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Expert System for the Design of Inherently Safer Processes. 2. Flowsheet Development Stage

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In part 1 of this series, we proposed a systematic methodology for inherent safety analysis during the process route selection stage. In this part, we present the methodology for inherent safety analysis during the flowsheet development stage. An expert system, called *i*Safe, that implements the methodology has also been developed. One key benefit of automation is substantial reduction in the time and effort required to perform safety analysis. The architecture of *i*Safe is described and illustrated using an acrylic acid process case study.

1. Introduction

In part 1 of this series, we discussed the methodology for inherent safety analysis during the product specification and route selection stage. Once the process route for manufacturing a product is decided, information on the desired product purity, production rate, process chemistry, catalyst, solvents used, etc., is used to develop alternate process flowsheets and evaluate their feasibilities. During the flowsheet development stage, unit operations, operating conditions, heat-transfer fluids, solvents, and the control and operational philosophy are decided. Once the process flowsheet is chosen, the process is simulated to investigate the necessity of recycles, effect of impurities on the process, and product quality and to refine the operating conditions in order to optimize the process yield, utilities, and cost. During the conceptual design stage, decisions regarding process equipment selection and sizing, materials of construction, inventory, storage and utility requirements, reliability and availability aspects of utilities and critical equipments, mode of transportation of chemicals, effective containment of process materials, minimization of fugitive emissions, and plant layout are made. Operational deviations are studied in order to define the regime within which the process can be operated safely.

The chemical process industry uses a wide range of process safety analysis tools to identify, quantify, and control risk and operational problems. These tools range from systematic “what if” analysis to detailed checklists. During flowsheet development, techniques such as Dow and Mond indices, HAZOP, quantitative risk assessment, etc., are used for hazard identification and quantification. A checklist is one of the general hazard identification tools that can be applied throughout the process life cycle. It is intended to prompt lateral thinking, question the rationale behind each alternative, and identify alternatives. The use of the Dow index for evaluation of latex plant design[1] and the Mond index to compare process alternatives[2] is reported in the literature. These traditional safety indices require detailed process and plant information such as layout, inventory, vessel size, etc., and therefore cannot be used at the exploratory stages of design. Another drawback of traditional indices is that they do not reflect improvements resulting from inherently safer measures such as a change of the reaction phase, temperature, etc. The commonly used HAZOP technique focuses on the identification of potential hazards and operability problems as a result of deviations from the design intent and is therefore not suitable for early design stages. The other limitations of traditional safety analysis include incompleteness, irreproducibility, inscrutability, experience dependence, and subjectivity.[3] Hence, there is a need for alternate methods for analyzing inherent safety nature of flowsheets. The adoption of proactive inherent safety analysis in early design stages will result in a safer process with reduced time and effort in the later ones.

In this paper, a systematic methodology for inherent safety analysis during the flowsheet development stage is presented. The stimulus to perform inherent safety analysis throughout the process life cycle can be provided by developing a computer tool that automates the analysis. Automation of the analysis also makes it more thorough and detailed, minimizes or eliminates human errors, facilitates documentation, and makes the study results available online for further detailed analysis and review in the later stages of the process design. The organization of the paper is as follows: In section 2, we describe the methodology for inherent safety analysis during the flowsheet development stage. An expert system, called *i*Safe, that automates inherent safety analysis from product specification to the flowsheet development stage is presented in section 3. The application of *i*Safe is illustrated in section 4 using an acrylic acid manufacture case study.

2. Inherent Safety Analysis during Flowsheet Development

After a process route has been selected, the flowsheet for the process has to be developed. The major difference between alternate flowsheets is the type and number of unit operations, reactors, number of recycles, and processing aids involved. Opportunities to substitute or eliminate hazardous materials and to alter process conditions are limited at this stage because these are largely determined by process chemistry. Despite the

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lower impact of design changes on inherent safety, opportunities for influencing the inherent safety of the process still exist. The choice of unit operations, the nature and amount of material handled, operating conditions, and operational philosophy determines the risk associated with equipments. Processing aids and utilities such as mass-separating agents and heat-transfer agents are also dependent on the unit operation. The inherent safeness of a process can be enhanced during the flowsheet development stage through application of inherent safety principles such as intensification, substitution, limitation of effects, and simplification.[4]

The effectiveness of inherent safety analysis largely depends on the knowledge available to identify hazards and alternative designs and to rank process flowsheets. Inherent safety analysis during the flowsheet development stage is envisioned to identify opportunities to eliminate or reduce the need for equipments and instruments, reduce the size of process equipments, identify unit operations that do not require processing aids and involve milder operating conditions, eliminate or reduce the use of hazardous utilities, and minimize the chance of fugitive emissions and accidental leaks. Using available information, the analysis must identify hazards under normal operating conditions as well as under foreseeable abnormal conditions, recommend design rectifications, and rank alternative flowsheets.

To identify the safety issues during the flowsheet development stage, the materials present in each stream and unit of the process have to be determined first. This can be achieved by using the process flowsheet information and material present at each input stream and by accounting for every physicochemical phenomenon occurring in different unit operations. The knowledge of the material present in each stream can be represented in a graphical form.

Similar to reaction graphs used in the chemistry evaluation, the process graph (P-graph) model of a flowsheet is a cause and effect representation of the materials in the process. The reaction graph is used during the detailed route evaluation stage and is based on reaction information, whereas the P-graph is used during the flowsheet development stage and is based on the flowsheet. In the P-graph model, a circle represents a material stream and a bar represents an operating unit. A directed arc represents a connection between a material stream and an operating unit. P-graph models are constructed by tracing the materials in the inlet and outlet streams of the process.

Once the materials in each equipment are known, inherent safety analysis can be performed either for the entire flowsheet or for the individual equipment. Flowsheets and equipment can be ranked based on their inherently safer nature using an index or analyzed to identify safety issues and alternatives. Both of these are explained in the following sections.

2.1. Inherent Safety Index for Flowsheets. Flowsheets are ranked using indices that are based on the scoring pattern proposed by Heikkila.[5] The flowsheet index (FI) is a measure of the hazardous nature of the process as a whole and is composed of the chemical index (CI) and the process index (PI).

$$\mathrm{FI} = \mathrm{CI} + \mathrm{PI} \tag{1}$$

The CI is based on the maximum index of parameters related to chemicals involved in the whole process. The CI is calculated by the summation of the following subindices: heat of main reaction subindex (R_M), heat of side reaction subindex (R_s), flammability subindex (N_f), toxicity subindex (N_T), explosiveness subindex (N_e), reactivity subindex (N_r), chemical interaction subindex (R_{CI}), and corrosion subindex[5] (R_C).

