SAFETY-ORIENTED RESILIENCE EVALUATION IN CHEMICAL PROCESSES

A Dissertation

by

LINH THI THUY DINH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2011

Major Subject: Chemical Engineering

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Approved by:

Chair of Committee,	Sam M. Mannan
Committee Members,	Mahmoud El-Halwagi
	Carl Laird
	Maria Barrufet
Head of Department,	Charles Glover

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ABSTRACT

Safety-oriented Resilience Evaluation in Chemical Processes. (December 2011)

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Chair of Advisory Committee: Dr. Sam M. Mannan

In the area of process safety, many efforts have focused on studying methods to prevent the transition of the state of the system from a normal state to an upset and/or catastrophic state, but many unexpected changes are unavoidable, and even under good risk management incidents still occur. The aim of this work is to propose the principles and factors that contribute to the resilience of the chemical process, and to develop a systematic approach to evaluate the resilience of chemical processes in design aspects.

Based on the analysis of transition of the system states, the top-level factors that contribute to Resilience were developed, including Design, Detection Potential, Emergency Response Planning, Human, and Safety Management. The evaluation framework to identify the Resilience Design Index is developed by means of the multi-factor model approach. The research was then focused on developing complete sub-factors of the top-level Design factor. The sub-factors include Inherent Safety, Flexibility, and Controllability.

The proposed framework to calculate the Inherent Safety index takes into account all the aspects of process safety design via many sub-indices. Indices of Flexibility and Controllability sub-factors were developed from implementations of well-known methodologies in process design and process control, respectively. Then, the top-level Design index was evaluated by combining the indices of the sub-factors with weight factors, which were derived from Analytical Hierarchical Process approach. A case study to compare the resilience levels of two ethylene production designs demonstrated the proposed approaches and gave insights on process resilience of the designs.

DEDICATION

To my family: parents, husband, and daughter

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It is difficult to express my deepest gratitude to my academic advisor, Dr. Sam Mannan, for his consistently great help not only in technical issues but also other things for the best outcome of my study program. This dissertation would not have been possible without his support. I have been so lucky to have such a remarkable advisor in the college years for my master's and doctoral programs.

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NOMENCLATURE

Abbreviations

ACP	administrative controls and procedures
AHP	analytical hierarchical process
BLEVE	boiling liquid expanding vapor explosion
CBR	case based reasoning
CN	condition number
CI	consistency index
COX	complexity value
CSB	chemical safety board
CR	consistency ratio
CV	controlled variables
CW	cooling water
DOF	degree of freedom
ERP	emergency response planning
F&EI	fire and explosion index
HAZOP	hazard and operability analysis
HSSES	hazardous substances emergency events surveillance
HX	heat exchanger
LEL	lower explosion limit
MV	manipulated variables
RHP	right half plane
RGA	relative gain array
RI	random consistency index
SVA	singular value analysis
TLV	threshold limit value
UEL	upper explosion limit

Variables

a_i	weighting factors
C	safety criteria limits
d	design parameter
D	design limits
e_{ij}	element located in row *i* and column *j*
e_{kj}	element located in row *k* of any normalized column *j*
I_i	index of the factor i
I_C	controllability index
I_{COR}	corrosiveness index
I_{EX}	explosiveness index
I_F	flexibility index
I_{FL}	flammability index
I_{IH}	inventory hazard index
I_{IS}	inherent safety index
I_{INT}	chemical interaction indec
I_M	material index
I_{MH}	material hazard index
I_{HMR}	heat of main reaction index
I_{HSR}	heat of side reaction index
I_P	process index
I_{PC}	process condition index
I_{COX}	process complexity index
I_{PE}	process equipment index
I_{PR}	process pressure index
I_{PS}	process structure index
I_R	resilience index
I_{RD}	resilience design index
I_{RH}	reaction hazard index

I_T	process temperature index
I_{TOX}	toxicity index
$\boldsymbol{K}$	gain matrix
M	amount of equipment accessible by the operator
O	number of measurement readings
P	number of input and output streams
Q	the number of interactions in the process
S	number of degrees of freedom
w_i	eigenvector of the comparison matrix
λ_{max}	eigenvalue
λ_{ij}	relative gain array element
σ_i	singular value
$\sum$	diagonal matrix of singular values
θ	impact value
z	control variable

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CHAPTER I
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

In the operation of an industrial process, three system states can be distinguished: normal, upset and catastrophic (Figure 1). The process systems should be maintained in the normal-state region. However, unwanted disturbances always exist, and tend to force the system state out of the normal-state region. If the system has the ability to detect disturbances and manipulate operating variables accordingly (a function of a process control system), it is likely to stay in the normal state. But the detection may fail, actions may be neglected, and even manipulation may be unable to keep the system state normal. These may cause unwanted events which make the system state upset or catastrophic. Upset state is the state that can create low impacts (i.e. a product not having proper specifications, small spills, and leaks). Catastrophic state is the state that may lead to high impact to people, environment or business (i.e. runaway reaction, fire, and explosion). From the upset state, the system can be recovered to a normal state through effective recovery methods.

If an upset system is not managed properly and is not able to recover to its normal state, then larger events (e.g. massive flammable or toxic material spills, BLEVEs) may follow and the system may cross over into a catastrophic state. This state may still be recovered to normal if action takes place within a certain reaction time. How fast and effective this recovery is will depend not only on recovery plans, but also on the resilience of the system design itself.

Most studies in the area of process safety aims to prevent the system state from transitioning downward (the right side of Figure 1). Increasing effort has been spent on

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This dissertation follows the style of *AIChE Journal*.

process safety, yet incidents still occur (Figure 2). Those incidents may be caused by technical and human failures and could cause considerable damage to process plants. Moreover, there are always other unmanageable threats to chemical plants. Some of these include natural causes (e.g., hurricanes) and intentional human acts (e.g., terrorism and sabotage). In large-scale and complex systems, such unexpected situations may occur even if risk management is fully carried out. When these situations occur, minimizing damages and getting operations back to normal are priorities for operators (the left side of Figure 1). This is the idea of the resilience concept in the industrial processes.

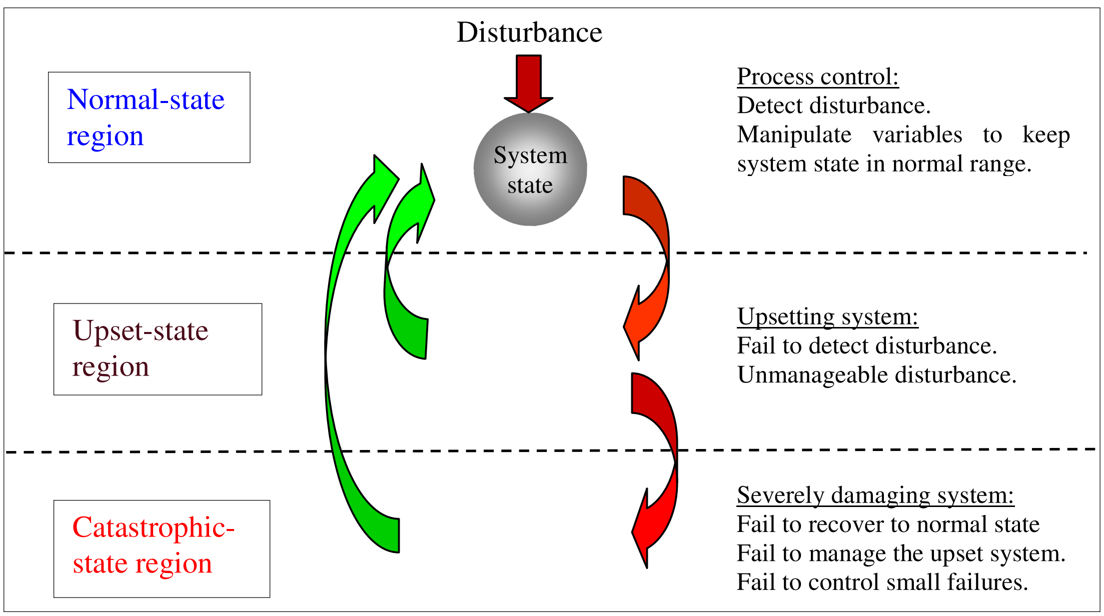
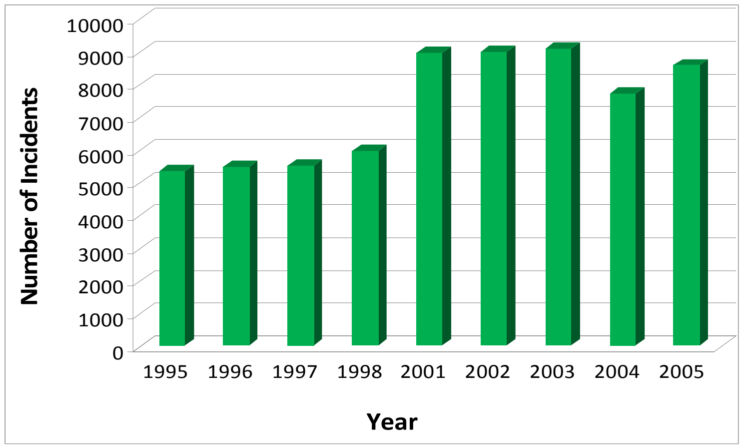


Figure 1. Transition of a system state between normal, upset, and catastrophic regions

Resilience engineering helps to recover system states after unwanted events happen rather than prevent them from occurring. Incident prevention is a subject of study in other process safety areas (e.g., risk assessment). However, it is impossible to foresee and avoid all threats. Therefore, resilience is needed as an additional safety measure. It should especially be recognized as an important characteristic of the process industry.



Source: HSEES database

Figure 2. Number of incidents 1995 – 2005

1.2 Literature review

The concept of resilience has been researched for many years in non-chemical disciplines, such as biology, psychology, organizational science, computer science, and ecology. In chemical engineering the concept remained relatively unknown. In general it is defined as "the ability to bounce back when hit with unexpected demands," which is vague.

Some researchers tried to derive more focused definitions to support their quantification approaches. Only a few publications closely related to process industry were found.

In management system, Carvalho et al.[1] proposed a qualitative resilience assessment of management system using a micro-incident analysis framework and applied it for nuclear power plant operation. The framework analysis provides an anticipation of the actions that are needed to improve the resilience and safety of organization. Costella et al.[2] proposed a new method for assessing health and safety management systems from the resilience engineering perspective. Four major principles of resilience engineering were identified: flexibility, learning, awareness and top management commitment which were used as assessment criteria during the evaluation of health and safety management systems.

In engineering systems, some quantitative methodologies have been developed to assess resilience. Slocum[3] used experimental disturbances to assess resilience along a known stress gradient. In this work resilience was measured as the recovery rate of the system from a known stress gradient applied. Even though experimental disturbances provide important information about the system and can be used as resilience “probes” by evaluating the recovery rate, it should not be used as a sole evaluation of the stress caused on the system because it also depends on other factors. Mitchell and Mannan[4] developed a concept of system resilience which was defined as “the amount of energy a system can store before reaching a point of instability”. If the input thermodynamic values change, then the absorbed exergy loads change. The authors borrowed this idea from material science to construct so-called “exergy stress and strain curves” to track those changes. The curves allow system resilience to be displayed, compared, and qualitatively assessed. The idea was demonstrated in four simple test systems from process engineering, including a steam pipe, water pipe, water pump, and heat exchanger.

Another related research area is flexibility of chemical processes which was developed by Morari et al. in the 1980s and Grossman et al. in 1990s. Morari[5] categorized process resilience into two categories based on operation modes: steady state and dynamic state, and treated them in different ways. In the steady state, process resilience is identical to process flexibility [6], i.e. the ability of a plant to handle different feedstock, product specifications, and operating conditions. Saboo et al.[6] introduced a new resilience index applied to heat exchanger networks to measure the largest disturbance that the network can tolerate without becoming infeasible. The index quantification was then extended by Karafyllis and Kokossis[7] and Skogestad and Wolff [8] as a controllability measure to determine the ability of the system to reject disturbances and prevent saturation in the manipulated variables.

In the dynamic state, process resilience is simply quantified by the quality level of its control system.[5,9] A similar idea is put forward by Morari and Woodcock, but is specifically related to the resilience (or flexibility) of heat exchanger networks with respect to inlet temperature variations.[6]

In the industrial processes, specifically chemical processes, resilience is the ability to minimize damages and get operations back to normal from adverse events rapidly. The more the resilience of an industrial process is, the lower the consequence is, and the sooner the recovery is. As a result, the risks (which comprises consequence and occurrence frequency) to people, environment and business are decreased. However, the resilience concept has not fully been adopted into the process industry, despite its clear potential benefits related to safety environment, and costs. There seem to be hurdles which limit the application of the concept, and which should be tackled to unveil its potential.

- First, the current difficulty in studying resilience is that it is conceptual. To theorize, manage – even engineer – resilience, it is necessary for basic principles and contributing factors of resilience be identified.
- Second, it is difficult to know when a process is designed according to resilience principles and measure the effects of changes due to the resilience approach. To implement resilience into practice, a method of estimating the resilience of different chemical process or design alternatives is needed.

The objective of this work is to propose the principles and factors that contribute to the resilience of a chemical process, and develop a systematic approach to evaluate the resilience of chemical process designs for relative comparison purpose. The following questions will be addressed:

- What are the principal features of positive resilience in a process operation when it is subjected to unexpected events?

- What are the contributing factors that minimize the damages and restore the system in a shorter time?
- How good resilience is this design compared to another?

The remaining chapters of this dissertation are organized as follows: Chapter II describes the problem statement for this research, discusses state transition of systems and then proposes an approach for evaluating resilience. Chapter III introduces principles to make systems more resilient and factors that contribute to resilience evaluations. Chapter IV focuses on sub-factors and quantitative methods of one main resilience contribution factor, resilient design. Literature review and proposed approaches to quantitatively calculate the sub-indices of resilient Design index are shown in Chapter V, VI, and VII. A case study of ethylene production processes demonstrates the quantitative approach in Chapter VIII. Last, the closing chapter discusses the conclusion, application, and future work.

CHAPTER II
PROBLEM STATEMENT
AND PROPOSED APPROACH

2.1 Problem statement

The problem statement for this research work can be described as follows. Given are chemical processes either in design or operation stage with information on process flow diagram, mass and energy balance, basic control systems, reaction, inventory, chemicals involved, safety management and culture and possible disturbances. Although many types of information are needed, their required levels of details are low. For example, only key control loops that are slow-response and likely significantly affect safety criteria and production specifications are needed; only heat of reaction is required for reaction information.

It is desired to develop a conceptual theory of safety-oriented resilience in chemical processes and a systematic approach to resilience evaluation of the chemical processes by a scalar resilience index. Specifically, the theory development regards to identifying resilience principles and contribution factors for better understanding the concept and indicating direction to develop the evaluation approach.

There are different types and ranges of possible disturbances. Some can be considered as unexpected input deviations. For example (Figure 3), the situations that flow rate of A is disturbed, D is introduced to the reactor instead of A, or cooling water is lost (i.e., flow rate of water reduces to 0) can create the unexpected input deviations.

The above unexpected input deviations may lead to another state of disturbances, upset state. One possible outcome is a runaway reaction; that means, the disturbances in upset state may create another state of disturbances, catastrophic state. If a runaway reaction occurs and cannot be controlled, a reactor can be ruptured. Consequently, an explosion or fire can occur. The scope of this research is to apply for all of those multilevel disturbances.

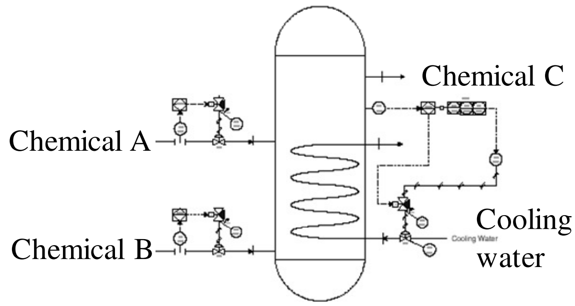


Figure 3. Examples of unexpected input deviations

2.2 Relationship between measures and process resilience

In an industrial process, at certain conditions even a small disturbance can upset the system, which can then become a catastrophic state. A resilient system can prevent such highly undesirable transitions through appropriate design, technology, human and management activities and well planned emergency procedures, which can reverse an incipient mishap and eliminate potential hazardous side effects. Factors or activities which can avoid the transition are called measures (which in terms of risk reduction are called barriers) because they block cause-consequence chains. The importance of the effects of barriers on the safety level has been noted in many studies.[10-13] In the context of resilience, measures will be discussed, because measures can not only stop a development, but also reverse it.

Figure 4 shows the effect of resilience measures on the transition of system states. If the measures between disturbance and upset states are effective, the system state goes back to normal. If those measures fail and upset still occurs, there will be protective measures in place which prevent harm to humans and equipment loss. The modeling concept used here is that those measures cannot only prevent loss (as some other process safety measures do) but also help the system to bounce back to a state of normal operation (which is unique to resilience measures). This model also reveals another new concept, resilience, a family of many different measures, not a single one. These different measures work and tie together to improve the ability of the system to tolerate derailing conditions, and to bounce back from disturbances or unexpected events instead of being broken. In general, although there are many different unexpected situations led to different consequence levels and response strategies, resilience measures are needed to prevent unwanted transitions and accelerate the desired transition back to a normal state.

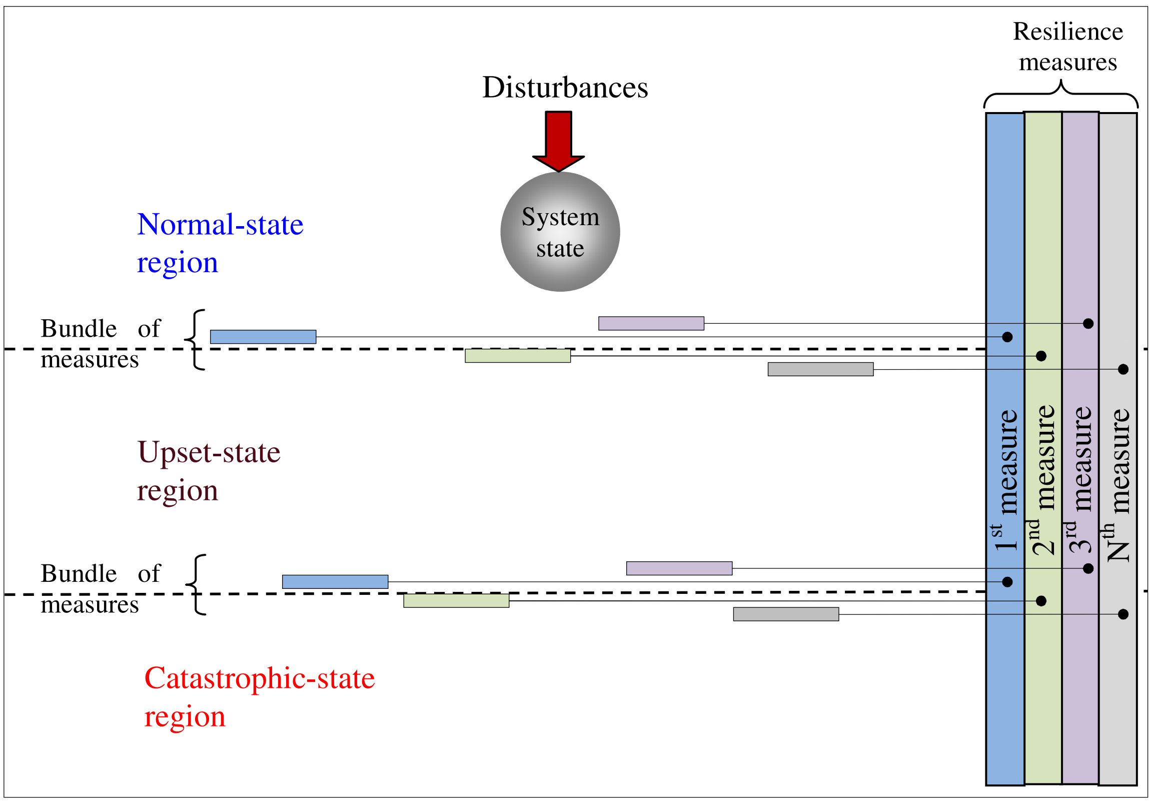


Figure 4. System bouncing back to normal state with presence of resilience measures

2.3 Multi-factor approach

It is assumed here that the complexity of resilience is derived from the interaction of several simple measures. Then, the evaluation framework is constructed based on a multi-level, multi-factor approach in which the complex (overall) objective (e.g. resilience or resilient design) is composed of many objectives and/or factors. Each factor contributes a resilience level due to its interaction and combination with other factors.

For the evaluation framework, all of the factors that contribute to resilience are basically arranged in a hierarchical tree (Figure 5). At the bottom of this tree, we desire to have one number which represents the resilient degree of a chemical process. It is named the "Resilience Index." The first level of the tree demonstrates the main contributing factors/ aspects to resilience, which can be considered resilience variables. Each of those aspects is represented by its sub-factors in level 2 of the tree. The value evaluation of sub-factors in level 1 is usually not simple because they themselves involve many other aspects. Therefore, we may need level 2, 3, or m, to evaluate values of the level 1 sub-factors. The upper levels are used as inputs for the lower levels.

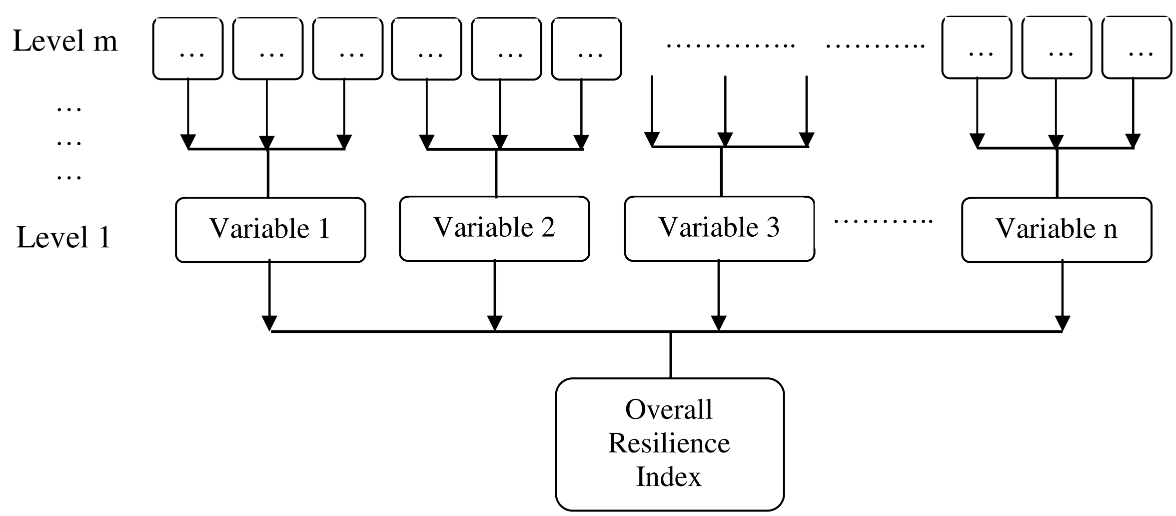


Figure 5. Hierarchical framework of evaluating resilience index

2.4 Proposed methodology to evaluate process resilience

The algorithm (Figure 6) is developed to capture the above multi-factor approach. To obtain one unique resilience index, the following steps need to be performed.

- Review the various concepts of resilience in different areas, and decide what definition of resilience will be used in this study.
- Identify strategies in the chemical process which represent the core concepts of resilience.
- Describe the basic resilience principles based on the strategies of resilience found in the chemical process.
- Identify the main factors that contribute to obtain the resilience principles as well as the process resilience after identifying the basic principles of resilience.
- Quantify the indices of each resilience contribution factor for obtaining final resilience index since resilience is the product of many process features or contribution factors.
- Identify the weights between the factors or sub-factors on different levels.
- Obtain the Overall Resilience Index (I_R) by adding together the multiplying results of the first level indices and their weighting factors (Equation 1). The weighting factors can be directly assigned by the designer to emphasize some aspects above others or calculated using Analytic Hierarchy Process (AHP) method.

$$I_R = \sum (a_i * I_i) \qquad \text{Eq. 1}$$

where a_i: Weighting factor of the factor i

I_i: The index of the factor i

Resilience index aims to be used as a screening test of a chemical process or plant. It is designed to give an indication of the level of resilience for comparison purpose, not for estimating resilience level of a single process. In Equation 3, there is an assumption of the independence of all resilience factors.

The resilience index indicates a quantitative assessment of resilience of a process or design. This index can be applied for three main purposes:

- Obtains a score to each chemical process or design, which serve as a tool for relative comparison of several processes or alternative designs in terms of resilience.

- Permits identification of the impact of individual elements to the resilience of a chemical process or design.
- Provides the direction to improve resilience by improving the sub-factors

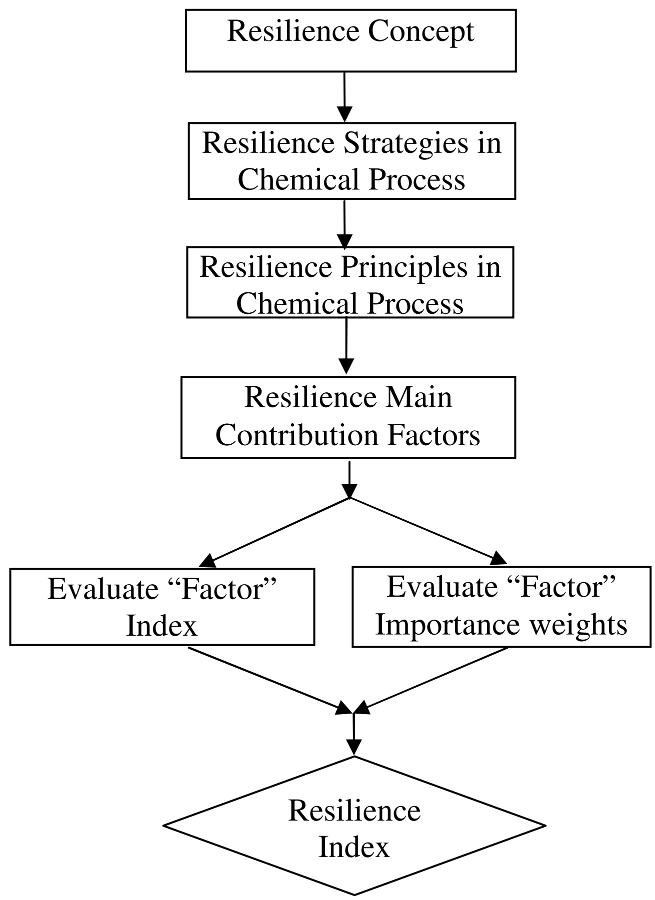


Figure 6. Research algorithm

CHAPTER III
RESILIENCE PRINCIPLES AND CONTRIBUTION FACTORS

3.1 Strategies and principles of resilience

Resilience can be viewed as a kind of forward, pro-active defense. From the general definition, a resilience strategy can be identified and developed. Resilience strives to control the situation by minimizing the probability of failure, the consequences and the restoration and recovery time. This can be considered a triple resilience strategy.

To execute the strategy and achieve resilience, the following basic principles are proposed: minimization of failure, early detection, higher flexibility, higher controllability, minimization of effects, and better administrative controls and procedures (ACP). By analyzing the state transition, it can be shown those principles need to be in places and work as layers to perform the resilience strategy (Figure 7).

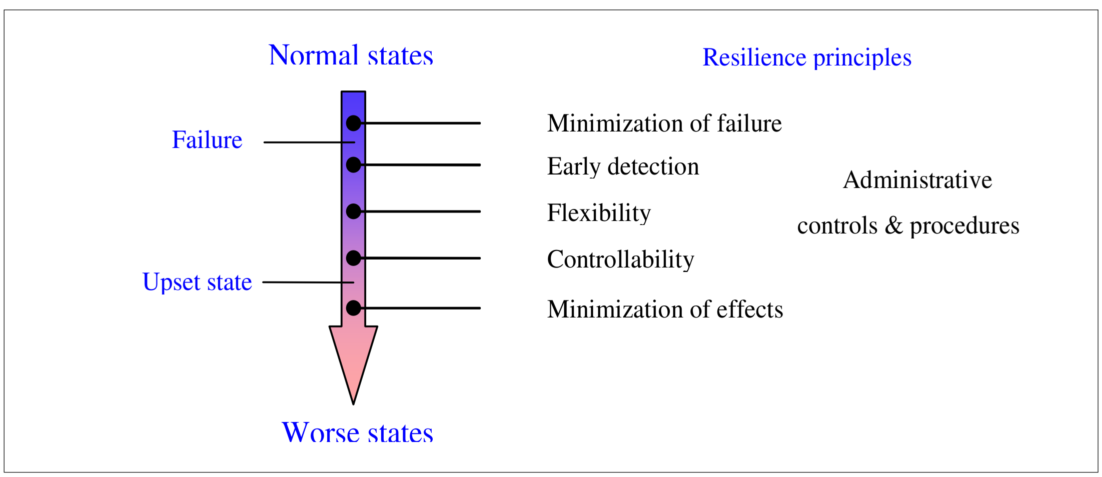


Figure 7. Resilience principles

To demonstrate how the principles contribute to achieve resilience, a leak of flammable gas is exemplified in the following description of the principle. When a flammable gas is leaked (i.e., process is in failure state), an explosive cloud can be formed. With an ignite source an explosion occurs (i.e., process is in an upset state), which may result in other flame and explosion and cause severe consequences to the process, operators, and environment

3.1.1 Minimization of failure

Failure is a state that does not meet a desired or intended objective, or which potentially creates a hazardous situation to people (e.g., toxic-gas release) and damage to equipment (e.g., leak, rupture, and suddenly increase of temperature). It is not healthy if safety only depends on operational measures and safeguards or mitigation measures. The Minimization of Failure principle is to prevent something bad from happening by preventive measures.

Inherently safer design, properly using protective equipment, and appropriate safety management should be performed to the maximum extent. In the example, some of preventive measures are choosing gaskets that minimize leak rates of hazardous substances, minimizing stockpiles of toxic substances, exercising careful maintenance [14], and replacing the flammable gas by a non-flammable one

3.1.2 Early detection

When the preventive measures cannot prevent a failure to occur, the role of principle Early Detection comes into place. The most dangerous disruption and most difficult situation to bounce back from is when disturbance is not detected until it is too late. No corrective actions will be initiated for failures that remain undetected [15]. Hence, accuracy and early detection is desired for all disturbances. In most cases, early response can be achieved by early detection resulting in a more effective response since operators have more time to consider and respond to the urgent situation.

Many authors (among others, Frese, 1991[16]; Zapf and Reason, 1994 [17]; Sellen, 1994 [18]; Kontogiannis, 1997 and 1999 [19,20]) have clearly stated detection is necessary before the rest of a recovery process can take place. The idea of the detection of the deviation being part of a recovery process was found in the literature.[21] Early detection of a disruption becomes a major determinant of resilience.[22, 23] The benefits of early detection in rapid response have also been mentioned in the area of emergency response management system.[24]

For the example, the leak should be detected as soon as possible to prevent the gas cloud formation, which may lead to worse situations. The detection is usually made by gas sensors

3.1.3 Flexibility

A process is called flexible if output variation can stay in desired range when input is changed due to disturbance within a defined range. More details on the flexibility concept are discussed in Section 7.1.

The Flexibility principle for resilience is to design a more flexible process that can operate under various disturbances. It is not necessary to return to the previous conditions under disturbance as long as the constraints and specifications are met.

Flexibility was considered as one of the attributes of resilience in previous work of Costella et al.[2], Sheffi[23], Saboo et al.[6], Morari[5]. Increasing flexibility can help a process not only respond to input fluctuations but also withstand significant disruptions. Some of common applications of flexibility are to design a plant producing the same product from various types of feedstock, a heat exchange network meeting output temperature specifications when input conditions are changed, and construction materials resistant to various types of corrosion and a wide range of physical conditions.

Refer to the gas leak example, a flexible design will allow to bypass the leaked equipment segment or to reduce gas pressure to minimize leak rate while production is maintained online. Both measures can prevent the hazard situation from escalading to cloud formation.

3.1.4 Controllability

Controllability is an ability of the system to achieve a specific target state.[25] A process is called controllable if the output parameters to be controlled can be tuned to target points in acceptable time when unexpected input deviate the parameters from the set points. More details on the controllability concept are discussed in Section 6.1.

Flexibility should be distinguished from controllability. The Controllability principle for resilience is to design a more controllable process. While the Flexibility principle allows processes to operate at various conditions, the Controllability principle allows changing the operation from one condition to another. Therefore, both Flexibility and Controllability are needed to achieve the resilience strategy.

Skogestad and Postlethwaite[26] introduced the term input-output controllability to address the ability to achieve acceptable control performance in which the controlled outputs and manipulated inputs are kept within specified bounds from their set points under any uncertainties. Controllability was also considered as dynamic resilience or as an attribute of resilience in the work of Morari.[5,9] The better the controllability is, the better the disturbance rejection capacity of the process is.[27]

In the gas leak example, the flexible design allows the process to operate in bypassed or pressure-reduced conditions. However, whether operators can perform the changes and how long to do that depend on controllability of the process. The cloud formation can be stopped only when the new condition is obtained. The sooner is new condition reached, the less is flammable gas released.

