Hybrid Framework for Hazard Identification and Assessment in Batch Processes

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A framework presented addresses the three main parts of a process hazards analysis study: hazard identification, hazard evaluation, and hazard mitigation. The framework utilizes a hybrid methodology that effectively combines a qualitative digraph model-based technique for performing hazard identification and a quantitative optimization-based technique for performing hazard evaluation and hazard mitigation. The combined framework circumvents the local minima problems faced by mathematical optimization algorithms, as well as the qualitative ambiguities that plague digraph models. The systems used to implement the framework are BatchHAZOPExpert, gPROMS, and gOPT. BatchHAZOPExpert is used for hazard identification, while gPROMS and gOPT are used for hazard evaluation and hazard mitigation. The application of the integrated framework is illustrated by implementing it on two industrial case studies.

Introduction

With today's chemical processes routinely handling a number of hazardous materials and operating at extreme conditions of temperature and pressure, the possibility of hazardous situations occurring in these processes has significantly increased (Kletz, 1985). This has led to an enhanced awareness of safety related issues in the chemical process industries (Lees, 1996a,b). Analyzing these processes to ensure safety has become more of a challenge with the increased complexity of their operation. Process hazards analysis (PHA) is the activity that addresses this challenging problem. PHA is defined as the systematic identification, evaluation, and mitigation of potential process hazards that could endanger the health and safety of humans and cause serious economic losses (Kletz, 1986). The primary purpose of PHA is to determine what deviations from normal operation can occur in a process, what are the possible causes of these deviations, what are the potential consequences of these deviations, the likelihood of these events, and what measures can be adopted to prevent these events or to mitigate their effects if they were to occur. The three parts of PHA: hazard identification, hazard evaluation, and hazard mitigation aim to address different parts of these areas of concern. In hazard identification, the possible deviations from normal operation are listed and the possible abnormal causes and the adverse consequences for these deviations are identified. The most popular methodology for performing hazard identification is hazard and operability analysis or HAZOP. Hazard identification is a qualitative reasoning phase of PHA that determines a preliminary set of hazards that can occur in a process. Based on quantitative information such as the bounds on inputs and disturbances and values of various process parameters, it is possible to obtain more detailed information about the identified deviations, and their causes and consequences. This phase of PHA where more detailed quantitative information is procured is hazard evaluation. Based on these detailed estimates on the various hazards, it is possible to come up with strategies including changes in operating policy to prevent or reduce the likelihood of an occurrence of the hazard and also suggests protective measures to be adopted in the event of the hazard. This is the hazard mitigation phase of PHA.

PHA needs to be performed in both continuous, as well as batch processes. Even though more major incidents bring to mind continuous processes, the possibility of hazardous situations is no less for batch processes (The Institution of Chemical Engineers, 1989). This is especially so because of the time varying and dynamic nature of apparently simple batch processes. Also, many products are routinely being manufactured in parallel and this multipurpose nature of a batch process makes it more likely for a hazardous situation such as

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cross contamination to occur. In this article we will therefore focus our attention on PHA for batch processes.

PHA is a laborious, time-consuming, and expensive activity. It requires specialized expertise and knowledge. PHA needs to be thorough and complete. Automating PHA would be very useful, because it would be less error-would take, and takes less time and human effort. In addition it would facilitate documentation for regulatory compliance by storing the results online. In this article we present a methodology that builds upon existing automated techniques for performing hazard identification, hazard evaluation, and hazard mitigation to provide an integrated framework for performing PHA for a batch chemical process. Related previous work that addresses the individual aspects of PHA is reviewed, and the necessity for an integrated framework is identified. The proposed integrated framework and its features are described. The framework is illustrated for two case studies. Finally, the results and scope for future work are discussed.

Review of Related Previous Work

HAZOP (Knowlton, 1989) is the most widely used methodology for hazard identification. The main principle behind HAZOP is that hazards in chemical processes arise as a result of deviations from normal operating conditions. During HAZOP, these deviations are systematically analyzed one by one by applying guide words like MORE OF, LESS OF, NONE, REVERSE, PART OF, AS WELL AS, and OTHER THAN in conjunction with process variables and parameters. There has been limited work to automate this reasoning mechanism adopted during HAZOP analysis. HAZOPExpert (Vaidhyanathan and Venkatasubramanian, 1995, 1996a) is a digraph model-based state of the art tool that facilitates automated qualitative HAZOP analysis for continuous plants. HAZOPExpert has successfully been tested on several industrial case studies and the results generated by the system compare favorably with those of the experts. Further extensions to HAZOPExpert (Vaidhyanathan and Venkatasubramanian, 1996b) have been proposed to incorporate semi-quantitative process information.

Recently, BatchHAZOPExpert (Srinivasan and Venkatasubramanian, 1998a,b) a system that performs HAZOP analysis for batch processes, has been reported. BatchHAZOPExpert, similar to HAZOPExpert, uses a qualitative digraph model-based mode of reasoning. Batch processes are inherently different from their continuous counterpart in their operation, with the different activities occurring in a hierarchical fashion. Hence, Batch-HAZOPExpert differs from HAZOPExpert in its process knowledge organization. A Petri Net based approach is used to represent the various hierarchical levels of batch operation (tasks, subtasks). The Petri Net based approach for modeling the batch process explicitly captures the discrete nature of the batch process operation. They tend to be equipment-centered in contrast to continuous processes which are operation-centered (Srinivasan and Venkatasubramanian, 1998a). The digraph models are associated with subtasks, unlike in HAZOPExpert, where they are associated with the equipment. This is necessary, because in batch processes the equipment is multipurpose and, during the different operations that can be performed within an equipment, the process dynamics occurring within the equipment change. The subtask digraph causal models capture the continuous dynamics that occur during each of these discrete operations. An advantage of explicitly modeling the discrete nature of the batch process operation using Petri Nets is that, in addition to reasoning about routine process variable deviations, it allows BatchHAZOPExpert to analyze maloperation scenarios that arise as a result of operator errors. These include incorrect sequence of operation, omission of operations, addition of wrong material, and so on. BatchHAZOPExpert has been extensively tested on several industrial case studies and has performed favorably well (Srinivasan, 1998).