Table 1. Scores for Equipment (ISBL) Safety Index Calculation[5]

equipment items	score
equipment handling nonhazardous materials	0
heat exchangers, pumps, towers, drums	1
air coolers, reactors, high hazard pumps	2
compressors, high hazard reactors	3
fired heaters, furnaces	4

$$\mathrm{CI} = \max(\mathrm{R_M}) + \max(\mathrm{R_S}) + \max(\mathrm{N_f}) + \max(\mathrm{N_T}) + \max(\mathrm{N_e}) + \max(\mathrm{N_r}) + \max(\mathrm{R_{CI}}) + \max(\mathrm{R_C}) \tag{2}$$

The chemical interaction index and corrosion index are additional subindices considered in the flowsheet stage along with those considered in the route selection stage. The chemical interaction index refers to an unintended reaction between raw materials, products, intermediates, byproducts, and processing aids. For example, interaction between chemicals might result in the generation of heat, rapid polymerization, generation of toxic, generation of heat and flammable gases, and fire and explosion. These consequences are identified with the help of CAMEO,[6] and the user assigns an index value for the interaction according to the scoring pattern developed by Heikkila.[5] An index value of 4 is assigned when there is a possibility of fire and explosion and 2 or 3 when there is a possibility of polymerization. The corrosion index takes into account the corrosive nature based on the material of construction used for the equipment. If the material of construction is carbon steel, the equipment is assigned a corrosion index of 0, if stainless steel an index of 1, and 3 for other materials.

The PI is calculated by taking into account the operating conditions, inventory, and nature of the equipment. It includes subindices for equipment safety (E_{ESI}), temperature (E_t), pressure (E_p), and inventory (E_I).

$$\mathrm{PI} = \max(E_t) + \max(E_p) + \max(E_I) + \max(E_{ESI}) \tag{3}$$

The PI is similar to the reaction index in the route selection stage with the exception that the yield subindex is replaced by the inventory subindex, which is calculated based on the inventory in each equipment. The inventory index is calculated based on the amount of material in the equipment. It is comprised of two subcategories: the inside battery limit (ISBL) subindex and the outside battery limit (OSBL) subindex. A subindex value of 1 is assigned to an ISBL tank if its inventory is less than 10 tons and to an OSBL tank with 10−100 tons of inventory. The equipment index is also divided into similar categories. The indices assigned for equipments in ISBL and OSBL are shown in Tables 1 and 2, respectively.[5] For example, raw material and product storage tanks are normally stored outside battery limits, while tanks that are used as buffer vessels or accumulators are located inside the plant.

The nature and type of equipment used in a process can also be evaluated and an equipment safety subindex assigned based on the statistics of the typical equipment involved in accidents. This is also based on the clas-

Table 2. Scores for Equipment Safety (OSBL) Index Calculation[5]

equipment items	score
equipment handling nonhazardous materials	0
atmospheric storage tanks, pumps	1
compressors, pressurized or refrigerated storage tanks, cooling towers, blow-down systems	2
flares, boilers, furnaces	3

sification of reactors, distillation column, furnaces, etc., as ISBL equipment and storage tanks, cooling towers, etc., as OSBL equipment. For example, an atmospheric storage tank in the OSBL category is assigned an equipment safety index value of 1.

FI is calculated for the overall process flowsheet. It is equal to the addition of maximum values of the each of the subindices calculated over each equipment in the flowsheet or the summation of CI and PI for the flowsheet. We have also introduced an individual equipment index (IEI) that represents the hazardous nature of the equipment. IEI accounts for parameters that influence the inherent safety of that equipment: temperature, pressure, toxicity, flammability, explosive nature, inventory, reactions (unit processes), corrosiveness, and the type of equipment. The IEI would help the designer focus on the most hazardous equipment in the process during the detailed safety studies. Similar to the FI, the IEI is also calculated based on the maximum of the individual subindices in that process equipment. The IEI and FI would be equal for a flowsheet that has only one equipment.

In addition to serving as a metric for inherently safe nature of a process flowsheet, we have used the inherent safety index in heuristics for deriving inherently safer alternatives with respect to operating conditions in a process unit. We have assumed that an index value of 0 or 1 is inherently safer while larger index values signal unsafe process conditions. Thus, when an index value is less than or equal to 1, the recommendation to maintain temperature, pressure, or inventory in the unit is proposed, whereas an alternative to decrease temperature, pressure, and inventory in the unit is recommended when the index value is greater than 1. For example, a reactor operating in the temperature range of 150−300 °C is assigned a temperature index of 2. Similarly, if the operating pressure is between 25 and 50 bar, a pressure index of 3 is concluded. The safety performance of every process unit is evaluated using this semiquantitative rating scheme. A qualitative hazard identification and alternative generation is also possible as described next.

2.2. Issue Identification and Alternative Generation. The P-graph provides a structure for diagnosing in more detail the origin of hazards in the process and identifying the phenomena, stream, or equipment that lead to the hazardous material. For example, the presence of an impurity in the inlet stream that catalyzes the formation of hazardous materials can be identified. It also allows for identification of the origin of hazardous materials that do not appear in the feed and process outputs. Also, inefficiencies in separation processes that result in the escape of hazardous raw materials or products to waste streams and unnecessary downstream processing can be identified.

Once the P-graph for a flowsheet has been generated, domain knowledge can be used to identify safety issues based on material properties and their interaction with other process elements. Alternatives for broad changes in a unit or its operation can also be proposed. Safety issues such as handling of material near phase change—freezing, boiling, or flashing—conditions, auto-ignition temperature, and thermal decomposition can be identified. The use of extreme operating conditions, the possibility of fire and explosion, the presence of impurity, catalyst poisons, inefficient separation, byproduct formation, handling of hazardous materials, the use of a large inventory of hazardous materials, etc., can also be identified using heuristics. Streams and process units can be classified as hazardous or nonhazardous based on the nature of the materials present in them. Phase generation such as boiling or freezing that could lead to overpressurization or blockage of equipment can be identified by evaluating the physical transformation of materials possible at the process conditions. For example, the possibility of freezing can be identified if the process temperature in a unit is less than the freezing point of the material handled in that unit. The change of operating conditions in the process unit can be proposed as an alternative. Similarly, handling of hazardous chemicals in a process unit can be identified, and the alternative to reduce the inventory can be highlighted. These heuristics are derived from chemical engineering principles, inherent safety index, and inherent safety principles.[4,7−12] In the following subsections, we describe the heuristic safety analysis knowledge for commonly used equipment.