3.1.5 Limitation of effects

Despite the low probability of failure, the precise moment when an even may occur cannot be known. If it is not possible to rule out failure or to prevent mishaps, it is important to limit them from becoming worse. The more severe the consequences are, the longer it will take for the process to recover. The Limitation of effects principle is to use safeguard or mitigation measures to limit the consequence of an upset event.

For the example, equipment can be designed in a small volume so that it can leak with only low amount, which would be easy to stop or control. Another measure of the limitation of effects principle can be a building fire wall between sections to restrict the spread of fire. A blast wall to protect control room is necessary in some cases.

3.1.6 Administrative controls and procedures

The upset-state or catastrophic state resulting from an unexpected event can be minimized or prevented by design aspects such as flexibility and controllability. However, for certain unexpected disturbances, a solution in the form of a resilient design may be infeasible. Moreover, not every risk can be foreseen by a detection system.[28] Therefore, the resilience principle should involve management systems through Administrative Controls and Procedures.

The principle is not a layer behind the previous principles. Instead, it can affect all the states during the transition from normal to catastrophic states. It is made as early as in design stage and continuously updated in operation stage.

Administrative controls, such as training and standard operating procedures, are another safeguard to prevent and recover from process deviation and accidental release. Training and certification of personnel on critical procedures should be a permanent activity. If operators have the right mental picture of the process and do not panic or neglect alarms, they may even cope with a developing incident by improvising.[29]

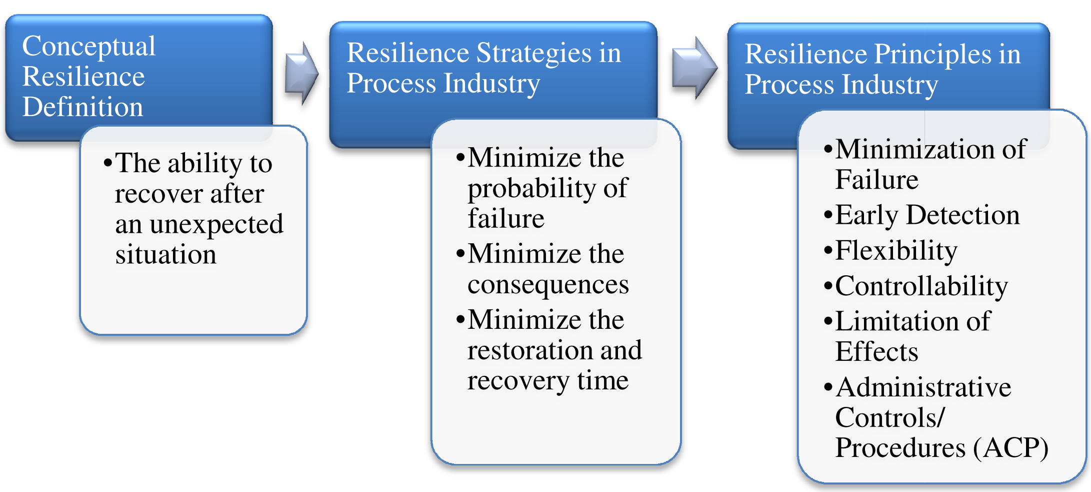


Figure 8. Development of resilience strategies and principles from resilience definition.

In the example, proper maintain procedure can even prevent leak from happening. As other measures, good emergency response plans help to fast stop the leak, isolate the unit, shut down the plant, evacuate the community to minimize the consequences to equipment damage and human loss.

In summary, the resilience definition in the context of industrial processes was used to develop the resilience strategy which in turn is a basis to develop the resilience principles. They are summarized in Figure 8.

3.2 Resilience contribution factors

3.2.1 Development of contribution factors

It is challenging to implement these principles when evaluating a process for its resilience because there is a lack of systematic attempts to identify factors that contribute to resilience in unexpected situations. Resilience levels of a plant can only be determined if the extent to which factors or attributes that contribute to the resilience of the plant are validated and exercised.

There have been many definitions of organizational resilience and, hence, the associated factors or attributes. Those definitions were found in numerous studies on how organizations dealt with situations that pushed them to the boundaries of competence. Woods (2006)[30] proposed a set of factors which contribute to the resilience developed in prior research, including buffering capacity, flexibility, margin, tolerance, and cross-scale interaction. These factors have been applied in the electric power and telecommunication studies. However, like with other extreme events in chemical engineering, these factors are difficult to evaluate.

In this work, factors or criteria to evaluate the resilience of a process are developed from the resilience principles. The factors must affect the associated principles directly. The major factors that are essential to resilience in global terms are discussed next.

From the Flexibility and Controllability principles of the process, the Design factor is developed. Process resilience is affected very significantly by the design of the process. For example, take the case study in which a batch reactor has a runaway reaction that is caused by the inability of the reactor to cool the accelerating rate of heat produced. If protective measures, such as the use of sufficient pressure relief systems and tanks designed to withstand high pressure and temperature, are in place, then the tank will not rupture or explode, and the system may be back to normal soon after it is cleaned out. Other design features known to increase resilience is increasing the range of heating/cooling capacity to improve flexibility, and fitting the right instrumentation to improve controllability. Several layers of safety systems, whether complementary or redundant, should be considered to enhance resilience as well. For example, in the BP oil spill disaster in the Gulf of Mexico, in the well there was a blowout preventer that was designed to seal off a well in the event of an emergency, but that device had not been working properly since the explosion aboard the Deepwater Horizon oil rig on April 20th 2010.[31] The BP oil spill disaster could have been recovered more quickly if the design would have included a redundancy in which the blowout preventer would perform its ultimate function of closing the well, or had other layers of timely ultimate protection beside this device.

For implementing the principle Early Detection, Detection Potential factor is introduced. Technically, in the run-away example mentioned previously, a special sensor, in combination with a suitable signal-processing device, may warn that a disturbance is emerging before any temperature or pressure deviation is noticeable. However, apart from technical features, here, organizational yardsticks become essential. The quality and implementation of a detection system has the crucial role not only to detect disturbances in time to activate proper safety measures but also, and perhaps even more importantly, to observe the level of resilience improvement or deterioration. Moreover, Detection Systems have also been recognized by Sheffi[22] as significant elements in building resilience, more specifically for the resilient enterprise through the vigilance concept.[32] According to Brizon and Wybo, vigilance is one of the key processes that participate in the resilience of industrial systems. The research of Hollnagel[33] also agrees with this and mentions "monitoring" as one of the key capacities of resilient engineering. The actions in the process industry to install process safety lagging and leading indicators after the 2005 BP Texas City explosion disaster can be seen as part of this.

A dedicated and well-designed detection system is not enough for a positive resilience. Without the proper management of the alarm system by operations personnel, crucial, quick and accurate detection, assessment and resolution of abnormal operating conditions may not be achieved. The human aspect plays an important role in the response to emergencies and in recovery processes (i.e., the identification and application of appropriate countermeasures).[15, 21] Operations personnel missing or misinterpreting alarms can contribute to a more difficult situation for a process to restore and recover from. Operators should be aware of the significance of every stage of the process and the safety procedure to be followed. They should be trained to recognize abnormal conditions or states that may occur. The Human factor also has an important role in detecting the unexpected situation, minimizing the failure and limiting the effects which are the resilience principles.

The final principle of resilience considers Administrative Controls and Procedures which is involved because carrying out a process under good safety management and good procedures makes the plant more resilient. For example, proper understanding of the process chemistry and thermochemistry by management and adequate operational procedures, including training, can help the plant recover quickly from incidents involving unexpected violent reactions and to prevent more severe consequences. A factor used to evaluate this component of resilience is the Safety Management factor. Employee training is a core aspect of this factor. Operator training supported by process simulation can frequently be improved by showing operators how to respond to upset conditions or process deviations.

Since unexpected situations combine many elements, they are challenging to plan for a respond too. Emergency Response Planning is another important factor that contributes to the characteristic of resilience. The Emergency Response Planning should be well prepared since a rapid and proper response usually results in a shorter recovery time. A situation will be mostly unexpected with regard to time and can be unexpected also with regard to nature. In principle it is impossible to have planned actions in the latter case; however, thorough planning and preparation for the other cases will lay the foundation for a collaborative response. Building joint processes, getting to know all organizations involved in a response, and assigning specific roles are necessary to recover quickly. Moreover, responding – the ability of knowing what to do and being able to do it –was also demonstrated as one of the key capacities of resilient engineering.[33] Chemical Safety and Hazard Investigation Board (CSB) has shown that many communities and companies need to be more knowledgeable and better prepared.

Based on the above discussion, it is clear that resilience is the product of many process features covering technical and organizational margins of safety. Five major factors including Design, Detection Potential, Emergency Response Planning (ERP), Human, and Safety Management, have been selected to contribute to resilience in this work (Figure 9).

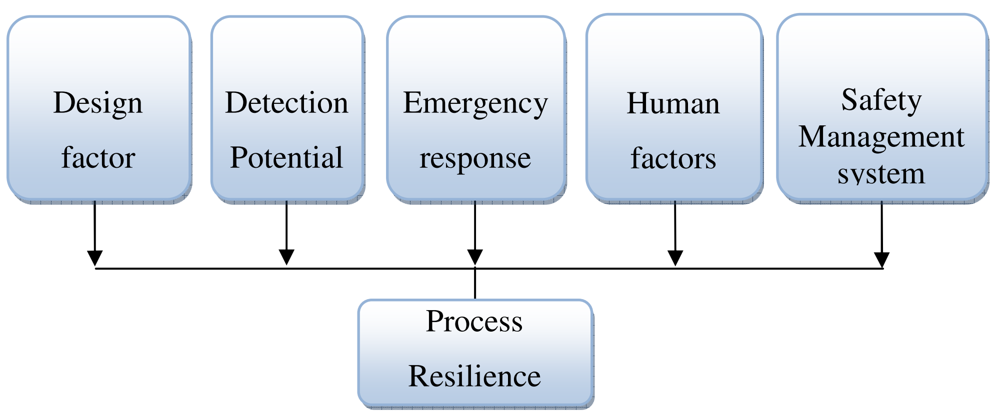


Figure 9. Contributing factors of process resilience.

In qualitative viewpoints, Figure 9 means that resilience in major hazard processes can be achieved through better design from a resilience viewpoint, better detection systems, better chemical process safety management, better behavior and quality of employees, and better emergency response procedures. These factors are essential elements in determining response time, and also reflect the fact that intrinsic resilience is affected by many different factors, including the technological, human and management factors. These factors are not sharply defined and tend to intermingle.

In quantitative viewpoints, Figure 9 means that resilience index of a chemical process is achieved if the indices of the factors contributing to resilience are obtained. The scope of the remaining chapters of this dissertation is limited to develop and demonstrate the evaluation method for Design factor. By just evaluating resilience design index, a better resilient design can be chosen by relative comparisons of different design alternatives or elements to improve resilience of a design can be identified.

3.2.2 Example demonstrating contribution factors

These types of resilience factors can be demonstrated in the following example and case study, which support the above selection of the main contributing factors.

Consider a simple example: a leak in a gas-phase heat exchanger (HX). The accident may occur due to a disturbance of the gas flow rate into the heat exchanger. If increased to a certain rate, the gas flow causes acoustic noise and unobserved tube vibration. Later the tube cracks due to prolonged vibration and fatigue. The gas in the high pressure area causes an increase the pressure in the downstream equipment that is connected to the tube side fluid. In the down-stream section, a pipe that was designed to operate at atmospheric pressure cannot withstand the higher pressure, and explodes.

In Design aspect, if the system was designed to eliminate or absorb vibration, then the failure is prevented. Also, if the down-stream section of the process was designed to withstand the higher pressure or to have a relief valve, the operator may have enough time to control the gas flow rate back to normal or isolate that HX to replace a new tube or fix the cracks. The recovery time will be faster when the explosion does not occur.

In Detection Potential aspect, if the process was designed with the control system to be able to detect abnormal pressure or temperature profiles due to the leak and control the pipe pressure, then the explosion can be prevented although leak occurred. The HX can be bypassed and process will continue to be in normal operating condition, rather than being shut down due to the explosion.

Human aspect may play a more important role to early detection for the resilience. If the operator can hear the acoustic noise due to vibration in a visual walk and was trained to suspect the vibration, then the HX can be bypassed for inspection and maintenance. Therefore, leak can be even prevented.

With a good ERP, operator is trained to respond to the detected issues by changing the gas flow (when vibration occurs), limiting the pressure increase in the pipe (when leak occurs), safely stopping the blowout flow in the relief valve (when gas is blown out), or closing the gas flow after the explosion.

Safety Management is an integral part to achieve resilience. A regular visual walk may result in the human detection on the acoustic noise. A Hazard and Operability Analysis (HAZOP) conducted in an earlier stage would have indicated where the acoustic noise could potentially come from. Besides, scheduled maintenance activity of the safety management may help to reveal the signs of prolonged vibration in the HX before leaks occur.

If any of those contribution factors are effective, the HX will be back to normal operation quicker without any leak, or with a leak but without an explosion. The system may accept the disturbance (gas flow rate increase), but management can make the HX resilient.

3.3 Case Study

3.3.1 Problem description

Consider the case where a release of flammable materials leads to an explosion following a runaway reaction and rupture of the reactor as a result of an increase in temperature. It is desired to show how the principles and contribution factors can prevent the hazard scenario from developing and assist in getting the system back to normal quicker, meaning the system is more resilient.

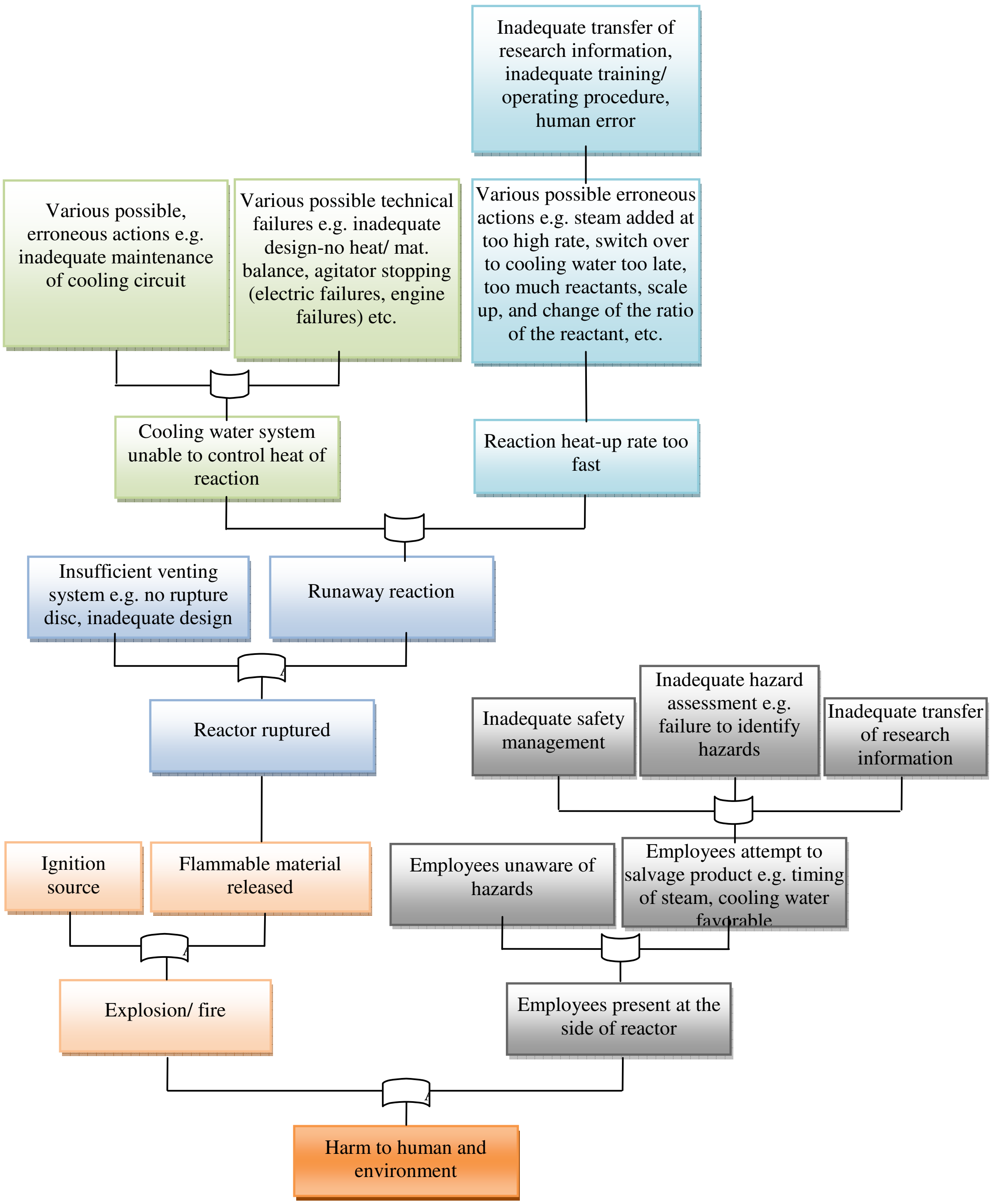


Figure 10. Sequence of the reactor run-away and flammable material release event.

3.3.2 Measures and factors contributing to resilience

To analyze the measures and factors that contribute to resilience, the transition of states is analyzed. The scenario will be considered at different levels of Disturbance, Upset, and Catastrophic consequences. Figure 10 shows the analyzed results of the state transition which is, in a simple way, the sequence of the events for this example.

Above all, the most effective tool to boost resilience is to prevent something bad from happening, which is based on the fact that there will be no recovery time if no unfortunate incident occurs. In this case study, conditions favorable to possible technical and erroneous failures can be prevented by adequate transferring of research information, hazard assessments, thorough knowledge of the reaction chemistry and thermochemistry, adequate hazard awareness, knowledge of the causes of overpressure, adequate operating procedures, including the order of ingredients, and carefully checked addition rates. Then, depend on a specific scenario, certain measures and factors can be applied to achieve positive resilience for this incident scenario. Those suggested measures and factors are summarized in Table 1.

Analyzing this case study demonstrates that the measures which cut short the chain of undesired events of the case study or contribute to a positive resilience of different scenarios fall into Design, Detection, Emergency Response Planning, Human, or Management categories.

Table 1. Measures, principles, and contribution factors for resilience of the case study.

Disturbance	*System state*	*Measure*	*Principle*	*Contribution Factors*
Erroneous actions such as an incorrect change in the feed ratio, an operator loading too much, loading in the wrong sequence or loading incompatible materials.	Upset: Reaction heat-up rate too high	Design processes, equipment and procedures to neutralize potential human error using inherently safer design e.g. interlocks	Minimization of Failure; ACP	Design; Safety Management
		Lock software based on values monitored	Controllability	Design
		Add chemicals to the vessel at a predetermined rate in order to control the rate of the reaction.	Controllability; Flexibility	Design
		Issue clear and precise process instruction sheets covering the action to be taken in the event of erroneous actions, e.g., incorrect feeding of reactants, delays in processing, under or over-charging, etc.	ACP	Safety Management; ERP
		Operators check product composition in order to recognize abnormal conditions early.	Early Detection; ACP	Human; Safety Management
Technical failures such as inadequate designs involving the heat/ material balance, the stopping of agitators due to electric failures and engine failures.	Upset: Water-cooling system unable to control the heat of the reaction	Design adequate heat transfer systems	Minimization of Failure	Design
		Design adequate control and safety back-up systems, e.g., a software action linked with heat excess alarms in case of power loss, agitator failure, and coolant failure.	Controllability; Minimization of Failure; Early Detection	Design; Detection Potential
		Operators recognize abnormal conditions and perform proper actions.	Early Detection; ACP	Human; ERP; Safety Management
		Issue clear and precise process instruction for abnormal conditions, e.g., loss of agitation, loss of cooling water.	ACP	Safety Management; ERP

Table 1. (Continued)

Disturbance	*System state*	*Measure*	*Principle*	*Contribution Factors*
Water-cooling system unable to control the heat of the reaction or the reaction heat rate is up too high.	Upset: Runaway reaction:	Fit a high temperature indicator and alarm system (e.g., high pressure alarm) to the vessel in give early warnings of potential runaway. Use smart signal processing to recognize abnormal temperature or pressure conditions.	Early Detection	Detection Potential
		Cut off the feed and heating from vessel when a predetermined maximum safe temperature or rate of temperature rise is reached,	Controllability;	Design; ERP
		Add chemicals to cancel the effects of the catalyst. Neutralize, quench with water or other diluents, or dump the contents into a vessel which contains a quench liquid programmed to be activated at a high pressure threshold.	Limitation of Effects	Design; ERP
		Issue clear and precise instructions for the operators to follow.	ACP	Safety Management
Runaway reaction.	Catastrophic: Reactor ruptured/exploded.	Provide sufficient relief systems, such as a suitable vents and bursting disc/ relief valves to be used when the safe working pressure of the vessel is exceeded.	Minimization of Failure;	Design;
		Use a tank designed to withstand high pressures and temperatures.	Flexibility	Design
		Recognize abnormal conditions and execute appropriate actions.	Early Detection; ACP	Human ERP Safety Management

Table 1. (Continued)

Disturbance	*System state*	*Measure*	*Principle*	*Contribution Factors*
Reactor ruptured.	Catastrophic: Flammable material released.	Design a suitable catch pot that can collect what is released and withstand the pressure of the discharge from the reaction vessel.	Limitation of Effects	Design
		Use a vent scrubber that is designed for treating atmospheric emissions in cases of high pressure in any catch tank that requires the release of products into the environment.	Limitation of Effects	Design
Flammable material released.	Catastrophic: Fire/ Explosion.	Area and equipment are classified to prevent ignition sources	Limitation of Effects	Design
		Reduce ignition probability by ignition source control by restricted access and permit to work system	ACP	Safety Management
		Install a device, e.g., a water spray, to rapidly cool the space above the reactor, so the hot reaction products do not self-ignite after mixing with air and generate a secondary vapor cloud explosion.	Limitation of Effects	Design
		Emergency response actions by operation, deluge, water spray, and fire brigade	ACP	ERP
Fire/ Explosion	Catastrophic: Harm to people.	Keep the number of people in the vicinity of the reactor to a minimum.	Limitation of Effects; ACP	Safety Management

3.4 Summary

Analyzing transitions of system states revealed that resilience is characterized by multiple factors or measures. These measures work and interact together to improve the ability of chemical processes to bounce back. The principles of resilience were proposed to be Flexibility, Controllability, Early Detection, Minimization of Failure, Limitation of Effects, and Administrative Controls/ Procedures. These principles act as guidelines to help develop the multiple contribution factors for numerically evaluating resilience. The first-layer of factors that contribute to resilience was proposed to be Design Factor, Detection Potential factor, Emergency Response Planning factor, Human factor, and Safety Management factor.

This section has investigated the resilience concepts in industrial process problems, and the roles of different factors to achieve resilience of different processes. In the ensuing sections, the scope of the remaining chapters of this dissertation is limited to develop and demonstrate the evaluation method for Design factor. The applicability of the multi-factor approach (Section 2.3 and 2.4) in evaluating the resilience of different chemical design alternatives will be provided. By just evaluating resilience Design index, a more resilient design can be achieved or elements to improve resilience of a design can be identified.

CHAPTER IV
RESILIENCE DESIGN FACTOR

In Chapter II, multi-level multi-factor approach was proposed to evaluate resilience of a chemical process quantitatively. According to this approach, process resilience index can be obtained with known indices of resilience contribution factors. Based on literature reviews and expert opinions, the specific factors contributing to process resilience developed and identified in Chapter III.

Among five main contribution factors to resilience of a chemical process or plant, resilient Design factor is chosen to demonstrate the applicability of the multi-factor approach in evaluating resilience index in design aspect. This chapter is a further step in identifying sub-factors contributing to resilience of different design alternatives, and then developing the equation to calculate resilience Design index.

4.1 Sub-factors of the Design factor

A resilient design is a design that has the ability to deal effectively with disturbances. Factors that need to be considered include the structure of the design (e.g. how many reactors are to be used and of what type they should be, the addition or removal of a recycle or heat exchanger [5]), the parameters (equipment sizing), and the control structure (what variables are to be measured, estimated, controlled or manipulated).

To improve resilience, a process needs to be inherently safe, flexible, and controllable. A resilient design is overarching and integrates all of these issues to limit undesired consequences of disturbances.

4.1.1 Controllability

Controllability, one of resilience principles, is the ability of a system to achieve a target state by determining whether it can be controlled effectively, either by feed-back or by feed-forward.[25]

A process should be controlled by the use of physical principles (i.e. the dynamics of the process should be favorable). If a process is difficult to control, one should look for ways of changing the process or the principles of control before an investment in complex control system is made.

Effective control is essential to minimize the hazards associated with particular reaction systems. Controllability can be attributed to the characteristics inherent in the system through the control structure (what variables are to be measured, estimated, controlled or manipulated). One problem there is how to select the appropriate set of manipulated variables to control a specified set of outputs via feedback.[5]

The development of measures in the controllability index is also important for the synthesis of control structures. Controllability was also considered as dynamic resilience or as an attribute of resilience in the work of Morari.[5]

4.1.2 Flexibility

Flexibility, another resilience principle, is clearly one of the components needed to be considered or integrated in a process design to achieve resilience since it is related to the capability of a process to cope with varying conditions and to achieve feasible operation over a wide range of uncertain conditions (e.g. different feedstock, product specifications, and changes in process parameters). Flexibility was also considered as one of the attributes of resilience in the work of Morari.[5]

4.1.3 Inherent safety

Although we designed a flexible and controllable system which can withstand in a wide range of temperatures, pressures, and flow rates, there are still unexpected situations resulting a leak or rupture of a unit/ system or even a control system. For these types of problems, to be resilient, flexibility and controllability are not enough. In these scenarios, the ability of a plant/ unit to recover quickly may depend on another design aspect, inherent safety design. An inherently safer design is a more resilient design, because inherently safer designs are created to eliminate hazards and prevent incidents from occurring.

Inherent safety can be considered a proactive approach to resilience because eliminating hazards eliminates the time and costs for recovery and restoration. A change in the plant design, such as a lower inventory of hazardous materials in the process, use of safer materials, less hazardous processing conditions, or the use of a semi-batch plant rather than a batch plant, makes it possible for the plant to avoid or significantly reduced hazards and operating problems with fewer opportunities for error.

Thus, the sub-factors of Design factor are Inherent Safety, Flexibility, and Controllability. In other words, a resilient design can be determined by these 3 elements (Figure 11).

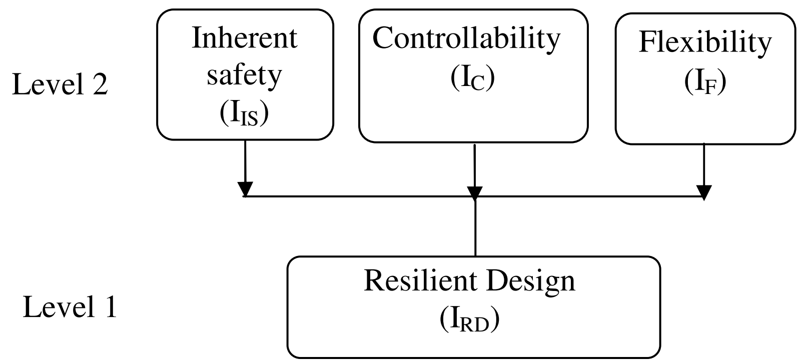


Figure 11. Contribution factors of resilient design.

In qualitative viewpoints, Figure 11 means that a more inherent safety, controllable, and flexible design is a more resilient design.

4.2 Resilience design index

A quantitative measure of resilience which is useful for design studies and satisfactory to both the practicing design engineer and the academic theoretician does not appear to exist at present. In seeking to engineer resilience, after identifying the factors that contribute to resilience there is a clear need to consider how these factors may be measured. Without this measure, it will be virtually impossible to make rational decisions on the "best" design in today's complex economic and physical environment.[5]

4.2.1 Quantitative formulation

In quantitative viewpoints, Figure 11 means that resilience design index can be obtained if the inherent safety, controllability, and flexibility indices can be calculated. Hence, the

Resilience Design Index (I_{RD}) is calculated by Equation 2, where the Total Resilience Design Index is the sum of the Flexibility Index (I_F), the Controllability Index (I_C), and the Inherent Safety index (I_{IS}).

$$I_{RD} = a_{IS} * I_{IS} + a_F * I_F + a_C * I_C \qquad \text{Eq. 2}$$

Where a_i is the weighting factors

This resilience design index aims to be applied in the early stage of a chemical process design to choose a more resilient design among different alternatives. Resilience design index is not designed to be extremely accurate and can give an indication of the level of resilience. In Equation 2, there is an assumption of the independence of all sub-factors of Design factor.

4.2.2 Weighting factors

To represent the relative importance between the sub-indices of the RI, weighting factors are introduced in Equation 2. To obtain the weight of each attribute, Analytical Hierarchical Process (AHP) can be used.[34] The main uniqueness of AHP is its inherent capability of weighting a great number of different nature factors. Although the purpose of this section is to identify the weighting of a few sub-factors of resilience design factor, the use of AHP is deemed suitable when considering its potential application for the overall resilience factor in the future. It is a multi-attribute evaluation method that is capable to extract the comments of experts and uses them as input to calculate the quantified weight of each attribute by pair-wise comparison with a nine-point scale. The advantages of pair-wise comparison are (1) it is systematic; (2) the results contain a greater degree of robustness since each factor is addressed (n-1) times in a set containing n factors; and (3) there is a way for consistency control.[35]

Using Saaty's AHP technique, the following steps need to be done to obtain the weights of contribution factors in Equation 2 after the hierarchy has been structured in Figure 11.

- Construct a pair-wise comparison matrix by asking the experts a series of questions (Table 2) to compare each element or sub-factor against one another based on a 9-point scale using pair-wise comparison method to indicate their relative importance.

The measure of intensity of importance is determined by a scale of 1 as 'equal importance' to 9 as 'absolute importance'. The selection of a number is done in accordance with the respondent's experienced opinion depending on the problem at hand (i.e. type of process); the purpose and criteria of the process designers; and the company policy.

Table 2. Questionnaire used to direct pair-wise comparison judgments

With respect to the overall goal "contribution to resilience of a chemical design", compare each of the following pair of the factors, and mark the place along the segment

Q1. How important is Inherent Safer Design when it is compared to Flexibility?

	1		3		5		7		9	
Inherent Safety Design	◆	◆	◆	◆	◆	◆	◆	◆	◆	Flexibility

Q2. How important is Inherent Safer Design when it is compared to Controllability?

	1		3		5		7		9	
Inherent Safety Design	◆	◆	◆	◆	◆	◆	◆	◆	◆	Controllability

Q3. How important is Flexibility when it is compared to Controllability?

	1		3		5		7		9	
Flexibility	◆	◆	◆	◆	◆	◆	◆	◆	◆	Controllability

- Calculate the eigenvector of the comparison matrix. An element of the eigenvector is as follows:

$$w_i = \frac{1}{n} . \sum_{j=1}^{n} \frac{e_{ij}}{\sum_{k=1}^{n} e_{kj}} \qquad \text{Eq. 3}$$

Where e_{ij} = element located in row i and column j of the comparison matrix, and e_{kj} = element located in row k of any normalized column j (i, j, k = 1, 2…n)

- Obtain relative weights of the factors in Equation 2 with regard to resilience of a design. According to Saaty, their weighting factors are the eigenvectors of their comparison matrix.[34] Hence, $a_i = w_i$
- Calculate the consistency ratio (CR) to measure the consistency of pair-wise comparisons since the responders sometimes make judgments inconsistently and discrepancies might occur between the results of the comparison. The CR is obtained by the following equation:

$$\mathrm{CR} = \frac{CI}{RI}$$

Where RI is random consistency index provided by Saaty's method

CI, consistency index, is identified by using the eigenvalue, λ_{max}

$$\mathrm{CI} = \frac{\lambda_{max} - n}{n - 1}$$

Where n is the matrix size

The CR is acceptable, if it does not exceed 0.10. If it is more, the judgment matrix is inconsistent.

In the case the comments of multiple experts are obtained, there are two different mechanisms to evaluate a single weight for each factor: (1) compute the mean weight for each factor; (2) compute the "mean" comparison matrix, then compute the weights using the routine AHP technique described above. The latter is preferred due to its priority to direct expert assessments rather than to inferential assessments, and therefore reflects the expert's judgment more authenticable.[35]

CHAPTER V
INHERENT SAFETY INDEX

5.1 Inherent safety concept

Inherent safety approach uses basic design measures to achieve hazard elimination, prevention, and reduction.[36] A plant considered as an inherently safe plant if its material and operating condition is harmless or its hazardous materials is in small inventory to cause no harm if released.

However, in the real industry, there always exists large inventory of hazardous materials under dangerous operating conditions. It is more practical to think of inherent safer processes instead of inherent safe processes. Inherent safer processes carry less inherent risk as compared to conventional process.[36]

5.2 Literature review

The most widely applicable principles of inherent safety are minimization, substitution, moderation, and simplification firstly introduced by Kletz.[28] These principles are also applied for this work, to evaluate an inherent safer design and then inherent safer index.