Both HAZOPExpert and BatchHAZOPExpert address the issue of hazard identification for chemical processes. There has been some work in the area of automating the hazard evaluation and hazard mitigation phases of PHA as well. A quantitative model-based approach (Dimitriadis, 1997) to this problem has been proposed that uses a state-transition representation to model chemical processes (both continuous and batch). The states have associated differential and algebraic equations. The transitions connecting states capture model discontinuities (such as laminar to turbulent flow), as well as those that arise because of control actions (such as opening and closing a valve). This state transition representation of the model is then translated into an equivalent Mixed Integer Linear Program (MILP). The decision variables for this MILP are the various process inputs and disturbances, and the objective function of the MILP tries to maximize the time for which the process is unsafe (such as variables that are above threshold values). Based on this safety verification or hazard evaluation, the troublespots of the process are determined and design recommendations are developed, again through optimization techniques, to prevent or mitigate the effects of the hazards. The systems that are actually used to implement the process models and the optimization scheme are gPROMS (Barton and Pantelides, 1994) and gOPT (Vassiliadis et al., 1994a,b).

Integrated Framework for PHA

The various phases of PHA, as outlined in the previous section, are currently being automated by different sets of tools. It would definitely be useful to have an unified framework that effectively combines these individual methodologies to perform all aspects of PHA. With this purpose, we propose in this article an integrated framework that combines the qualitative digraph-based hazard identification methodology and the quantitative optimization-based hazard evaluation approach to efficiently perform PHA. Recently, there has been an effort to provide such a unified framework for performing PHA for continuous processes (Srinivasan et al., 1998). We extend upon this earlier effort to encompass batch processes as well. The first extension is the more detailed consideration of phenomenological models. This is very important for batch processes, because nearly 35% of all batch process hazards are reaction-based (Barton and Rogers, 1997). The second extension to the framework is the ability to consider maloperation scenarios that arise primarily in batch processes because of the active role played by the operator during batch operation.

The knowledge organization and the inference mechanisms in the unified framework are shown in Figure 1. The

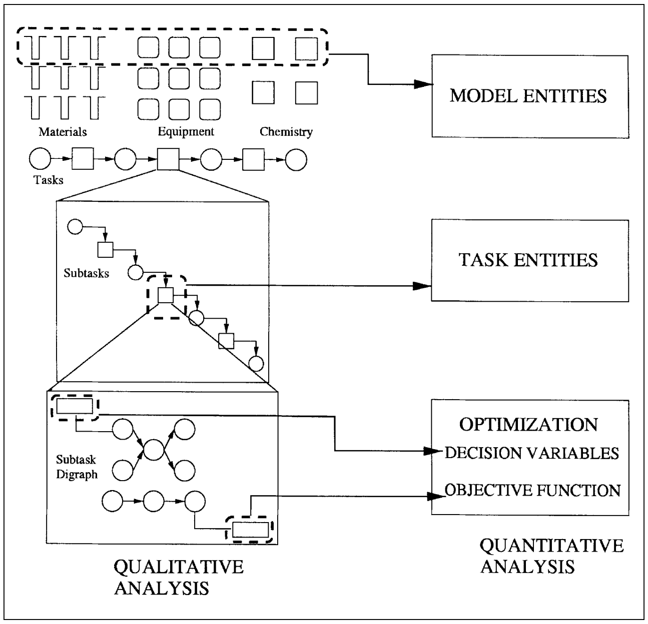

Figure 1. Unified framework for process hazards analysis.

framework proposes a method that effectively combines the qualitative digraph-based hazard identification methodology with the optimization-based hazard evaluation and mitigation technique. The primary idea is to intelligently guide the formulation of the hazard evaluation and hazard mitigation based on the hazard identification results. This would result in smaller sized optimization problems that are numerically tractable and whose solutions are practically relevant, apparent, and applicable. The working of the framework consists of the following steps:

- Process modeling for qualitative analysis;
- Qualitative digraph-based hazard identification;
- Filtering of identified hazards for further evaluation;
- Focused process modeling for hazard assessment; and
- Focused development of optimization problem for hazard evaluation and mitigation.

A more detailed explanation about the knowledge organization in the framework and the various steps in the working of the framework are described below.

Process modeling for qualitative analysis

The knowledge necessary for qualitative analysis is divided into two parts: process specific information and process generic information. Process specific knowledge consists of information about material, equipment, chemistry, and operating procedures. The material, equipment, and chemistry knowledge is represented using an object-oriented methodology. The operating procedures are represented using Petri Nets in a two-tier scheme: tasks and subtasks. Tasks represent operations such as reaction, filtration, while subtasks consist of operations such as charge, heat, stir, and so on, which when combined together make up a single task. The process generic knowledge needed for qualitative analysis are the subtask digraph models. These are causal models that capture the interactions between the process variables that describe the dynamics occurring in a subtask. The nodes in a digraph model correspond to the process variables, and the arcs, with associated arc gains, depict the interaction between these process variables in a qualitative manner. Within the subtask digraph models, in addition to the digraph nodes and digraph arcs, there are cause and consequence nodes associated with all the relevant process variables. These contain information about the hazards that could arise if the value of the process variable were to become high, low, or zero. A set of these digraph models, consisting of digraph nodes, digraph arcs, cause and consequence nodes, associated with different subtasks are stored in a subtask digraph model library within the framework.