2.2.1. Reactors. The inherent safety analysis for reactors includes identifying opportunities for (1) reduction of the inventory, (2) elimination of processing aids such as diluents, solvents, and inerts, (3) change of operating conditions, (4) selecting appropriate reactor types such as packed-bed, fluidized, or continuous stirred-tank reactors, (5) change of the size and configuration of reactors, and (6) external coolers that minimize the possibility of ignition, decomposition, runaway, boilover, and byproduct formation. Table 3 shows a part of the knowledge base for reactor analysis. Hazard identification is done by evaluating the reaction phase, type of reactor, unit process involved, reaction schemes (series or parallel), thermal nature of the reaction, hazardous nature of chemicals, and whether the reaction is catalytic or not. For example, fluidized-bed reactors provide improved temperature control and are therefore suitable for a exothermic, gas-phase, catalyzed reaction. Similarly, packed-bed reactors are suggested when reactions are in series and result in byproduct formation. The exothermic nature is identified based on the heat of reaction values of the reaction involved, and the possibility of runaway, fire, and explosion hazards are identified based on the presence of flammable materials. The alternatives proposed for such situations include the use of excess nonhazardous reactants to increase conversion, optimize reactor conditions, and improve heat and mass transfer through proper distribution and avoidance of stagnant zones. Various means to remove heat are recommended to reduce the runaway conditions. In the case of liquid-phase exothermic reaction, use of a solvent to remove heat from the reaction system is suggested.

2.2.2. Separator. The knowledge base for separators is applicable for distillation, absorption, and extraction (see Table 4). Hazard evaluation in separators includes identification of (1) hazardous materials, (2) separation inefficiencies, (3) extreme operating conditions, (4) necessities of processing aids, and (5) the possibility of

Table 3. Heuristics for Reactor Analysis

applicable item	condition	safety issues	alternative
reactor	reaction temperature > auto-ignition temperature of the material	material under ignition conditions	change the operating conditions of the reactor to a safer regime to avoid ignition of materials
reactor	exothermic reaction + liquid phase	loss of temperature control might lead to uncontrolled boiling and over-pressurization leading to rupture	increase the robustness of the reactor to withstand the maximum pressure; use the solvent to remove the heat of reaction
reactor	inventory index > 1	large inventory of chemicals	reduce the residence time in the reactor
			look for the possibility of changing configuration or reducing size of without affecting throughput
			look for the possibility of changing the configuration or reducing the size without affecting throughput
reactor	exothermic reaction and vapor-phase reaction	loss of temperature control might lead to runaway because the reactor involves exothermic reaction	add a nonhazardous inert material or diluents to remove the heat of reaction; add excess nonhazardous reactants to the feed stream to remove the heat of reaction
	byproduct formation	byproduct formation results in a need for more separation units, use of more raw material, and waste of energy in process	optimize the operating conditions (flow rate, temperature, residence time, pressure, etc.) to increase the selectivity toward product formation
	low conversion	reduced conversion of raw materials resulting in a need for recovery and recycle unit and an increase in the in-process inventory of materials	use of an excess of nonhazardous reactants to increase conversion; change the reactor which will improve heat and mass transfer; improve contact between reactants by ensuring proper distribution and mixing of reactants and by avoidance of stagnant zones

Table 4. Heuristics for Separator Analysis

applicable item	condition	safety issues	alternative
separator	BP of material < operating temperature	possibility of flashing in the case of a leak	reduce the inventory of flammable material in the separator
	presence of thermally/ polymerizable unstable materials	possibility of thermal decomposition and polymerization	keep the operating temperature away from the decomposition temperature
			conduct the separation process under low pressure
			add inhibitor material to avoid unintended reactions
	use of a mass-separating agent	use of a mass-separating agent and a need for an additional unit to recover the mass-separating agent which increases process inventory	use the separation process which does not use a mass-separating agent
			replace the mass-separating agent in the separation unit with a less hazardous material
			replace the mass-separating agent in the separation unit with a less hazardous material and with a material that is easy to recover and has higher selectivity
			replace the mass-separating agent in the separation unit with an in-process material

decomposition and polymerization. For example, hazardous chemicals in a distillation column are identified through P-graph analysis and alternatives such as change of column internals so that holdup can be minimized without sacrificing efficiency, use of an internal baffle in the base section, use of a reduced base diameter column, use of an internal reflux condenser and reboiler, and use of a smaller reflux accumulator and reboiler can be recommended. For extraction columns that use a hazardous mass-separating agent, alternatives such as use of a safer extraction agent or use of an alternative separation process that does not involve such an agent can be suggested. The possibility of thermal decomposition or polymerization of material is detected based on the properties of materials handled in the column, and the alternative to conduct the separation at low pressure is proposed.

2.2.3. Heat Exchangers. The knowledge base used for analysis of heat exchangers and utilities shown in Table 5 is capable of identifying (1) hazards associated with a heat-transfer medium, (2) the possibility of unintended reactions and phase change, and (3) handling of hazardous chemicals in heaters, coolers, condensers, and reboilers. For example, in the case of a heater, use of steam is suggested as an alternative to any other hazardous special heat-transfer fluid, and the possibility of using tempered water instead of steam can be recommended. Similarly, in the case of coolers that

Table 5. Heuristics for Heat Exchangers and Utilities Analysis

applicable item	condition	safety issues	safety alternative
heat-transfer equipment	use of a heat-transfer medium other than steam or cooling water	use of a heat-transfer liquid or refrigerant	change the heat-transfer medium
	presence of hazardous chemicals	inventory of hazardous chemicals	use compact heat exchangers
equipment	temperature > 150 °C or pressure > 25 bar	use of extreme operating conditions	decrease the temperature in the equipment; decrease the pressure in the equipment
utilities and processing aids	use of a hazardous inhibitor	handling of a hazardous inhibitor	change the operating conditions to eliminate use of an inhibitor
	use of a hazardous solvent	handling of a hazardous solvent in the process	use in-process materials (raw materials, product, intermediates, byproducts) as solvents in the process use water as the solvent use a less hazardous solvent with desirable properties
	hazardous heat-transfer medium	handling of a hazardous heat-transfer medium	replace the hazardous heat-transfer medium with a safer material
	use of coolant other than water	use of coolant other than water in the reactor	change the operating conditions in the reactor such that the coolant could be replaced by cooling water
	use of a heating agent other than steam	use of a heating agent other than steam	change the operating conditions in the reactor such that the heating agent could be replaced by process steam
	use of steam as the heating agent	use of steam as the heating agent	change the operating conditions in the reactor such that the process steam could be replaced by hot/tempered water
	corrosive material	corrosion of equipment in the process	use of less corrosive material; change the material of construction to withstand the corrosive effects; remove the material as early as possible

use refrigerated water, the use of cooling water is recommended as a substitute. If the heat-transfer medium is a refrigerant, the use of refrigerated water is recommended as an alternative. If hazardous chemicals are handled, the use of compact heat exchangers is proposed. The possibility of freezing or decomposition is identified based on the properties of chemicals handled, and the alterative to limit the temperature of the heat-transfer medium used in the condenser or reboiler is proposed.