Due to the benefits of inherent safer design to remove or reduce hazards, there have been several researches in developing a systematic methodology for the evaluation of inherent safety index. Some of those methodologies was based on other well-known indices such as Dow Fire and Explosion Index, Mond Index and do not attempt the aggregation of individual indices under a unique index.[37-39] Several researchers did attempt to obtain an overall index for inherent safety assessment. Lawrence proposed the overall inherent safety index for a chemical synthesis route in 1996.[40] Then, the index for chemical route selection was extended and applied for more overall inherent safety index for process synthesis by Heikkila.[41] Khan et al. proposed a risk-based approach for inherent safety evaluation in 1998.[42] In 2003, Gentile et al. proposed the fuzzy-based inherent safety index, which used fuzzy logic system to evaluate inherent safety index based on if-then rules.[43] In 2005, Khan and Amyotte[36] developed an integrated inherent safety index which used a structured guideword based approach. Abedi and Shahriari[44] added some missing important criteria and the consideration of the interactions between different factors more explicitly on the basis of Heikkila's study and Dow F&EI in 2005.

The methods for assessing inherent safety of chemical processes vary in goal, scope, structure and the way the safety aspects are considered. Since the desired results of inherent safety evaluation in this research is a unique index. The following paragraphs review in detail the advantages and disadvantages of the inherent safety evaluation methodologies with the attempts to obtain an overall inherent safety index.

The first method, Dow F&EI, was designed for identifying of contributed equipment in an incident for process or plant involved in processing, and handling flammable chemicals. Then, the Mond Index method is a modification of the Dow F&EI method. The risks and hazards of a chemical plant can be identified well by the Dow and Mond F&EI methods, but the aspects relevant to inherent safety were not evaluated.[44] Lawrence's method was designed for identifying and selecting inherent safety chemical synthesis route, which is very reaction oriented and does not consider properly the other parts of inherent safety process. To fill the gaps of Lawrence's method, Heikkila et al. proposed a method which considered many other aspects relevant to inherent safety process. Heikkila's method was intended for evaluating inherent safety index of different process alternatives. This method is quite suitable for the early design stage of the process with low information requirements and subjective process. Some of the subjective factors in Heikkila's method were later improved by Fuzzy logic based index developed by Gentile et al. However, this method becomes difficult to apply for the problems involving the evaluation of more than one linguistic variable at the same time.[44] The integrated inherent safety index by Khan and Amyotte was identified based on hazard potential identification as well as economic evaluation.

After reviewing the advantages and disadvantages of different methodologies, Heikkila's model[41] was considered as a basis methodology to evaluate inherent safety index in this work since the scope of this work is the same to that of Heikkila (which for comparison of two or several alternative processes with low information requirements). Heikkila's method was a development of several common indices such as Dow F&EI,

Mond index, Lawrence's index and based on the principles of inherent safety as well as well-accepted engineering knowledge.

Heikkila's method[41] for process synthesis is reviewed in details as follows. The method was proposed in 1996..The objective of this index development was to be applied during preliminary process design. Heikkila's index consists of chemical and process inherent safety indices. The chemical safety index contains several sub-indices of chemical interaction, flammability, explosiveness, and corrosiveness. The process inherent safety index has two sub-indices, process conditions including inventory, process temperature, process pressure and process system including process equipment, process structure. All of the sub-factors in Heikkila's study are carefully selected based on well-accepted engineering knowledge.

For each one of the selected sub-factors, a possible range of variation is selected and divided into several sub-ranges that receive a score between zero and six. The scores represent the positive or negative contribution on the inherent safety level. The higher the score is, the more hazardous the situation is.

5.3 Proposed approach

Figure 12 shows the hierarchical model which is applied to calculate ISI in this work. The selection of sub-factors of inherent safety factor was based on the studies by Heikkila with the consideration of an additional important criteria, process complexity, and the interactions between different factors more explicitly pointed out by Abedi.[44] This model is constructed based on a multi-level, multi-attribute approach.

As Heikkila's methods, in this model, the inherent safety index is also splited into two sub-indices related to material and process. The material index includes the inventory hazard index which used to be a sub-factor of process index in Heikkila's method. This modification is performed due to the consideration of the interaction between I_{MH} and I_{IH} suggested by Abedi in which the material hazard index is compounded by the magnitude of the inventory index.[44] The process index includes all the selected sub-factors in Heikkila's method with the addition of the complexity index involving amount of equipment, number of DOFs, interactions requiring operator invention and number of external disturbances. This complexity index is chosen based on the last principles of inherent safety, simplication, and was also suggested as one of inherent safety attributes by Abedi and Shsriari.[44] The detail of this index will be discussed more in Section 5.4.2.

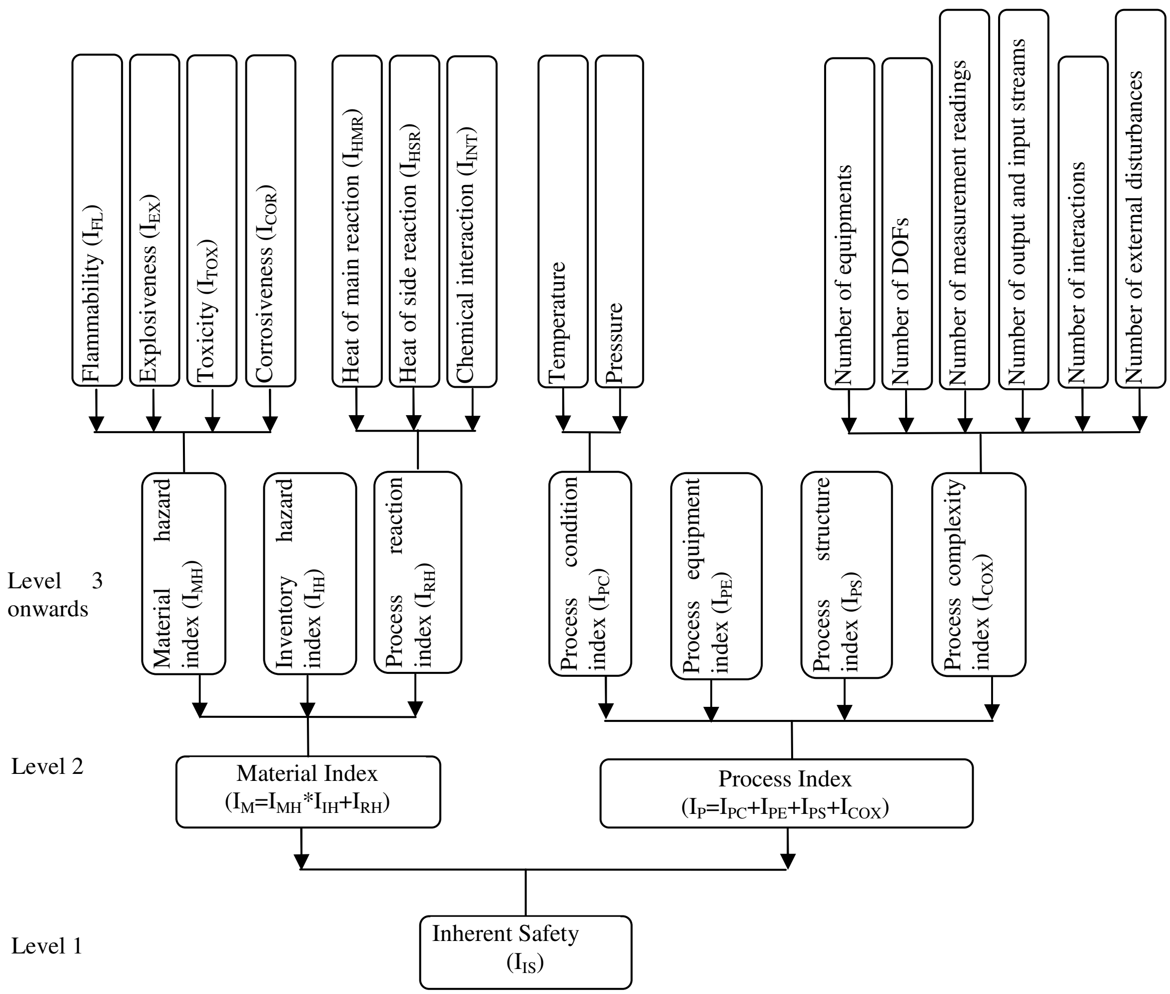


Figure 12. Hierarchical model of Inherent Safety sub-index[44]

With this evaluation model and its selected sub-factors, four widely inherent safety principles have been satisfied. The sub-factor of inventory which is the quantity of the material present in the process has covered the first principle of minimization. If there is a fire, explosion, or tank rupture, small inventories are favorable. The sub-factor of material hazard including flammability, explosiveness, toxicity, corrosiveness and reactivity places an important role to fulfill the second principle, substitution. An inherent safer process or more resilient process is a process with less hazardous materials. The sub-factors of process condition and process reaction demonstrate the third inherent safety principle, moderation. The process condition including process temperature and pressure covers the fact that an inherent safer process carries out a reaction under less hazardous conditions, or storing or transporting a hazardous material in a less hazardous form. The process reaction demonstrates the hazard of the heat released by the reaction between materials existing in the process as well as their reactivity characteristics which are another moderation concern. An inherent safer process carries out a reaction with less heat released. The last principle is simplification. The important criterion is the level of complexity of a unit in a chemical process plant.

When it is not possible to make plants safer by minimization, substitution, moderation, or simplification, there is a need to measure the possibility that a piece of equipment is unsafe which is demonstrated by process equipment sub-factor in Figure 12. The selection of safer equipment alternatives is preferred since the type of equipment used in a process has an important role for the process safety. This sub-factor considers the safety of all major pieces of equipment such as pump and vessels etc. but not piping, valves as separate entities, and without interactions through the process with other equipment. The effects of those interactions to the safety of the process are reflected through the process structure and process complexity sub-factors. The process structure describes the inherent safety of the process configuration; in the other words, it describes how well certain unit operations and other process items work together in a total process perspective.[41] The complexity factor describes how easy the process can be operated from human interaction perspective, and from the equipment / system and their interactions. Numbers of components (i.e. equipment), number of input and output streams, number of interaction, and number of external disturbances have been considered in the complexity factor. From an operational perspective, other issues such as the degree of freedom (DOFs), the number of measurement readings are also assessed in the process complexity. It is understood that the operation is less complex when less degrees of freedom are available for the operator.[45]

Since the scope of the quantitative section to obtain resilience index as well as inherent safety index is for different alternative process designs, the other issues such as process layout, onsite transportation are not considered in the calculation of inherent safety index in this work.

The advantages of this method are well coverage of the risks and hazards as well as the aspects relevant to inherent safety existing on a chemical process, low information requirement which are suitable in the design stage.

5.4 Inherent safety index and sub-indices assessment

The I_{IS} calculations are made on the basis of the worst situation. The approach of the worst case describes the most risky situation that can occur. A low index value represents an inherently safer process. In the calculations, the greatest sum of the flammability, explosiveness and toxic exposure sub-indices are used. For inventory, process temperature and pressure, the maximum expected values are used. The worst possible interaction between chemical substances or pieces of equipment and the worst process structure gives the values of these sub-indices.

In general, the Inherent Safety index (I_{IS}) is calculated by Equation 4, where the Total Inherent Safety index is the sum of the Material Index (I_M) and the Process Index (I_P).

$$I_{IS} = I_M + I_P \qquad \text{Eq. 4}$$

These two indices are calculated for each design alternative and the results can be used to compare with each other if desired. The methodology to obtain each sub-index value is described in the ensuing sections in detail.

Table 3. Inherent safety sub-indices and their score range.[41]

Sub-factors	Symbol	Score
Flammability	I_{FL}	0-4
Explosiveness	I_{EX}	0-4
Toxicity	I_{TOX}	0-6
Corrosiveness	I_{COR}	0-2
Inventory	I_{IH}	0-5
Heat of main reaction	I_{HMR}	0-4
Heat of side reaction	I_{HSR}	0-4
Chemical interaction	I_{INT}	0-4
Process temperature	I_{T}	0-4
Process pressure	I_{PR}	0-4
Process equipment	I_{PE}	0-4
Process structure	I_{PS}	0-5
Process complexity	I_{COX}	0-5

Another issue of multi-factor approach is the weighting between sub-indices of inherent safety index. In Heikkila's method, the importance of the specific sub-index was reflected by the score ranges which were made on the basis of the expert judgment collected by Lawrence.[40] And in this work, the scoring systems for calculating all inherent safety sub-indices (Table 3) are taken from Heikkila's study.[41] That means the weighting factors have been considered and integrated into the current work to calculate inherent safety index by using the scoring systems suggested by Heikkila. Basically, the minimum score for each sub-factor is set to zero, while the maximum scores are set in order to reflect the importance of the specific sub-index to the process safety. A wider range means greater impact for the overall safety evaluation. The most important factor on inherent safety are inventory and toxicity with the greatest score range. The one has lowest impact to inherent safety is corrosiveness with the score range of 0-2. The most other sub-indices had the score range of 0-4. The process structure is also considered as an important factor with the maximum score of 5. The process complexity is a new factor which has not been introduced in Heikkila's method. This factor demonstrates how the process's is constituted and operated easily from the interactions of other process equipment together and from operational perspective. The number of potential errors increases when the number of connections increases.[45] The importance of the process complexity is considered to be the same as the process structure resulting in its score range of 0-5.

5.4.1 Material index

The material index is based on the material, inventory, and reaction hazard indices in which the material hazard index is compounded by the magnitude of the inventory. Therefore, I_M is calculated as the addition of reaction hazard index and the product of material hazard index and inventory hazard index (Equation 5).[44]

$$I_M = I_{MH} \cdot I_{IH} + I_{RH} \qquad \text{Eq. 5}$$

5.4.1.1 Material hazard index

The Material Hazard Index is the greatest sum of flammability, explosiveness, toxic exposure, and corrosiveness sub-indices.[41]

$$I_{MH} = (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR,\,max} \qquad \text{Eq. 6}$$

The flammability index is identified based on the value of the flash point and the sub-ranges from nonflammable up to very flammable (i.e., flash point < 0^oC and boiling point ≤ 35^oC)

The Explosiveness index is determined based on the difference between the upper and lower flammability limits and the sub-ranges from non-explosive up to the difference of UEL and LEL of 70-100vol%.

The toxicity index is evaluated based on the Threshold Limit Values (TLV) and the sub-ranges between lowest toxicity (TLV >10000 ppm) up to really toxicity (TLV ≤ 0.1 ppm).

The corrosiveness index is found out on the basis of the required construction material. The lowest score of I_{COR} is for carbon steel, and the highest one is for needed material better than stainless steel.

5.4.1.2 Inventory hazard index

The score for the evaluation of inventory index is based on the sub-ranges of process vessels from volumes between 0-1 ton up to volumes larger than 1,000 ton. The mass flows and residence time in the process are used to estimate the inventory of each design alternative.[41]

5.4.1.3 Process reaction index

It is important to know how exothermic the reaction is. Hence, the process reaction index consists of both the maximum values of indices for the heat of the main and side reactions, and the maximum value of chemical interactions, which describes the unintended reactions between chemical substances present in the process area studied

$$I_{RH} = I_{HMR,\,max} + I_{HSR,\,max} + I_{INT,\,max} \qquad \text{Eq. 7}$$

The values of indices for the heat of main and side reactions are assigned based on the heat of reaction and its sub-ranges from endothermic or thermally neutral reactions with heat of reaction $\leq$ 200 J/g up to extremely exothermic reactions with heat generation $\geq$ 3,000 J/g. If there are several main reactions (in a series reaction) or side reaction, these indices is determined on the basis of the greatest heat release.[41]

The interaction hazard index evaluated the hazard associated with the consequences of chemical incompatibility among chemical substances. It is assumed that fire and explosions are most hazardous consequences of an interaction with the score 4.

5.4.2 Process index

5.4.2.1 Process condition index

The process condition index is the sum of process temperature and pressure sub-indices.[41]

$$I_{PC} = (I_T + I_{PR})_{max} \qquad \text{Eq. 8}$$

The process temperature index is identified based on the maximum temperature in the process area under investigation and the sub-ranges from the harmless range to people of 0-70 ^{o}C up to the range of larger than 600 ^{o}C. The temperatures below 0^{o}C are also considered as a hazard with the assigned I_T of 1 due to mechanical problems and freezing.

The process pressure index is determined based on the maximum pressure in the process area under normal operation and the sub-ranges from the lowest range of 0.5-5 bar for the score of 0 up to 200-1000 bar for the score of 4.

5.4.2.2 Process equipment index

This index is assigned based on the score system developed from engineering practice and recommendations on layout recommendations, and quantitative accident and failure data by Heikkila. Furnaces and fired heaters which have the highest impact to safety of the process receive the score of 4, while the equipment that handle nontoxic and nonflammable chemicals receive the score of 0. The process equipment index is determined on the basis of worst case of different equipment in the process under investigation.[41]

5.4.2.3 Process structure index

The process structure index is evaluated based on the scoring system involving incident reports and database, sound engineering practice, accepted engineering standards as well as expert knowledge suggested by Heikkila. Basically, this sub-factor falls into one of six following groups of equipment and systems. The first group for process and equipment solutions recommended by safety standards has the score of 0. Process cases selected with basis in sound engineering practice and known reliable are in the second group with the score of 1. The third group for the process cases that lacks information regarding hazardous operation receives the score of 2. The fourth group receives the score of 3 and is for the configurations which are probably questionable on the basis of safety even accidents have not occurs yet. The fifth and sixth groups are for the process cases with documented minor or major incident respectively.[41]

While the scoring system is ready, the problem is to identify which group the investigation process belongs. With no explicit way, one has to depend on experience based data such as incident reports and databases, engineering standards and practice. And when problem solving is based on experience which is difficult to define as explicit rule, it is possible to apply case-based reasoning (CBR). CBR is a methodology which uses directly solutions of old problems to solve new problems.

Using this CBR approach, incident reports and databases are analyzed, the process cases which are similar to the investigation process in any levels (process, sub-process, system, subsystem, equipment, and detail) are retrieved and serve as case-bases to compare with the investigation process. Input data using retrieval parameters such as raw material, product, reaction type etc.

The process structure index is determined on the basis of worst case of different levels of reasoning.

5.4.2.4 Process complexity index

While the process structure index demonstrates which process configurations and operations are safe from system engineering point of view on the basis of experience based data such as incident reports and databases, engineering standards and practice, the process complexity index describes how easy process items work together, how they should be connected and controlled together from an operational perspective on the basis of process characteristic itself. All the interconnections among different equipment, a source for disturbance and interaction, are added to the process complexity. The process structure and complexity index seem overlapped, but actually they are different. The latter one helps to evaluate new process which does not has experience based data and therefore could not evaluate in the process structure index.

A system is complex when it has many interacting elements of a variety of kinds, in such a way that no evidence can be found of the characteristics of single elements in the overall result.[46] The number of components in the technical system, number of connections between the components of the system, number of common modes, and type of component and the connections can affect the process complexity level.[46] For a design or unit in a chemical process, the amount of equipment is an important factor indicating the level of complexity in a system. The number of input and output streams becomes important when the interaction of different equipment is assessed. Fewer degrees of freedom (DOFs) result in more simplified operation, which in practice is realized by the introduction of automation (less opportunity for human error).[45]

To evaluate the complexity of a chemical process, Koolen[45] has suggested a complexity value as a function of complexity factors including amount of equipment accessible by the operator (M), number of degrees of freedom (DOFs) (S), number of measurement readings (O), number of input and output streams including energy streams (P), interactions in the process requiring operator intervention (Q), and number of external disturbances (for the unit) requiring action from an operator (R). A summation of complexity factors with their weighting factors obtains the following formula:

$$\text{Complexity value (COX)} = m \cdot M + s \cdot S + o \cdot O + p \cdot P + q \cdot Q + r \cdot R \qquad \text{Eq. 9}$$

where m, s, o, p, q, r are the weighting factors per item.

Equation 9 is simplified by using 1 as the weighting factor for all terms in this work. Thus, the complexity value is now calculated by the following equation:

$$\text{Complexity value (COX)} = M + S + O + P + Q + R \qquad \text{Eq. 10}$$

Finally, to obtain a complexity index from the complexity value, a scoring method is proposed in this work. This method requires at least two processes for the inherent safety or resilience evaluations. Due to the score range of the process complexity index of 0 to 5 (lower is better), the highest complexity index which is a value of 5 is assigned to the highest complexity value. Then, the process complexity index is determined based on the scoring system in Table 4.

After all sub-indices have been identified, the inherent safety index (I_{IS}) can be obtained by Equation 4. Then, the inherent safety index of the process k is normalized for resilience evaluation as:

$$ISI_k = \frac{(I_{IS})_k \cdot 10}{114} \qquad \text{Eq. 11}$$

The factor 10 is involved to normalize the index range from 0 to 10 so that it is evaluated at the same scale to the other factors. The factor 114 is appeared in the normalized equation since it is the maximum value of I_{IS} which is corresponding to the score of 10.

Table 4. Determination of the process complexity index I_{COX}

Process complexity value (COX)	Score of I_{COX}
$1-\left(\frac{COX_{max}}{6}\right)$	0
$\left(\frac{COX_{max}}{6}\right)-\left(\frac{COX_{max}}{3}\right)$	1
$\left(\frac{COX_{max}}{3}\right)-\left(\frac{COX_{max}}{2}\right)$	2
$\left(\frac{COX_{max}}{2}\right)-\left(2\frac{COX_{max}}{3}\right)$	3
$\left(2\frac{COX_{max}}{3}\right)-\left(5\frac{COX_{max}}{6}\right)$	4
$\left(5\frac{COX_{max}}{6}\right)-\left(COX_{max}\right)$	5

CHAPTER VI
CONTROLLABILITY INDEX

In this chapter, an approach to controllability assessment is developed, based on well-established theory of process control. Under impacts of disturbance, it is desired to bounce back the changes by keeping operating conditions at the previous state or at a new steady state. The controllability index measures the ability of the process to obtain desired operating conditions using control systems.

6.1 Controllability concept

Process control has been developed to become an indispensable part of process operation for a long time. Some plants have better "built-in" disturbance rejection capabilities than others, that is, their controllability with respect to disturbance rejection is better.

There have been two research areas of controllability: steady–state and dynamic control. This work of resilient evaluation is based on steady-state controllability concept. Controllability is referred to as an ability of a chemical process to achieve acceptable control performance in which the controlled variables (outputs) can steadily reach target values by manipulating other variables when disturbance (inputs) occurs.

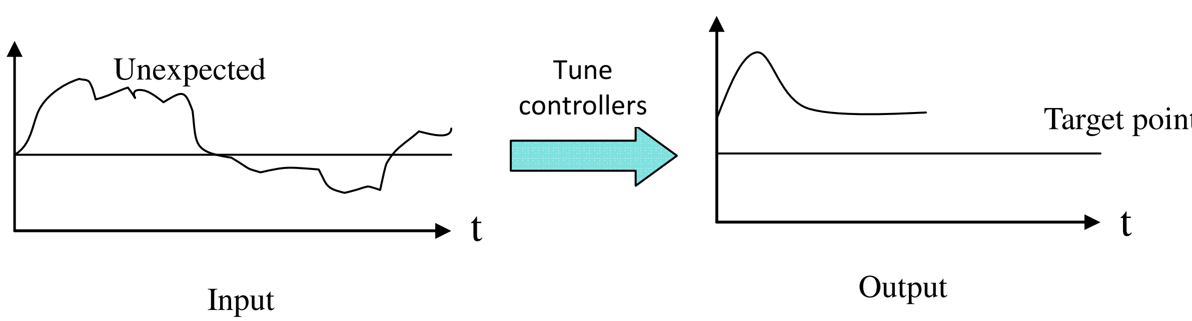


Figure 13. Controllability concept

Figure 13 depicts those changes to demonstrate the controllability concept. Suppose impacts results in unexpected input deviates from set point with respect to time, operators are allowed to tune controllers to cope with the input changes. In general, both the inputs and outputs are objects of the control systems such as temperature, pressure, and flowrate of process and utility streams. If the outputs can be easily controlled to reach target points, the process controllability is considered high (i.e., good). Although time t involves, the controllability in this work considers how easy the outputs can be steady at desired targets (steady-state control), rather than investigate how long the transition can be done (dynamic-control).

In literature of process system engineering, various controllability definitions and expressions have been suggested. For example, some of them are:

- Controllability was defined as an ability of the process to achieve and maintain the desired equilibrium values by Ziegler and Nichols in the 1940's.[47]
- Controllability was referred to as "state controllability" to address the capability of a system changing from a given initial state to an arbitrary final state within finite time by Kalman in the 1960's.[26]
- A more general definition of controllability as the possibility of a system to achieve the specified aims of control was introduced by Rosenbrock in1970.[25]In the other words, the system is more or less controllable according to the ease or difficulty of exerting control.
- Controllability also introduced under the term dynamic resilience to address the input-output controllability of the process without any confusion with state controllability.[9] A drawback with the name "dynamic resilience" is that it does not reflect its relation to control.[48]
- Controllability was mentioned as "input-output controllability" to address the ability to achieve acceptable control performance in which the controlled outputs and manipulated inputs are kept within specified bounds from their setpoints under any uncertainties by Skogestad and Postlethwaite. [26]

Compared to those definitions, controllability concept in this work is similar to some extents. However, the purpose of evaluating controllability for resilience assessment in this work is unique.

6.2 Literature review

Controllability analysis plays an important role in integrated approaches to design and control dynamical systems.[49] There are two types of controllability evaluation methods. One type is based upon linear model analysis, whereas another type needs physical chemical insights and thus provides nonlinear information. To evaluate the controllability in process design stage, a common controllability analysis is based on steady-state consideration or linear model analysis. By steady-state consideration, one can cut through to the essence of some very complex problems and solve them in a simple and straightforward manner. The possibility of this method in assessing how easy a plant is controlled has been proved in some research.[8,26,50,51]

There exist several available tools for evaluating linear controllability, including right half plane (RHP)-zeros and time delays, RHP-poles, partial disturbance sensitivity, relative order and phase lag, disturbance sensitivity, relative gain array, singular value analysis and condition number. A review of those tools was done by Wolff et al.[8] Morari and coworkers made significant contribution to this research area with the following work: the effect of RHP zeros on dynamic resilience,[52,53] the effect of dead time on dynamic resilience,[54] the effect of model uncertainty on dynamic resilience,[55] and the relations of pole direction to state controllability.

In this section, the review is focused on theories of some methods for evaluating controllability including relative gain array (RGA), singular value analysis, and condition number. These methods are commonly used tools in controllability analysis and are the basis of the proposed approach in this work.

6.2.1 Relative gain array analysis

Control systems are preferably designed in pairs of controlled variables and manipulated variable either in feed-back or feed-forward configurations such that those pairs are independent and the relationship of each pair is as less nonlinear as possible. However, the interaction between them is unavoidable because of dependency characteristics of process flows. The interaction levels relate to how easy the process is controlled. Therefore, interaction analysis is an important way to perform control analysis.

Among available techniques, Relative Gain Array (RGA) is well developed for interaction analysis. It requires little effort in its application but can yield a great deal of very useful and practical information.[50] The relative gain which was first introduced by Bristol[56] is one of the most widespread techniques to appear in the process control literature.[50] One important advantage of the RGA is that it is independent of input and output scaling.[27,57]

Bristol's relative gain is a systematic approach to the analysis of multivariable process control problems. Consider a process of multivariable control systems with n manipulated variables (inputs) and n controlled variables (outputs). The ij^{th} element of RGA is defined as the ratio of the open loop gain from input j to output i when all other loops are open and the closed loop gain from input j to output i when all other loops are perfectly controlled.[27,50,58]

$$\lambda_{ij} = \frac{\left(\partial y_i / \partial x_j\right)_x}{\left(\partial y_i / \partial x_j\right)_y} = \frac{gain(open-loop)}{gain(closed-loop)} \qquad \text{Eq. 12}$$

The numerator is a partial derivative with all the manipulated variables held constant except x_j. The denominator is evaluated with all of the control variables held constant except y_i. The values of λ_{ij} provides two important pieces of information:[58]

- A measure of process interactions.
- A selection criteria for the most effective pairing of controlled and manipulated variables.

Based on the equation above, relative gain elements (λ_{ij})can be quantified by calculating all the partial derivatives for all possible pairings. However, a more convenient way is to derive from evaluation of process open-loop gain matrix ***K*** which is defined as

$$\boldsymbol{y} = \boldsymbol{K} \cdot \boldsymbol{x} \qquad \text{Eq. 13}$$

It was proved that RGA element (λ_{ij}) is equal to multiplication of the open-loop gain matrix element (K_{ij}) and the corresponding element ${K_{ij}^{-1}}^{T}$ of the inverse transpose matrix of the gain matrix.[56]

$$\lambda_{ij} = K_{ij} \cdot {K_{ij}^{-1}}^{T} \qquad \text{Eq. 14}$$

To calculate K_{ij}, Nisenfeld and Schultz[59] proposed an approach based on on-line test. Measurement is performed with an assumption that perfect steady-state operation is achieved. Only one controlled variable y_i of loop i is allowed to change at a time by manipulating all variables x_j. This measurement is repeated for every loop i. Then the gain matrix can be calculated from this relationship:

$$K_{ij}^{-1} = \left(\frac{\Delta y_i}{\Delta x_j}\right)_{on-line\ test} \qquad \text{Eq. 15}$$

Another way is to employ a simulation model. For a multivariable process, a step change (Δx_j) is set for the input while holding all other input $j' \neq j$ constant. The resulting changes in the controlled variables (Δy_i) are recorded. From this information the gain matrix element K_{ij} can be obtained by the formula:[26]

$$K_{ij} = \left(\frac{\Delta y_i}{\Delta x_j}\right)_{simulation} \qquad \text{Eq. 16}$$

The latter approach can be performed at design stage using simulation model of the design while the former operation of existing plant. For this reason, the proposed approach will use the idea of the latter one.

The overall recommendation from RGA analysis is to pair the controlled and manipulated variables so that corresponding relative gains are positive and as close to one as possible. From the RGA analysis, a decision in pairing the controlled and manipulated variables can be made. Particularly, RGA values can fall into five following ranges:

- $\lambda_{ij} = 1$.The closed-loop and open-loop gains between y_i and x_j are identical. So, y_i and x_j should be paired.
- $\lambda_{ij} = 0$. It indicates that x_j has no effect on y_i and they need not be paired.

- $0 < \lambda_{ij} < 1$. The closed-loop gain is larger than the open-loop gain. Within this range, the interaction between the two loops is greater when $\lambda_{ij} = 0.5$.
- $\lambda_{ij} > 1$. The pairings with positive RGA-values and closer to one are favorable. Plants with large RGA-values are difficult to control.[8]
- $\lambda_{ij} < 0$. This is a case in which the open-loop and closed-loop gains between y_i and x_j have opposite signs. The closed-loop system may become unstable. Hence, y_i and x_j should not be paired

For the evaluation of resilience, there is a need to represent the controllability in one scalar. Hence, condition number which can be derived from $\boldsymbol{K}$ will be used. The condition number is calculated via ensuing singular value analysis (SVA).

6.2.2 Singular value analysis

One important property of process gain matrix $\boldsymbol{K}$ is its singular values which are nonnegative numbers. SVA can be used to analyze the robustness of a control system and to determine the best multi-loop control configuration.[26] A procedure to calculate SVA of the gain matrix $\boldsymbol{K}$ is as follows.

Consider a process model: $\boldsymbol{y} = \boldsymbol{K} \cdot \boldsymbol{x}$

Singular values of $\boldsymbol{K}$ are the positive square roots of the eigenvalues of the matrix product $\boldsymbol{K}^{\mathrm{T}}\boldsymbol{K}$. To determine the singular values, $\boldsymbol{K}$ matrix is decomposed.[58]

$$\boldsymbol{K} = \boldsymbol{W} \sum \boldsymbol{V}^{\mathrm{T}}$$

where $\boldsymbol{W}$ and $\boldsymbol{V}$ are unitary matrices: $\boldsymbol{W}\boldsymbol{W}^{\mathrm{T}} = \boldsymbol{I}$; and $\boldsymbol{V}\boldsymbol{V}^{\mathrm{T}} = \boldsymbol{I}$

$\sum$ is the diagonal matrix of singular values;

$$\Sigma = \begin{bmatrix} s & 0 \\ 0 & 0 \end{bmatrix} \quad \text{where} \quad s = \begin{bmatrix} \sigma_1 & 0 & 0 & \cdots & 0 \\ 0 & \sigma_2 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \sigma_r \end{bmatrix}$$

$\sigma_1, \sigma_2 \ldots \sigma_r$ are called the singular values of $\boldsymbol{K}$

Nowadays, using computer software such as MATLAB, singular values of $\boldsymbol{K}$ can be easily computed. The meaning of singular value comes from its condition number which is discussed in the next section.

6.2.3 Condition numbers

Condition number of a matrix provides information on sensitivity of the matrix properties to the changes of its element values. Condition number is therefore a measure of interaction analysis.[26] To be able to evaluate controllability in one single number as early as in design stage, condition number is definitely a suitable measure.

The condition number is determined from the singular values decomposition of the steady – state gain matrix which is the ratio of the largest and smallest nonzero singular values:[27,58]

$$CN = \frac{\sigma_1}{\sigma_r} \qquad \text{Eq. 17}$$

where σ_1 is the largest and σ_r is the smallest singular values

One disadvantage of the condition number (as well as SVA) derived from gain matrix is that it dependent of input and output scaling. It is essential to eliminate this dependency when it comes to evaluate and compare resilience of more than one process.

From condition number the controllability of the system is evaluated on how well controllable the system is. A system with a small condition number will be more controllable than a system with a higher condition number. A large condition number indicates an ill-conditioned plant which is believed to be too sensitive to disturbance. Plants with a larger condition number are more likely to be more sensitive to disturbances, and this result in a poorer resilience performance.[51]

6.3 Problem statement

Given process designs with simplified control systems, it is desired to develop an index that can indicate how effective the control is. This index is called controllability index of the resilience evaluation.