Qualitative digraph-based hazard identification

After the process specific knowledge has been specified, hazard identification is then performed in the framework using this knowledge and the subtask digraph model library. Systematically, a set of deviations such as HIGH TEMPERATURE, LOW FLOW RATE, ZERO AGITATION are introduced in the various subtasks that constitute the process. The deviations are then propagated within and across the subtask digraphs (upstream and downstream of the subtask) to determine the effect of the deviation on all the process variables. Then, the relevant portions of the cause and consequence nodes of the various process variables are activated and the hazards are identified based on the information in these cause and consequence nodes. In addition to generic hazards, the cause and consequence nodes also have cause and consequence functions associated with them that report a hazard or not based on more process specific information (such as low agitation will cause solids settling in a stir subtask only if there is a solid component during the subtask). The hazards identified by the qualitative digraph-based analysis are then stored in a systematic object-oriented fashion.

Filtering of identified hazards for further evaluation

Not all the hazards identified through the qualitative analysis need to be evaluated further. Most of them are routine and can be reported as such. There are some, however, which require more detailed consideration. These include scenarios that have very serious potential consequences and those that seem spurious and not likely to happen. In this effort, we have concentrated on filtering hazards that have serious potential consequences for further evaluation. Of the hazards identified, it is necessary to filter out the ones that are critical and need to be evaluated further. There is a degree of manual judgment required here, because there is no precise definition of a critical hazard. This may vary from process to process. There are, however, some measures and properties that are useful indicators of whether a hazard is critical or not. The methodology adopted in this framework to filter hazards requires interactive, but intelligent, search through the identified set of hazards to determine which ones need to be evaluated further. To facilitate an intelligent search through the identified hazards, the PHA framework categorizes them based on several criteria. These criteria include consequence class, cause class, materials involved, severity measure, and likelihood of occurrence measure. The PHA framework also provides graphical utilities that allow fast and efficient navigation through the identified hazards based on the above listed criteria. Using these utilities, the set of hazards that require further detailed evaluation are determined.

Focused process modeling for hazard assessment

For each of the filtered hazards, it is necessary to model only those sections of the process that are relevant to the hazard. The relevant section of the process or the extent of the process that needs to be modeled is determined by the cause (initial point) and the consequence (final point) of the hazard. For the extent of the process, thus determined, more detailed chemistry (reaction kinetics), material (thermophysical properties), and equipment (process dynamics) model entities are constructed. Also, for the extent of the process considered relevant for each filtered hazard, the corresponding sequence within the operating procedures are modeled as task entities.

Focused development of optimization problem for hazard evaluation and mitigation

Once the process model for a particular filtered hazard has been developed, it is necessary to specify the optimization problem to analyze and evaluate the hazard. Here again, the hazard identification stage guides the hazard evaluation stage. The causes identified by the qualitative phase determine the decision variables for the optimization problem, while the objective function of the optimization problem is determined by the consequences of the hazard. Once the optimization problem is developed, it is solved through standard solution methodologies that are available. The solution to the optimization problem determines if the situation is credible and if there is a need for any recommendations. If the need for a recommendation is identified, then another optimization problem is posed that tries to search for a better operating policy that helps prevent the hazard or mitigate its effect were it to occur.

The above framework was realized by performing qualitative analysis using BatchHAZOPExpert and quantitative analysis using gPROMS (process model) and gOPT (optimization). Currently, the filtering of the results for further evaluation is being done manually. The results of using these tools to realize the integrated framework are illustrated in the next section.

Case Studies

The case studies considered in this section were obtained from Monsanto Pharma. The details of the case study such as material and equipment names, however, have been suitably modified.

Case study I

The first case study used to illustrate the framework is a semi-batch process. It consists of eight process materials (three reactants (A, B, C) a solvent (D), two byproducts (E, F), one main product (G), and a purge gas (H)), five equipment items (two stills, a filter, a dryer, and a scrubber), four tasks with associated chemistry (a reaction, a filtration, a drying, and a scrubbing), and 27 subtasks which make up these four tasks. The process consists of reaction of A, B and C in a solution of D to yield E, F and G. E and F are scrubbed from the reaction mixture using purge gas H. The remaining solution is then filtered and dried to yield the pure product G.

The process details, described above, were modeled in BatchHAZOPExpert, through its user interface, as shown in Figure 2. Then, the hazard identification was done in a batch mode for all the standard deviations in the various subtasks which were considered by experts during manual HAZOP. The HAZOP performed using BatchHAZOPExpert identified a total of 75 causes and 90 consequences. Most of the causes and consequences were routine. To illustrate the working of the framework, one of the hazards was considered for further evaluation. The details of this hazard are shown in Table 1. This was chosen because temperature control hazards occur frequently in batch process operations and account for nearly 20% of batch process incidents (The Institution of Chemical Engineers, 1989).

As can be seen from Table 1, the deviation introduced was high reaction rate. It has a total of six possible causes and one major consequence. Out of the six possible causes, those relating to the temperature control, namely the high ramp rate and low hold time causes, were considered in more detail during the hazard evaluation phase. The effect of variation in these temperature control causes on the one major consequence, that of rapid gas evolution, was studied during the hazard evaluation stage.

For this particular scenario, the section of the process that is of importance is the reaction task. The subtasks within the reaction task that are important are the heat, hold, and reaction subtasks. The equipment of importance are the reactor and the scrubber. All the materials need to be considered for this particular hazard. The relevant chemistry to be considered is that pertaining to the one reaction. So, only these details of the process (eight materials, two equipment, one reaction, one reaction task, and four subtasks) were modeled in gPROMS for the purposes of the hazard evaluation. The process model developed for this case study is shown in Appendix A. As one can observe, the model size is significantly smaller than would be for the entire process by intelligently formulating it based on the identified hazard.