2.2.4. Storage Tanks. Inventory of materials in the storage tank is a major hazard contributor in any chemical plant. The need for intermediate storage tanks and the conditions at which chemicals are stored are evaluated based on the (1) nature and function of chemicals, (2) storage conditions, and (3) amount of chemicals. The hazards identified include (1) a large inventory of hazardous chemicals, (2) unintended reactions such as thermal decomposition and polymerization, and (3) use of high-pressure storage tanks. Storage tanks are classified as ISBL or OSBL tanks as described earlier. In the case of intermediate storage within the plant battery limit, alternatives such as (1) modification of the reactor that allows the in-process consumption of intermediates as soon as it is produced, (2) reduction of the inventory by using a close-coupled reactor arrangement instead of an individual reactor arrangement, (3) modification of the process configuration such that downstream units draw directly from the plant, and (4) change of the operation philosophy such that downstream would be shut down or run at the lowest possible throughput when the upstream unit is shut down and vice versa can be proposed. The knowledge base for analysis of storage tanks is shown in Table 6. Pumps are similarly evaluated for (1) the possibility of deadheading and (2) leakage of hazardous chemicals, and alternatives such as the use of gravity and seal-less pumps to avoid leakage are proposed. The reader would note that these alternatives can help the designer brainstorm and seek alternative reactors, separators, heat exchangers, storage tanks, fluid transportation equipment, and utilities.

The inherent safety analysis methodology described in part 1 of this series for the product selection and route selection stages and in section 2 above for the flowsheet stage has been implemented as a unified expert system, called *i*Safe, as described in the next section.

3. Expert System for Inherent Safety Analysis of Chemical Processes

*i*Safe is envisioned as an expert system that enables the designer to identify downstream implications of process alternatives at early stages of design by performing inherent safety analysis, thereby reducing the time and effort spent on detailed safety analysis at later stages of design and obviating the need for add-on protection systems. The task for *i*Safe can be defined as follows: Given the details available about the process at any design stage (materials involved, process chemistry, and the reaction and separation schemes or flowsheet), the goal is to (1) identify the inherent hazards in the process, (2) identify opportunities to minimize them, and (3) rank various process alternatives. The other characteristics of the tool are its capability to coexist with existing design methods and procedures, to evaluate retrofit and existing plants, to work with limited information, and to manage process information in a simple and easy to use fashion.[13] *i*Safe has an object-oriented architecture and is implemented as an expert system using Gensym's G2. It consists of three main components: knowledge base, user interface, and inference engine. *i*Safe is similar in structure to ENVOPExpert, an expert system developed for waste minimization analysis.[14,15] In the interest of space, the detailed algorithms are not described here and only an

Table 6. Heuristics for Storage Tank Analysis

applicable item	condition	safety issues	alternative
storage	hazardous intermediate/raw material supply from OSBL/tanker/pipeline/shipment	inventory of hazardous chemicals	reduce the inventory to the minimum required level by adopting a just-in-time approach; in situ manufacture of material
	temperature index > 1	storage of materials at higher temperature	consider the possibility of storing at or near atmospheric conditions
	pressure index > 1	storage of materials at higher pressure	use of refrigerated storage instead of pressurized storage by reducing the vapor pressure of the material; consider the possibility of storing at or near atmospheric conditions; reduce the storage pressure by the addition of a high boiling point inert chemical, thereby reducing the partial pressure of the material wherever possible
	hazardous intermediate/raw material supply from ISBL	inventory of hazardous chemicals	reduce the inventory of the material to the minimum practicable level
	hazardous intermediate from ISBL	inventory of hazardous chemicals	modify the reactor, which allows the in-process consumption of intermediate as soon as it is produced; reduce the inventory by using aclose coupled reactor arrangement instead of an individual reactor arrangement; modify the process configuration such that downstream units draw directly from the plant; change the operation philosophy such that downstream would be shut down or run at the lowest possible throughput when the upstream unit is shut down and vice versa

overview is presented. The reader is referred to work by Palaniappan[16] for in-depth descriptions of *i*Safe's implementation.

3.1. Knowledge Base. The knowledge embedded in *i*Safe can be classified into process-general and process-specific parts. The process-general knowledge includes the knowledge required for the identification of hazards and alternatives to minimize them through evaluation of materials, reactions, and equipment as well as the interactions between them. This also provides the structure for the process-specific knowledge, which is specified by the user for each case study and includes information about process materials, reactions, phase change, separations, equipment, and streams. The information related to each of these is stored in separate objects. The materials information required from the user is the function of each material and its properties. A material could function as a raw material, product, coproduct, intermediate, processing aid, impurity, or byproduct. Processing aids include catalyst, inert, diluent, solvent, inhibitor, heat-transfer agent, refrigerant, separating agent, and utilities such as steam, cooling water, process air, etc. The properties of materials needed for the analysis include boiling point, flash point, threshold limit value, auto-ignition temperature, etc. Information about different categories of materials becomes available at different stages. For example, the product is chosen in the product specification stage; raw materials, byproducts, and intermediates get fixed once the process chemistry is decided; and processing aids are decided at different stages. At each stage, the hazards associated with each material and the alternatives to reduce or eliminate them are identified based on their function and properties.

In *i*Safe, reactions are classified as main reactions and side reactions. The information needed for each reaction includes its reactants, products, catalysts, solvents, yield, temperature, pressure, etc. While information related to equipment varies with unit operations, the operating conditions and equipment type have to be specified for each equipment. Equipment is classified based on its function as a reactor, separator, transportation equipment, mixer, heat exchanger, or storage unit. Streams are classified as inlet and outlet streams. Inlet streams include utility cooling water inlet to the cooler and feed stream to the reactor, while outlet streams include the waste stream from the process, purge stream to vent, and product stream to storage.

3.2. Inference Engine. The inference engine uses the process-specific and process-generic knowledge to conduct the inherent safety analysis at each design stage. The inference engine performs the analysis with the help of methods for (1) reaction graph analysis, (2) material propagation, (3) P-graph analysis, and (4) inherent safety index calculation. The inference engine also contains heuristics and the metaknowledge required to systematically use them along with the methods to identify issues and alternatives.