Because the evaluation is preferred at design stage and there is no plant available for testing, simulation software is an integral tool. However, it does not mean the approach is not applicable during operation stage where more information about the process is available.

For the purpose of resilience comparison, the controllability index must be independent on scaling or unit of measurement. In addition, it can be normalized to a scale that is equal to other Design sub-factors (Inherent Safety and Flexibility) to calculate the Resilience index.

6.4 Proposed approach

In this section, an approach is developed to address the controllability aspect for the resilience evaluation of the plant. The reviewed process control theories are the basis to develop an index for quantifying how good the control performance is to bounce back effect of disturbances on operating conditions. The key of the proposed approach is to combine advantage of scaling independence found in relative gain array and the convenient simplification of the condition number. It is important that these tools are also independent of the controller in order to reflect the control performance limitations of the plant.

6.4.1 Controllability evaluation

Although there exist several available tools for evaluating linear controllability[8], new approach to assess controllability needs to be developed in this work based on two reasons. First, controllability index is parameter scalar, which is satisfied using condition number. Second, it is crucial that the variables of being scaling-independent to make the comparison in controllable aspects of different alternatives. RGA with its main application of best pairing controlled variables with manipulated variables is independent with scale; but it does not meet the first criterion. On the other hand, the condition number which derived from gain matrix and its singular values satisfy the first criterion only.

The proposed methodology is structured around a newly define term *relative gain matrix*, different from relative gain array and gain matrix to describe the relationship between input and output change. Next, a procedure called Singular Value Analysis is applied to determine minimum singular value, maximum singular value. Then, a measure of controllability called Condition Number (CN) is obtained for each design. Condition numbers indicate more-resilient design in terms of controllability among alternatives.

6.4.1.1 Definition of proposed relative gain matrix

To avoid the scaling dependence, the controlled variables and manipulated variables are given in dimensionless form

$$Y_i = \frac{y_i - y_{i,0}}{y_{i,0}} \qquad \text{Eq. 18}$$

$$X_j = \frac{x_j - x_{j,0}}{x_{j,0}}$$

Where $x_{j,0}$ is the steady-state or optimized values of the manipulated variable x_j

$y_{i,0}$ is the steady-state or optimized values of the controlled variable y_i

x_j is the changed/ new values of the manipulated variable x_j

y_i is the values of the controlled variable y_i with respect to x_i obtained while holding all other manipulated constant.

Assume one is dealing with a process with a (multivariable) *n*-loop control system. The input-output relation to address the effect of relative change in manipulated variables on relative change of controlled variables can be expressed as

$$\boldsymbol{Y} = \boldsymbol{K} \cdot \boldsymbol{X} \qquad \text{Eq. 19}$$

Where ***Y*** is an n-element vector of relative change of controlled variables, ***X*** is an *n*-element vector of relative change of manipulated variables

$$\boldsymbol{Y} = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ \cdots \\ Y_n \end{bmatrix}, \ \boldsymbol{X} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ \cdots \\ X_n \end{bmatrix}$$

K is the $n \times n$ relative gain matrix (not relative gain array – RGA – which is commonly found in the literature) to address the gain between relative values of ***Y*** and ***X***

$$\boldsymbol{K} = \begin{bmatrix} K_{11} & \cdots & K_{1n} \\ \vdots & \ddots & \vdots \\ K_{n1} & \cdots & K_{NN} \end{bmatrix}$$

6.4.1.2 Determination of relative gain matrix K

The simulation approach is employed to calculate matrix ***K***. A steady-state model needs to be built in simulation software (e.g., Aspen Plus). The simulation model considers all mass and energy balances. In the simulation, unit specifications are set up in such a way that control loop is opened. For example, in a heat exchanger heat duty is specified instead of process stream outlet temperature. With this way, the outlet temperature is calculated accordingly whenever the inlet temperature changes, due to interaction. This steady-state scenario is referred to as a base case (X_{i0}; Y_{i0}).

Suppose the control loops are paired so that controlled variable Yi is primarily controlled with manipulated variable X_j. A step change of only manipulated variable X_j is made for loop j while all other manipulated variables are kept constant. The values of controlled variables are calculated and recorded from the simulation results. For this scenario, the measure is obtained as follows:

$$\boldsymbol{Y} = \begin{bmatrix} \Delta Y_1 \\ \Delta Y_2 \\ \Delta Y_3 \\ \\ \vdots \\ \\ \Delta Y_n \end{bmatrix}, \ \boldsymbol{X} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ \Delta X_j \\ \vdots \\ 0 \\ 0 \end{bmatrix}$$

Because $\boldsymbol{Y} = \boldsymbol{K} \cdot \boldsymbol{X}$, *a column of the matrix* $\boldsymbol{K}$ is calculated:

$$\begin{bmatrix} \Delta Y_1/\Delta X_j \\ \Delta Y_2/\Delta X_j \\ \Delta Y_3/\Delta X_j \\ \\ \vdots \\ \\ \Delta Y_{n/\Delta X_j} \end{bmatrix} = \begin{bmatrix} K_{1j} \\ K_{2j} \\ K_{3j} \\ \\ \vdots \\ \\ K_{nj} \end{bmatrix}$$

The step changes are repeated for every loop j, then the whole matrix $\boldsymbol{K}$ is derived:

$$K_{ij} = \frac{\Delta Y_i}{\Delta X_j}$$

If step changes are performed with various levels (e.g., ±0.1%; ±0.2%; ±0.5%…), then sensitivity of controllability measure to disturbance impact can be obtained.

The proposed measure has several important properties:

- Relative gain matrix takes into account of the interaction of multivariable in control system

- Relative gain matrix is dimensionless and thus not affected by choice of units or scaling of variables
- Relative gain matrix can be easily and straightforward calculated using simulation sensitivity analysis tool. Thus, it requires little effort in its application and can yield a great deal of very useful, practical information. Other interaction methods require detailed, dynamic models which in turn require a large effort

6.4.2 Controllability index evaluation algorithm

This work evaluates steady-state controllability via an analysis of the relative gain matrix. The proposed steps to calculate the controllability index are described in Figure 14.

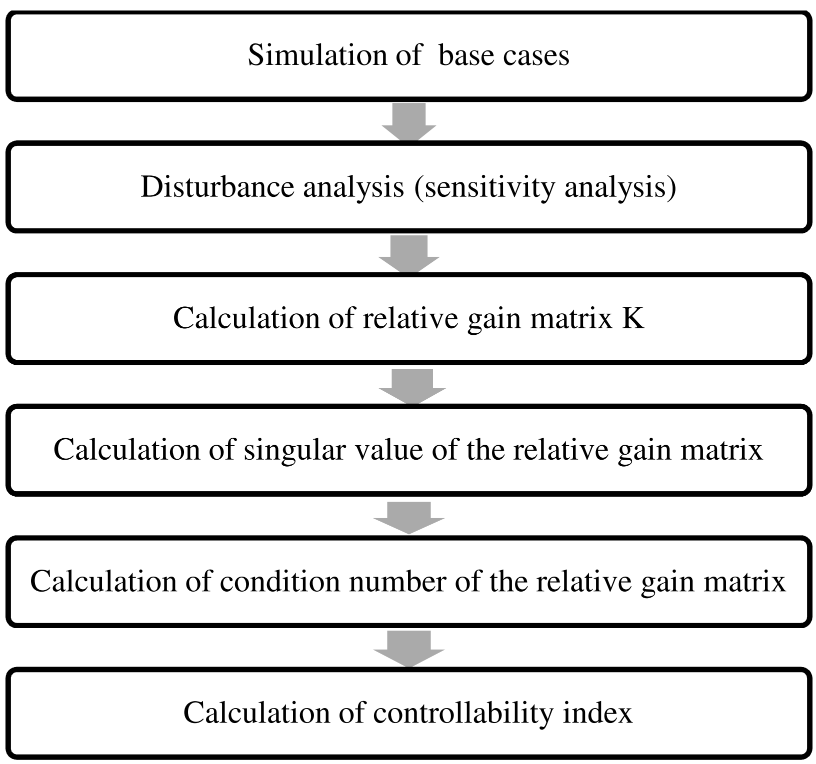


Figure 14. Algorithm to assess the controllability index

First, the calculation procedure starts with the simulation of base cases in a process simulator (e.g. Aspen Plus, Pro/II, Hysis, etc.). From the simulation, mass balance, energy balance, and operating conditions (temperature, pressure, flow rate, concentration) are determined. Optimization has been performed to minimize or maximize the objective function (e.g. cost) subject to a number of restrictions (called constraint) when needed. Then, the "best" scenario with (Y_{i0}; X_{jo}) from among the set of candidate solutions is assigned the base case.

Second, sensitivity analysis tool of the software is used to simulate interaction by changing the values of one manipulated variable (X_j) at a time in small ranges and recording the values of other variables (Y_i). Only variables of the evaluated control systems (including controlled variables and manipulated variables) need to be tracked.

Third, relative gain matrices $\boldsymbol{K}$ of the control systems are obtained from the sensitivity analysis by the following expression.

$$K_{ij} = \frac{(Y_i - Y_{i0})/Y_{i0}}{(X_j - X_{j0})/X_{jo}} \qquad \text{Eq. 20}$$

where K_{ij} = element of the i^{th} row and the j^{th} column of the matrix, or the ratio of the relative change of controlled variable i to that of manipulated variable j.

Y_i, Y_{i0} are dimensionless controlled variables

X_j, X_{j0} are dimensionless manipulated variables.

The gain matrix indicated the interaction of the control loops. In this research, multivariable control systems are analyzed at a plant-wide level (i.e. not limited to every equipment boundary). However, not all of the control loops are analyzed. Pairs of controlled and manipulated variables that have a fast response were neglected to simplify the interaction analysis. The exclusion of such control loops does not affect the conclusion of the controllability evaluation.[50] In the simulation, the fast-response control loops are closed loops and excluded from the controllability analysis while the others involved in the relative gain matrix calculation are open loops.

Fourth, singular values of the gain matrix are calculated. For practical cases with a large number of controlled and manipulated variables, numerical computing software (e.g. MATLAB, Maple) can be used for the quick and accurate calculation.

Next, the condition number of the gain matrix is derived from the maximum and minimum of the found singular values using the definition:

$$CN = \frac{Maximum\ singular\ value}{Minimum\ singular\ value} \qquad \text{Eq. 21}$$

Finally, to obtain a controllability index from the condition numbers, a novel scoring method is proposed in this work. This method requires at least two processes from the resilience evaluations or a standard condition number of a known process for comparison. The controllability index, on a scale of 0 to 10 (lower is better), assigned the averaged value of the condition numbers $\underline{CN}$ a value of 5. Considering N condition numbers from N processes, the averaged condition number is defined as:

$$\underline{CN} = \frac{\sum_1^N CN_k}{N} \qquad \text{Eq. 22}$$

where CN_k is the condition number of process k

A system with a smaller condition number is considered more controllable and therefore more resilient. Using a linear scale, the scoring of the controllability index (I_C) of process k is defined as:

$$(I_c)_k = \begin{cases} 10\left(\dfrac{CN_k}{2 \cdot \underline{CN}}\right) & for\ CN_k \le 2\underline{CN} \\ 10 & for\ CN_k > 2\underline{CN} \end{cases} \qquad \text{Eq. 23}$$

CHAPTER VII
FLEXIBILITY INDEX

In this chapter, an approach is developed to measure the ability of a process to accommodate impacts. In other words, this chapter evaluates the ability to bounce back and keep production online under operation disturbance.

7.1 Flexibility concept

There are several different viewpoints of flexibility definitions in different problems (e.g., dynamics, steady state, uncertainty design). In this work of resilient evaluation, flexibility is referred to as an ability of a chemical plant to satisfy all performance specifications and safety criteria while unwelcomed variations of operations occurs due to external impacts. The performance specifications are, for example, product concentration, production rate, temperature and pressure of output streams. Safety criteria are requirements to avoid hazards of equipment failure; for example, operating conditions must not exceed design temperature and pressure to avoid mechanical failure (crack, leak, and rupture) and potential run-away reactions.

Figure 15 demonstrates the flexibility concept. Suppose impacts results in input changes to a process within a defined range, operators are allowed to tune controllers to cope with the input changes. Inputs can be temperature, pressure, flowrate of certain process streams and/or utility streams. The outputs are the performance specifications and safety criteria. If the output variation stays in desired ranges, the process is considered flexible.

In process system engineering, flexibility has been usually arisen in context of process design with uncertainty. For example, some of the flexibility definitions are:

- Flexibility is an ability of a design to operate at a wide range of operating conditions and parameter variations while satisfying product quality and quantity.[5]
- Flexibility of chemical plants is an ability to achieve feasible operation over a given range of uncertain variations of external and internal parameters.[60]

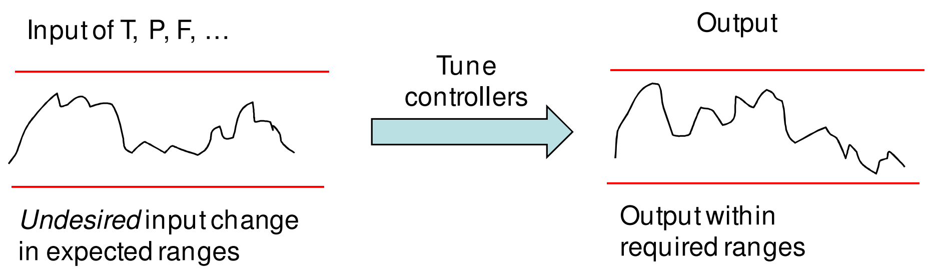


Figure 15. Flexibility concept

Compared to the definitions of those pioneers, flexibility concept in this work has implementation. This work is oriented to process safety. It additionally investigates the ability of the process to operate under impacts of safety-related issues such as leak, spill, and rupture which may result in loss of stream or utility flow rates. Those types of impacts have never been mentioned in literature. Pistikopoulos[61] categorized impacts (in term of uncertainty sources) into four types: model-inherent, process-inherent, external, and discrete uncertainties. The safety-related impacts do not perfectly fall into any of those categories; therefore, they can be referred to as another category.

7.2 Literature review

Flexibility levels of a process design have been quantified in a scalar called flexibility index. There are many definitions and determination methods for flexibility index. The three approaches of Morari and Grossmann's groups are systematic and commonly cited on the literature. They are best described in graphs of impact (uncertainty) space.

Morari[5] proposed an index to evaluate flexibility of design of heat exchanger networks. The author defined resilient processes as those which satisfy all physical constraints (nonnegative exchanger loads) and performance specifications (target T, P, product specifications, etc.) for every value of the uncertain variables in the uncertain range despite undesired changes to the process (e.g. environmental disturbances in supply temperatures, fouling of heat transfer surfaces). Although the author used the term "resilience," that work was actually referred to flexibility aspect. Developed from this definition, the index was characterized in some sense of the largest disturbance that the network can tolerate without becoming infeasible. In the space of impact variables (θ) in Figure 16, the round envelop is an actual flexibility region that cannot be determined explicitly. Inside this envelops, all physical constraints and specifications are satisfied. The rectangles are varying ranges of the impacts. The flexibility index is characterized as the largest rectangle inside the flexibility region. It is a function of the distance S between vertex of rectangle and boundary of the region.[6]

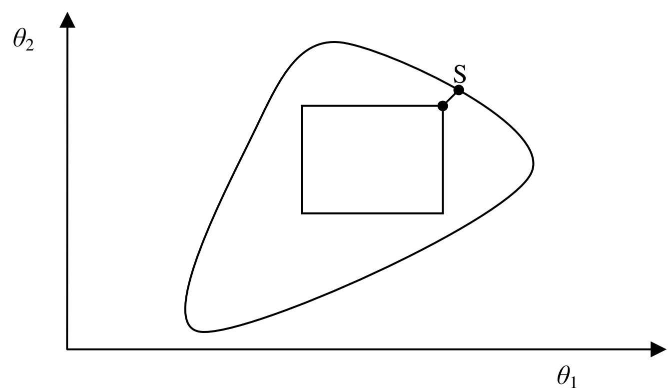


Figure 16. Flexibility index of Saboo and Morari[6]

As for the second approach, Swaney and Grossmann[62] scaled down the investigated rectangle range of impact variables (the largest rectangle in Figure 17) until it inscribes the flexibility region and at least one of the vertices lies on the flexibility boundary (the smaller rectangle in Figure 17). The scaling is based on a fixed nominal point (A) which usually corresponds to a base-case operating condition. The flexibility index was defined as a ratio between the sides of inscribing rectangle and original rectangle, i.e., the ratio of AB/AC. This approach is the basis for the method developed in this work.

In the two previous approaches, the values of impact variables must be given in continuous ranges. If they are described in discrete sets, stochastic flexibility index is more suitable for those cases. Stochastic flexibility was defined as the probability that operation is feasible.[63] It was quantified by a ratio between the areas of flexibility part (the shaded area in Figure 18) and the rectangle of investigated region of impact variable values. The rectangle is derived from the upper and lower bounds of the impact values.

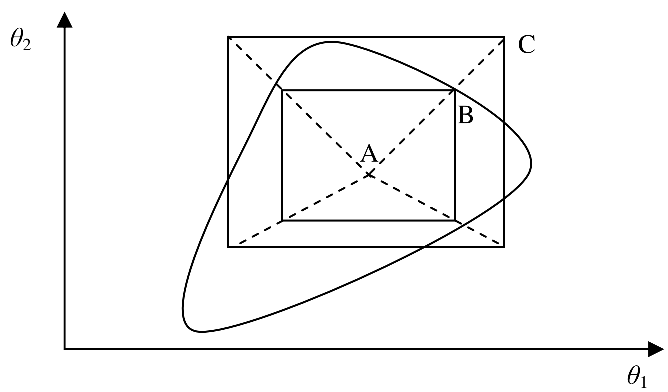


Figure 17. Flexibility index of Swaney and Grossmann[62]

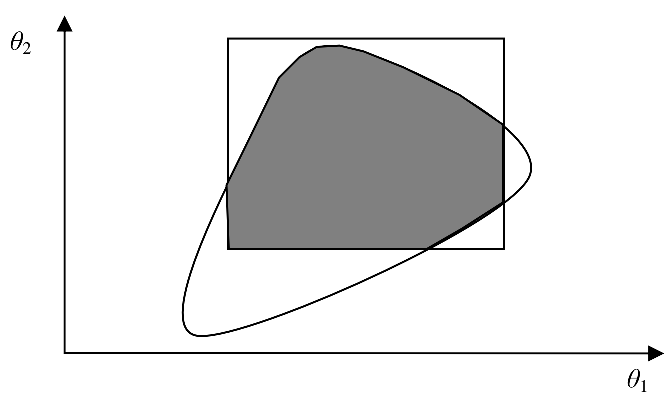


Figure 18. Stochastic flexibility index[64]

Although their methods are systematic approaches, there are still some limitations. They are practically good for a small part of a chemical process (e.g., heat exchanger network, reactor unit) but not a whole plant because of the requirement of all process-modeling equations and the increasing computing costs exponentially with number of external impacts. Also, safety related issues were out of their scopes.

Therefore, a new method is needed for the resilience evaluation problem that involves the whole process with a large number of physical constraints. In this research, a new approach is proposed to develop based on the integration work of Grossmann with a powerful aid of process simulator software (e.g., Aspen Plus).

7.3 Problem statement

In a design stage of a process, design parameters such as equipment sizes and process structure are to be determined. In a follow-up operation stage, those design parameters are not changed (unless the process is retrofitted) because the process is already built. Only control parameters such as stream flow rates, temperature, and pressure are allowed to change to achieve production objective. The common problem with flexibility design in the literature is how to determine the design parameters in the design stage under uncertainty of inputs such that the operation is optimum (e.g., profit is maximized).

Different from flexibility design, the objective of this chapter is to develop a method to evaluate flexibility of a given design (flexibility analysis). The problem is stated as follows:

A design of a chemical process (d) is given. That means, equipment sizes and process structure are known and unchanged.

Control variables (z) are allowed to vary in given bounded ranges. Flow rate, temperature, and pressure are considered control variable because they can be varied to control the process. They can be tuned by certain means. For example, flow rates are adjusted by control valves; pressure is controlled by throttle valves, pumps, compressors; temperatures are controlled using heat exchangers. Flow rates can be changed by adjusting openings of valves; and state variables (temperature and pressures) can be indirectly controlled through operating valves.

These changeable variables are degrees of freedom to accommodate the process with unexpected changes of external impacts, such as: environmental conditions, leaks, ruptures. Ranges of the impacts are expressed in terms of process flow rates, temperatures, and pressures. For example, rupture is described by a zero flow in the ruptured pipe.

The process is flexible when it can be kept in operation under effects of the impacts while all the performance specifications and safety criteria are met. The problem is to quantify the flexibility of the design in form of one scalar index which is a function of ranges of external impacts that the process can tolerate

7.4 Proposed approach

7.4.1 Theory

The following theory is based on the work of Swaney and Grossmann.[62] A simple calculation algorithm will be proposed in the next section. However, the theory behind the algorithm is complicated with some assumptions.

In mathematic view point, the process is described by sets of constraints:

- Physical constraints :

$$\boldsymbol{f}_m(\boldsymbol{d},\boldsymbol{z},\boldsymbol{\theta}) = 0 \qquad \text{Eq. 24}$$

- Specifications:

$$\boldsymbol{g}_n(\boldsymbol{d},\boldsymbol{z},\boldsymbol{\theta}) \leq 0 \qquad \text{Eq. 25}$$

Physical constraints are shown in Equation 24, for example, mass and energy balance, phase equilibrium, kinetics equations, and so on. Specifications have two types: product specifications (e.g., optimum concentration, production rates) and safety criteria to avoid safety-related issues such as run-away reactions, leaks, rupture and other mechanic failures. The process is feasible operable when all of these constraints and specifications are met.

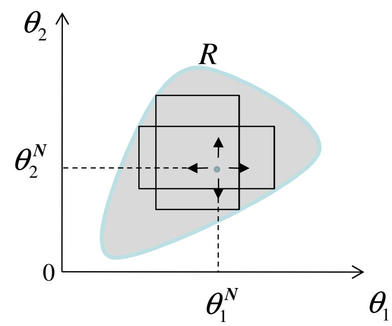


Figure 19. Feasible region and inscribed hyper-rectangles of impact ranges.

In the space of impacts θ (Figure 19), the state of process operation is normal if the impacts are at nominal values (θ_1^N, θ_2^N). When impacts values increases or decreases, the operating points move away from the nominal value. Assume external impacts vary independently of each other. *Flexibility index* is a measure of a rectangular operating region inscribing the feasible region *R*.

To quantify the index, the problem must be formulated. Let Region *R* be the set of impact values θ such that there is at least one control state z in which the operation satisfies all the constraints and specifications.

$$\boldsymbol{R} = \{\theta \mid [\exists z \mid \boldsymbol{f}_m(\boldsymbol{d}, z, \theta) = 0 \wedge \boldsymbol{g}_n(\boldsymbol{d}, z, \theta) \le 0, \forall \boldsymbol{m}, \boldsymbol{n}]\} \qquad \text{Eq. 26}$$

There are many rectangles inscribing in region *R* and touches the boundary as shown in Figure 19. Hence, the first step is to standardize the way of changing θ such that there is only one rectangle touching the boundary, which defines a unique index.

The largest rectangle in the figure is the given ranges of impact values. If we call *T* the searching rectangle, then the standardization means *T* is a scale-down of the large rectangle based on the nominal point (Figure 20). In other words, when scaling is performed, the rectangle vertices are always on the lines connecting the nominal point and vertices of the largest rectangle.

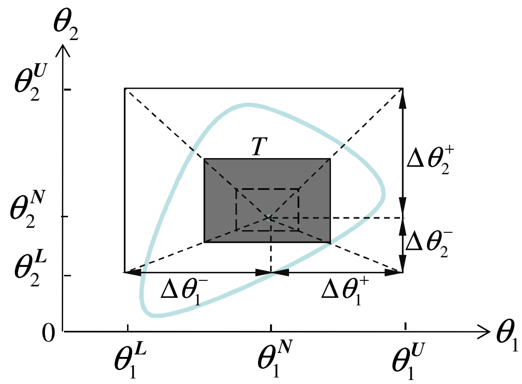


Figure 20. Scaling standardization of the hyper-rectangles of impact ranges.

Let δ be the ratio between sizes of T and the large rectangle. The size of T depends on value of parametric δ. T increases as δ increases. When T is largest, touches and inscribes the boundary of R, the value of δ is maximum and therefore is the flexibility index. Mathematically, flexibility index I_F is the solution of the optimization problem

$$\boldsymbol{I_F} = max\delta \qquad \text{Eq. 27}$$

subject to:

Feasible operating conditions:

$$\forall\theta \in \boldsymbol{T}\,(\delta)\{\exists\boldsymbol{z}|\boldsymbol{f}_m(\boldsymbol{d},\boldsymbol{z},\theta) = 0 \,\cap\, \boldsymbol{g}_n\,(\boldsymbol{d},\boldsymbol{z},\theta \,\leq 0, \forall\boldsymbol{m},\boldsymbol{n}\} \qquad \text{Eq. 28}$$

Parametric region of T:

$$T(\delta) = \{\theta|(\theta^N - \delta\Delta\theta^-) \leq \theta \leq (\theta^N + \delta\Delta\theta^+) \qquad \text{Eq. 29}$$

Constraint shown in Equation 24 is the feasibility operating conditions. It means that for all θ inside T, there is at least one control state z such that all physical constraints and specifications are satisfied.

The above formula is a complete formulation to determine flexibility index. It is very difficult to solve. To be solvable, the above logic language is translated into conventional optimization formulation by transforming the variable θ to $\tilde{\theta}$ with the relationship:

$$\theta = \theta^N + \delta\tilde{\theta} \qquad \text{Eq. 30}$$

The formulation above becomes a two-stage optimization programming:

$$I_F = \min_{\tilde{\theta} \in \tilde{T}} \delta^*(\tilde{\theta}) \text{with} \tilde{T} = \{\tilde{\theta} | -\Delta\theta^- \leq \tilde{\theta} \leq \Delta\theta^+\} \quad \text{Eq. 31}$$

where $\delta^*(\theta)$ is determined from the optimization problems:

$$\delta^*(\theta) = \max\delta \quad \text{Eq. 32}$$

Subject to

$$f_m(d, z, \theta) = 0, \forall m \quad \text{Eq. 33}$$

$$g_n(d, z, \theta) \leq 0, \forall n \quad \text{Eq. 34}$$

The idea of this transformation is to introduce vector $\delta\theta^{\sim}$ which originates from the nominal point and always touch the boundary of *T* (not only vertices of *T*). The direction of the vector is defined by $\theta^{\sim}$ and its length depends on δ. In the inner-stage problem (Equations 32 – 34), δ increases to scale up *T*. When its arrow touch boundary of R (δ is maximum), we obtain δ^*. In outer-stage problem (Equation 31), the found δ's from various direction $\tilde{\theta}$ are compared for the minimum, which is the value of flexibility index.

The problem is now easier to solve but its size is large because we need to investigate infinite values of direction $\tilde{\theta}$ ($0 \leq \tilde{\theta} \leq 360^o$). To reduce the size, an assumption that Rectangle *T* touches boundary of *R* only at a vertex of *T* is applied. The benefit is the reduction of search space from infinitive to a manageable finite set and only $\tilde{\theta}$ in the vertex directions to be investigated. In Figure 21, there are four vertices because is *T* is a rectangle. If *T* is a hyper-rectangle in *p*-dimension space, the number of vertices is $2p$.

The assumption is actually true when Region *R* is one-dimensional convex (i.e., if a vertical or horizontal straight line cuts R boundary at two points or less). The assumption is difficult to be verified since we do not explicitly know *f* functions. However, even the conditions are not satisfied, the solution in engineering problems is still very likely to lie at a vertex.[62]

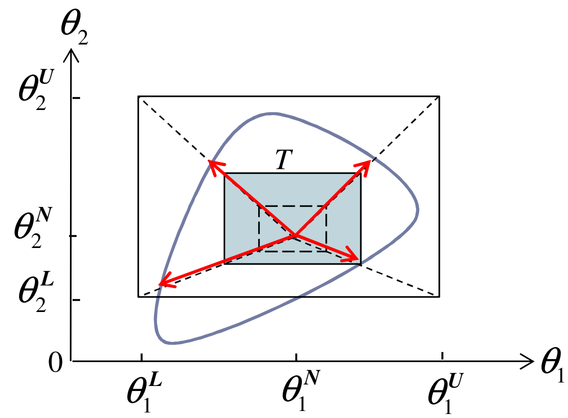


Figure 21. Searching direction of transformed impact variables.

7.4.2 Implementation

The final formulation above is not ready to be applied in flexibility analysis for resilience evaluation because it is very difficult (if not impossible) to define all physical constraint $f_m(\boldsymbol{d},\boldsymbol{z},\boldsymbol{\theta}) = 0$ for a whole plant. A novel approach is proposed with the powerful aid of process simulator (e.g., Aspen Plus) to easily verify these constraints.

In this work, whole process is simulated in Aspen Plus in various scenarios of external impacts and control variables. Those scenarios are generated in systematic way to search for the operating condition that associates with the flexibility index. The algorithm is shown in next section.

The benefits of this approach are to eliminate hassle determination of all functions $f_m(\boldsymbol{d},\boldsymbol{z},\boldsymbol{\theta}) = 0$, to obtain rigorous and quick calculations. However, it requires adequate knowledge of using process simulation software.

7.4.3 Flexibility index evaluation algorithm

Based on the theory (Section 7.4.1) and proposed implementation (Section 7.4.2), a calculation algorithm is proposed in Figure 22.

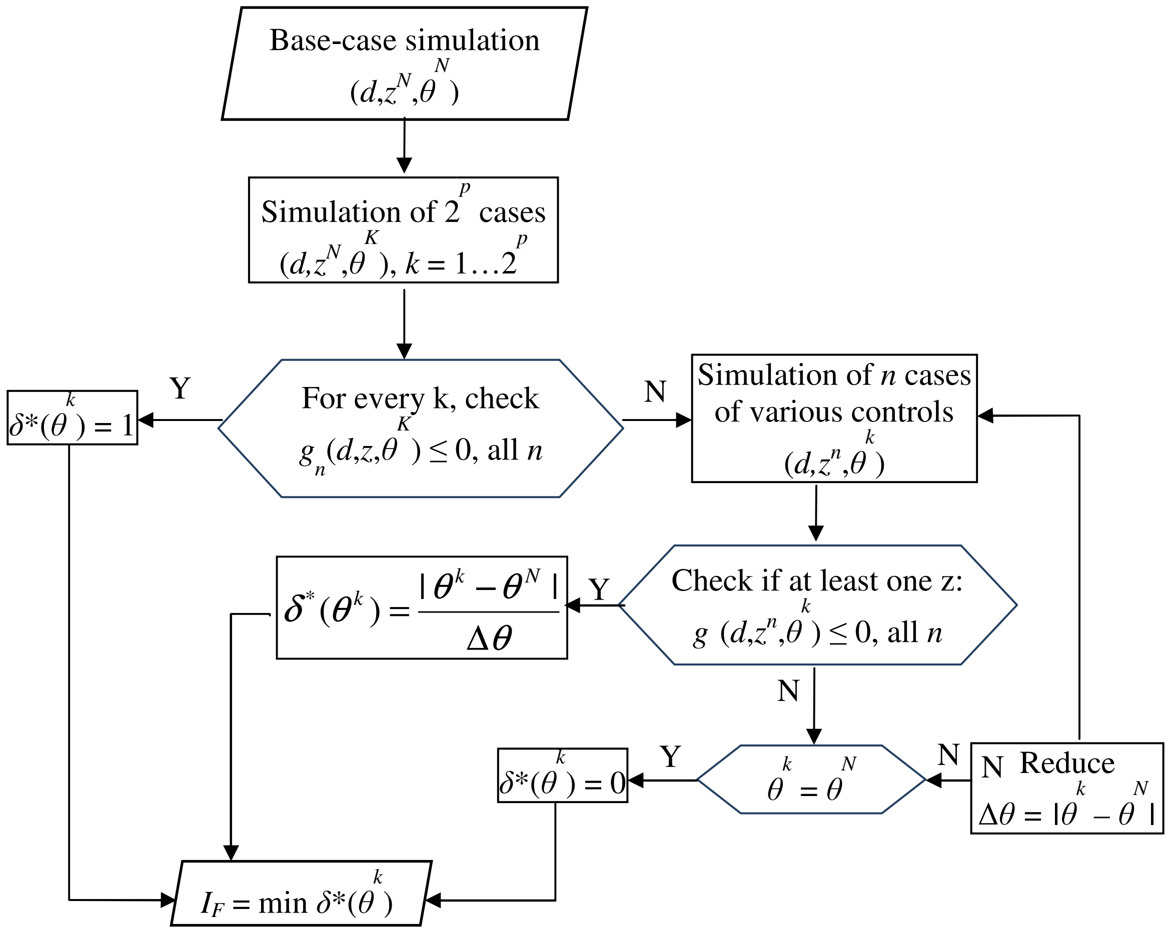


Figure 22. Flexibility calculation algorithm

First, the whole process is simulated in a base case with determined design parameter *d* and nominal values of control variables z^N and impact parameters θ^N. There are more than one way to specify performance of a unit in the simulation. However, the way to allow sensitivity analysis in the next steps should be chosen. For example, to investigate the effect of changing utility duty on process stream temperature in a heat exchanger, heat duty should be specified in the simulation. Other parameters such as temperature, pressure, vapor fraction related to the heat exchanger are calculated accordingly.