The optimization problem was determined by the three causes and the one consequence. The decision variables for the optimization were the two ramp rates of the two heat subtasks and the duration of the hold subtask. Reasonable bounds on the decision variables were imposed based on the bounds on the heating utilities in the process. The objective function was to maximize the unsafe time, that is, the time for which the flow rate from the reactor to the scrubber was above the scrubber capacity limit. This objective function was sufficient, because the process returns to the safe operating regime at the end of the reaction task. The optimization problem developed for this case study is shown in Appendix B. The hazard evaluation was then done over two stages using this formulation in gOPT. First, the effect of each of the causes on the consequence was considered independently. This was followed by a study of the effect of all the causes simultaneously (multiple fault scenario). The results of the study are shown in Table 2 and the temperature control, and the corresponding inlet flow rate to the scrubber are shown

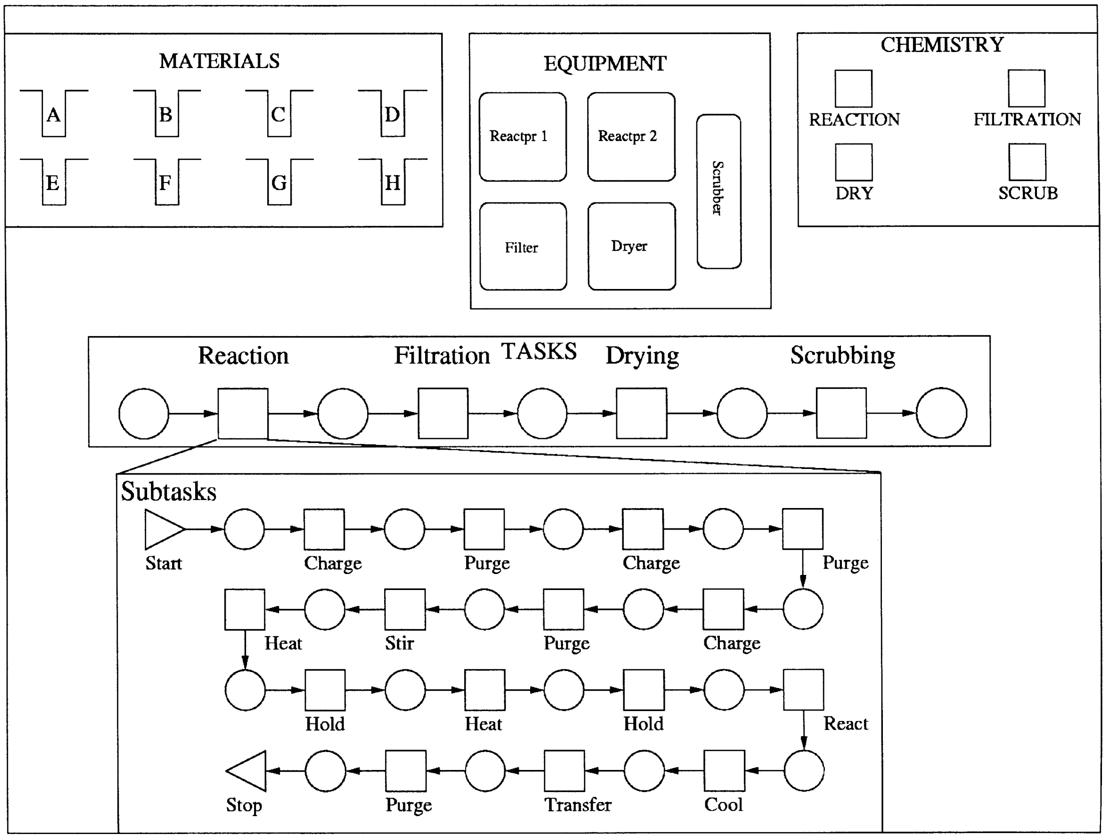

Figure 2. Case Study 1: process modeling in BatchHAZOPExpert.

in Figures 3 and 4. The values of the ramp rates in the heat subtasks when allowed to vary independently (scenarios 1 and 3) hit the maximum value of 0.08 in the worst case, and the unsafe times for these two scenarios are of the order of 3,000 s. The unsafe time when the duration of the hold operation is allowed to vary independently (scenario 2) is 4,900 s and the decision variable value for the duration of the hold subtask hits its minimum value of 0.0 s. The maximum value of the vapor flow rate in the case of scenarios 1 and 3 is less than 440,000 L per hour, while for scenario 2 it is greater than 440,000 L per hour. From these observations, one can conclude that the duration of operation of the hold subtask seems to be the predominant factor that affects the unsafe time of operation. The ramp rates also have an effect on the unsafe time, but not to the extent of the hold subtask duration. So, it is necessary for the operator to ensure that the hold subtask

Table 1. Case Study 1: Hazard Identification Using BatchHAZOPExpert (Causes and Consequences for High Reaction Rate Deviation During Reaction Subtask)

Causes	Consequence
Heat Subtask 2: High Ramping Rate Hold Subtask 1: Low Duration of Operation Heat Subtask 1: High Ramping Rate Charge Subtask 3: High Amt of Reactant A Charge Subtask 2: High Amt of Reactant B Charge Subtask 1: High Amt of Reactant C	Reaction Subtask 1: Rapid gas evolution

Table 2. Case Study 1: Hazard Evaluation Using gOPT (Maximizing Unsafe Time by Varying Ramp Rates and Hold Duration)

Scenario	Decision Variable (DV) Bounds	Optimal DV Values	Total Unsafe Time
1	Heat Subtask 1 Ramp Rate (0:0.08°C/s)	0.08 until T 308	3,100 s
2	Hold Subtask 1 Duration of Operation (0:10800)	0.0 s	4,900 s
3	Heat Subtask 2 Ramp Rate (0:0.08°C/s)	0.08 until T 323	3,200 s
4	Heat Subtask 1 Ramp Rate (0:0.08°C/s)	0.00167 for 10 s	
	Hold Subtask 1 Duration of Operation (0:10,800)	0.0 s	
	Heat Subtask 2 Ramp Rate (0:0.08°C/s)	0.0571592 for 4,546 s	5,500 s