During the product specification stage, the product is analyzed for hazards using heuristics. In the preliminary route selection stage, the index values for different routes are calculated as described in part 1 of this series and the main reactions analyzed for hazards and alternatives using heuristics. After the routes are screened, the information on the possible side reactions in the routes is used for detailed study. The reaction graph is developed and analyzed to locate the cause of each hazardous material, and alternatives to reduce hazardous materials and reactions are proposed.

During the flowsheet development stage, the material propagation method performs a qualitative simulation when materials in each unit are not known by propa-

Table 7. Details of Acrylic Acid Process Routes

process name	reaction name	reactions involved	reaction conditions: temp (°C)	pressure (atm)	ΔH_R (kJ/g)	catalyst	reaction phase	process yield (%)
one-step process	main 11	propylene + oxygen → acrylic acid + water	190−310	3−5	−17.08	metal oxides	vapor	50−60
	side 11	propylene + oxygen → acetic acid + water	190−310	3−5		metal oxides	vapor	
	side 12	propylene + oxygen → carbon dioxide + water	190−310	3−5		metal oxides	vapor	
two-step process	main 21	propylene + air/O_2 → acrolein + water	300−350	1.5−2.5	−8.29	metal oxides	vapor	90
	main 22	acrolein + air/O_2 → acrylic acid + water	250−300	1	−8.797	metal oxides	vapor	
	side 21	acrolein + air/O_2 → carbon dioxide + water	250−300	1		metal oxides	vapor	
	side 22	propylene + oxygen → carbon dioxide + water	300−350	1.5−2.5		metal oxides	vapor	

Table 8. Summary of Index Calculation for Acrylic Acid Process Routes[16]

process name	PI	CI	PI + CI	worst reaction index	worst material index	no. of materials	total index of all materials	no. of reactions: main	side	route index
one-step process	10	9	19	14	11	6	23	1	2	19
two-step process	14	26	40	12	14	6	28	2	2	40

gating material from the process inlet streams to the outlet streams while taking into account the physicochemical phenomena occurring in the units. The algorithms for material propagation follow the principles of the sequential modular approach commonly found in process simulators. P-graph models for each material are then generated by backward propagation of the material from the outlet stream to the inlet stream, and each model is evaluated to determine the source of the materials, inefficiencies in separation, etc. Using the P-graph models and the heuristics described above, analysis is performed to identify issues and generate alternatives for each process unit. The current version of *i*Safe includes heuristics for the inherent safer design of reactors, extraction column, absorbers, distillation columns, pumps, heat exchangers, and storage tanks. The inherent safety index is calculated at every stage to rank the process routes and flowsheets taking into account the parameters known at that stage.

3.3. Graphical User Interface. A graphical user interface (GUI) enables the user to input process-specific information, view and edit the models, and browse the analysis results. The GUI provides for input of other necessary process-specific information such as the properties of materials, reactions, separations, and phase changes. The GUI enables the user to construct a flowsheet by selecting the unit operations from the library, connecting them using streams, and specifying operating conditions and the material present in each inlet stream. The GUI also enables the user to add and edit inherent safety analysis knowledge in the form of heuristics and models. Once all of the necessary process-specific information has been specified, inherent safety analysis can be performed. The GUI allows the results to be viewed based on different categories such as materials, reactions, equipment, and design stages. Each issue and alternative identified by *i*Safe is stored as a separate object. Each alternative object is characterized by attributes such as guide word (the change required in the process elements based on inherent safety principles), context (variables related to material, process phenomena, or equipment), and applicable item (description of the process element). One-to-many relationships are established between an issue and the corresponding alternative objects. This allows the results to be organized in different categories, facilitating the design team to concentrate and retrieve required and relevant information from a large number of issues and options. The balance between detail and usability of the information is the principal problem in information management. The detailed documentation and information management provided by *i*Safe enables a better understanding of the design while reducing the analysis time, avoiding errors, and preventing modifications that could result in accidents. *i*Safe can thus supplement concurrent process engineering by providing the designer with a comprehensive understanding of the process from a safety perspective.

4. Acrylic Acid Process Case Study

*i*Safe has been tested on an acrylic acid process during the synthesis route selection and flowsheet development stages of the process. Two process routes for manufacture of acrylic acid, one- and two-step routes, are evaluated during the synthesis route selection stage. The one-step route involves the production of acrylic acid through a single reaction at relatively lower temperature albeit at low process yield, whereas the higher yield, two-step process involves the use of higher temperature and the hazardous intermediate acrolein. The reaction conditions, materials involved, catalyst used, products, yield, and reaction phase involved in both of the routes are shown in Table 7. Physical and chemical properties of materials and their hazardous properties were obtained from property databases, while reaction characteristics were obtained from the literature.[17−20] The number of main reaction steps is a simple measure of complexity of the process and foretells the need for more reactors, fluid transportation equipment, and heat exchangers. The number of side and unintended reactions is an indirect measure of the need for more separation units and recovery units, handling of chemicals, and increased probability of accidents.

The inherent safety indices for the two routes were calculated as shown in Table 8. The safety issues associated with each process route and alternatives to rectify them are identified using *i*Safe. From this, it is

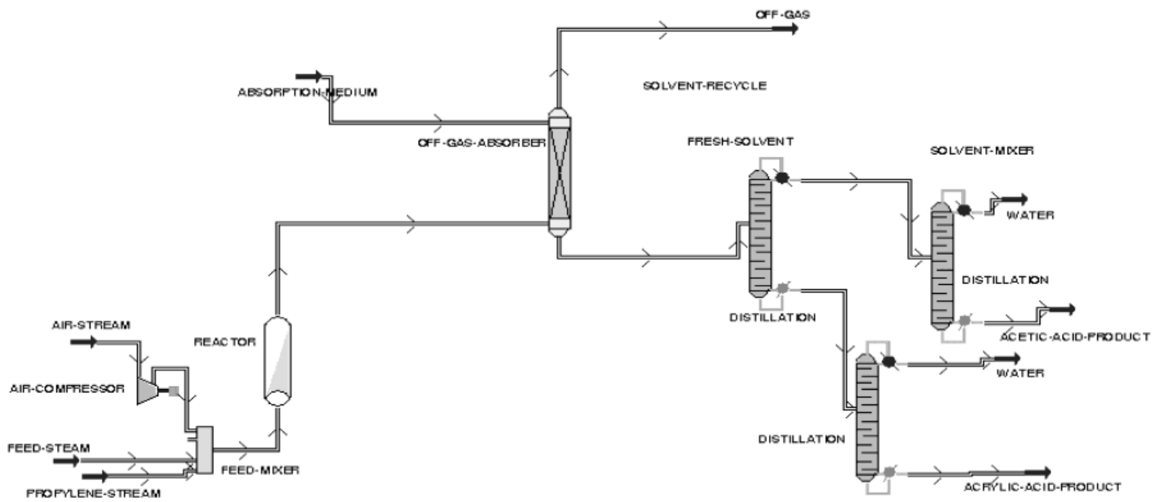

Figure 1. One-step acrylic acid process flowsheet: option 1.

