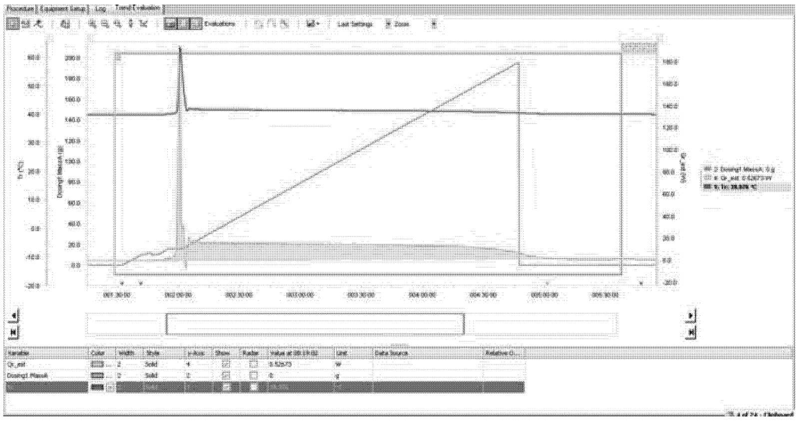

*__Figure 8__: grignard reaction monitored in real time: The blue curve shows the mass of the reaction mixture mr, i.e. the dosing of parabromtoluene and toluene. In green the heat of reaction obtained in real time based on RTCalTM, in red the reaction temperature Tr.*

As Figure 8 shows, RTCal$^{TM}$ monitors a very strong peak of reaction heat at the beginning of the reaction up to *Qr* = 150W in the reaction mixture. The reaction enthalpy resulting in real time fits nicely with former values of the standard method as shown in the table below.

***Table 4:*** *Reaction enthalpies for the Grignard experiment.*

| **Experiment integration based on** | **Qr** | **Qrtc** |
|---|---|---|
| Grignard integration results | -510 kJ/mol | -487 kJ/mol |

## 3. Conclusions

The new RTCal™ principle has been used to characterize two reactions examples. The esterification of propionic anhydride was performed in order to demonstrate the feasibility, precision and advantage of following the reaction with a strong heat of dosing. The Grignard reaction demonstrate instead that RTCal$^{TM}$ could be used for safety studies to characterize and optimize in real time dangerous reactions.

RTCal™ heat flow profiles therefore allows the user to make adjustments to the actual chemistry and optimization of process parameters online.

RTCal™ is complementary to the traditional heat flow method and adds additional data which translates into better information. The ease-of-use makes RTCal™ a true walk-up tool that substantially enhances the capabilities and applications of the Reaction Calorimeter RC1e™ (Mettler-Toledo).

iControl is the new evaluation and control software which combines functionality with flexibility and a simple and straightforward graphical user interface. This modern and state-of the-art user interface reflects the personal way to run experiments and offers what was always expected from the control software.

In summary, regardless of whether you are looking for immediate thermal data, searching for specific details within your process, generating data to develop a kinetic model or simply optimizing a process RTCal™ will help to find the answer in an efficient and cost effective manner.

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# Failure Simulation and Pool-fire Radiative Effects on Nearby Process Units

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This manuscript shows how the connection and interaction between a process dynamic simulator and a dynamic accident simulator allow improving operators training, accident investigation, and safety management, by better modeling the feedbacks existing among process units and accidental events.
In this perspective, the manuscript presents a rather simplified case study that allows simulating the process dynamic response to an industrial accident comprising a continuous leakage of flammable liquid, the pool spreading, and its final ignition and fire. Interactions between dynamic models of both process and the pool-fire allow investigating radiative effects on nearby process unit.

## 1. Introduction

Chemical and industrial facilities handling dangerous materials should comply with high levels of process safety. Primary objective of safety programs, within chemical facilities, is the prevention of accidents. In this field, the goal should be to improve the safety by acting on technological issues, management systems, and staff skills in order to approach the ultimate objective of zero accidents. On the other hand, when an industrial accident occurs, the main goal is limiting the damages.
The manuscript discusses both the operations and operator actions that must be carried out when an industrial accident occurs. This requires three sequential phases: (i) dynamic simulation of an industrial process; (ii) dynamic simulation of an industrial accident; and (iii) process response understanding.
These phases involve different process system issues as well as the biunique interaction of a dynamic simulation program with an accident simulation one, according to:

- The dynamic simulation of industrial processes requires developing a detailed mathematical model as well as the defining an adequate plant-wide control system. The dynamic simulation suite DYNSIM$^{TM}$ (Simsci-Esscor, 2004) may been adopted for these purposes;
- The development of an accident simulator capable of interacting and exchanging information with a process dynamic simulator (Brambilla and Manca, 2007);
- Process response understanding means coupling both the process simulators to investigate what happens in case of accident while assessing the robustness and quality of the control loops.