Second, based on the base-case process model, sensitivity analysis is performed to simulate 2^p cases with of impact values θ^K being at their bounds. This task can be easily performed using the Sensitivity Analysis tool in Aspen Plus.

The third step is analyzing those simulation results. In every case, if all specifications and safety criteria are met, then the index of that case is $\delta^* = 1$. For cases where not all specifications are met, Sensitivity Analysis tool is employed to simulate scenarios of various values of control variables z^n. Then the specifications and safety criteria are verified. If the specifications and criteria are met, the index is still maximum:

$$\delta^*(\theta^k) = \frac{|\theta^k - \theta^N|}{\Delta\theta} = \frac{\Delta\theta}{\Delta\theta} = 1. \qquad \text{Eq. 35}$$

If not all specifications are met, vector of impact values θ^k need to be changed towards vector θ^N in the next step. Although there may be only one impact violating the constraints, all the impact must be reduced at the same scale ratio (rectangle T is scaled down). Those steps are repeated until all constraints on specifications and safety are met or θ^k reaches θ^N in which index equals to zero ($\delta^* = 0$).

The minimum index found among all simulation scenarios is the flexibility index of the process. The index is bounded in the range of 0 and 1.

For the case that hyper-rectangle T completely inscribes in region R without scaling-down step, the index is assigned to 1 although T can be scaled up and still inscribes in R. the value of flexibility index using this method is dependent on the range of impacts to be investigated.

To evaluate resilience, the flexibility index of process k is converted so that it is in the same scale with the other indices and the lower of I_F is the better:

$$(FI)_k = 10 \cdot \{1 - (I_F)_k\} \qquad \text{Eq. 36}$$

The factor 10 is involved to normalize the index range from 0 to 10 so that it is evaluated at the same scale to the other factors (inherent safety index and controllability index).

7.4.4 Safety criteria

A process is considered flexible in a scenario when all process specifications and safety criteria are satisfied ($g_n(d,z,\theta) \leq 0$). Let rewrite the safety criteria in an equivalent form: $g'_n(d,z,\theta) \leq C$ (where C is constant). C can be referred to as limits of the safety criteria.

Importantly, one should understand that C is not limits of design system. Value of C is set by evaluators, therefore subjective, and is not necessary equal to design limits (say D). For example, a piece of equipment is design to withstand a maximum temperature of 500^o Celsius (i.e., D = 500). But evaluators may specify that the equipment should not operate over 300^o Celsius (i.e., C = 300) to avoid mechanical failure in flexibility analysis. The value of 300^o Celsius is a safety criterion in the flexibility analysis.

If D is increased while C is fixed, operation of the equipment is safer but its flexibility level is unchanged because the level is calculated from C. If C is increased while D is fixed, the operation is concluded more flexible; however, the operation is likely less safe because operating temperature is closer to the limits. Therefore, evaluators should choose suitable values of safety criteria.

CHAPTER VIII

CASE STUDY: EVALUATION OF RESILIENCE DESIGN FACTOR IN ETHYLENE PRODUCTION ALTERNATIVES

Ethylene is the most produced organic compound in the world with a global production of ethylene expected to reach 162 million tonnes in 2012 including both current and planned new construction projects.[65] Due to the important but hazardous characteristics of ethylene product and its production processes, and due to the data availability, ethylene production alternatives were chosen in this work to demonstrate the proposed methodology in evaluating the Design index.

There are some criteria to choose case studies for this work. To be able to demonstrate the methodology well, the design alternatives in producing the same product were preferred to have very different main pathways and different operating conditions, and to involve at least typical equipment such as pump, reactor, heat exchanger, vessel, column etc. Most importantly, their information or data (i.e. PFD) are available in publications.

In Eupore and Asia, ethylene is produced mainly from steam cracking naphtha, gasoil and condensates. While in US, Canada, and Middle East, ethylene is obtained from the steam cracking of ethane. Recently, oxydehydrogenation technology is being developed to compete with the conventional steam-cracking technology and attracts more attention by a number of researches.[66-71] In the meantime, another ethylene production pathway, bioethanol dehydration, also has the support from the industry and researchers motivated by the growth of renewable chemicals and by the low carbon footprint of the product obtained.[72-74] With their satisfaction on the criteria above, they were chosen for demonstration of resilience evaluation and comparison.

In this case study, the quantitative methodology to obtain resilience Design index is applied for the two following processes producing ethylene via:

- Catalytic dehydration of bio-ethanol (Process 1)
- Oxydehydrogenation of ethane (Process 2)

8.1 Process description

Both of the processes are designed at a capacity of 20,000 tonnes per year ethylene. The ethylene product meet chemical grades which requires ethylene molar composition at least 95%. The feedstock compositions are given in Table 5.

Table 5. Molar fraction of the two process feedstocks.

Component	Dehydration process	Oxydehydrogenation process
Ethanol	0.990	
Ethane		0.997
Carbon dioxide	0.010	0.003
Total	1.000	1.000

8.1.1 Catalytic-dehydration of bio-ethanol

The production of ethylene from bio-ethanol employs some key processing steps as shown in Figure 23. First, ethanol is preheated before being converted into the main product ethylene in an endothermic dehydration reaction. Then, because the output of the reactor contains some impurities, it must go through downstream purification steps, including water wash, caustic wash, absorption, and drying, to obtain desired chemical-grade ethylene.

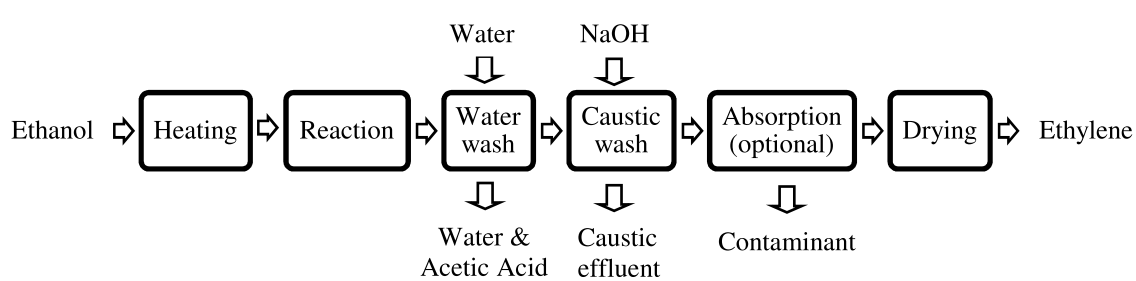


Figure 23. Conversion of bio-ethanol to ethylene via dehydration

There have been four technologies available for commercialization, including Lummus fixed-bed, Lummus fluidized-bed, Syndol[75] and Petrobras[72] (APPENDIX B). The design of Petrobras (Figure 24) is chosen for this case study investigation as it is the latest technology among those available and a plant using the technology has been built in Brazil

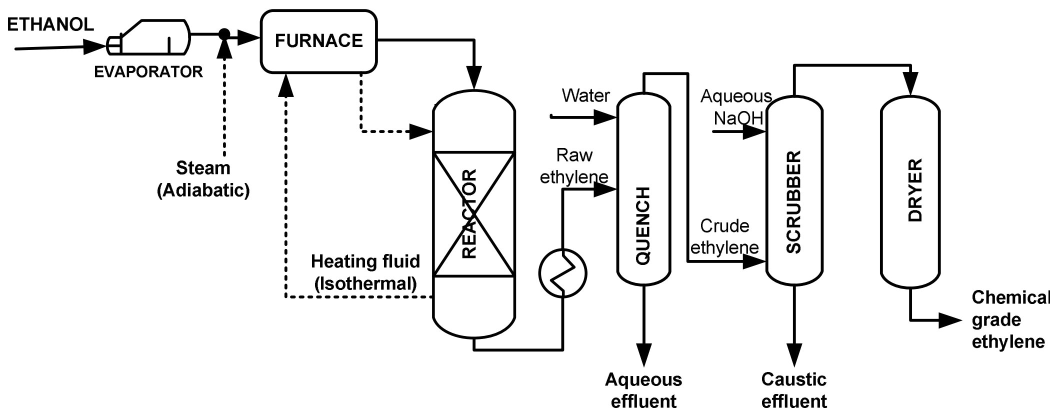


Figure 24. Simplified flow diagram of the Petrobras dehydration process.[72]

The bio-ethanol feedstock is preheated to the reaction conditions (330 – 380 ^{o}C) through an evaporator, steam mixing, and a furnace. The Petrobras design uses a single isothermal reactor for the ethanol-to-ethylene conversion. Bio-ethanol is dehydrated using the endothermic reaction as follows:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O + 46 \text{ kJ/mol} \quad \text{Eq. 37}$$

The reaction occurs in an isothermal fixed-bed reactor in which catalysts are packed inside multi-tubes. The temperature is maintained by circulation of a heating fluid between the reactor shell and the furnace. For this design, it is important to control the operating temperature keep reaction rate and selectivity of main product high.

After the reactor, the product stream is quenched by water to remove the produced water, non-reacted ethanol and some of other by-products such as acetaldehyde and acetic acid. Then, the ethylene product with remaining gaseous contaminants (e.g., acid acetic, carbon dioxide, water) exits the top of the quench tower and passes the scrubber to remove the contaminants. Finally, remaining water vapor in the product stream is removed in drying packed-bed columns.

8.1.2 Oxydehydrogenation of ethane

The feedstock of this process is ethane which is an important petroleum derivative. Oxydehydrogenation of ethane is a technology that is still in research phase focusing on development of catalysts. It is expected to be in competition with the conventional naphtha steam-cracking technology thanks to its higher yield. The main reaction (oxydehydrogenation) is as follows:

$$C_2H_6 + ½O_2 \rightarrow C_2H_4 + H_2O \text{ - } 105 \text{ kJ/mol} \qquad \text{Eq. 38}$$

The only commercial technology that is available from the literature is the design created by Union Carbide. Figure 25 shows the process blow diagram with its key conversion and separation steps. Figure 26 depicts the simplified flow diagram which is adapted from Manyik et al.[66]

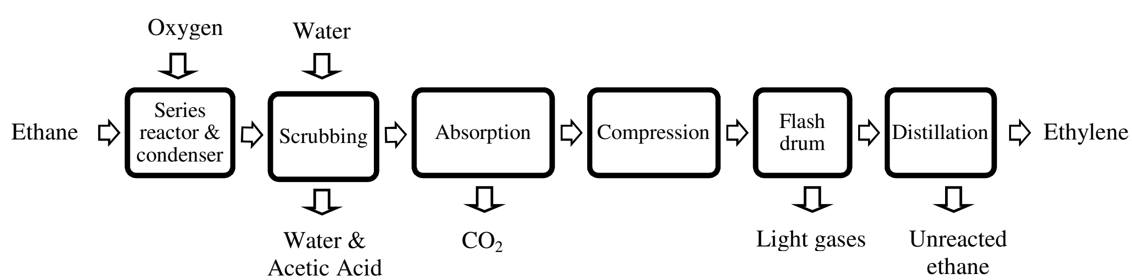


Figure 25. Block diagram of ethane to ethylene via oxydehydrogenation.

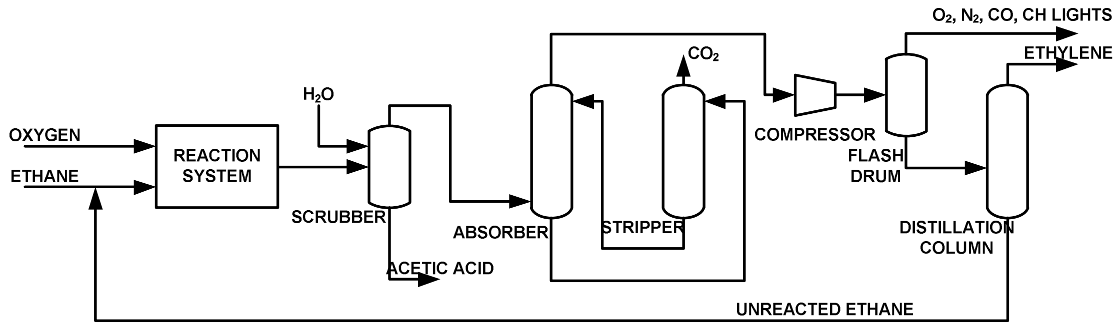


Figure 26. A simplified flow diagram adapted from the Union Carbide oxydehydrogenation process [66]

In this process, the ethane and oxygen that is supplied from an air separation unit are compressed, mixed, and preheated before fed to the reactors. The oxygen concentration must be less than about 6 mole percent of the total input gaseous stream. The oxydehydrogenation reaction occurs in a series of reactors in which ethane is introduced to the first reactor and oxygen is fed in parallel (to every reactor inlet). In every stage, the feed streams are preheated to around 250 °C, converted into ethylene in free-radical reactions at 300 – 400 ^{o}C, and partially condensed to remove acid acetic and water. In this case study, a configuration of three reactors in a series is investigated.

The product stream from the final stage comprises of ethylene, acetic acid, water, unreacted ethane, unreacted oxygen, gases produced by side reactions (such as carbon monoxide and carbon dioxide), and other gases which are present in commercial ethane. The final stage is followed by a scrubber to separate out the remaining aqueous acetic acid. Then, the gases from the scrubber go through an amine adsorption system to remove carbon dioxide. Next, the gas stream is compressed and introduced to the distillation column where ethylene is distillated in the top product; ethane and other gases are in the bottom product. The ethane from the distillation column is recycled to the reaction system.

In this process, the introduction of oxygen into a gaseous stream containing ethane, and possibly ethylene, poses a safety issue. To prevent the occurrence of unwanted situations (i.e. explosion, fire), the introduction of oxygen into a gaseous hydrocarbon must be carried out at a temperature lower than the auto-ignition temperature of the mixed gas stream. Based on their study, Manyik et al[66] suggested that temperature of the gaseous stream is less than 250 ^{o}C and oxygen composition is less than 6% mol..

8.2 Results and discussions

8.2.1 Inherent safety index

8.2.1.1 Material hazard index

The chemical substances in both processes are all flammable and/ or toxic in varying degrees. The hazards are posed according to the type and quantity of chemicals present. Table 6 summarizes the substances potentially presented in the processes.

Table 6. Substances involving in the processes

Pathway	Dehydration process	Oxydehydrogenation process
Raw Material	Ethanol	Ethane
Main reaction:	$2CH_3CH_2OH \rightarrow H_2C{=}CH_2 + 2H_2O$ + (CH_3CHO by-product)	$CH_3CH_3 + 1/2O_2 \rightarrow H_2C{=}CH_2 + H_2O$
Raw material	Ethanol	Ethane, O_2
Desired product	Ethylene	Ethylene
Main by-product	Acetaldehyde and Acetic acid	Acetic acid
Other by-products or gases		CO and CO_2

Table 7. Substance characteristics

Substances	Flash point	Boiling point	UEL-LEL (vol%)	TLV (ppm)
Ethane	-135.15 °C (-211.3 °F)	-88.2 °C (-126.8 °F)	3.0-12.4	1000
O_2		-183.1 °C (-297.6 °F)		
Ethylene	-136 ^{o}C (-212.8 ^{o}F)	-103.8 ^{o}C (-154.8 ^{o}F)	2.7-36	200
Acetic acid	39°C (102.2°F)	118.1 °C (244.6 °F)	4-19.9	15
CO	-119°C	-312.7 ^{o}F (-191.5 ^{o}C)	12.5-74	25
CO_2		-78.55 °C (-109.4 °F)		5000
Ethanol	16.6°C (61.88°F)	78 °C	3.3-19	1000
Acetaldehyde	-38°C (-36.4°F)	21 °C (69.8 °F)	4.0-60	25

Table 8. The values of sub-factor indices

Substances	I_{FL}	I_{EX}	I_{TOX}	$I_{FL} + I_{EX} + I_{TOX}$	I_{COR}
Ethanol catalytic dehydration					
Ethanol	3	1	2	6	
Ethylene	4	2	2	8	
Acetaldehyde	4	3	3	**10**	
Acetic acid	2	1	3	6	**1**
Oxydehydrogenation of ethane					
Ethane	4	1	2	7	
O_2			-		
Ethylene	4	2	2	8	
Acetic acid	2	1	3	6	**1**
CO	4	3	3	**10**	
CO_2			1	1	

Based on the flash points and boiling points, the difference between the upper and the lower explosion limits, the TLV of the substances in Table 7, the flammability, explosiveness, and toxicity indices of each substance are determined, respectively (Table 8). For the corrosiveness index, the most potential corrosive material of both processes is similar, acetic acid. It is assumed that the need of stainless steel is for both processes. Hence, the score of 1 is assigned for the corrosiveness index of both processes.

Finally, all indices in Table 8 are summed for every substance separately. The maximum sum is the sub-index value. For both processes, the material hazard indices are equal:

$$I_{MH} = (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR,\,max} = 10 + 1 = 11$$

Table 9. Heat release and reaction hazard sub-indices.

Pathway	Dehydration of Ethanol	Oxydehydrogenation of ethane
Main reaction ΔH	$2CH_3CH_2OH \rightarrow H_2C{=}CH_2 + 2H_2O$ + 46 kJ/mol (1,000 J/g)	$CH_3CH_3 + 1/2O_2 \rightarrow H_2C{=}CH_2 + H_2O$ – 105 kJ/mol (-2,283 J/g)
Side reaction 1 ΔH	$CH_3CH_2OH \rightarrow CH_3CHO + H_2$ + 69 kJ/mol (+1,500 J/g)	$CH_3CH_3 + 3/2O_2 \rightarrow CH_3COOH + H_2O$ – 591 kJ/mol (-7,577 J/g)
Other side reaction ΔH		$CH_3CH_3 + (3/2+x)O_2 \rightarrow 2CO_x + 3H_2O$ -1,429 kJ/mol (-10,063 J/g, for CO_2) -863 kJ/mol (-7,845 J/g, for CO)
$I_{HMR,\,max}$	0	3
$I_{HSR,\,max}$	0	4
$I_{INT,\,max}$	0	1
I_{RH}	**0**	**8**

8.2.1.2 Reaction hazard index

The heat release of the main and possible side reactions are calculated and used to assign the scores for I_{MR} and I_{SR} of both processes (Table 9). The chemical interaction considers the unexpected reactions among process materials in the process. These reactions are not expected to take place in the reactor and hence they are not discussed in the side reaction. In the oxydehydrogenation, acid acetic and acetaldehyde which are the main by-products can create a potential unwanted reaction. Small amounts of acetic acid will cause the acetaldehyde to polymerize, releasing large amounts heat. Since the quantity of by-products could be insignificant, the heat released by this chemical interaction may not significant and therefore the chemical interaction sub-index is assigned to 1 for the oxydehydrogenation and 0 for the dehydration of ethanol.

The maximum values of individual indices are summed to obtain the reaction hazard index for every process

Oxydehydrogenation of ethane: $I_{RH} = I_{HRM, max} + I_{HSR, max} + I_{INT, max} = 3 + 4 + 1 = 8$

Catalytic dehydration of ethanol: $I_{RH} = I_{HRM, max} + I_{HSR, max} + I_{INT, max} = 0 + 0 + 0 = 0$

In these case studies, the reaction hazard index of oxydehydrogenation is high because of the exothermic reactions, while that of dehydration case is zero since it involves only endothermic reactions.

8.2.1.3 Inventory index

The mass flows of the processes are known from the design capacity simulated in Aspen simulation. The inventories for each process vessel are estimated based on the maximum mass flow among the streams of that vessel and one hour nominal residence time (Table 10). The total inventory, the sum of inventories of all process vessels, is used to identify the inventory index.

The mass flows of both processes are on the basis of the production capacity of 20,000 tonnes of ethylene/ year. Since the conversion of ethane to ethylene in the oxydehydrogenation reactions (once-through yield in the reaction system is 59%) is lower than in the dehydration of ethanol (95%), the oxydehydrogenation process needs to recycle a large volume of unreacted ethane. Thus, the inventory of the oxydehydrogenation process is significantly larger than that of the dehydration of ethanol. This issue can be clearly seen in Table 10 and therefore the inventory hazard index of the oxydehydrogenation is 4 while that of the dehydration is 2.

8.2.1.4 Process condition index

The process condition index includes the process temperature and pressure indices which are identified on the basis of the maximum temperature and pressure in the process. Table 11 shows the temperature and pressure for each process vessel obtained in publications and Aspen simulations. Later, the process temperature and pressure sub-indices which are determined based on the obtained maximum temperature and pressure are summed to obtain the process condition indices.

Table 10. Process vessel inventories and inventory sub-indices

Process vessels	Mass flow (kg/hr)	Inventory (tonnes)	Inventory Indices (I_{IH})
Dehydration of Ethanol			
Reactor	6406	6.5	
Quench	6406	6.5	
Scrubber	4165	4.2	
Dryer	3832	3.8	
Evaporator	4604	4.6	
Cooler	6406	6.4	
Furnace	6406	6.4	
Total		38.4	2
Oxydehydrogenation of ethane			
Reactor 1	20069	20	
Reactor 2	20706	21	
Reactor 3	20461	20	
Scrubber	20461	20	
Absorber	18968	19	
Stripper	15312	15	
Flash drum	18968	19	
Distillation column	17145	17	
Compressor	19376	19	
Cooler 1	21637	22	
Cooler 2	21102	21	
Cooler 3	20856	21	
Cooler 4	14879	15	
Total		249	4

Table 11. Process temperature/ pressure and process condition sub-indices

	Temperature (°C)	Pressure (bar)	Process condition index (I_{PC})
Dehydration of Ethanol			
Reactor	350	3	
Quench	77	1	
Scrubber	77	1	
Dryer	77	1	
Evaporator	108	3	
Cooler	350 to 105	3	
Furnace	116 to 350	3	
Process temp./ pres., max	350	3	
Process temp/ pres. indices	3	0	3
Oxydehydrogenation of ethane			
Reactor 1	244	10	
Reactor 2	299	10	
Reactor 3	304	10	
Scrubber	43	1.5	
Absorber	42	45	
Stripper	93	1.3	
Flash drum	20	44	
Distillation column	-28	43	
Compressor	318	44	
Cooler 1	85	10	
Cooler 2	85	10	
Cooler 3	75	10	
Cooler 4	44	1	
Process temp./ pres., max	318	44	
Process temp/ pres. indices	3	2	5

8.2.1.5 Process equipment index

The process safety also depends on what type of equipment existing in the process. From engineering practice and recommendations on layout spacing between the equipment and from incident reports and database on the equipment involved in the incidents, Heikkila et al. suggested a scoring system to identify the process equipment index based on the types of equipment. Table 12 summarizes the main equipment present in the processes. Finally, the process equipment index is determined on the basis of worst case of different equipment in the process under investigation.

Table 12. Equipment present in the processes

Process	Type of equipment	Process equipment indices (I_{PE})
Dehydration	Reactor, Quench, Scrubber, Dryer, Evaporator, Cooler, Furnace	4
Oxydehydrogenation	Reactor 1, 2 and 3, Scrubber Absorber, Stripper, Flash drum Distillation column, Compressor Cooler 1, 2, 3, and 4	3

Among different equipment in the oxydehydrogenation process, compressor is the most unsafe equipment since it is subject to vibration, very vulnerable process equipment and can release flammable gas in case of failure.[41] As a result, the process equipment of the oxydehydrogenation is assigned to 3, while that of the dehydration of ethanol is assigned to 4 due to the furnace in the process. Furnace is a source of ignition for flammable leaks from other equipment.

8.2.1.6 Process structure index

The process structure index looks at the process from a system engineering point of view and therefore it is much more difficult to estimate. One potential approach is to depend on experience based data (standards, design recommendations and accident report). Hence, firstly, an experience based data which contains the base cases for the ethylene production needs to be developed by applying CBR method. CBR is applied in different incident databases such as HSEES, RMP, OSHA, MARS as well as many other useful websites such as hse.gov.uk, Kolmetz.Com, and csb.gov to retrieve the relevant cases for the ethylene production process. Proceedings of the Ethylene Producers Conference also provided a good source of information on several safety incidents.

According to CBR method, there must be input data and output requirements to retrieve the base cases. Due to the lack of the details of the incident itself in the database, the base cases are retrieved based on several input variables: the involved substance including ethylene (desired product); and ethane or ethanol (required raw material); type of industry (ethylene production, not polyethylene process); and type of system (fixed facility, not transportation). Despite of limited input variables, a few base cases for CBR are found and shown in APPENDIX A.

All of the base cases in APPENDIX A occurred in ethylene unit or ethylene production plant; however, there is no clue to identify if any of them was in the ethanol dehydration process. Moreover, the design of Petrobras (Figure 24) chosen for this case study is quite new technology. Therefore, no incident has been found for the dehydration of ethanol so far. From the reasoning on the process level, the score of 2 (no data or neutral) is assigned for the Process Structure Index of the ethanol dehydration process.

It is also very difficult to conclude if any of the base cases in APPENDIX A occurred in the ethane oxydehydrogenation process due to the lack of the details of those incident data. Those incidents could happen in a common ethylene production process, the dehydrogenation process with the raw materials of ethane, naphtha, or condensate. The ethane oxydehydrogenation is a new technology which has a similar flow diagram and basic equipment as the naphtha dehydrogenation. Both of them have absorber, compressor, flash drum and distillation or purification unit (different in catalyst).[69,76] Even incidents could not identify or have not occurred yet; the process configuration of the oxydehydrogenation is probably questionable on the basis of safety due to its similar process equipment and configuration to the naphtha dehydrogenation process which used to have a major incident. Therefore, the score of 3 corresponding to the fourth configuration group is assigned for the Process Structure Index of the ethane oxydehydrogenation process.

8.2.1.7 Process complexity index

To obtain the process complexity index, the complexity values need to be calculated from the values of many complexity factors using Equation 10. Most of these values are quite straightforward to estimate since they are i.e. based on the P&ID of the process. For instance, degree of freedom is the number of variables that can be controlled. The mathematical approach in evaluating the degree of freedom is to subtract the number of independent equations from the total number of variables. In practice, to identify the degree of freedom for a process, an experienced and easier method is to simply add the total number of properly placed control valves. One factor, the interaction in the process requiring operator intervention (Q), would require more detail design information to be estimated. In this case study, the interactions requiring operator intervention in both processes are assumed to be 0 due to the unavailable data. The other parameters calculated straightforward based on P&ID are provided in the ensuing paragraphs.

For the dehydration process, the number of equipment (M) is 8 including evaporator, furnace, reactor, cooler, quench, scrubber, 2 dryer. The degree of freedom (S) is 6 since there are 6 control valves as evaluated in controllability index for dehydration process. The number of measurement readings (O) is 10 (5 temperature, 1 flowrate, 2 concentration, 1 pressure, and 1 level measurement readings). Number of input and output streams (P) is 10 which include energy streams as recommended by Koolen (ethanol + steam + fuel + water + NaOH + cooling water in and out + aqueous effluent + caustic effluent + ethylene). The number of external disturbances asking for action from an operator (R) is 6 (feed stream (ethanol flow), and heating and cooling media (steam flow, fuel flow, cooling water temperature, water flow, NaOH flow). So, the complexity value for the dehydration process is: $COX_d = 8 + 6 + 10 + 10 + 0 + 6 = 40$.

For the oxydehydrogenation process, the number of equipment (M) = 17 (3 reactors, 3 condensers, scrubber, cooler, absorber, compressor, stripper, 2 reboiler, flash drum, distillation column, condenser, drum). The degree of freedom is 10 since there are 10 control valves as evaluated in controllability index for oxydehydrogenation process. The number of measurement readings is 28 (9 temperature, 5 flowrate, 3 concentration, 5 pressure, and 6 level measurement readings). The number of input and output streams is 30 (ethane + 3 oxygen + water + 5 cooling water in and out + 2 steam in and out + 1 refrigerant in and out + 3 acetic acid/ water + acetic acid solution + CO_2 + CH lights +

non-condensibles + ethylene + unreacted ethane). The number of external disturbances asking for action from an operator (R) is 13 (feed stream (ethane flow, 3 oxygen flow), and heating and cooling media (5 cooling water temperature, water flow, 2 steam temperature, 1 refrigerant flow) need the action from an operator if there is any disturbance). So, the complexity value for the dehydration process is: $COX_o = 17 + 10 + 28 + 30 + 0 + 13 = 98$.

The value of the oxydehydrogenation is higher corresponding to the complexity index of 5 resulting in the score system in Table 13. The values of the different terms and complexity indices for two processes have been summarized in

This case study was given only to demonstrate the suggested methodology in calculating Complexity Index. In the real industry, equipment complexity, or piping complexity should be considered as well. Other equipment such as pumps, blinds, safety devices, vents, and drains should be included in evaluating number of equipment. Manual/ actuated valves/ switches and set points of control loops can be included in Table 14.

Table 13. Scoring system for the process complexity index (I_{COX})

Process complexity value (COX)	Score of I_{COX}
1-16	0
17-33	1
34-49	2
50-65	3
66-82	4
83-98	5

Table 14. Complexity factor index for both processes

	Dehydration	Oxydehydrogenation
Number of equipment	8	17
Number of DOFs	6	10
Number of input and output streams (P)	10	30
Number of measurement readings (O)	10	28
The interaction in the process requiring an operator intervention (Q)	0	0
The number of external disturbances asking for action from an operator (R)	6	13
Complexity values (WFs = 1 for each) (COX)	40	98
I_{COX}	2	5

8.2.1.8 Discussion

Table 15 shows the results of all indices of inherent safety index. The results showed that the oxydehydrogenation seems to have higher values which contribute negative to inherent safety aspect. This observation seems logically since in the dehydration process the material in use is less hazardous and the process is simpler and requires more moderate conditions.

All indices in Table 15 are combined to achieve the final inherent safety index as follows:

For the ethanol dehydration process, $I_{IS} = 33$

For the ethane oxydehydrogenation process, $I_{IS} = 68$

To be able to combine all indices for an overall resilience Design index, inherent safety indices of both processes are normalized in the scale of 0 to 10. The normalized inherent safety indices (ISI) were calculated as follows:

For the ethanol dehydration process

$$ISI_d = \frac{33 \cdot 10}{114} = 2.9$$

Table 15. Inherent safety sub-indices of two ethylene production processes

Pathway	Dehydration of Ethanol	Oxydehydrogenation of Ethane
$(I_{FL} + I_{EX} + I_{TOX})_{max}$	10	10
$I_{COR,\ max}$	1	1
Material Hazard Index, I_{MH}	11	11
Inventory Hazard Index, I_{IH}	2	4
$I_{HMR,\ max}$	0	3
$I_{HSR,\ max}$	0	4
$I_{INT,\ max}$	0	1
Reaction Hazard Index, I_{RH}	0	8
$I_M = I_{MH} \cdot I_{IH} + I_{RH}$	22	52
Process temperature index	3	3
Process pressure index	0	2
Process condition index	3	5
Process equipment index	4	3
Process Structure Index	2	3
Process Complexity Index	2	5
I_P	11	16

For the ethane oxydehydrogenation process

$ISI_o = \frac{68 \cdot 10}{114} = 6.0$The lower the inherent safety index is, the more resilient the process design achieves. Therefore, the ethanol dehydration process is more resilient with regard to the inherent safety design perspectives.

8.2.2 Controllability index

This section demonstrates how to perform the proposed controllability analysis via evaluation of relative gain matrix, its singular value, and condition number. The controllability index indicates how easy to control the process in response to disturbances

For the demonstration purpose, the case study only investigates typical feedback control configurations (Section 8.2.2.1). Although not all pairs of controlled and manipulated variables are considered in the analysis, the variations of the investigated pairs significantly affect production specifications and therefore are critical to the control performance.

Simulation models in Aspen Plus were constructed in Section 8.2.2.2. Those models are able to simulate not only base-case operations but also sensitivity of the processes to variations of manipulated variables.

The latter advantage allows testing how controlled variables are affected and interacted by the variations on manipulated variables. Multiple scenarios of variations were simulated. The manipulated variables were varied by ±0.1%, ±0.2%, ±0.5%, ±1%, ±2%, ±5%, ±10%, ±20%, ±30%. Responses in values of controlled variables were recorded to construct the relative gain matrices (Section 8.2.2.3).

In the next calculation step, singular values of the relative gain matrices were determined with the aid of the numerical computing software MATLAB[77] (Section 8.2.2.4). The controllability index is scored from the calculated values of the condition numbers.

Table 16. Analyzed pairs of manipulated and controlled variables in the dehydration process.

Manipulated variables			Controlled variables		
No.	Parameter	Value	No.	Parameter	Value
MV1	Evaporator steam flow rate (kg/h)	2,425	CV1	Evaporator outlet temperature of cold stream (kg/h)	108.4
MV2	Furnace fuel flow rate (kg/h)	66.58	CV2	Furnace outlet temperature of cold stream (^oC)	350.0
MV3	Reactor heating fluid flow rate (kg/h)	11,047	CV3	Reactor temperature (^oC)	350.0
MV4	Cooler cooling water flow rate (kg/h)	37,041	CV4	Cooler outlet temperature of hot stream (^oC)	160.0
MV5	Quench water flow rate (kg/h)	34,000	CV5	Quenched vapor phase temperature (^oC)	83.1
MV6	Scrubber caustic inlet flow rate (kg/h)	1,755	CV6	OH^- molar fraction in scrubber caustic effluent ()	0.00112

Table 17. Analyzed pairs of manipulated and controlled variables in the oxydehydrogenation process.