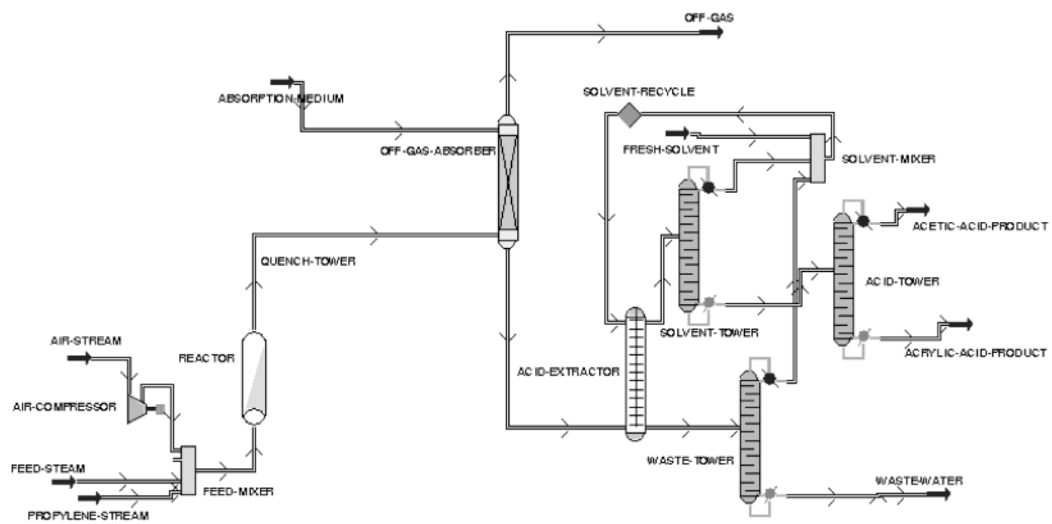

Figure 2. One-step acrylic acid process flowsheet: option 2.

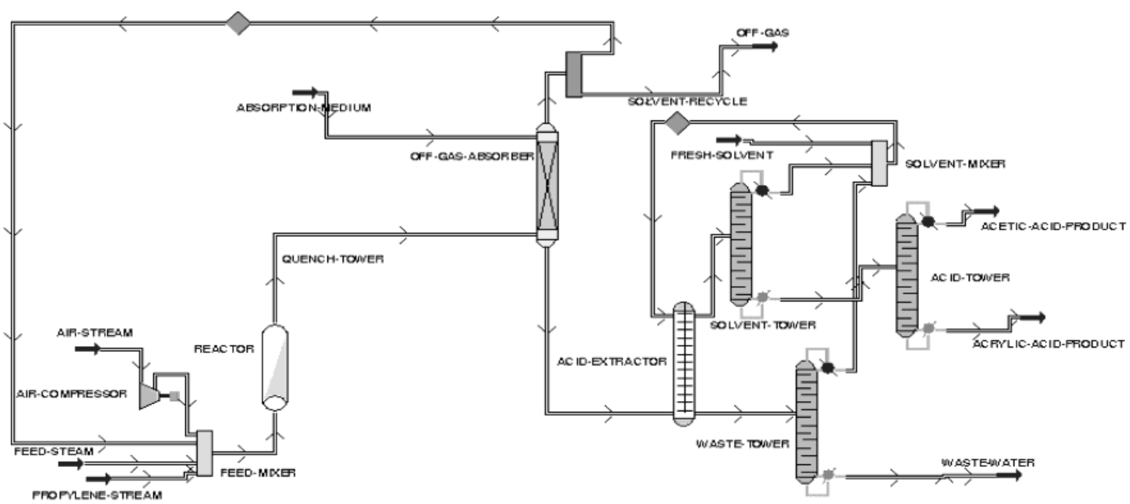

Figure 3. One-step acrylic acid process flowsheet: option 3.

clear that the one-step process is inherently safer with a route index value of 19 compared to the two-step process, which has a route index value of 40. Therefore, the one-step process is further evaluated. Three different flowsheets for the one-step process were synthesized as shown in Figures 1−3. The chemicals involved in the three flowsheets are almost the same, and the major difference is in the number and type of unit operations and recycles. Based on the number of reactors, separation unit, and recycle block, the three flowsheets were ranked as shown in Table 9. The criteria for ranking the flowsheets are as follows: the worse is the inherent safety of the process, the higher is the number of reactors and separation units. Figure 4 shows a detailed

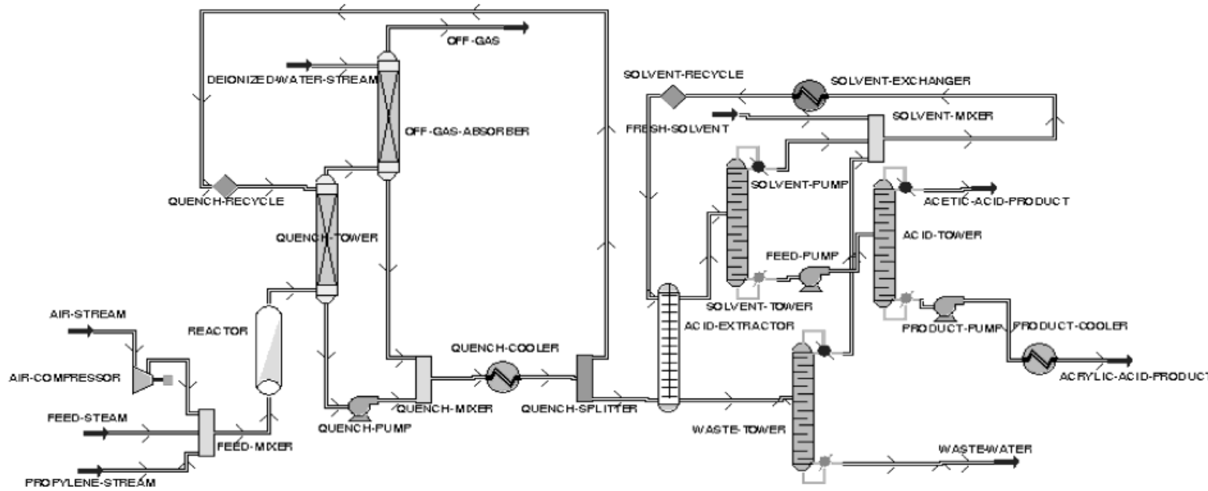

Figure 4. Detailed flowsheet for an acrylic acid process.