In the literature, a number of papers discuss just one of the first two points. Some authors (Gani and Grancharova, 1997; Bezzo *et al*., 2004; Manenti, 2007; Signor *et al.*, 2007) developed detailed dynamic models and *ad hoc* control schemes for chemical plants by using widespread process simulators. Others (Webber, 1990; Fay, 2007; Raj, 2007) discussed in detail the liquid leakage and pool-fire modeling as well as fire dynamics.

Nevertheless, there are not any publications on interactions between process dynamic simulation and industrial accident simulation, except for a recent paper (Brambilla *et al.*, 2008), which explains some significant concepts on which is based the present research activity.

Section 2 describes the methodology adopted in the integration of chemical process and pool-fire. The case study is discussed in Section 3 and preliminary results are explained in Section 4.

## 2. Interactions of Dynamic Models

The main benefit coming from the integration between a process dynamic simulation and an industrial accident simulation is the opportunity to study process unit behaviors when a specific failure occurs. This goes beyond ordinary and static HAZOP, FTA, or What-If analyses, since it involves the dynamic response of the process units, by taking into account their interactions with the accidental event as well as offering a valid and field-proven support to risk assessment.

Let us consider the following scenario: in a LNG train, a rupture occurs on an intermediate tank storing normal-butane. As a consequence, a leakage of flammable liquid occurs instantaneously and produces a pool which is fed by the storage tank. After some minutes, the pool is ignited and a pool-fire starts. A few minutes later, both control-room and field operators detect and solve the problem. The pool-fire is no longer fed by fresh butane and the fire extinguishes in few minutes.

The dynamic models, applied to both process and accident investigation, allow understanding how the radiative flux (emitted by the pool-fire) affects the behaviour of the process units. On the other side, it is also possible to evaluate the effects of these disturbances on pool-fire where different operating conditions in the storage tank lead inevitably to the variation of the emitted flowrate.

### 2.1 Closed-loop Technique

The interactions between a process dynamic simulation and an industrial accident simulation require the complete integration of two different packages in real time. A mixed-language approach was adopted to connect AXIM© (a proprietary package mainly coded in Fortran 90) to DYNSIM™. An *ad hoc* interface was developed in C++ where AXIM is implemented in DYNSIM as an added-module (see also Figure 1).

This integration gives a twofold benefit: AXIM potentialities can be indiscriminately exploited to simulate accidents and failures in every kind of process dynamic simulation and industrial field. Furthermore, any future upgrading of AXIM should not require any modification to the DYNSIM environment and to the dynamic models already developed.

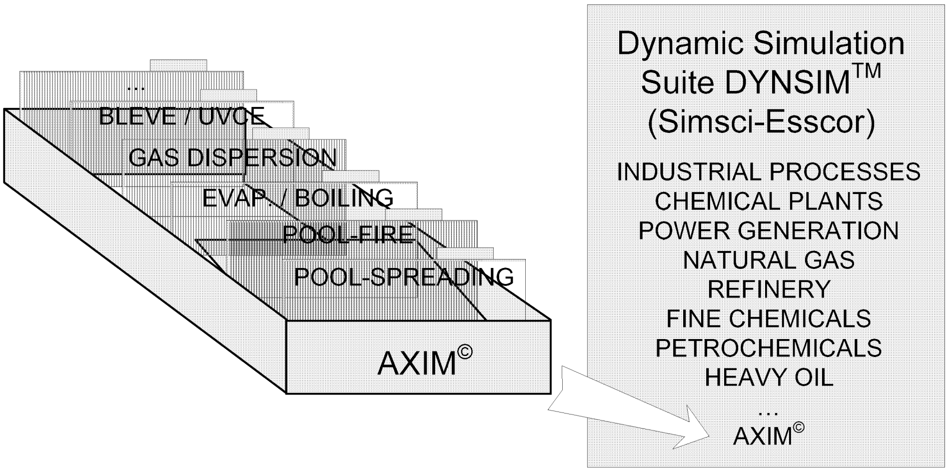


Figure 1: AXIM is integrated as a DYNSIM added-module

## 3. Case Study

The case study is based on the dynamic simulation of a LNG plant subsection, specifically an intermediate storage tank containing n-butane, placed before the final large-size LNG storage. The proposed industrial accident is a continuous flammable liquid leakage, which lasts for about 15 min, and the subsequent pool-fire, in accordance with the aforementioned scenario.