Manipulated variables			Controlled variables		
No.	Parameter	Value	No.	Parameter	Value
MV1	Heater steam flow rate	6,611	CV1	Heater outlet temperature of cold stream(^oC)	149.7
MV2	Condenser C-1 CW flow rate (kg/hr)	245,737	CV2	Condenser C-1 outlet temperature of hot stream (^oC)	396
MV3	Condenser C-2 CW flow rate (kg/hr)	211,529	CV3	Condenser C-2 outlet temperature of hot stream (^oC)	90
MV4	Condenser C-3 CW flow rate (kg/hr)	161,025	CV4	Condenser C-3 outlet temperature of hot stream (^oC)	160
MV5	Scrubber water flow rate (kg/hr)	34,000	CV5	Scrubbed vapor temperature (^oC)	71.0
MV6	Compressor power (kW)	1,140	CV6	Compressed pressure (bar)	46.02
MV7	Absorber lean stream flow rate (kmol/h)	1,679	CV7	Molar fraction of MDEA in effluent stream	0.0670
MV8	Flash drum refrigerant flow rate (kg/hr)	133,940	CV8	Flash drum temperature (^oC)	-24.0
MV9	Deethane reflux flow rate (kmol/hr)	704	CV9	Ethylene concentration in distillate stream (%mol.)	96.7
MV10	Dethane bottom flow rate (kmol/h)	380	CV10	Ethane concentration in bottom stream (%mol.)	99.3

8.2.2.1 Control systems

Since detailed information on the investigated processes (such as process flow diagrams and pipe & instrument diagrams) is not available in the literature, simplified process flow diagrams with control systems were developed for this case study based on published operating conditions and performance.

The control systems were designed from the common arrangement of feedback control. They did not result from a design optimization which usually involves much more effort not related to the objective of this research. Optimization should include, for example, alternative evaluation for optimal selection of control type (P, PI, or PID),[26] manipulated variables, and controlled variables, and detailed interaction analysis for optimal pairing controlled variables with manipulated variables. APPENDIX B sketches the control configurations used in the case study of the key processing units. The controlled variables are temperature, pressure, flow rate, and concentration of the process streams and utility streams. The manipulated variables are flow rates of those streams. Some of fast-response control loops (e.g. level control, reflux rate control of distillation and absorption units) are excluded to simplify the controllability analysis without sacrificing the conclusion because control performance is usually limited by slow response.

In this case study, the analyzed multivariable control configurations are 6×6 (i.e., there are 6 controlled variables and 6 manipulated variables) and 10x10 for the dehydration and oxydehydrogenation processes, respectively. Those controlled and manipulated variables are paired in the chosen designs are shown in Table 16.

8.2.2.2 Simulation models

In this work, process controllability evaluation relies on the use of mathematical models although it can be performed with online tests on practical plants. These models are developed to describe the steady-state operation under various scenarios for both controllability and flexibility analyses.

Optimization was performed in some units, including quench, absorber, stripper, and deethanizer to determine the optimal flow rates of supporting streams such as quench water, caustic solution, stripper reboiler steam, deethanizer reflux. It is necessary to determine those optimal conditions which are usually close to practical operation and fall in transition region of linearity. For example, rate of caustic solution is optimal when it is just enough to saturate carbon dioxide in the rich stream; that means, less carbon dioxide is absorbed for less caustic rates but no more carbon dioxide is available to react with excess sodium hydroxide.

The models were built in Aspen Plus[78] The simulation flowsheets, input data summary, and specifications are reported in APPENDIX C. Except the Dryer unit of the dehydration process is simulated as a "black box", all other units are simulated with thermodynamic models to predict their performance. The global property method is NRTL – a non-ideal gas equation of state. Specifically in some units involving ionized component, a more appropriate method – ELECTNRTL – was employed. Also in those units, multiple equilibrium and dissociation equations were involved in absorbing and desorbing reactions. They are simulated using special add-on packages for accurate prediction. The equations and associating parameters are shown in APPENDIX C.

The two plants are designed at a capacity of 20,000 tonnes per year. Product concentrations are required not lower than 95% mol ethylene. The simulation results for the base cases are given in the Tables 16 and 17. Those results were compared to the published data[66,72] for reasonable conversion, yields, and operating conditions (if available).

8.2.2.3 Controllability analysis

Scenarios of variations of manipulated variables were investigated without any controllers in place (i.e., all loops were open). It can be referred to as the natural response of the process to changes in the manipulated variables. Open-loop tests were performed to calculate the relative gain analysis once the manipulated and controlled variables are chosen. Those tests were done using Sensitivity Analysis tool of Aspen Plus.

For open loop tests, disturbances have been made to the process by changing the input values of all manipulated variables out of their base-case values (Table 16 and Table 17), one at a time.

The following disturbances ranges were performed: ±0.1%, ±0.2%, ±0.5%, ±1%, ±2%, ±5%, ±10%, ±20%, and ±30%. Changes in controlled variables were calculated accordingly in the Sensitivity Analysis tool.

Figure 27 plots the effects of manipulated variable disturbances to the values controlled variables in the dehydration process when all the control loops were open (i.e., no control actions). All the cases are reported in the same scale for comparison. Controlled variables that were not affected are represented by horizontal straight lines through the origin. From MV1 to MV6, less controlled variables were affected by disturbances because the positions of manipulated variables locate more towards the back-end of the process which has no recycle loops.

The most affected controlled variable of MV1 (evaporator steam flow rate) disturbances was CV1 (evaporator outlet temperature of the cold stream) as shown in Figure 27a. This relationship was partially proportional with positive disturbances (+0.1%, +0.2%, +0.5%, and +10%) but it was independent with negative disturbances and large positive disturbances (+20% and +30%). The reason is explained as follows. The outlet cold stream was at saturated vapor condition in base case operation. When more steam was introduced due to the positive disturbances, the vapor is superheated and therefore its temperature was proportionally increased. When the vapor temperature reaches steam temperature, it does not change due to the second law of thermodynamics no matter how much more steam was added. This constant temperature obviously resulted in unchanged temperatures in the downstream units, including the tracked temperatures of Furnace (CV2), Reactor (CV3), and Cooler (CV4) (Figure 27a). When the steam rate was shortened due to the negative disturbances, the saturated vapor was condensed at a constant temperature.

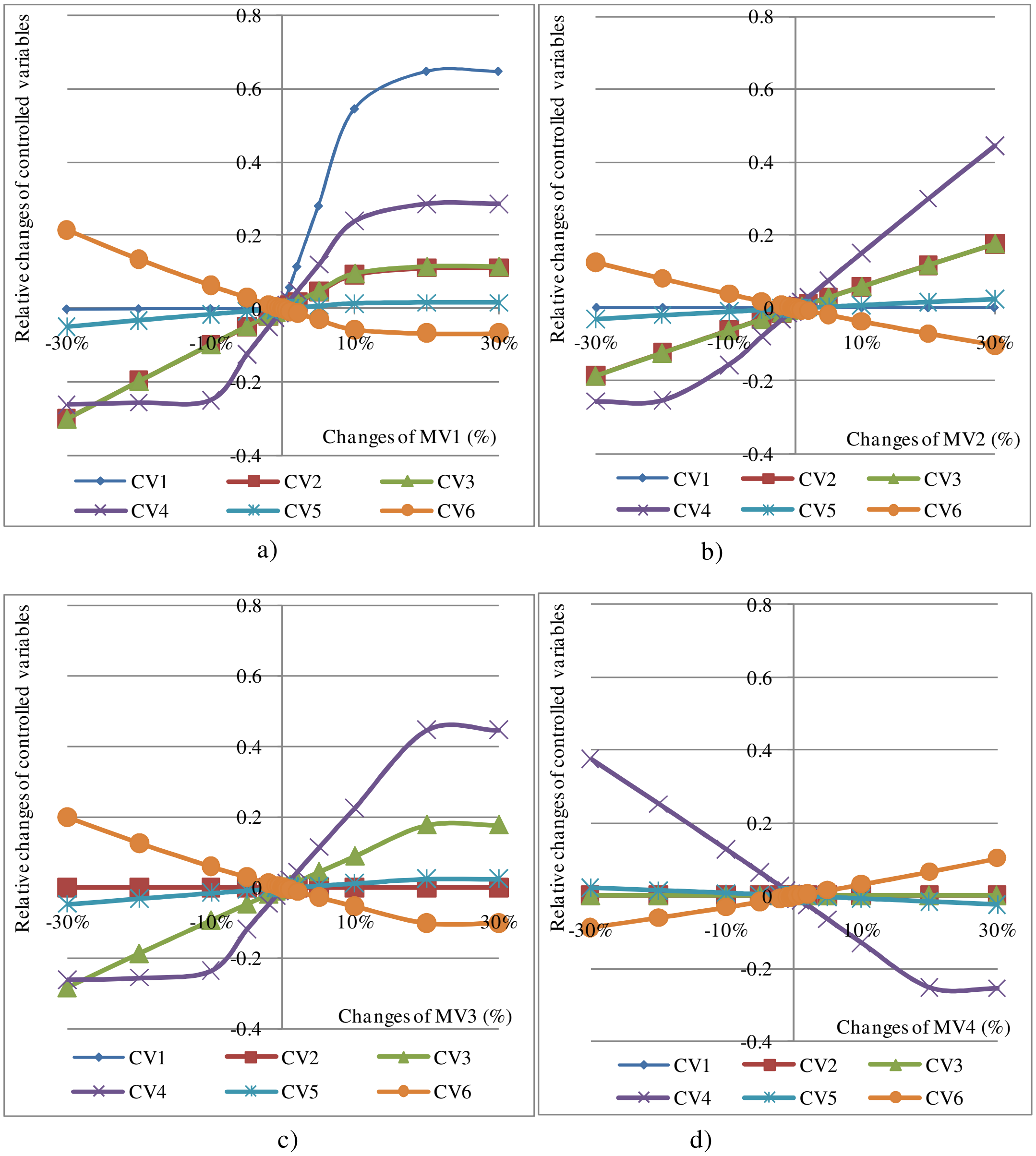
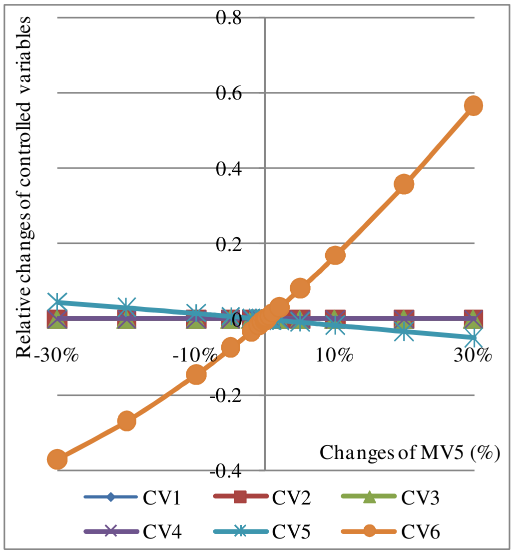


Figure 27. Relative changes of controlled variables in open-loop with respect to disturbances of manipulated variables in the dehydration process. a) Evaporator steam flow rate (MV1); b) Furnace fuel flow rate (MV2); c) Reactor heating fluid flow rate (MV3) d) Cooler cooling water flow rate (MV4); e) Quench water flow rate (MV5); and f) Scrubber caustic flow inlet rate (MV6).



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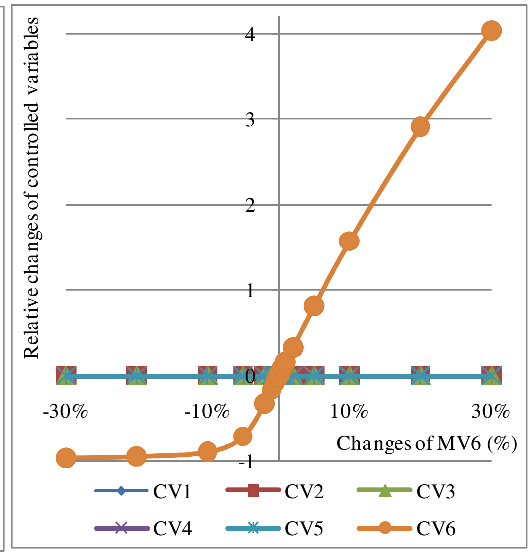


f)

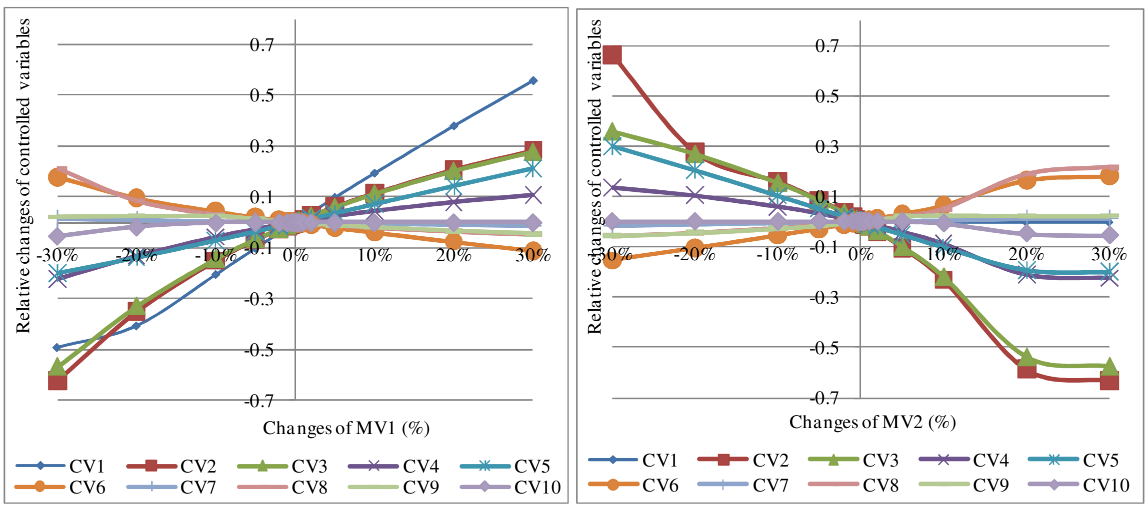
Figure 27. (Continued)

Similarly, the reactor temperature (CV3) reached associating heating utility temperature at the +20% disturbance (Figure 27c). That resulted in unchanged temperature in the downstream cooler (CV4).

The Cooler temperature (CV4) was significantly affected by the heat duty perturbation due to the disturbances on upstream manipulated variables (MV1 – MV4). Positive disturbances of MV1 – MV3 (on heating utility) result in more heat supply to the process streams while positive disturbance of MV4 (on cooling utility) results in less heat supply. Therefore, CV4 changes with respect to MV4 are in opposite direction to those with respect to MV1 – MV3 (Figure 27a – d). In all of the cases, the CV4 lines turned horizontal for because of isothermal condensation at large negative disturbances of MV1 – MV3 and at large positive disturbance of MV4.

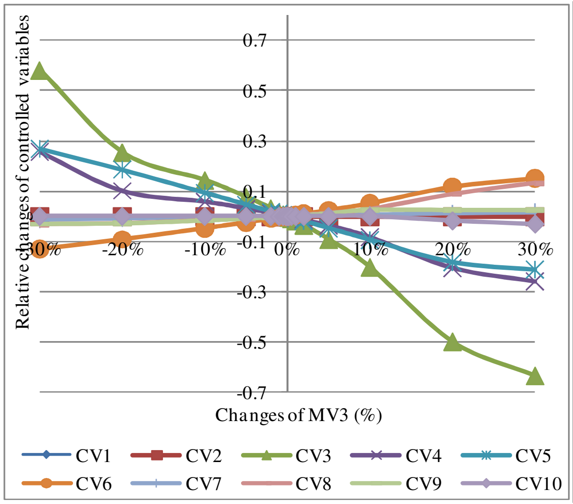
Controlled variable CV5 in general did not change much compared to other controlled variables. Its changes were within the range of -0.1% and 0.1%.

Molar fraction of ion OH^- (CV6) which corresponds to pH of scrubber effluent was sensitive to all manipulated variable disturbances, especially for MV5 (Quench water rate) and MV6 (Caustic inlet rate). Quench water rate directly and linearly affects amount of CO_2 physically absorbed in liquid phase of the quench vessel, and therefore in the stream going to the absorber. Caustic soda reacts with CO_2. If caustic rate is reduced, unreacted CO_2 amount increased until it reached the inlet CO_2 concentration corresponding to certain pH, which represents by a horizontal line between -10% and -30% in Figure 27f. However, if caustic rate increases, the pH keeps increase because more base is introduced to the column. There is also an upper limit of the pH; however, it has not been reached in the investigated disturbance ranges.



a) b)

Figure 28. Relative changes of controlled variables in open-loop with respect to disturbances of manipulated variables in the oxydehydrogenation process. a) Heater steam flow rate (MV1); b) Condenser C -1 CW flow rate (MV2); c) Condenser C-2 CW flow rate (MV3); d) Condenser C-3 CW flow rate (MV4); e) Scrubber water flow rate (MV5); f) Compressor power (MV6); g) Absorber lean stream flow rate (MV7); h) Flash drum CW flow rate (MV8); i) Deethane reflux flow rate (MV9); and j) Dethane bottom flow rate (MV10).



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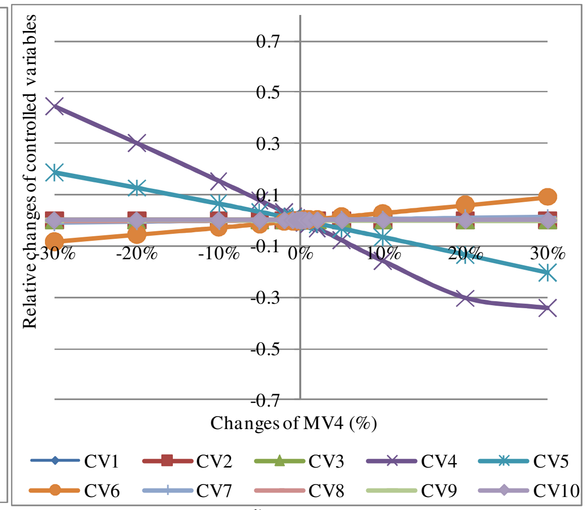

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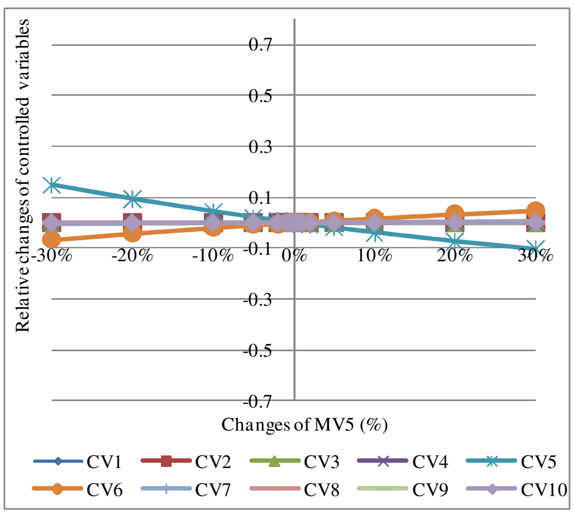

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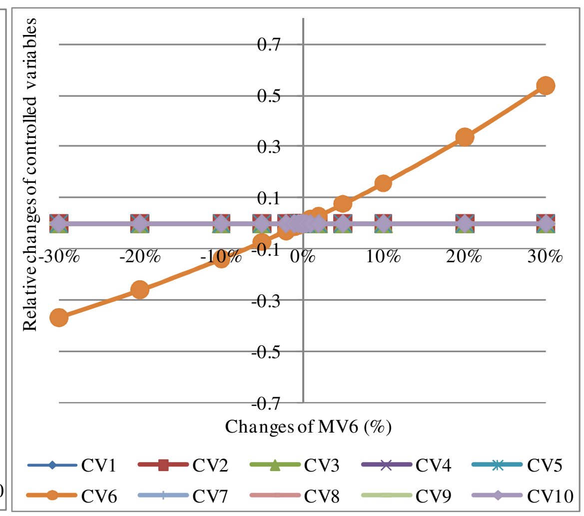
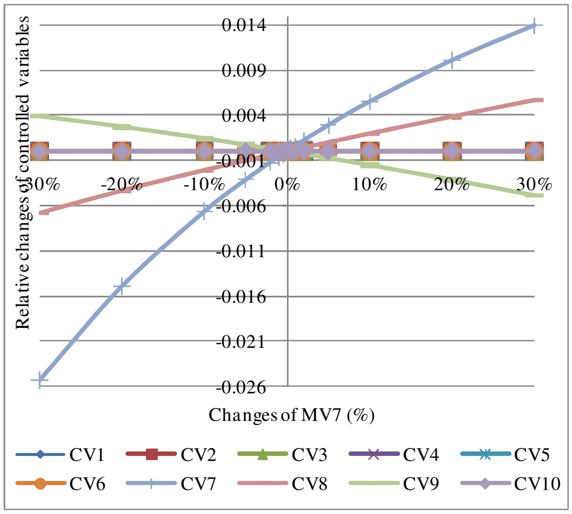


f)

Figure 28. (Continued)



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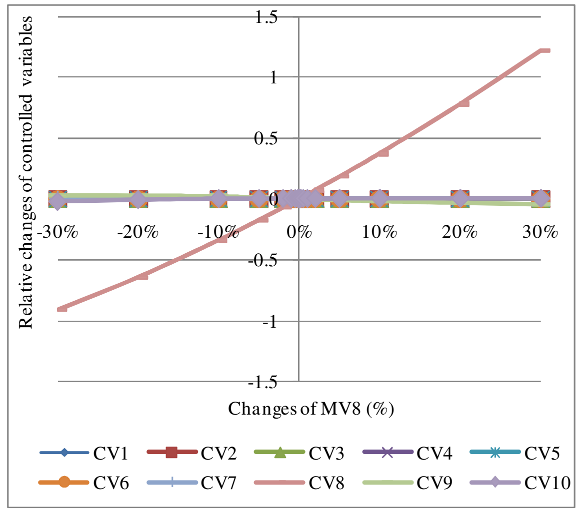

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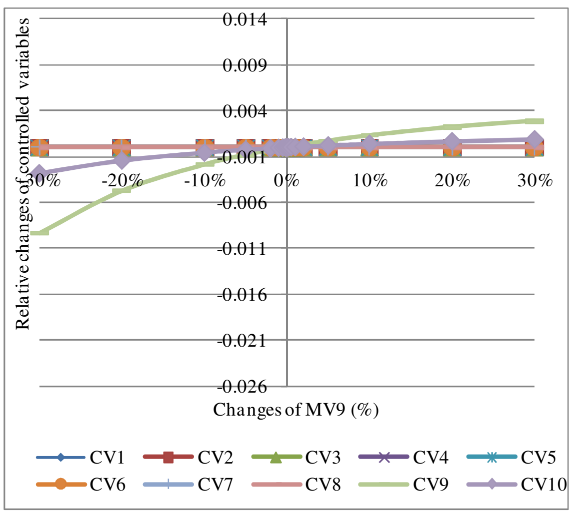
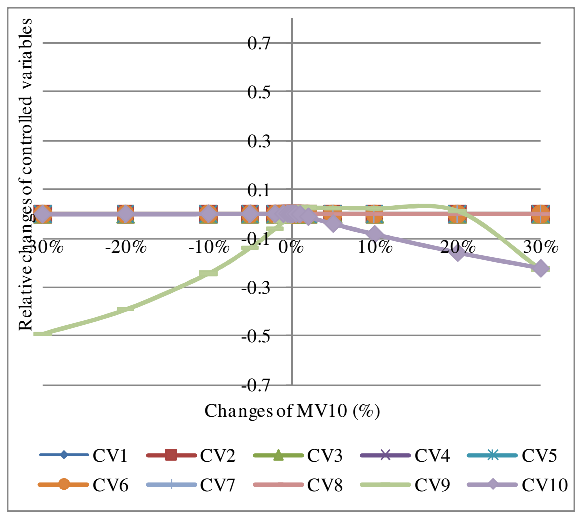


i)



j)

Figure 28. (Continued)

Figure 28 shows the effects of manipulated variable disturbances to controlled variables in the oxydehydrogenation process. Similar to the dehydration process, the upstream MVs interacted with more CVs than the downstream MVs did.

In general, the i^{th} MV affected most on the i^{th} CV, which indicates that the controlled and manipulated variables were reasonably paired. One exception was found for MV10 disturbance where CV9 was affected most (Figure 28j) because they both were part of the distillation column – highly integrated equipment.

The line of CV1-MV1 is not straight at -30% disturbance of MV1 (Figure 28a) as the feed stream was partially condensed. The condensation was not at constant temperature because the stream contained multiple components.

The disturbance of cooling water rate in Cooler 1 (MV2) linearly affected the hot stream outlet temperature (CV2) and other controlled variables downstream until the rate reached +20% disturbance (Figure 28b). At the disturbance of +20% or more, the outlet temperature was close to the cooling water temperature; therefore, it was independent on the cooling water rate.

The line of CV3-MV3 (Figure 28c) is not straight because multiple-component condensation occurred in the whole investigated range of MV3 disturbance. This is different from the straight line CV4-MV4 (Figure 28d) where the condensation only occurred at cooling water rate disturbance of +20% or more.

In Figures 28e – i, the CVs shows their nearly dependence on their paired MVs.

Figure 28j shows special relationships of ethylene molar fraction in distillate (CV9) and ethane molar fraction in bottom stream (CV10) with respect to bottom rate (MV10). They all belonged to control system of the distillation column. When bottom rate was reduced (from 0 to -30%), composition of main component in bottom stream was unchanged (i.e., it reached its separable limit by distillation), and composition of main component in distillate was decreased because other components were additionally recovered. O the other side, when the bottom rate was increased (from 0 to 30%), a reverse observation was expected, i.e., the components were more directed to the bottom stream, which decreased CV10 and kept CV9 unchanged. However, the ethylene composition (CV9) was reduced at +30% disturbance of MV10 because too much ethylene was lost in the bottom while the light component carbon monoxide stayed in the distillate and diluted the ethylene.

The special relationships in Figure 28j showed two insightful facts about the design of the oxydehydrogenation process. Firstly as a result of the steady-state optimization mentioned earlier, the distillation reflux rate (MV9) and bottom rate (MV10) were optimal because both of the compositions reached their limits at the base case. Secondly, the design would be better (more controllable) if a vapor outlet was added in the top section of the column to remove light carbon monoxide and keep the ethylene concentration at its best. This shows the benefits of the controllability analysis to the ability of the process to bounce-back the disturbance.

8.2.2.4 Relative gain matrices and condition numbers

The tracked values of controlled variables (CV) and manipulated variables (MV) obtained from the simulation results in the previous section were used to construct the relative gain matrices. Using Equation 22, the components of the gain matrices were calculated straightforward for every disturbance scenario. Table 18 is an example of what the relative gain matrices are. Elements zero indicate no interaction between the associating controlled and manipulated variables.

The property of those relative gain matrices was investigated by calculating their singular values and condition numbers, the results are reported in Tables 19 and 20. The singular values were calculated using the command "*svd*([matrix name])" in the Matlab software while the condition numbers for various disturbance scenarios were derived using Equation 17.

Figure 29 plots the values of condition numbers with respect to different disturbance ranges for both processes. The ranges of the disturbances do affect the values of the relative gain matrices, and therefore condition numbers, which has been confirmed by McAvoy.[50] Larger condition number indicates the matrix is more poorly conditioned and hence the process is more difficult to control with the chosen controlled and manipulated variables.[26] The results show that the dehydration process was very sensitive to small negative changes of the manipulated variables; that means, it is difficult to control the process. In other words, it requires a very large change in one or more manipulated variables, or controlled variables change largely for a small variation of one or more manipulated variables. The condition numbers in those scenarios were up to more than 8,000 which were much higher than those in other scenarios. The condition numbers in the positive disturbances for both processes were low and generally stable, indicating that it is easy to control the processes.

Table 18. Relative gain matrix of dehydration process for disturbance +10%

		Controlled variables (VC)									
		CV1	CV2	CV3	CV4	CV5	CV6	CV7	CV8	CV9	CV10
Manipulate variables (MV)	MV1	1.93925067	1.15263493	1.11960915	0.44405069	0.71895047	-0.39082861	-0.03576057	-0.20344217	-0.19838619	-0.00010760
	MV2	0.00000000	-2.30721881	-2.19013841	-0.88214812	-1.01128644	0.64508695	0.05328795	0.49790787	0.25304046	-0.07438346
	MV3	0.00000000	0.00000001	-2.01106659	-0.82738129	-0.93833223	0.52210988	0.04842960	0.27116078	0.25104524	-0.00357882
	MV4	0.00000000	0.00000000	-0.00000112	-1.59718163	-0.66283796	0.29294880	0.03306556	0.00301303	-0.00133990	0.00001744
	MV5	0.00000000	0.00000000	0.00000007	0.00000000	-0.38827866	0.17622991	0.02382504	0.00455842	-0.00060204	0.00002276
	MV6	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	1.57476704	0.00383629	-0.00182854	0.00275811	-0.00001653
	MV7	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.05458784	0.01948252	-0.01517357	0.00017238
	MV8	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	3.73112881	-0.17729597	0.00458663
	MV9	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000129	0.01285987	0.00387143
	MV10	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.22394831	-0.83785975

Table 19. Singular values (SV) and condition numbers of the dehydration process with manipulated variable disturbances

MVs Changes	**-30%**	**-20%**	**-10%**	**-5%**	**-2%**	**-1%**	**-0.5%**	**-0.2%**	**-0.1%**
Maximum SV	3.736	5.090	9.122	14.293	16.319	16.530	16.619	16.651	16.657
Minimum SV	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002
CN	1167.469	2036.160	3966.130	6806.095	7770.857	8265.000	8309.550	8325.700	8328.400
MVs Changes	**0.10%**	**0.2%**	**0.5%**	**1%**	**2%**	**5%**	**10%**	**20%**	**30%**
Maximum SV	16.644	16.651	16.651	16.650	16.625	16.406	15.858	14.683	13.624
Minimum SV	0.165	0.165	0.162	0.163	0.163	0.163	0.164	0.165	0.164
CN	100.688	100.731	102.528	102.462	102.310	100.587	96.754	89.040	83.326

Table 20. Singular values (SV) and condition numbers of the oxydehydrogenation process with manipulated variable disturbances.

MVs Changes	**-30%**	**-20%**	**-10%**	**-5%**	**-2%**	**-1%**	**-0.5%**	**-0.2%**	**-0.1%**
Maximum SV	4.718	4.186	4.176	4.232	4.291	4.319	4.331	4.342	4.365
Minimum SV	0.009	0.007	0.006	0.005	0.005	0.005	0.005	0.005	0.004
CN	512.804	589.549	732.614	829.784	893.938	899.708	941.522	943.935	992.000
MVs Changes	**0.10%**	**0.2%**	**0.5%**	**1%**	**2%**	**5%**	**10%**	**20%**	**30%**
Maximum SV	4.356	4.360	4.362	4.359	4.380	4.485	4.711	5.471	4.518
Minimum SV	0.003	0.005	0.005	0.006	0.010	0.014	0.013	0.011	0.005
CN	1405.194	927.702	948.217	751.517	429.441	327.387	365.186	511.346	1405.194

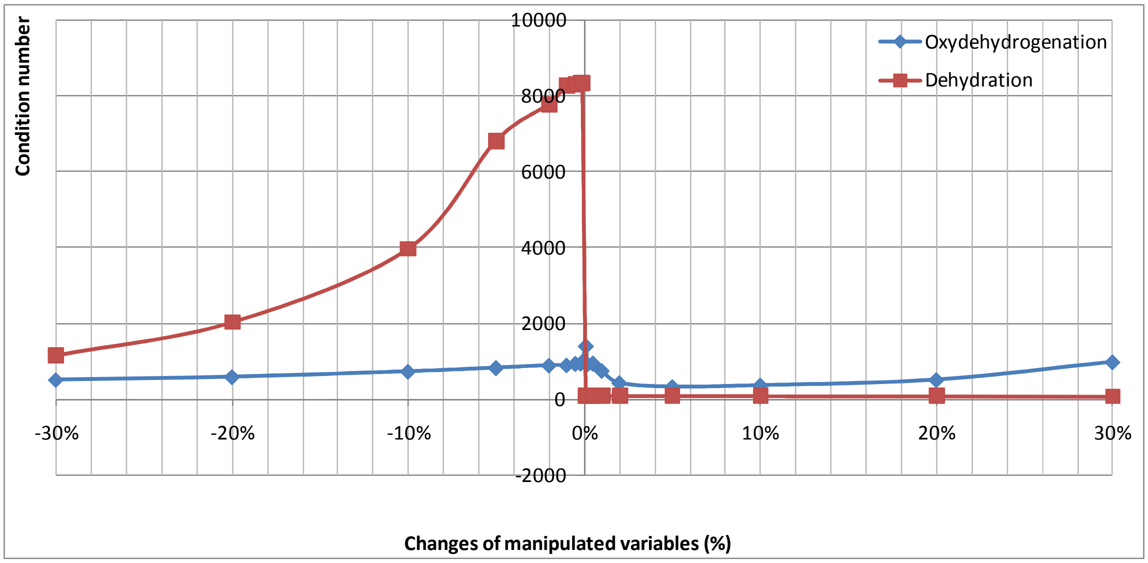


Figure 29. Condition numbers with respect to disturbance ranges

Most of the investigated manipulated variables were utility flow rate. Hence, the results also indicate that both processes are vulnerable to reduction of either heating or cooling utility flow rates as the condition numbers were high in negative disturbance. The effects of utility rate reduction will be further investigated in Section 8.2.3 in the viewpoint of flexibility.