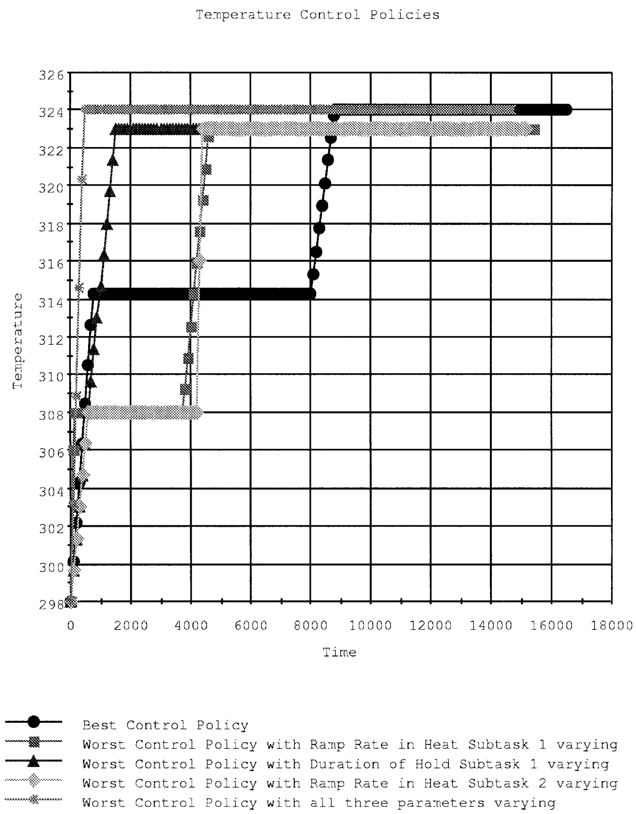

Figure 3. Case Study 1: operating policies for the different scenarios.

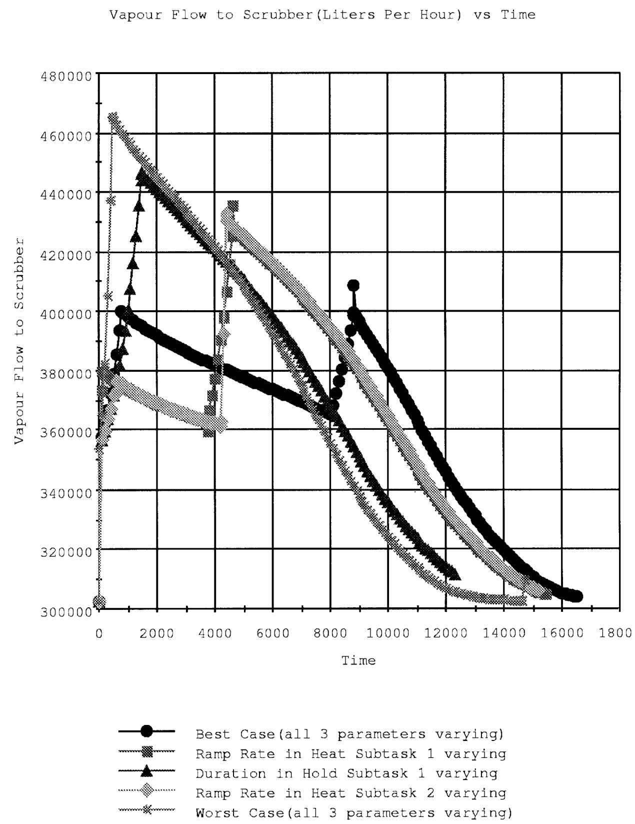

Figure 4. Case Study 1: vapor flow to scrubber for the different scenarios.

is performed properly, as it is crucial for the safety of the process and personnel and this is one possible recommendation that could be included in operating records. This sort of inference is possible through the rigorous quantitative hazard evaluation part of the framework and is one of its main advantages.

A second optimization problem was posed to determine if there was an optimal operating policy that keeps the plant safe while ensuring minimum processing time. This optimization problem can be visualized as a fault avoidance formulation that ensures that the plant does not enter an unsafe state during the operation. This formulation is shown in Appendix C. The optimal temperature control policy that was determined through this formulation is shown in Table 3. From the control policy, we can see that the recommended mode of operation is ramp at a relatively faster rate initially (0.02°C/s) and hold for a sufficiently long duration (order of 2 h) and then ramp at a slower rate (0.01°C/s) during the second heat subtask. This operating policy can be explained by the fact that at lower temperatures the rate of reaction is lower and; hence, the gas evolution rate is lower. So it is safe and optimal to operate at a higher ramp rate. At higher temperatures, however, the rate of reaction is higher so the ramping rate has to be slower in order to ensure that the gas evolution rate is not too high. Based on the hazard evaluation study, it was observed that the duration of the hold subtask was crucial to the operation and this is corroborated by the value of the duration of the hold subtask determined by the hazard mitigation analysis.