The dynamic simulation assumes that, before the occurrence of the accident, the plant is in steady-state conditions. When the accident occurs, the ignition is not synchronous with the liquid leakage. Actually, the liquid spreads up to an ignition source that is 2.5 m far from the center of the pool. By performing the simulation, we can assess that the pool starts burning 9 min and 42 s after the occurrence of the hole in the pipe when the aforementioned ignition source is reached by the spreading pool. The flame radiates a time-varying heat flux towards the surrounding process units, according to the amount of liquid in the pool, evaporation rate, and atmospheric and wind conditions.

In particular, we focused on the effects of the radiated heat to a small storage tank of one meter diameter, 2 m height, and an internal liquid level of 0.5 m. The flame distance from the storage tank is 4 m. The perforated pipe receives the process butane flowrate from the intermediate process drum.

## 4. Preliminary Results

Figure 2 shows the radiative effects of the pool-fire on the nearby storage tank. Pool-fire is characterized by four distinct stages: ignition, radiative peak, radiative plateau, and extinction. With reference to the radiative effects on the neighboring process units, only the radiative peak and plateau have a significant impact, whilst both ignition and extinction phenomena may be neglected.

The radiative peak reaches a flame radiation higher than 60 kW, although for a reduced time (about 30 s). Conversely, the radiative plateau is characterized by a flame radiation of about 20 kW, for a longer period (about 5 min).
When the pool is ignited, the n-butane temperature increases inside the drum. The higher temperature derivative corresponds to the radiation peak. On the other hand, when the pool fire reaches a more stable regime (radiative plateau), the tank temperature is characterized by a negligible derivative.
When the upstream emergency-valve is closed and the liquid emission is halted, the storage tank temperature reaches its maximum value, about 307 K, before starting to decrease to the original steady-state value.
In this perspective, the proposed research activity is useful in training both the field and control-room operators. It is also helpful to train the operators and make them aware of unconventional and emergency conditions while defining the most appropriate and robust plant-wide control systems. Finally, these tools allow identifying and quantifying the transient procedures to better control the plant and assure the process safety when an accident occurs.

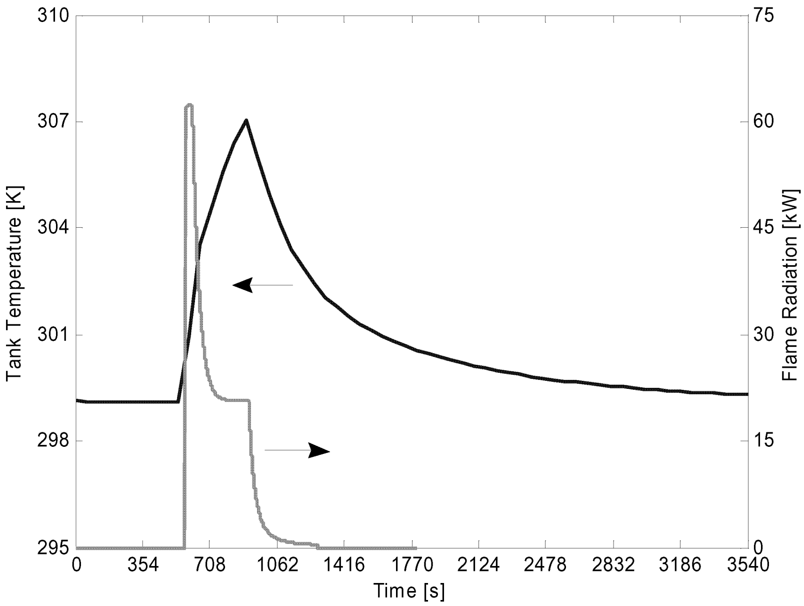


Figure 2: Pool-fire effects on a nearby process tank

## 5. Conclusions and Future Challenges

The paper described the interactions between a commercial and field-proven process simulation package and a proprietary industrial accident simulator via a closed-loop technique. This means that the dynamic interaction between these simulators is allowed

and active in both directions and biuniquely, *i.e.* from the dynamic process model to the industrial accident tool and vice versa.
Specifically, a n-butane storage tank was modeled and controlled in DYNSIM and a pool-fire was simulated in AXIM, with the main objective of studying the process dynamics subject to radiative effects.
Preliminary encouraging results showed some of the potentialities deriving from coupling a process dynamic simulation with an industrial accident tool, especially in terms of process understanding, analysis of process dynamics, and discussion and validation of the process control system.
Future challenges will concern the interactions between more complex industrial plants and multifaceted accidents, with a significant impact on plant safety and reliability, operator training, and human factor issues.

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