8.2.2.5 Calculation of controllability indices

In the last step, the controllability index was quantified. The indices are based on values of the condition numbers which were varied in different scenarios as shown in the previous section. To evaluate the general controllability of the processes, it was desired to use averaged values of those condition numbers.

For the dehydration process, the averaged valued of the condition numbers from the 18 scenarios of manipulated variable disturbance is:

$$CN_d = 3{,}103$$

For the oxydehydrogenation, the averaged condition number is:

$$CNo = 800$$

The averaged condition number for both processes is:

$$\underline{CN} = \frac{CN_d + CN_o}{2} = 1952$$

Using Equation 23, the controllability indices of the dehydration and oxydehydrogenation are, respectively:

$$(I_c)_d = 8.0$$

$$(I_c)_O = 2.0$$

The final results show that the oxydehydrogenation process is significantly more controllable than the dehydration process. That result implies a relative difference in controllability between the two processes rather than whether the control systems are acceptable or not. However, the controllability analyses indicate some insights on the processes.

8.2.3 Flexibility index

To evaluate the flexibility indices of the two processes, many impacts should be investigated to make reliable conclusions. However, only one impact is considered in this case study for the purpose of demonstrating the approach. A rupture is assumed to occur on a supply pipeline of the utility systems. The rupture may make the flow rate through the pipe reduce to zero due to loss or local shut-down.

For simplification, only utility systems that can cause significant consequences under the impact are considered. Particularly, dehydration is an endothermic reaction; therefore, heating utility is critical to keep high conversion of the reaction of the dehydration process to satisfy production specifications. Scenarios of losing steam, heating oil, and quench water flow rates are evaluated for this process.

On the other hand, the process using oxydehydrogenation which is an exothermal reaction is vulnerable to the lack of cooling utility. Uncontrolled exothermic reaction can lead to severe violation of safety criteria such as run-away reactions, overheated and overpressure reactors. Mixture of ethane and oxygen in the feed stream can be overheated and violate its flammability limits. This process is investigated in scenarios of losing cooling water and quenching water.

8.2.3.1 Flexibility index of the dehydration process

Four pieces of equipment using steam, heating oil, or boiling feed water are affected by the impact of the pipeline rupture. The effects of impact are transformed into the flow reduction of those utility streams. Their ranges are given in Table 21.

Table 21. Ranges of impact utility flow rates in dehydration process.

Impact utility	Equipment using the utility supply	Lower limit (kg/h)	Nominal rate (kg/h)	Upper limit (kg/h)
Steam	Evaporator	0	2,425	2,425
Heating oil	Reactor	0	35,578	35,578
Boiler feed water	Boiler	0	1,136	1,136
Steam	Mixer	0	1,802	1,802

Under the impact, all the control system can be used to tune operating conditions to bounce back the effect. However, assume only three following control variables are effective to tackle the impact: furnace fuel rate, valve opening position, and water for the quench unit. For controllable flow rates, they are assumed to be able to vary from zero to a maximum of 130% of the nominal values. For throttle valve, it can be adjusted all the way of position. Their values are shown in Table 22.

Table 22. Ranges of adjustable control variables in the dehydration process.

Variables (unit)	Lower bound (by %)	Nominal value	Upper bound (by %)
Furnace fuel (MCal/h)	0 (-100%)	732	952 (+30%)
Valve opening (%)	0 (-100%)	46.3	100 (+116%)
Quenching water(kg/h)	0 (-100%)	30,000	39,000 (+30%)

The product specifications are ethylene purity (minimum purity level: 95% mol) and production rate (minimum flow rate of ethylene: 80% of nominal value). Because the dryer can not be simulated in Aspen Plus, it was assumed that dryer can process satisfied purity from a wide range of inlet purity. It was further assumed that the reaction conversion is assumed too low and therefore production rate is not met if reactor temperature is lower than 100^{o}C. For this reason, reactor temperature was the only specification of the simulation. The process specifications are given in Table 23.

Table 23. Production specifications of the dehydration process.

Parameter	Minimum value
Product (ethylene) purity	95% mol.
Production rate	80% of nominal value
Reactor temperature	100^{o}C

Table 24. Safety criteria of the dehydration process.

Equipment	$T_{nominal}$ (^{o}C)	T_{design} (^{o}C)	P_{design} (bar)
Pump	25	120	10
Evaporator	108	250	10
Mixer	116	250	10
Furnace	350	700	10
Reactor	350	700	10
Boiler	350	500	10
Throttling valve	160	250	10
Quench	83	250	10
Scrubber	81	150	10

Safety criteria are the ranges of operating temperature and pressures not to cause mechanic failure of equipment. Highest normal operating pressure of the process is 3 bar. All pieces of equipment were designed to withstand a maximum pressure of 10 bar. Table 24 lists the design temperatures and design pressures which are specified as upper limits of the safety criteria.

The simulation results are reported in APPENDIX E. The calculation procedure was performed as follows:

- First, the base case was simulated. It is referred to as Scenario 1 in the report.
- Second, the Sensitivity Analysis tool in Aspen Plus was used to simulate 16 cases corresponding to the combination number of two extreme values of the four external impact parameters. Those simulation results are marked as Scenario 2-17 in the report. 11 cases out of them were converged and met all the specifications and criteria. The flexibility indices for those 11 cases were 1.
- Third, the control variables were adjusted in the remaining 5 cases (Scenarios 7 and 10 – 13) violating the minimum temperature requirement of reactor or yielding unreasonable simulation results. Because their linear relationships, furnace fuel duty was preferred maximized to increase reactor temperature. There was no need to adjust valve openings and quench water rate as the related units operated within accepted specifications and criteria. With the furnace duty adjustment, 3 out of the 5 cases satisfied the constraints; therefore, their flexibility index is 1.
- Next, the remaining 2 cases still violating reactor temperature limits need reduction of impact levels. The search for the threshold level was performed until reactor temperature is at 100^{o}C. The result shows that the minimum mixer steam the plant can withstand is 487 kg/h, i.e., if the steam is lost more then reactor temperate can not be met for any values of the control variables. The flexibility index of this case is

$$\delta^*(\theta^k) = \frac{|\theta^k - \theta^N|}{\Delta\theta} = \frac{|487 - 1802|}{|0 - 1802|} = 0.73$$

Compared all the found indices, the flexibility index of the dehydration process is 0.73, which is the smallest of indices from all cases. Figure 30 tracks the number of cases in the calculation steps.

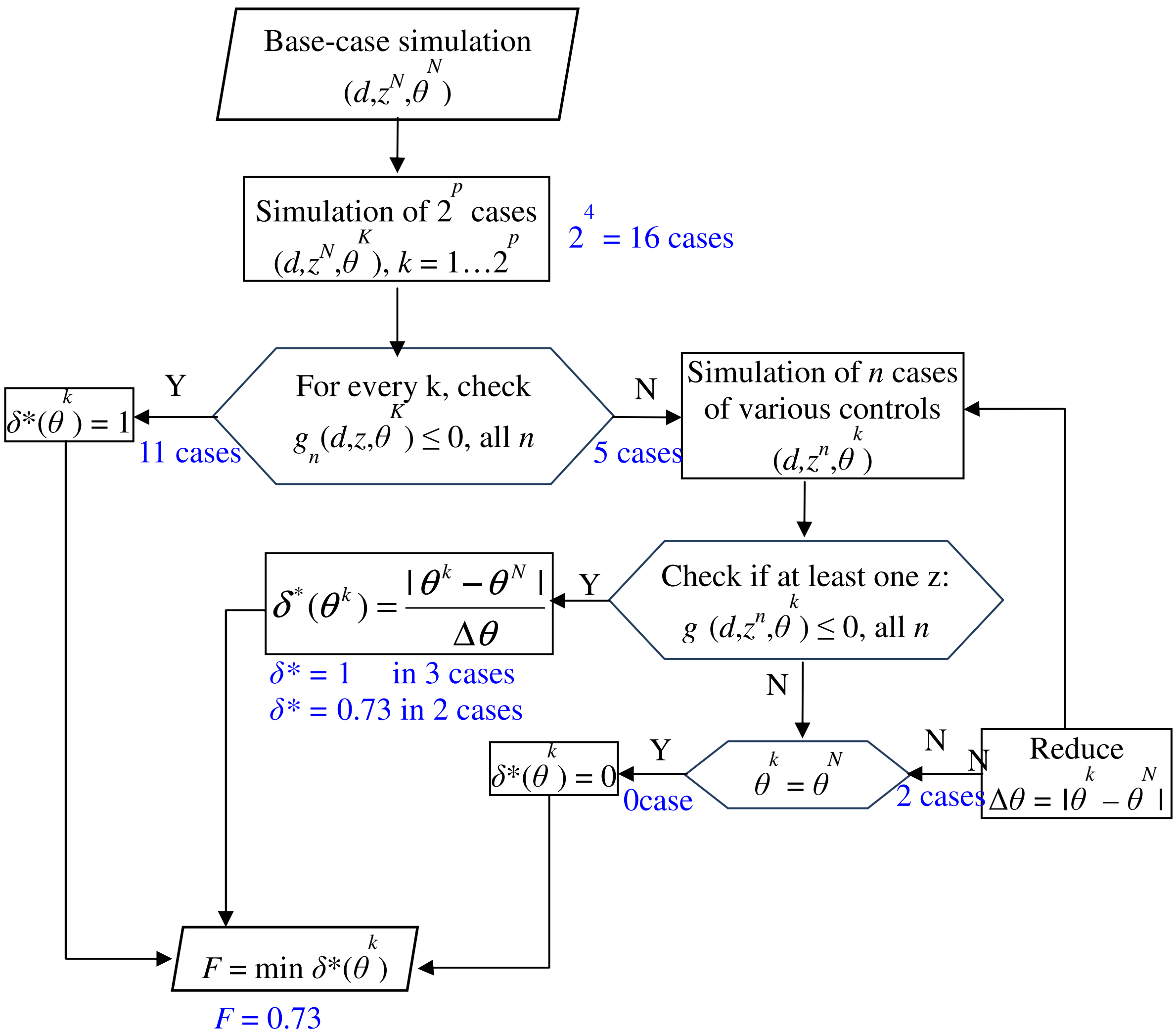


Figure 30. Tracking number of cases in calculation of dehydration flexibility index.

8.2.3.2 Flexibility index of the oxydehydrogenation process

As discussed at the beginning of Section 8.2.3 the oxydehydrogenation process is vulnerable to loss of cooling utility because of its highly exothermic reaction and oxygen presence in the feed mixed streams. In this case study, it was assumed that three pieces of equipment using cooling water are affected by the impact of the pipeline rupture. Their ranges of the impact are given in Table 25.

Table 25.Ranges of impact utility flow rates in oxydehydrogenation process.

Impact utility	Equipment using the utility supply	Lower limit (kg/h)	Nominal rate (kg/h)	Upper limit (kg/h)
Cooling water	Reactor 1 cooler	0	245,737	245,737
Cooling water	Reactor 2 cooler	0	211,529	211,529
Cooling water	Recycle amine	0	161,025	161,025

Among the control variables, assume only two following control variables are effective to tackle the loss of the cooling utility: steam rate of the heater, and water for the scrubber unit. (Process flow diagram with the control systems is shown in APPENDIX B.) As in the other process, controllable flow rates are assumed to be able to vary from zero to a maximum of 130% of the nominal values, which are shown in Table 26.

Table 26. Ranges of adjustable control variables in the oxydehydrogenation process.

Variables (unit)	Lower bound (by %)	Nominal value	Upper bound (by %)
Heater HP steam (kg/h)	0 (-100%)	6,611	8,594 (+30%)
Quenchingwater(kg/h)	0 (-100%)	34,000	43,000 (+30%)

The product specifications are ethylene purity and production rate. Minimum flow rate of the product stream is 80% of the nominal value). The process specifications are given in Table 27. They can be checked directly from Aspen simulation results.

Table 27. Production specifications of the oxydehydrogenation process.

Parameter	Unit	Nominal value	Minimum value
Product purity	% mol.	96.7	95.0
Production rate	kg/h	3,301	2,641

Safety criteria in this process are not only equipment design temperature and pressures but also temperature of the reactor feeds to reduce flammability hazards. The reactor inlet stream is a mixture of ethane, ethylene, and oxygen. Flammability limits of a mixture of ethane and oxygen at atmosphere pressure is 3-12.4%, while that of ethylene and oxygen is 2.7-36%. These flammability limits are affected by the temperature and pressure of the ethane and ethylene stream. Higher temperature results in lower LFL and higher UFL, while greater pressure increases both values. As recommended in the patent[66], to avoid the flammability region under high temperature and pressure operating condition, the conversion of ethane to ethylene was divided into three stages (three reactors in series). Oxygen was introduced to the inlet of every stage such that the oxygen content is less than 6%mol.[66] The temperature of that inlet gaseous stream is also limited at 250^{o}C.[66]

Because pressure-changing valve was not involved in this analysis, the criteria on maximum pressures were not considered. In the simulation, pressures were specified inputs.

To avoid the excess vaporization of water in the scrubber which may result in failure of the following compressor, the scrubber temperature must be less than 95^{o}C. The maximum temperature of compressor outlet is 300^{o}C to avoid upset and failure in the absorber. Table 28 lists the safety criteria.

Table 28.Safety criteria of the oxydehydrogenation process.

Equipment and stream	$T_{nominal}$ (^oC)	$T_{maximum}$ (^oC)
Reactor 1 cooler	396	500
Reactor 2 mixed inlet	90	250
Reactor 2 cooler	368	500
Reactor 3 mixed inlet	90	250
Reactor 3 cooler	375	500
Scrubber temperature	71	95
Compressor temperature	193	300

The simulation results are reported in APPENDIX E. Similar to the dehydration calculation procedure, the calculation procedure was performed as follows:

- First, the base case was simulated. It is referred to as Scenario 1 in the report. Its operation satisfied all the requirements.
- Second, the Sensitivity Analysis tool in Aspen Plus was used to simulate 8 cases corresponding to the combination number of two extreme values of the four external impact parameters. Those simulation results are marked as Scenarios 1 – 8 in the report (One of the scenarios is identical to base case). Only two of those 8 cases (Scenarios 1 and 2) met all the specifications and criteria. The flexibility indices for those 2 cases were noted as 1. The violated safety criteria were temperatures of Reactor 2 feed, Reactor 3 feed and cooler, and Scrubber. The specification of product concentration was also not met.
- Third, the control variables were adjusted in the violating 6 cases (Scenarios 9 – 14). Because their linear relationships, heater duty was minimized and quench water is maximized to reduce the violated temperatures. With those adjustments, all the 6 cases still did not satisfied the constraints; therefore, their impact ranges must be reduced.

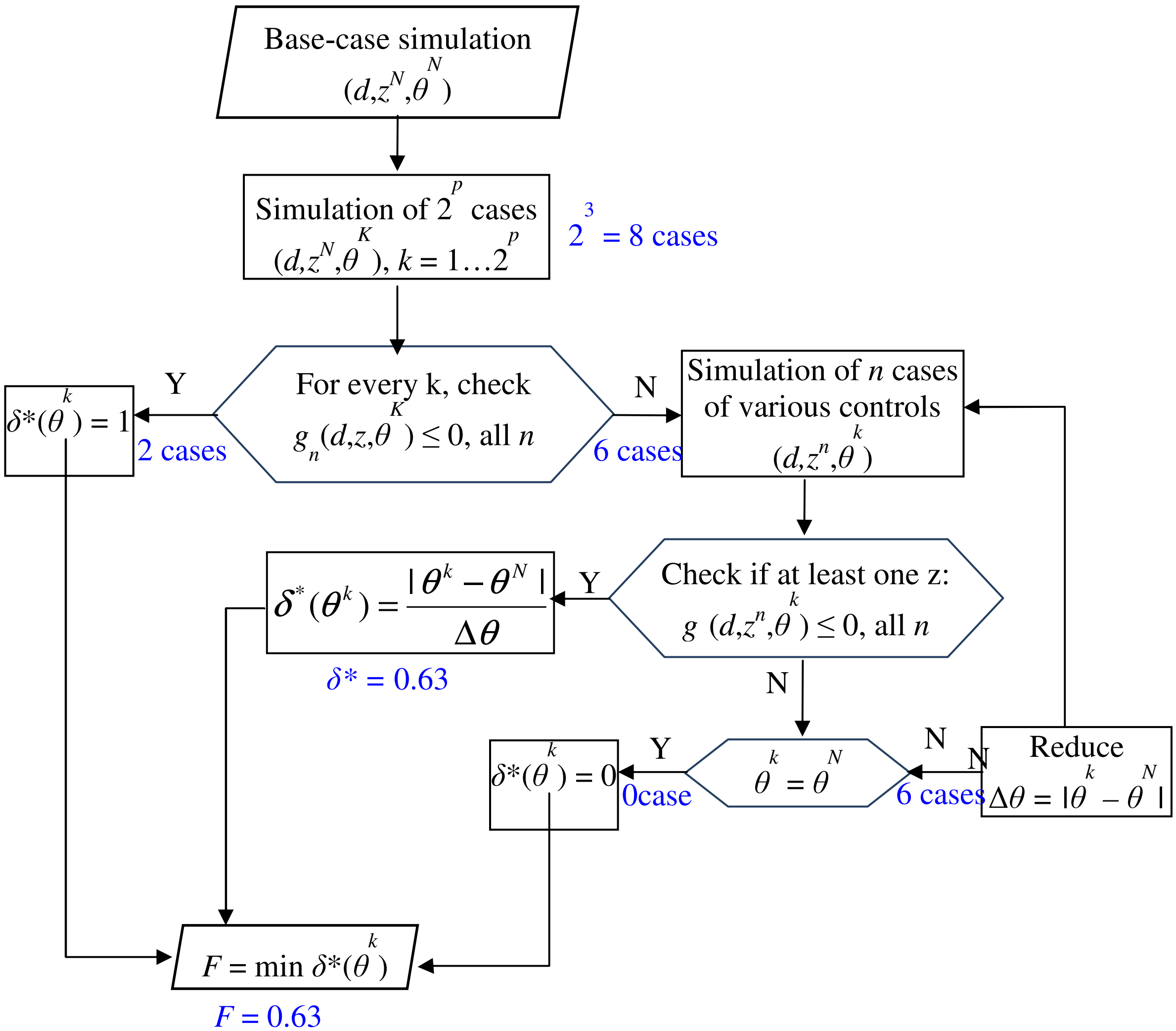


Figure 31. Tracking number of cases in calculation of oxydehydrogenation flexibility index.

- Next, the impact variables were reduced in the same ratios with the preferred extreme values of the control variables. The search showed that the limitation of Scrubber temperature was an active constraint. To meet this temperature requirement, the cooling water rates for Cooler 1, 2, and 4 can be reduced to no less than 91, 78, and 60 tonne per hour, respectively (scenario 15). The flexibility index of this case is

$$\delta^*(\theta^k) = \frac{|\theta^k - \theta^N|}{\Delta\theta} = \frac{|90{,}925 - 245{,}737|}{|0 - 245{,}737|} = 0.63$$

Compared all the found indices, the flexibility index of the oxydehydrogenation process is 0.63, which is the smallest of indices from all cases. Figure 31 tracks the number of cases in the calculation steps.

The methodology leads to the higher the obtained flexibility index is, the more resilient the process design achieves. As a result, the ethanol dehydration process is more resilient with regard to the flexibility perspectives. Then, to evaluate an overall resilience index, flexibility index needs to be in the same scale and consistent with other indices which are in the score of 0 to 10 and in the form that the lower is the better. Therefore, the obtained flexibility indices of both processes were normalized as below:

For the ethanol dehydration process: $(FI)_d$ = (1-0.73) ·10 = 2.7

For the ethane oxydehydrogenation process: $(FI)_O$ = (1-0.63) ·10 = 3.7

8.2.4 Weighting factors

The AHP method in Section 4.2.2 was applied for this case study to obtain the relative weights of inherent safety, controllability, and flexibility sub-factors with regard to the resilience factor of the ethylene production design. The questionnaire in Table 2 was sent to a safety expert who has a lot of years of working experience in process safety and knowledge about resilience in chemical processes. The answers or the selection of a number shown in Table 29 was done in accordance with the expert's experienced opinion.

The above preferences or priority of each factor in terms of how contributes to resilience of a design is demonstrated into the following comparison matrix:

$$\begin{array}{cc} & \begin{array}{ccc} \text{IS} & \text{F} & \text{C} \end{array} \\ \begin{array}{c} \text{IS} \\ \text{F} \\ \text{C} \end{array} & \begin{vmatrix} 1 & 7 & 3 \\ 1/7 & 1 & 1 \\ 1/3 & 1 & 1 \end{vmatrix} \\ \text{Column sums:} & \begin{array}{ccc} 1.48 & 9 & 5 \end{array} \end{array}$$

The following steps were performed to obtain the weighting factors of Inherent Safety, Controllability, and Flexibility to the resilience of a design.

Table 29. The expert's judgments on pair-wise comparison

	Questions	Answers
Q1.	How important is Inherent Safer Design when it is compared to Flexibility? Inherent Safety Design 1 3 5 7 9 Flexibility	7
Q2.	How important is Inherent Safer Design when it is compared to Controllability? Inherent Safety Design 1 3 5 7 9 Controllability	3
Q3.	How important is Flexibility when it is compared to Controllability? Flexibility 1 3 5 7 9 Controllability	1

- Normalizing the pair-wise comparison matrix is performed by dividing each cell of the matrix by is column total.

$$
\begin{array}{r c}
 & \begin{array}{ccc} \text{IS} & \text{F} & \text{C} \end{array} \\
\begin{array}{c} \text{IS} \\ \text{F} \\ \text{C} \end{array} & \begin{vmatrix} 0.677 & 0.778 & 0.600 \\ 0.097 & 0.111 & 0.200 \\ 0.226 & 0.111 & 0.200 \end{vmatrix} \\
\text{Column sum:} & \begin{array}{ccc} 1.00 & 1.00 & 1.00 \end{array}
\end{array}
$$

- Obtain the eigenvector by averaging the normalized scores of all the cells in the same row to determine the final score of an alternative

$$
\begin{array}{c c}
\begin{array}{c} \text{IS} \\ \text{F} \\ \text{C} \end{array} & \begin{vmatrix} 0.685 \\ 0.136 \\ 0.179 \end{vmatrix}
\end{array}
$$

- Estimate the consistency ratio to check the consistency of the pair-wise comparison matrix to check whether the responder's comparison were consistent or not. Consistency ratio is estimated through several steps as follows:
  - Obtain the weighted sum matrix:

$$0.685\begin{bmatrix}1\\1/7\\1/3\end{bmatrix} + 0.136\begin{bmatrix}7\\1\\1\end{bmatrix} + 0.179\begin{bmatrix}3\\1\\1\end{bmatrix} = \begin{bmatrix}2.174\\0.413\\0.543\end{bmatrix}$$

  - Dividing all the elements of the weighted sum matrices by their respective eigenvector element, we obtain:

$$\frac{2.174}{0.685} = 3.174; \frac{0.413}{0.136} = 3.037; \frac{0.543}{0.179} = 3.034$$

  - Then, computing the average of the above values to obtain λ_{max}

$$\lambda_{max} = \frac{3.174 + 3.037 + 3.034}{3} = 3.082$$

  - Calculating the consistency index, CI, as follows

$$CI = \frac{\lambda_{max} - n}{n - 1} = \frac{3.082 - 3}{3 - 1} = 0.041$$

  - From the work of Saaty, the appropriate value of random consistency ratio, RI, for a matrix size of three is 0.58. The consistency ratio, CR, for this case is:

$$CR = \frac{CI}{RI} = \frac{0.041}{0.58} = 0.071$$

- As the value of CR is less than 0.1, the judgment on the weights of the contribution factors is acceptable.
- Hence, the relative weights of inherent safety, controllability, and flexibility are 0.685, 0.179 and 0.136, respectively.

Since the contribution of Flexibility to Design was assessed as being inferior to that of Inherent Safety by a value of 7 i.e., Inherent Safety is favored very strongly over

Flexibility, this factor also has the lowest computed weight 0.136. The contribution of Controllability was assessed as being inferior to that of Inherent Safety by a factor of 3 i.e., the latter are favored slightly, and its weight computed as 0.179. It is evident that with 68.5%, Inherent Safety is leading sub-factors of the Design factor.

8.2.5 Discussions

The indices of each contribution factors to a resilience design including Inherent Safety, Controllability, and Flexibility as well as their important weights have been calculated. The final resilience design index is obtained by adding the products of the normalized indices and their weighting factors. Table 30 summarizes all indices in a scale of 0 to 10 and the final resilience design indices of two processes.

Table 30. Normalized values of all indices to scale of 0 to 10

Contribution factors	Ethanol dehydration	Ethane dehydrogenation	Weighting factors (%)
Normalized Inherent Safety index	2.9	6.0	68.5
Normalized Controllability index (CI)	8	2	17.9
Normalized Flexibility index (FI)	2.7	3.7	13.6
Overall resilience Design index (I_{RD})	3.8	5.0	

The final results show that the ethanol dehydration process design is more resilient than the ethane oxydehydrogenation process design. This index methodology can also be used to compare each individual index for the resilience improvement purpose. For instance, the ethanol dehydration process is more resilient with regard to the inherent safety and flexibility perspectives. In the other hand, the ethane oxydehydrogenation process is more resilient with regard to the controllability perspectives. That means, the dehydration process has a wider operation range (more flexible) but it is more difficult to change the operation from one state to another (lower controllability index). To improve overall resilience for the oxydehydrogenation, the inventory should be reduced by finding a way to increase the product yield.

CHAPTER IX
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

9.1 Conclusion

This work revealed the importance of resilience characteristics in the chemical process, an undeveloped research area. The aim of this work is to develop new principles and contributing factors that constitute resilience, and propose a new method for resilience evaluation of the chemical processes.

In the pursuit of the first objective, analyzing transitions of system states unveiled that resilience is characterized by multiple factors or measures. These measures work and interact together to improve the ability of chemical processes to bounce back. In developing this area of research, the principles of resilience were proposed to be Flexibility, Controllability, Early Detection, Minimization of Failure, Limitation of Effects, and Administrative Controls/ Procedures. These principles act as guidelines to help develop the multiple contribution factors for numerically evaluating resilience. The first layer of factors contributing to resilience was proposed to include Design factor, Detection Potential factor, Emergency Response Planning factor, Human factor, and Safety Management factor.

As for the second objective, multi-level multi-factor approach was proposed to quantify resilience of a chemical process. Among five main contribution factors to resilience, the Design factor was further developed to demonstrate the applicability of the multi-factor approach in evaluating Design index. Its sub-factors were proposed to be Inherent Safety, Controllability, and Flexibility.

- The Inherent Safety index accounted for the effects of material and process design on the process' resilience from an inherent safety viewpoint. The proposed framework showed that the Inherent Safety index takes into account all the aspects of process safety design via various sub-indices.
- The calculation procedure of the Controllability index, using proposed relative gain matrix analysis, is systematic and applicable for controllability evaluations.

The index values indicate a reliable comparative conclusion on the controllability between two or more processes.

- New approach was developed to quantify flexibility of chemical process. The theory is based on optimization programming. With a few assumptions on the function characteristics, the solution approach can be performed in a process simulator like Aspen Plus.

The proposed quantification methodology was demonstrated in a case study of evaluating and comparing resilience of two processes producing ethylene via dehydration of bio-ethanol and oxydehydrogenation of ethane. It was found in the results that the dehydration process was inherently safer and more flexible yet less controllable in the viewpoints of safety-oriented resilience. At the bottom line, the dehydration process design has index values that are more positive to resilience characteristics than those of the oxydehydrogenation process.

The case study results for resilience Design factor showed the applicability of the propose method for assessment and comparison of resilience levels of chemical processes, and at the same time to guide effort to achieve a more resilient design. The method can be further developed at different levels including process, sub-process, subsystem level, or sub-levels of the factors in order to find least resilient points in the design.

It is also very important to understand that process may be resilient with respect one criteria, but not resilient in another point of view or the other criteria. Two processes may seem equally resilient in terms of the final index, but the scores of the sub-indices can be significantly different. By this way, the improvement opportunities can be identified to increase the resilience of chemical processes by modify early the process designs.

It should be noted that this method is not designed for estimating resilience level for a single process because no zero-absolute resilience was established. In that case, a reference level which refers to a standard similar process can be used. In addition, the proposed method is applicable for different types of unexpected situations.

9.2 Recommendations for future work

The proposed methodology can be further improved. The proposed multi-level multi-factor approach has been developed to evaluate the resilience index in terms of the design aspect. Evaluation of other sub-indices including Emergency Response Planning factor, Human factor, and Safety Management factor in terms of resilience point of view should be studied and developed to have better understanding resilience in chemical processes.

The approach to assess controllability is simple but lacks full insights on the control system. It may not hinder many other aspects of process control.

To achieve a higher resilient design, it may require to invest more equipment, piping, interconnections (which lead to complexity) and oversized equipment (which leads to operational problems) and resulting in more capital with none or very limited pay-back. In economic view point, the whole plant should be analyzed not only from the process viewpoint but also from the capital and operating cost viewpoint to understand where and how resilience has been reduced (or increased) and the economic impact of the changes.

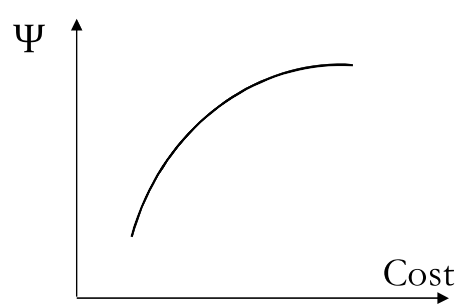


Figure 32. Expected curve of a resilience level Ψ and cost.

Figure 32 shows an expected relationship of a resilience level Ψ and process costs. In general, cost increases as more resilient is gained. From this expectation, the following problems arise to incorporate costs into resilience optimization problem.

- Maximize resilience index and impose a cost limitation (i.e., COST $\leq$ Budget). The solution will be the most resilience design within a budget.
- Replace object by a minimization of COST which is a function of resilience index. The solution is a least costly design with an acceptable resilience level.

Specifically, the process complexity of inherent safety factor can be done in more details if additional data is available. For instance, the factors of equipment complexity can be different when detailed designs of heat exchangers are considered (spiral heat exchanger can be scored more complex than sign-pass steel-tube heat exchanger.) Piping is the other issue needs to be considered in complexity term when possible since it can make the overall system complicated, and affect the inherent safety of the process. Fewer lines and connections improve safety because it can lead to less operational errors. The piping complexity factors can be number of lines plant, number of connections modeling, number of piping items. The relationship between complexity and weighting factors can also be done to address more accurately.

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APPENDIX A

INCIDENT DATABASE FOR CBR METHOD

Table 31.Incident database for CBR

Outlet components		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
Input data	Database	MARS	RMP	RMP	RMP	HSEES	HSEES	HSEES
	Type of industry	Ethylene Production Plant	Ethylene unit	Ethylene Unit	Ethylene Producer		2869 ethylene production	2869, mfg ethylene
	SYSTEM	Fixed facility				Fixed facility	Fixed facility	Fixed facility
	Substance involved	Ethylene, Propylene,	Ethylene	Ethylene	Ethylene	Ethylene Ethane	Ethylene	Ethylene
Output data	ID		9122	7678	6510	4871	LA20011807	LA20020828
	Location		Sunoco, Inc. Marcus Hook Refinery, Marcus Hook, PA	Sunoco, Inc. Marcus Hook Refinery, Marcus Hook, PA	Westlake Petrochemicals, Sulphur, LA	Calcasieu, LA	LA	Baton rouge, LA
	Date	18/01/1985	May 17 2009	Aug 18 2000	Jan 05 2002	2001	12/2/2001	6/26/2002
	Incident	Release and explosion				Air Emission		

Table 31. (Continued)

Cause	Unused by-pass failure	Equipment failure	Equipment failure	Equipment failure	System startup and shutdown	Equipment failure	Deliberate damage/intentional
Consequences	43 people injured						
Details	The accident occurred during normal operation in a distillation unit of the Ethylene Production Plant in a petrochemical industry.		10lbs	1,300lbs ethylene released			System start-up. Release amount unknown. Exact end time unknown.