Case study II

The second case study that was used to test the framework was a larger one. It has a total of 11 materials, 10 equipment, 10 tasks and related chemistry, and 100 subtasks. These were modeled in BatchHAZOPExpert. Out of the identified hazards one hazard was filtered for further evaluation. This hazard corresponds to an overcharging of reactants. Overcharging reagents like temperature control incidents accounts for around 20% of the incidents in batch processes (The Institu-

Table 3. Case Study 1: Hazard Mitigation Using gOPT (Minimizing Unsafe Time and Total Processing Time by Varying Ramp Rates and Hold Duration)

Decision Variable (DV) Bounds	Optimal DV Values	Optimal Obj Fn Value
Heat Subtask 1 Ramping Rate (0:0.08°C/min)	0.020907	0.0 s
Hold Subtask 1 Duration of Operation (0:10,800)	7,235.44 s	
Heat Subtask 2 Ramping Rate (0:0.08°C/min)	0.0120076	

Table 4. Case Study 2: Hazard Identification Using BatchHAZOPExpert (Consequences for Reactant Overcharge Maloperation Scenarios)

Consequences
High concentration of unreacted gas in scrubber outlet
Boiloff of scrubber media due to high temperature in scrubber

tion of Chemical Engineers, 1989). Another reason why this hazard was chosen for evaluation is because it illustrates the ability of the framework to handle maloperation scenarios. In Table 4 the results for this hazard from BatchHAZOPExpert are presented. There are three maloperation scenarios—overcharging of each of the reactants—that will result in the same two consequences: insufficient scrubbing due to high gaseous flow rate to scrubber, and boiloff of scrubber media because of high scrubber temperature that is a result of the high exothermic reaction rate. The high reaction rate again is due to the high flow rate of the gaseous reactant into the scrubber.

The section of the process that was modeled for evaluating this hazard consists of 11 materials, 2 equipment, 2 tasks, and 6 subtasks. The optimization problem for hazard evaluation was posed based on the three causes and the two consequences. The decision variables were the initial amount of each reactant that enters the reaction subtask, and the objective function was to maximize the cumulative amount of gas that enters the scrubber. The objective function captures both the consequences: insufficient scrubbing due to high gas flow rate and boiloff of scrubber media. As for the first case study, the evaluation was conducted over two stages: independently considering the effect of overcharging of each of the reactants and simultaneously considering the effect of overcharging all the reactants. The results of these analysis are shown in Table 5 The first scenario is overcharge of the limiting reagent, and the next two scenarios are the independent overcharge of the other two reactants. The last scenario is the simultaneous overcharge of all three reactants. From an analysis of the four scenarios, it can be seen that the overcharging of the limiting reagent is more important than the overcharge of the other two reactants and that overcharging of other two reactants has an effect only if the limiting reagent is overcharged. The maximum amount of gas that can be released to the scrubber is realized in the event of a simultaneous overcharge of all three reactants and the value of the cumulative amount of gas that is discharged from the reaction in this worst case scenario is of the order of 1,700 mols of gas. The cumulative amount of gas discharged to the scrubber from the reactor for the two scenarios of overcharging the limiting reagent and simultaneous overcharge of all three reagents is shown in Figure 5.

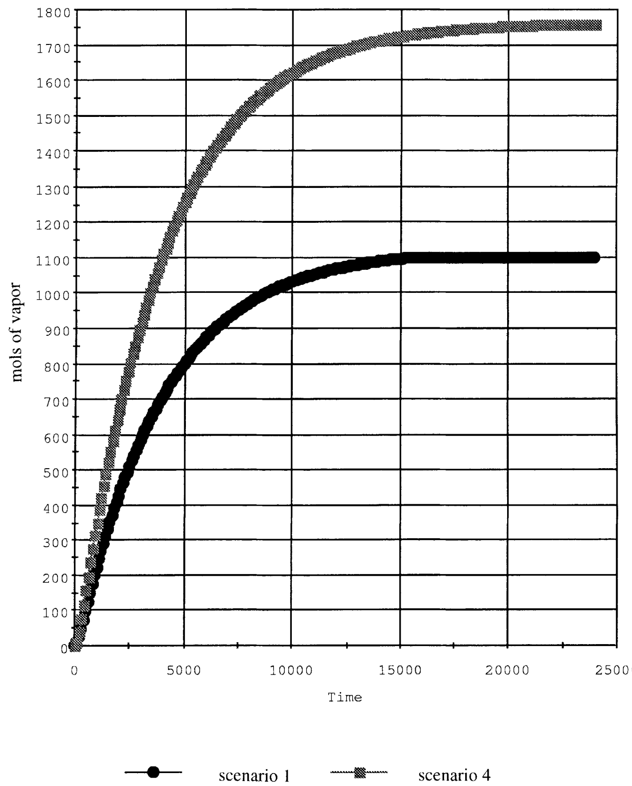

Figure 5. Case Study 2: cumulative vapor discharged to scrubber for two scenarios.

Table 5. Case Study 2: Hazard Evaluation Using gOPT (Maximizing Outlet Gas Flow Rate from Reactor by Varying Reactant Overcharge Amounts)

Scenario	Decision Variable (DV) Bounds	Optimal DV Values	Optimal Obj Fn Value
1	Charge Subtask 1 Overcharge Amount (0:441 mol)	120	1,100 mols of vapor
2	Charge Subtask 2 Overcharge Amount (0:1,100 mol)	0.0	882 mols of vapor
3	Charge Subtask 3 Overcharge Amount (0:550 mol)	0.0	882 mols of vapor
4	Charge Subtask 1 Overcharge Amount (0:441 mol)	441	
	Charge Subtask 2 Overcharge Amount (0:1,100 mol)	0.0	1,750 mols of vapor
	Charge Subtask 3 Overcharge Amount (0:550 mol)	332	

Table 6. Case Study 2: Hazard Mitigation Using gOPT (Minimizing Scrubber Media Amount While Ensuring Temperature Rise and Unreacted Gas Amount Constraints are not Violated for Worst Case Inlet Gas Flow Rate)

Decision Variable Bounds and Constraint Specs	Optimal DV Values and Constraint Values
Charge Subtask in Scrub Task Total Amount (0:1,500 kg)	1,204.5 kg
Charge Subtask in Scrub Task Bleach Concentration (5:15 mass %)	10.87
Temperature Rise in Scrub Task $< 75°C$	Temperature Rise = 75°C
Unreacted Gas in Scrub Task < 1 mol	Unreacted Gas = 1.0 mols

