the movement of temperature to help isolate hot spots that could initiate the undesired reaction. We were also able to determine the effects of using external means to hold the wall of the reactor at a constant temperature.

In this more complex model, three physics interfaces in COMSOL Multiphysics are used. First, the non-isothermal flow interface describes the free convection caused by the different densities due to the exothermic dimerization reaction. Second, the convection and conduction interface defines the heat transfer resulting from the extended reaction net involving the six reactions under study. Third, the convection and diffusion interface represents the mass balance by linking the reaction kinetics.

Fig. 2 shows the geometry for the model and some results. A hot zone in the upper part of the vessel is clearly visible; this is due to the buoyancy effect generated by local temperature differences which are created by the heat of the dimerization reaction. There are also several small downward streams which form at the top and move to the walls where they disappear. In fact, even if at the beginning of the process the walls are the hottest area where the dimerization reaction is initiated, once the hot dense gases move toward the top, the walls become a cooling function. This cooling effect at the walls produces turbulence in the gas leading to a continuous supply of non-reacted TFE from the lower part of the vessel to the hot upper reaction area. Beside the pressure the dimerization reaction strongly depends on the temperature and in the hot zone a self-accelerating process takes place.

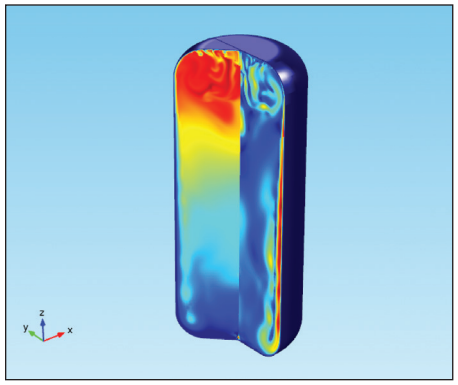

**Fig. 2. Temperature (K) in a 3-dm³-vessel, shown in the left cross-section, after 21 s; note the hot zone building up in the upper section. The cross-section at the rightshows the complex velocity field caused by free convection in the vessel.**

Validation of the model was done by comparing the experimentally determined MITD with the simulated MID given by the model (figure 3), and good agreement was found.

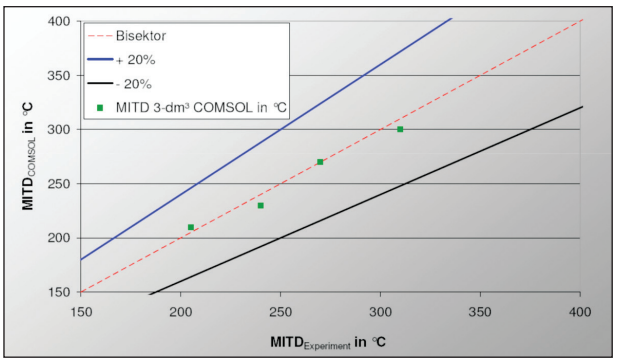


**Fig 3. Direct comparison of the MITD for a 3 dm³ vessel at various temperatures showing how the experimental and simulated temperatures are very close across a wide range.**

## Industrial-Sized Reactors

We are now embarking on a series of validation tests using industrial-sized reactors. The benefits of having a validated model are plentiful. Companies could determine if for a given reactor a specific pressure/temperature setting is not safe and consequently adapt the process. Plant engineers could use the model to determine if and how they should change their process conditions. Furthermore, with a working model we can study additional aspects such determining the geometric dependence of the self-ignition temperature. Finally, we can study forced convection, add piping of various diameters, different flow regimes and vessels orientations as well the effect of internal features/obstacles. ■

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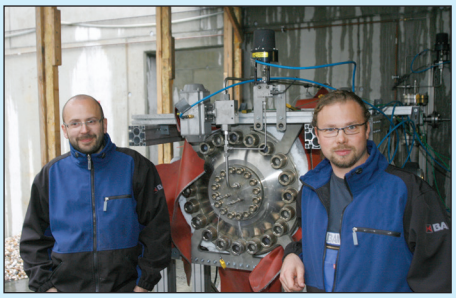

**The authors Dr. Fabio Ferrero (left) and Martin Beckmann-Kluge (right) standing in front of an autoclave.**

Dr. Fabio Ferrero is a researcher at the BAM German Federal Institute for Materials Research and Testing. He received a degree in Chemical Engineering at the Politecnico di Torino in Italy and then his PhD from the Universitat Politècnica de Catalunya in Barcelona for work on hydrocarbon pool fires. He started his career at BAM in 2007 and has since dealt with different aspects related to the safety in chemical plants including research topics addressing decomposable gases such as TFE and acetylene.