Table 9. Analysis of Various Flowsheet Options for a One-Step Acrylic Acid Process

flowsheet	no. of reactors	no. of unit operations	separations involved	use of solvent/ heat-transfer fluid	no. of recycle units	rank
option 1 (Figure 1)	1	4	absorption, distillation	heat-transfer media		1
option 2 (Figure 2)	1	6	absorption, distillation, extraction	heat-transfer media and solvent	1	2
option 3 (Figure 3)	1	6	absorption, distillation, extraction	heat-transfer media and solvent	2	3

flowsheet corresponding to the flowsheet option 3 in Figure 3. This detailed flowsheet was reported by Turton[17] and includes accessories such as pumps, heat exchangers, and mixers in the process.

Acrylic acid is produced by partial oxidation of propylene in a fluidized-bed catalytic reactor. Products from the reactor are quenched immediately using cold recycle to avoid side reactions. Off-gas from the quench tower, containing acetic acid, acrylic acid, unreacted propylene, and byproducts, is absorbed using deionized water in the off-gas absorber. The quenched stream is sent to the acid extractor for liquid−liquid extraction to separate the acid from water using diisopropyl ether as the solvent. The organic phase from the extractor is sent to the solvent tower, where diisopropyl ether is recovered and recycled. The bottom stream from this solvent tower is sent to the acid tower, where acetic acid and acrylic acid are separated, cooled, and sent to storage. The aqueous phase from the acid extractor is sent to a waste tower where the solvent is recovered and recycled. The bottom wastewater stream, containing acetic acid and small amounts of solvent, is sent to wastewater treatment.

The inherent safety index for each equipment (IEI) is calculated using *i*Safe based on material of construction, operating conditions, type of equipment, unintended chemical interaction, inventory, and hazardous characteristics of the chemicals handled, and equipment is ranked based on the index. Hazardous interactions, such as the possible polymerization of acrylic acid and fire and explosion due to the presence of propylene and oxygen in the reactor, which can take place between the chemicals present, were derived using CAMEO, and the corresponding inherent safety index value is used for calculation. The worst-case scenario for each factor is taken for the calculation of the equipment and FI. The index of chemicals, equipment involved in the one-step process, and summary of FI calculation are shown in Table 10. The equipment index for the reactor is the

Table 10. Summary of FI Calculation for a One-Step Acrylic Acid Process Flow Diagram[16]

FI			
PI		CI	
pressure index	1	chemical interaction index	4
equipment safety index	3	toxicity index	4
temperature Index	3	reactivity index	2
flowsheet inventory index	3	explosiveness index	1
		flammability index	4
		corrosion index	3
		heat of main reaction index	4
		heat of side reaction index	4
PI	10	CI	26
PI + CI			36
worst equipment index			21
worst material index			11
worst chemical interaction index			4

highest; therefore, the reactor is considered the most hazardous equipment and should be studied in detail during later design stages.

*i*Safe was used to analyze this detailed flowsheet, and several hazards related to the unit operations, type of reactor, operating conditions, and processing aids were identified as shown in Table 11. For example, the use of hazardous extraction agent diisopropyl ether in the extraction column is identified and alternatives such as the use of a safer extraction agent, use of in-process materials, and use of a different separation operation are proposed. The presence of hazardous propylene, acetic acid, and acrylic acid in the off-gas stream is identified, and the alternative to change the stream to a nonhazardous stream is proposed. The handling of hazardous acrylic acid and acetic acid in the quench pump and the possibility of leaks through the seals are identified. The use of gravity instead of pumps, use of seal-less pumps, and use of a robust sealing arrangement are recommended as alternatives. The handling of hazardous chemicals in the acid tower, the solvent

Table 11. Inherent Safety Analysis of a One-Step Acrylic Acid Process during the Flowsheet Development Stage

applicable item	issue	alternative
fresh solvent	use of the hazardous solvent diisopropyl ether in fresh solvent	use the in-process material instead of the solvent diisopropyl ether; replace the solvent diisopropyl ether with a safer material
off-gas	unconverted reactant in the outlet of off-gas resulting in wastage	recover and recycle the material propylene
reactor	involves a large inventory of hazardous materials	reduce the inventory of the reactor; reduce the residence time in the reactor; use the compact novel reactors with increased heat and mass transfer
acid tower	handling of corrosive materials acetic acid and acrylic acid in the acid tower	use robust material of construction to withstand the corrosive effects of materials handled in the acid tower
acid tower	handling of thermally sensitive material acrylic acid in the acid tower	keep the operating temperature away from the decomposition temperature of acrylic acid; conduct the separation process under low pressure; limit the temperature of steam in the reboiler of the acid tower
solvent tower	handling of acetic acid near freezing conditions in the distillation column of the solvent tower	keep the operating temperature in the distillation column of the solvent tower away from the freezing temperature of acetic acid; limit the temperature of cooling water in the condenser of the solvent tower
reactor	use of higher temperature conditions in the reactor	look for the possibility of reducing the temperature in the reactor
reactor	byproduct formation in the reactor due to side reactions, resulting in a need for separation units to separate them from the product	increase the in-process inventory and decrease the process yield
quench tower	possibility of unintended reactions due to acrylic acid vapor	add an inhibitor in the quench tower to avoid unintended reactions
reactor	use of molten salt in the reactor as a heating agent	change the operating conditions in the reactor such that heating agent molten salt could be replaced by process steam

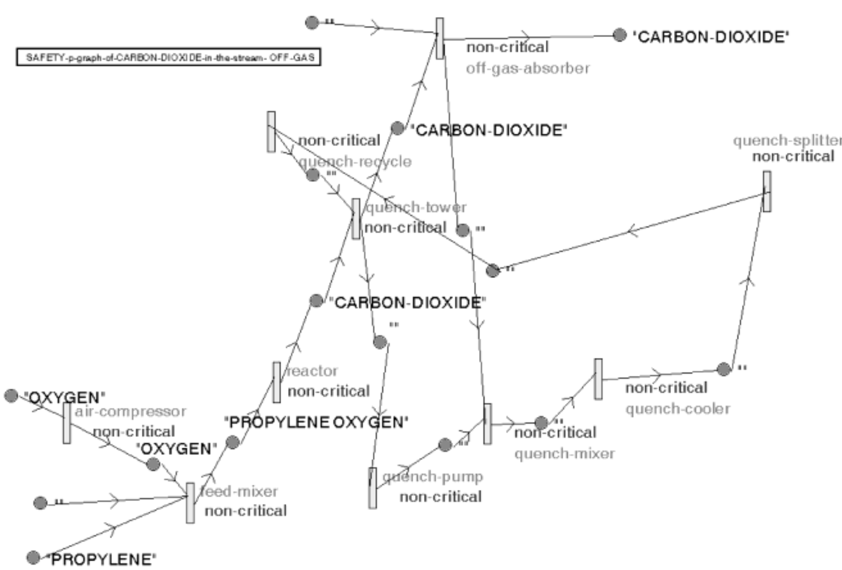

Figure 5. P-graph for carbon dioxide in an off-gas stream.

tower, and the waste tower are identified, and the alternatives to change column internals that will minimize holdup without sacrificing efficiency, to use a reduced base diameter column, and to use a smaller reflux accumulator and reboiler are suggested. To reduce the inventory of hazardous chemicals handled in the reactor, reduction of the residence time, a change of configuration, and the use of compact reactors are proposed.