A second optimization problem was posed that would mitigate the effect of the hazard if it were to occur. This formulation is a fault tolerance formulation to design the scrubber so that it can handle the worst case scenario of the gas flow rate that was observed during the hazard evaluation study. In this optimization problem the objective is to use the minimum amount of scrubber media that ensures that the temperature rise in the scrubber and the amount of unreacted gas that leave the scrubber are less than certain threshold values for the worst case scenario of gas inlet flow rate. The results of this optimization problem are shown in Table 6. The results of the optimization indicate that around 1,200 kg of total scrubber solution is necessary with the actual bleach amount being 11% by mass of the solution. In the event of the worst case cumulative gas amount of 1,700 mols the maximum allowed temperature rise of 75°C will occur. This temperature rise, however, still does not cross the boiling point of the scrubber media (110°C) and the amount of unreacted gas, with the optimal amount of scrubber media and bleach concentration, that will escape the scrubber in the event of the worst case scenario is less than 1 mol and this is an acceptable and safe gas discharge amount.

Conclusion

We have presented in this article a unified framework that performs all aspects of process hazards analysis for batch processes. It effectively combines the existing state of the art tools—BatchHAZOPExpert, gPROMS, and gOPT—to provide a useful technique for performing hazard identification, evaluation, and mitigation. The advantages of this framework are that it efficiently utilizes the complementary strengths of these systems. BatchHAZOPExpert results are comprehensive and can be obtained quickly so it is used in this framework for exhaustive hazard identification. The results are then filtered and evaluated using an optimization-based safety verification scheme implemented in gPROMS and gOPT. The modeling necessary for this stage is very focused and driven by the hazards identified in BatchHAZOPExpert. Only sections of the process that affect the filtered hazards are modeled in gPROMS. This greatly facilitates the modeling task by significantly reducing the model size. Also, the size of the optimization problem that needs to be solved is smaller making the computation faster, more efficient, and less wrought by numerical difficulties. The parts of the optimization problem—namely the objective function and the decision variables—are again dictated by the causes and consequences of the filtered hazards and the results generated by the focused optimization problem are more tractable and practically relevant. Due to this, the optimization of the process for the purpose of hazard mitigation can also be easily visualized and formulated rigorously. Another advantage of the framework is that it allows the consideration of both single fault and multiple fault scenarios with simple manipulations to the formulation during the hazard evaluation stage. The framework is also capable of handling both physical equipment failures and maloperation scenarios. This is possible because of the explicit representation of the discrete nature of batch process operation using Petri Nets during hazard identification and by use of discrete variables while formulating the hazard evaluation optimization problem. Currently, there is a significant amount of manual input during the hazard filtering stage and this is something that needs to be looked into in future efforts.

Literature Cited

Barton, P. I., and C. C. Pantelides, "Modeling of Combined Discrete/Continuous Processes," *AIChE J.*, **40**, 966 (1994).

Barton, J., and R. Rogers, *Chemical Reaction Hazards: A Guide to Safety*, Institution of Chemical Engineers, Rugby, London (1997).

Dimitriadis, V., "Modelling, Safety Verification and Design of Discrete/Continuous Systems," PhD Thesis, Univ. of London (1997).

Institution of Chemical Engineers, *Hazards X: Process Safety for Fine and Speciality Chemicals*, MIST, Manchester (1989).

Kletz, T. A., *What Went Wrong? Case Histories of Process Plant Disasters*, Gulf Publishing, Houston (1985).

Kletz, T. A., *HAZOP and HAZAN Notes on the Identification and Assessment of Hazards*, Institution of Chem. Eng., Rugby, U.K. (1986).

Knowlton, R. E., *Hazard and Operability Studies*, Chematics International Co., Vancouver, WA (1989).

Lees, F. P., *Loss Prevention in Process Industries, Volume 1*, Butterworths, London (1996a).

Lees, F. P., *Loss Prevention in Process Industries: Volume 2*, Butterworths, London (1996b).

Srinivasan, R., "PHAZER: An Intelligent Multiple Models-Based Process Hazards Analyzer," PhD Thesis, Dept. of Chemical Engineering, Purdue Univ. (1998).

Srinivasan, R., V. Dimitradis, N. Shah, and V. Venkatasubramanian, "Safety Verification Using a Hybrid Knowledge-Based Mathematical Programming Framework," *AIChE J.*, **44**, 361 (1998).

Srinivasan, R., and V. Venkatasubramanian, "Automating HAZOP Analysis of Batch Chemical Plants: I. The Knowledge Representation Framework," *Comput. Chem. Eng.* (1998a).

Srinivasan, R., and V. Venkatasubramanian, "Automating HAZOP Analysis of Batch Chemical Plants: II. Algorithms and Application," *Comput. Chem. Eng.*, **22**(9), 1357 (1998b).

Vaidhyanathan, R., and V. Venkatasubramanian, "Digraph-Based Models for Automating HAZOP Analysis," *Reliability Engineering and System Safety*, **50**, 33 (1995).

Vaidhyanathan, R., and V. Venkatasubramanian, "HAZOPExpert: An Expert System for Automating HAZOP Analysis," *Process Safety Prog.*, **15**, 80 (1996a).

Vaidhyanathan, R., and V. Venkatasubramanian, "A Semi-Quantitative Reasoning Methodology for Filtering and Ranking HAZOP Results in HAZOPExpert," *Reliability Engineering and System Safety*, **53**, 185 (1996b).

Vassiliadis, V. S., R. W. H. Sargent, and C. C. Pantelides, "Solution of a Class of Multistage Dynamic Optimisation Problems: I, Problems Without Path Constraints," *Ind. Eng. Chem. Res.*, **33**, 2111 (1994a).