The inefficiencies in separation of acrylic acid and acetic acid vapor in an off-gas absorber are identified through P-graph analysis of the materials in the off-gas stream and alternatives such as increase the number of trays or the height of packing, improve the control system, and optimize the separation conditions are proposed. The presence of impurity moisture and inert nitrogen in the feed stream is also identified through P-graph analysis of the off-gas stream, and the recommendation to improve the quality of the feed and remove the impurity as early as possible is proposed. The P-graph of carbon dioxide is shown in Figure 5. The source of carbon dioxide is identified as the reactor, and the alternative to reduce byproduct formation in the reactor through optimization of reactor conditions is proposed. A snapshot of *i*Safe's GUI for this case study is shown in Figure 6.

From these results, the reader should note that *i*Safe identifies the hazards in the process and proposes

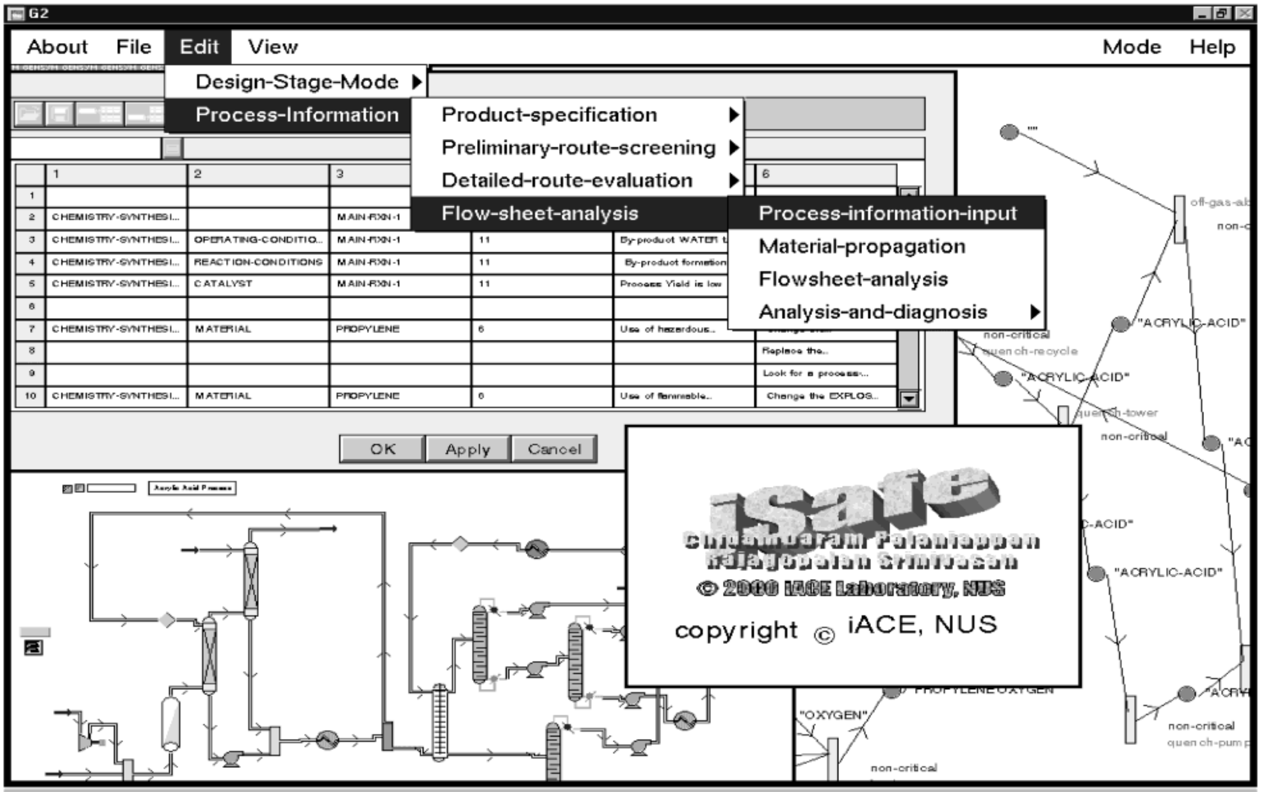

Figure 6. GUI of *i*Safe.

suitable alternatives to minimize them. Process equipment with the highest inherent safety index is the most hazardous area in the process. *i*Safe enables the designer to focus on most hazardous areas through the calculation of IEI. This will prompt the designer to brainstorm for changes that will make the process equipment inherently safer. In addition to the case study described above, *i*Safe has also been tested on 10 different process routes for acetic acid manufacture at the preliminary route screening stage and three different synthesis routes for phenol manufacture at detailed route analysis.[16] Through these case studies, it has been established that *i*Safe can act as a supplement to conventional process design tools in the early stages of process design and development and provide the designer with a comprehensive understanding of the process from an inherent safety perspective. Another key benefit is that *i*Safe implicitly incorporates the iterative nature of process design. By repeating the analysis for the modified process, a user can assess the effect of implementing an alternative.

5. Conclusions

The choice of equipment, operating conditions, and processing aids is crucial during the flowsheet development and conceptual design stage. In this paper, we have proposed an inherent safety analysis methodology for the development and evaluation of process flowsheets. We have also illustrated an automated tool, called *i*Safe, that performs inherent safety analysis to identify safety issues and derive inherently safer alternatives. *i*Safe is implemented in an object-oriented architecture using the G2 expert system shell and uses a combination of P-graph analysis, property databases, and a domain-specific knowledge base comprising models, methods, and heuristics to perform safety analysis. We have illustrated the application of *i*Safe using an acrylic acid process. *i*Safe reduces the time and effort spent in safety analysis at later stages, complements the traditional design tools, and offers the concurrent engineering capability to consider safety throughout process design. We envision *i*Safe to lead or direct the design team toward a safer design for a wide variety of processes.

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