Vassiliadis, V. S., R. W. H. Sargent, and C. C. Pantelides, "Solution of a Class of Multistage Dynamic Optimisation Problems: I, Problems With Path Constraints," *Ind. Eng. Chem. Res.*, **33**, 2123 (1994b).

Appendix A: Hazard Evaluation for Case Study I—Process Model

Component material balance equations

$$\frac{dM_A}{dt} = -\frac{M_l}{\rho_l} r_1$$

$$\frac{dM_B}{dt} = -Vy_B - \frac{M_l}{\rho_l} r_1$$

$$\frac{dM_C}{dt} = -Vy_C - \frac{M_l}{\rho_l} r_1$$

$$\frac{dM_D}{dt} = -Vy_D$$

$$\frac{dM_E}{dt} = \frac{M_l}{\rho_l} r_1 - Vy_E$$

$$\frac{dM_F}{dt} = \frac{M_l}{\rho_l} r_1 - Vy_F$$

$$\frac{dM_G}{dt} = \frac{M_l}{\rho_l} r_1$$

$$\frac{dM_H}{dt} = F - Vy_H$$

$$M_i = M_l x_i + M_v y_i,\ i = A, B, C, D, E, F, G, H$$

Overall energy balance equations

$$\frac{dU}{dt} = Fh_f - Vh_v + Q + \frac{M_l}{\rho_l} r_1 \delta H_1^R$$

$$U = M_l u_l + M_v u_v$$

Equipment free volume constraint

$$\frac{M_l}{\rho_l} + \frac{M_v}{\rho_v} = \nu$$

$$\nu = 1.14$$

Mol fraction equations

$$\Sigma x_i = 1$$

$$\Sigma y_i = 1$$

$$y_A = 0$$

$$y_B = K_B x_B$$

$$y_C = K_C x_C$$

$$y_D = K_D x_D$$

$$x_E = 0$$

$$x_F = 0$$

$$y_G = 0$$

$$x_H = 0$$

Thermophysical property equations

Specific Enthalpies and Internal Energies

$$h_l = \Sigma x_i h_{l,i}^0(T)$$

$$h_v = \Sigma y_i h_{v,i}^0(T)$$

$$u_l = h_l - \frac{P}{\rho_l}$$

$$u_v = h_v - \frac{P}{\rho_v}$$

$h_{l,i}^0(T)$ and $h_{v,i}^0(T)$ are available, but not shown here for reasons of confidentiality.

Liquid and vapor densities

$$\frac{1}{\rho l} = \Sigma \frac{x_i}{P_{l,i}^0(T)}$$

$$P_v = \frac{P}{RT}$$

$\rho_{l,i}^0(T)$ are available, but not shown here for reasons of confidentiality.

K-Values

$$K_i = \frac{P_i^0(T)}{P}$$

$$P_i^0(T) = A_i + \frac{B_i}{T + C_i}$$

A_i, B_i and C_i are available but not shown here for reasons of confidentiality.

Reaction kinetics

$$r_1 = ke^{\frac{-AE}{RT}}$$

k, AE are available but not shown here for reasons of confidentiality.

Heat profile specification

$$\frac{dT}{dt} = \text{Ramp}$$

Purge and gas stream flow rate specifications

$$F = 3.75$$

$$P_{\text{downstream}} = 101325$$

$$\delta P = P - P_{\text{downstream}}$$

$$V = F(1 + \max(0, \delta P))$$

Unsafe time and processing time specification

$$\frac{dt_{\text{unsafe}}}{dt} = \frac{\max(0, V - V_{\text{scrubber-capacity}})}{V - V_{\text{scrubber-capacity}}}$$

$$\frac{dt_{\text{processing}}}{dt} = 1$$

$$V_{\text{scrubber-capacity}} = 400{,}000$$

Objective specifications

$$OBJ_{\text{worst}} = t_{\text{unsafe}}$$

$$OBJ_{\text{best}} = t_{\text{processing}} + t_{\text{unsafe}}$$

Initial conditions

$M_A = 355.3$

$M_B = 722$

$M_C = 2{,}495.5$

$M_D = 8753$

$Y_E = 0.000$

$Y_F = 0.000$

$X_G = 0.0$

$P = 101325$

$T = 298$

$t_{\text{unsafe}} = 0$

$t_{\text{processing}} = 0$

Appendix B: Hazard Evaluation for Case Study I—Optimization Problem in gOPT

HORIZON

15,900 : 25 : 45,000

INTERVALS

4
600 : 125 : 6,000
3,600 : 0 : 10,800
900 : 187 : 9,000
10,800 : 0 : 27,300

PIECEWISE-CONSTANT

Ramp

INITIAL-PROFILE

0.01667 : 0.001667 : 0.08
0.0 : 0.0 : 0.0
0.01667 : 0.001667 : 0.08
0.0 : 0.0 : 0.0

ENDPOINT-INEQUALITY

T
323 : 324

ENDPOINT-INEQUALITY

M_A
0 : 1

MAXIMIZE

$\text{OBJ}_{\text{worst}}$

Appendix C: Hazard Mitigation for Case Study I—Optimization Problem in gOPT

HORIZON

15,900 : 25 : 45,000

INTERVALS

4
600 : 125 : 6,000
3,600 : 0 : 10,800
900 : 187 : 9,000
10,800 : 0 : 27,300

PIECEWISE-CONSTANT

Ramp

INITIAL-PROFILE

0.01667 : 0.001667 : 0.08
0.0 : 0.0 : 0.0
0.01667 : 0.001667 : 0.08
0.0 : 0.0 : 0.0

ENDPOINT-INEQUALITY

T
323 : 324

ENDPOINT-INEQUALITY

M_A
0 : 1

MINIMIZE

OBJ_{best}

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