APPENDIX B
PROCESS DIAGRAMS

B.1 Commercial ethylene production process diagrams

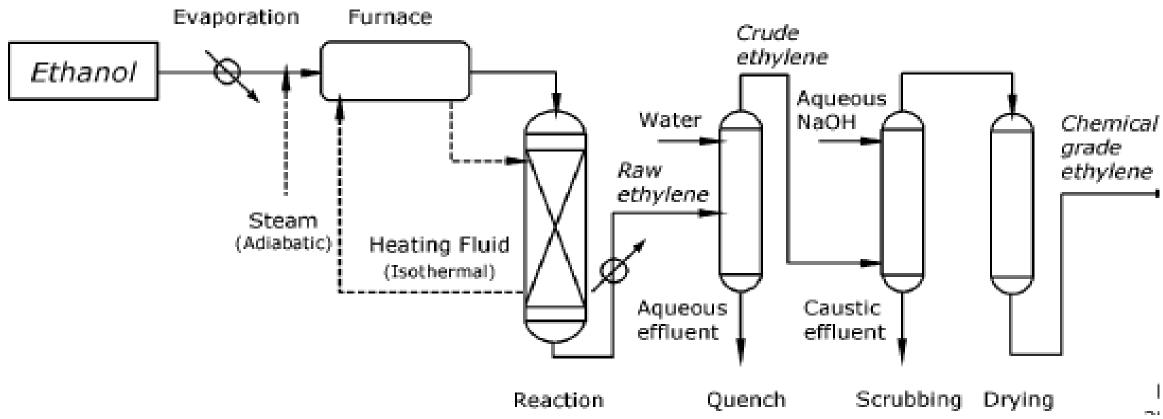


Figure 33. Petrobras process for ethanol dehydration.[72]

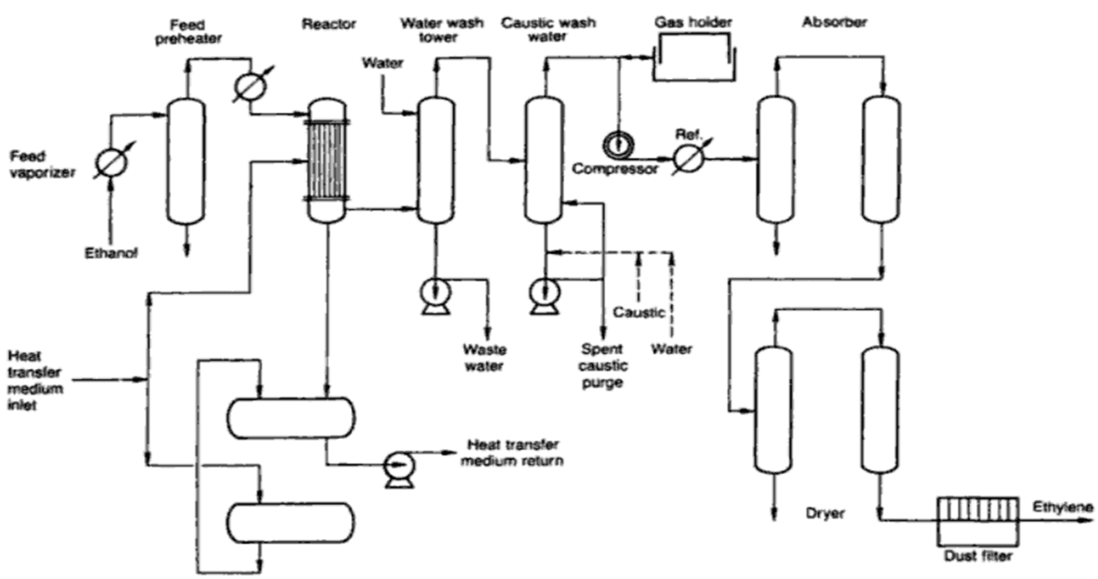


Figure 34. Lummus fixed-bed process for ethanol dehydration.[75]

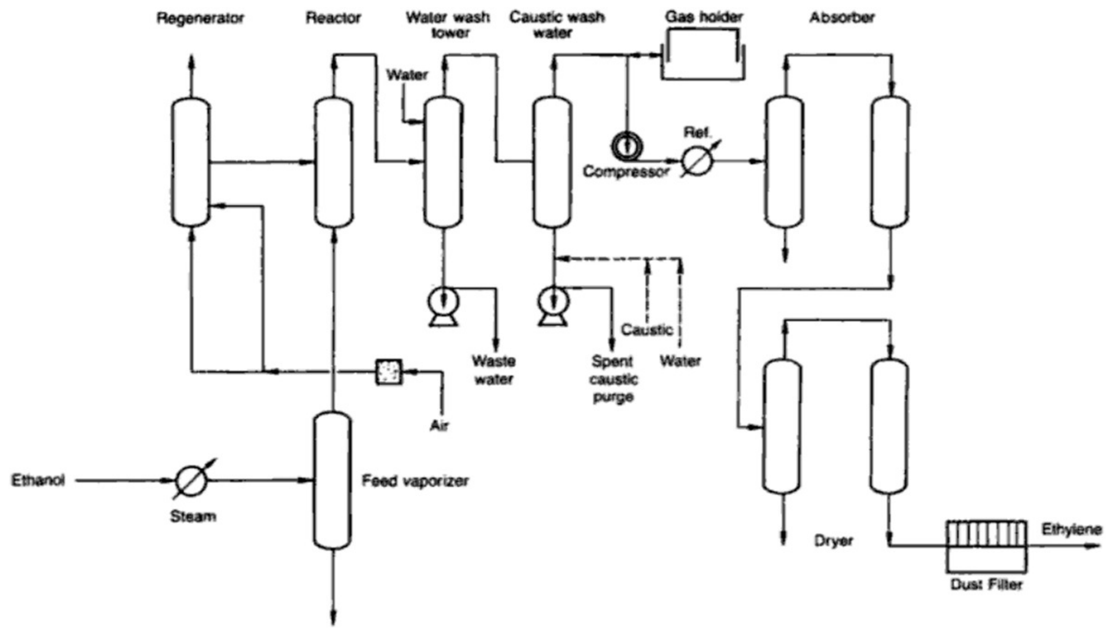


Figure 35. Lummus fluidized-bed process for ethanol dehydration.[75]

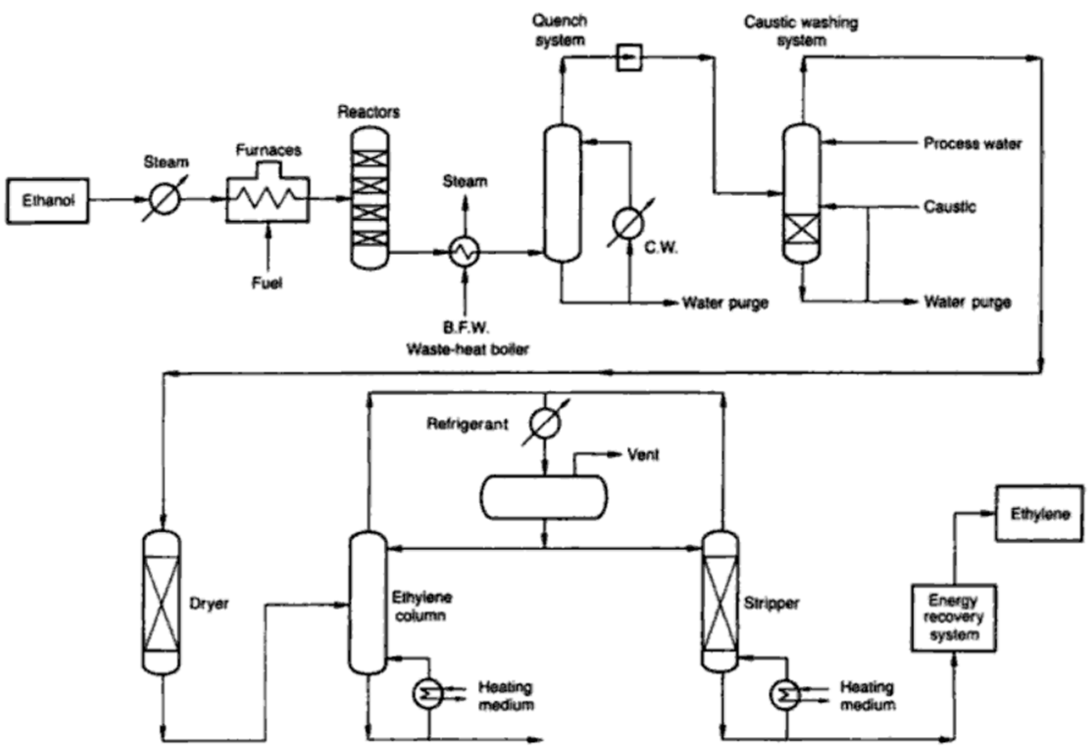
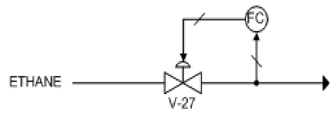
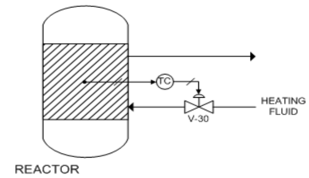


Figure 36. Halcon SD process for ethanol dehydration.[75]

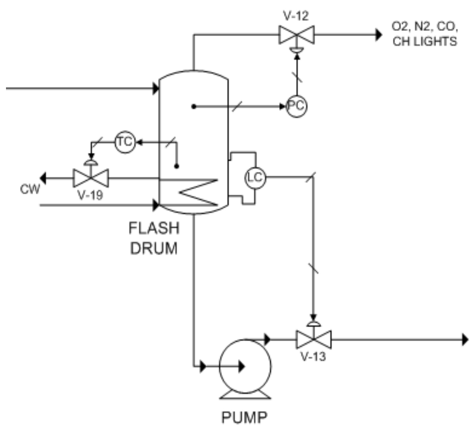
B.2 Typical control system investigated in the case study



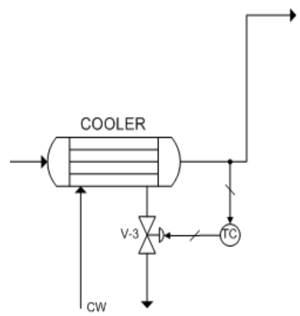
(a) Flowrate control



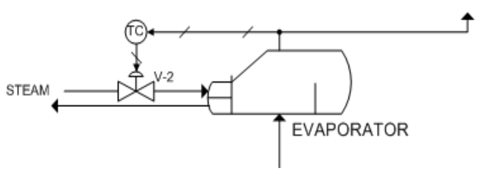
(b) Reactor temperature control



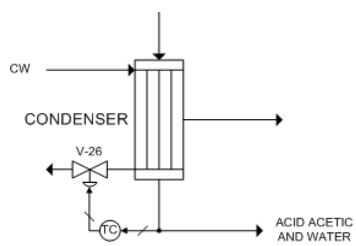
(c) Flash drum control



(d) Cooler control

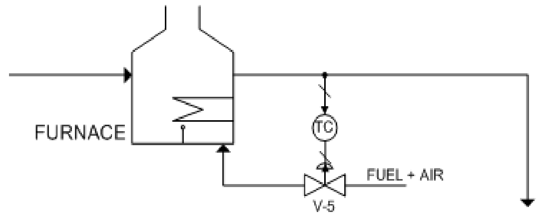


(e) Evaporator control

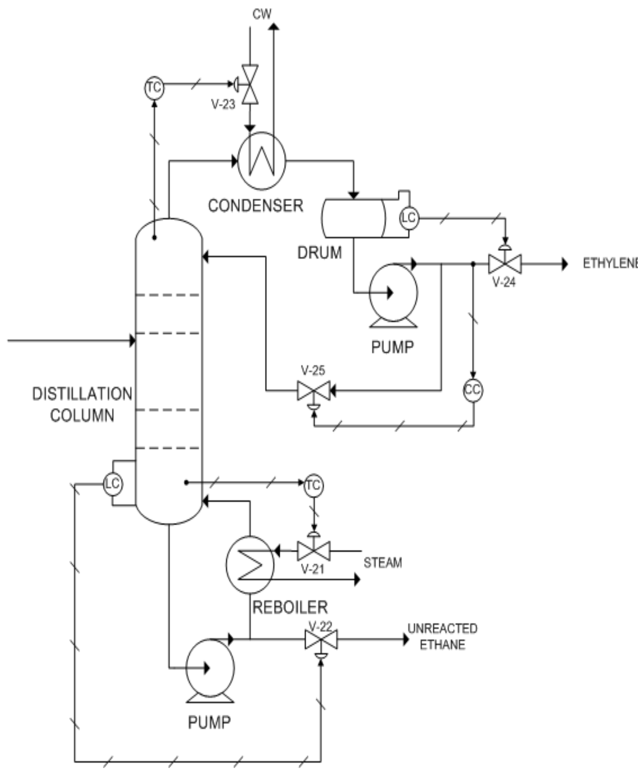


(f) Condenser control

Figure 37. Typical feedback control systems.



(g) Furnace control



(h) Distillation column control

Figure 37. (Continued)

B.3 Ethylene process diagram with control systems

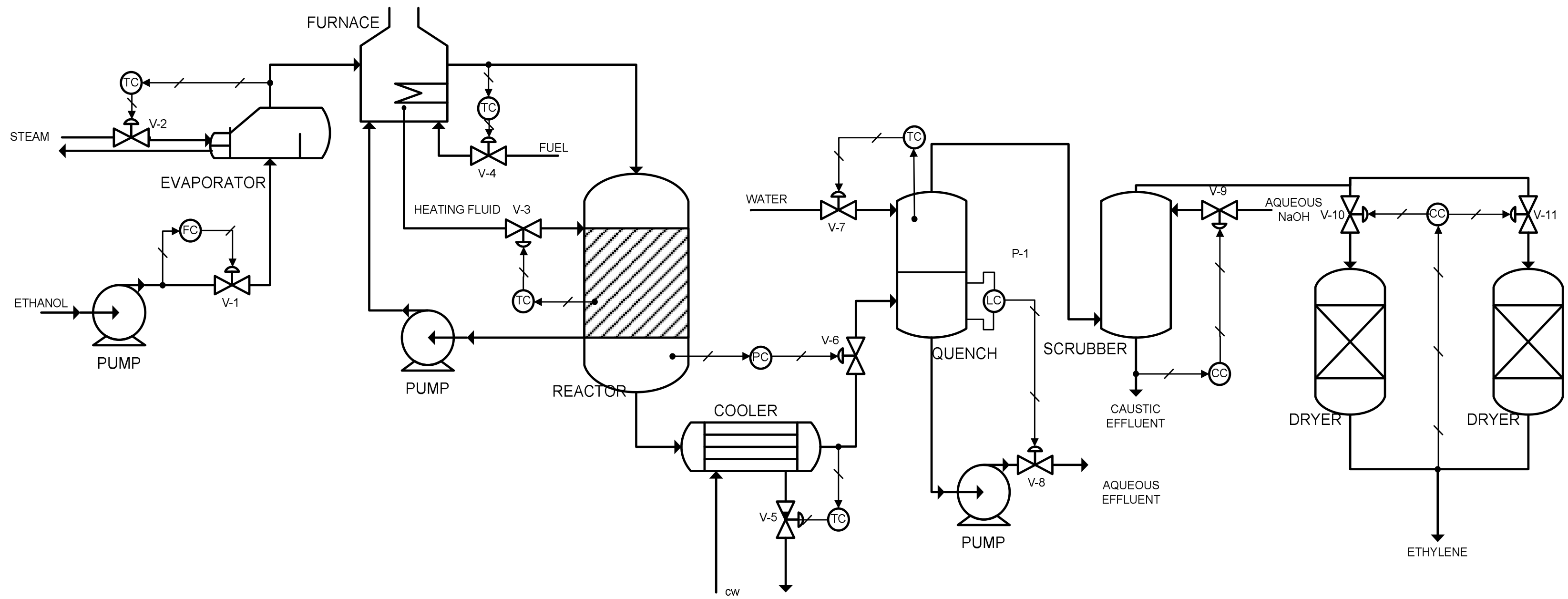


Figure 38.Dehydration of bioethanol to ethylene process with designed control systems

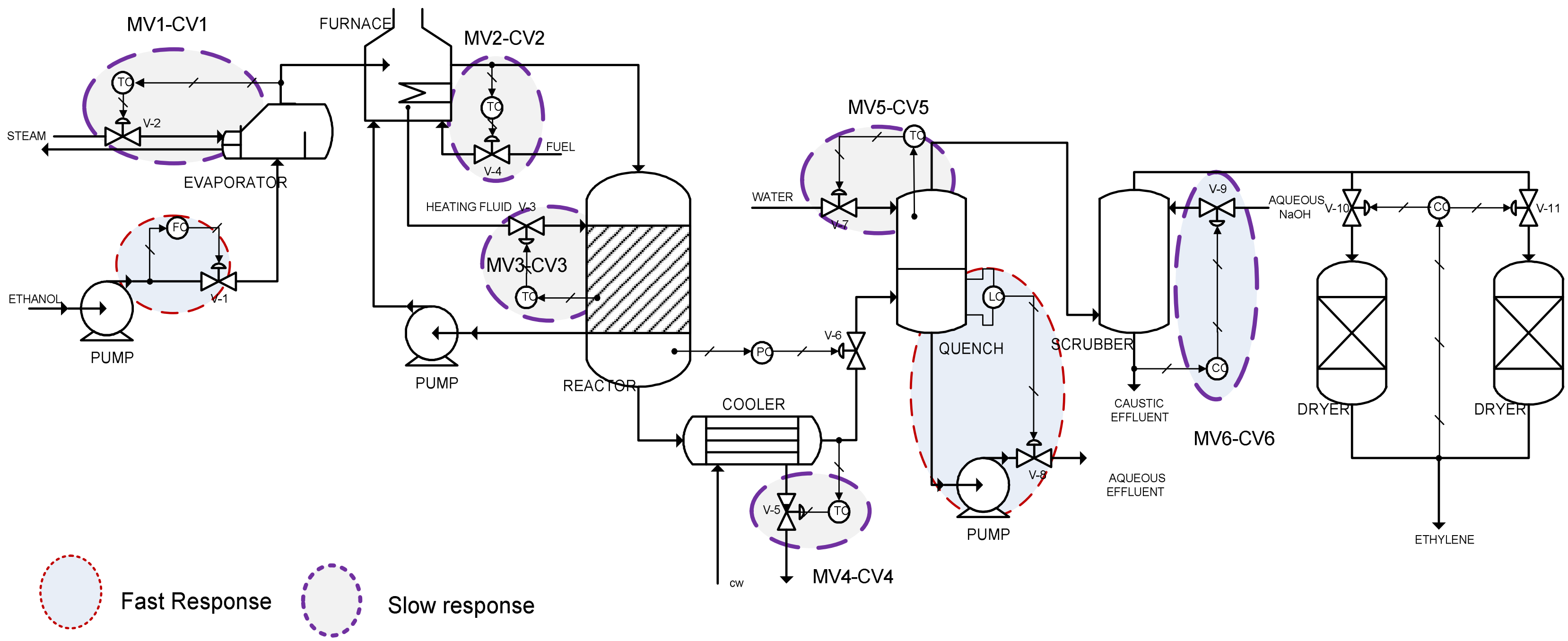


Figure 39. Dehydration of bioethanol to ethylene process with the slow and fast response pairs of control.

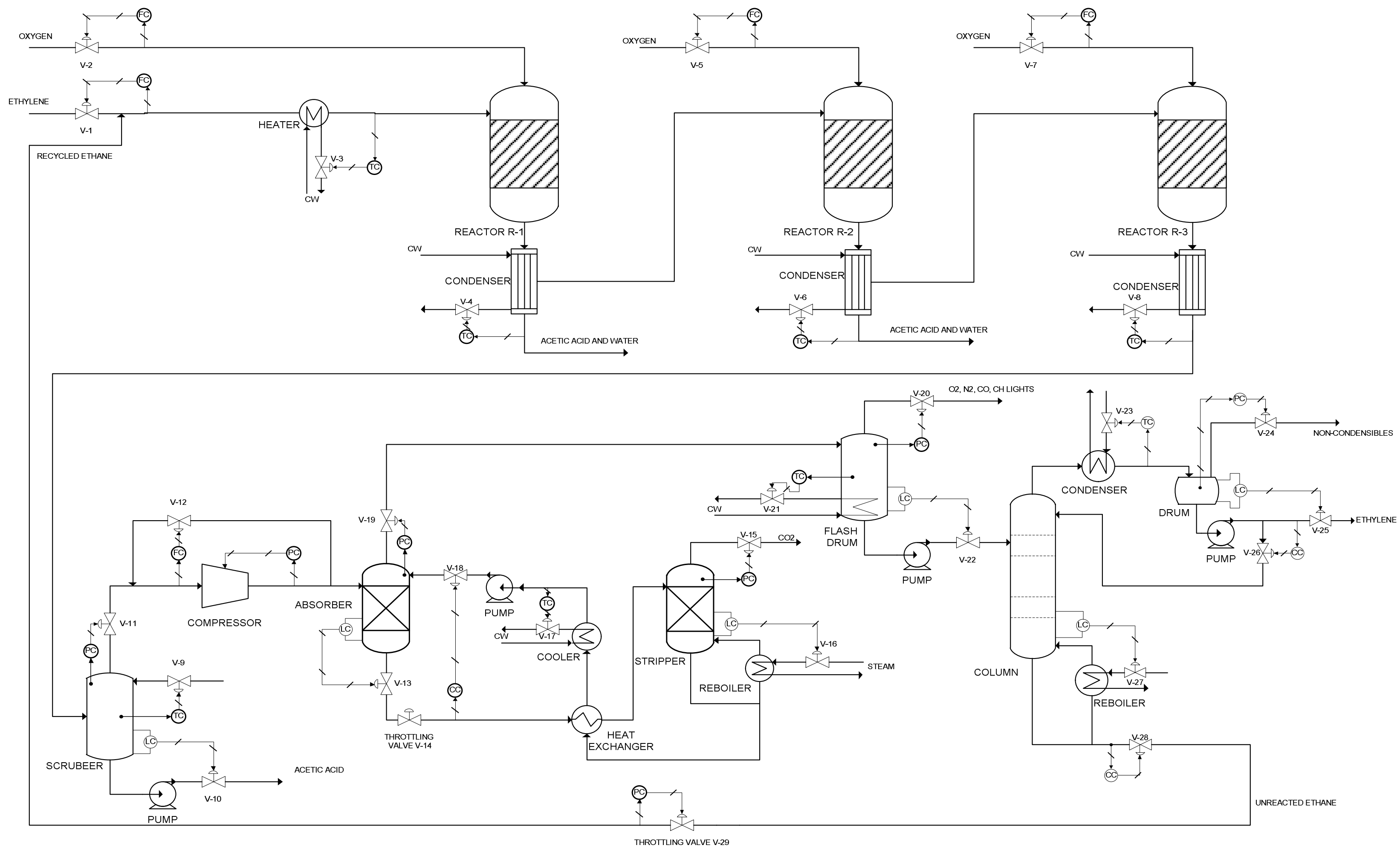


Figure 40. Oxydehydrogenation of ethane to ethylene process with designed control systems.

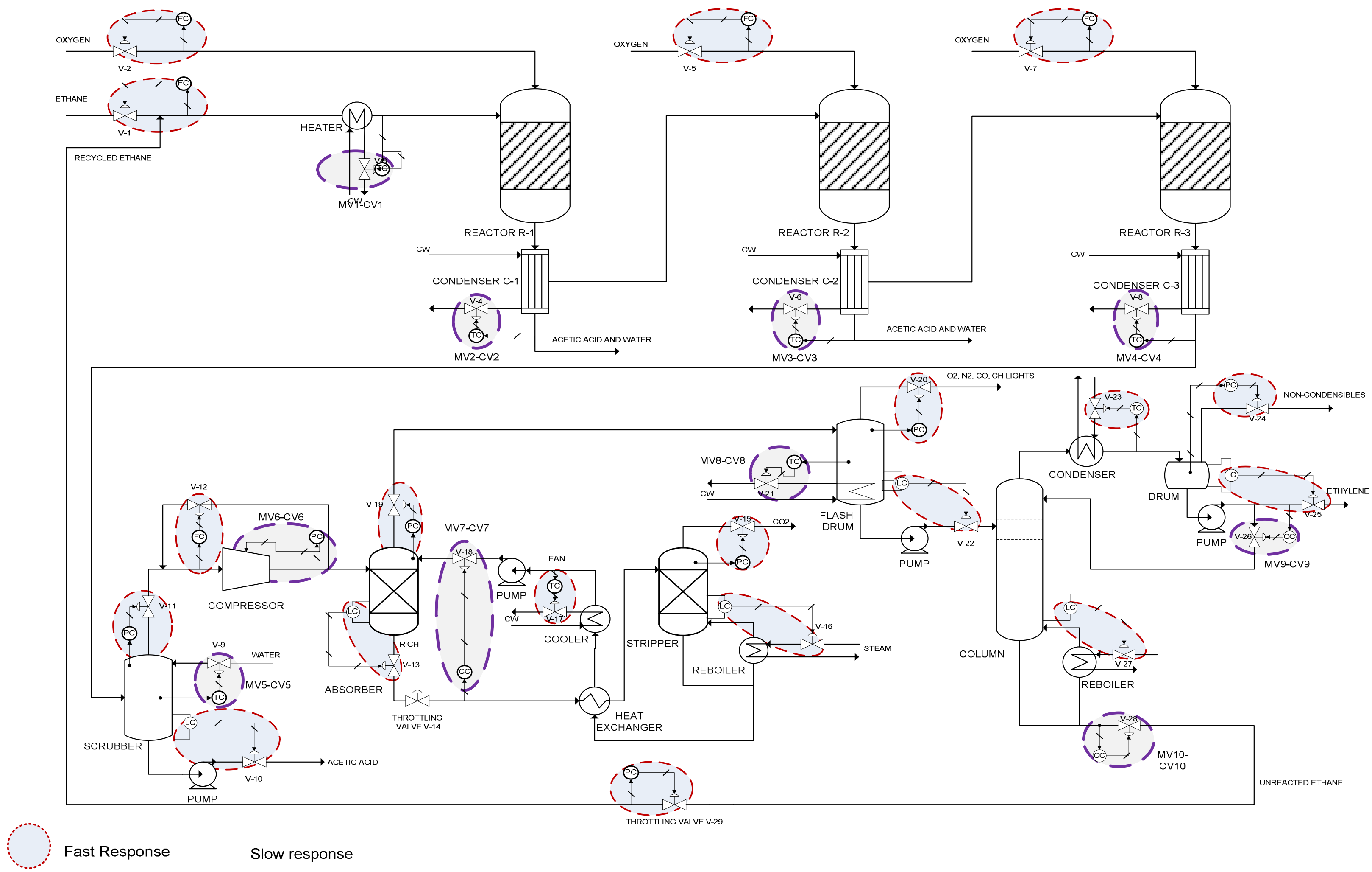


Figure 41. Oxydehydrogenation of ethane to ethylene process with the slow and fast response pairs of control.

APPENDIX C

ASPEN MODELS AND INPUT DATA FOR THE CASE STUDY OF ETHYLENE PRODUCTION PROCESSES

C.1 Aspen model

Equipment	Aspen model	Property method	Equilibrium package	Specified parameter
Pump	PUMP	NRTL	(none)	Outlet pressure
Evaporator, cooler, condenser	HEATER	NRTL	(none)	Outlet pressure Heat duty
Furnace	HEATER	NRTL	(none)	Outlet pressure Heat duty
Reactor	RSTOIC	NRTL	(none)	Conversion Outlet pressure Heat duty
Flash drum, , quench	FLASH	NRTL	(none)	Pressure drop Heat duty
Valve	VALVE	NRTL	(none)	Outlet pressure
Scrubber	FLASH	ELECNRTL	CAUSTIC	Pressure drop Heat duty
Dryer	Separation	NRTL	(none)	Split fractions
Absorber	RADFRAC	ELECNRTL	KEMDEA	Pressure profile
Stripper	RADFRAC	ELECNRTL	KEMDEA	Pressure profile Bottom rate
Distillation	RADFRAC	NRTL	(none)	Bottom rate Reflux rate
Compressor	COMPRESSOR	NRTL	(none)	Duty

C.2 Aspen flowsheets

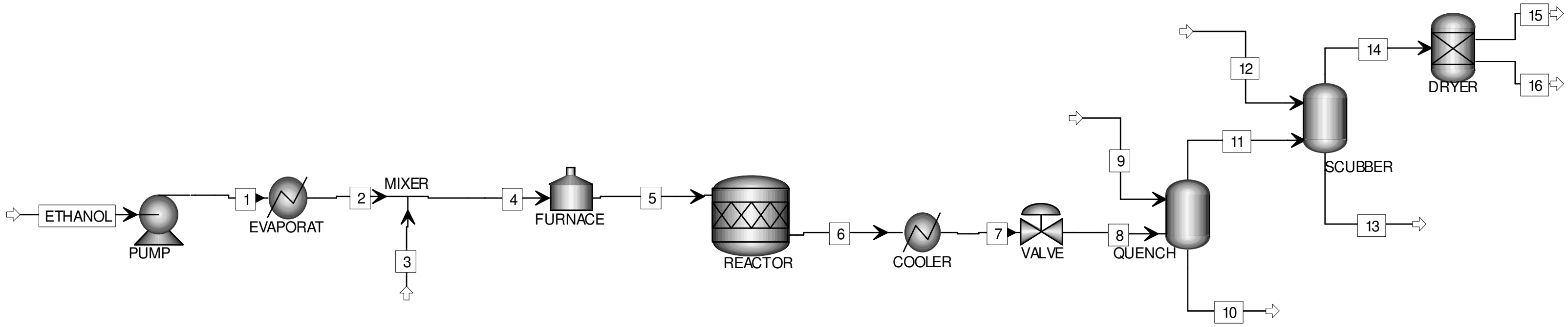


Figure 42. Aspen flowsheet of the dehydration process.

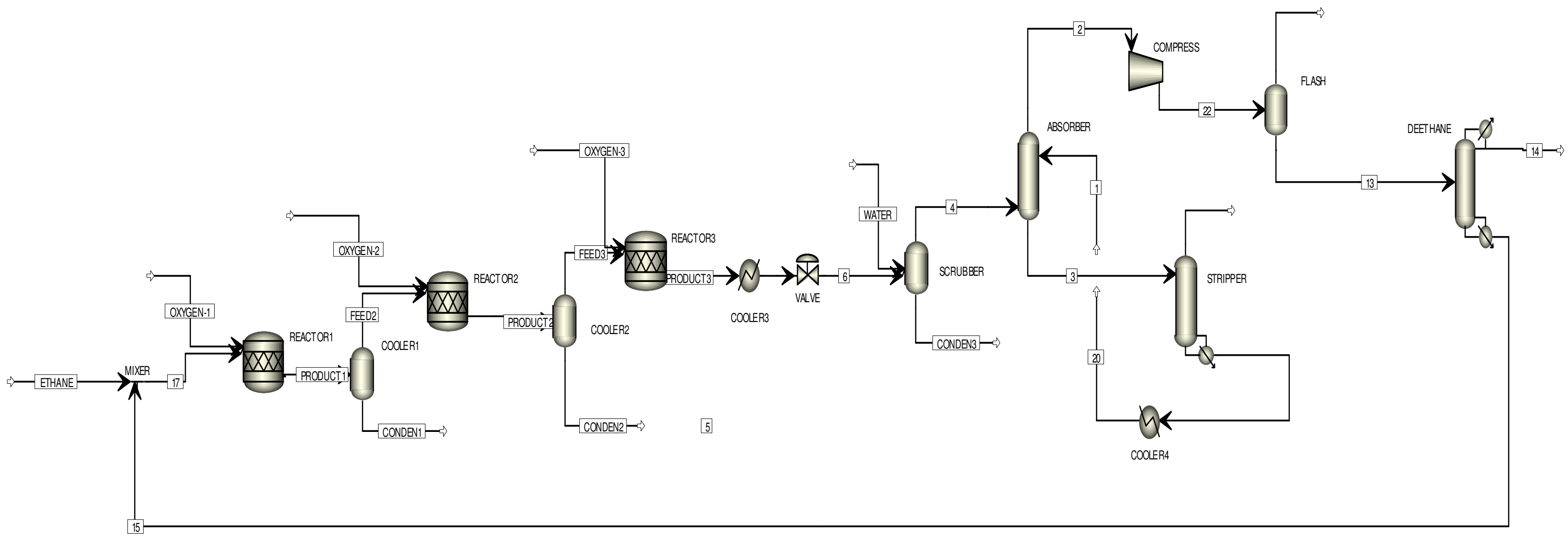


Figure 43. Aspen flowsheet of the oxydehydrogenation process.

C.3 Input summary in Aspen Plus

C.3.1 Dehydration process

```
DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' PDROP=bar

DEF-STREAMS CONVEN ALL

SIM-OPTIONS OLD-DATABANK=NO

DESCRIPTION " "

DATABANKS 'APV72 PURE24' / 'APV72 AQUEOUS' / 'APV72 SOLIDS' /  &
        'APV72 INORGANIC' / 'APV72 ASPENPCD' / 'APV72 PURE856'

PROP-SOURCES 'APV72 PURE24' / 'APV72 AQUEOUS' / 'APV72 SOLIDS' &
         / 'APV72 INORGANIC' / 'APV72 ASPENPCD' /  'APV72 PURE856'

COMPONENTS
    ETHANOL C2H6O-2 / ETHYLENE C2H4 / H2O H2O / ACETAL C2H4O-1 /
    HYDROGEN H2 / ACETIC C2H4O2-1 / ETHYLACE C4H8O2-3 /
    ACETONE C3H6O-1 / METHANOL CH4O / METHANE CH4 / ETHANE C2H6 /
    PROPANE C3H8 / PROPYLEN C3H6-2 / N-BUTANE C4H10-1 /
    I-BUTANE C4H8-5 / CO CO / CO2 CO2 / NH3 H3N / H2S H2S /
    NAOH NAOH / NA+ NA+ / H3O+ H3O+ / NH4+ NH4+ / OH- OH- /
    HCO3- HCO3- / CO3-2 CO3-2 / HS- HS- / S-2 S-2 / NH2COO- NH2COO- /
    CH3COO- CH3COO- / NA2CO3 NA2CO3 / NAHCO3 NAHCO3

HENRY-COMPS ESOURO NH3 H2S CO2 ETHYLENE

SOLVE
    PARAM

CHEMISTRY CAUSTIC

CHEMISTRY ESOURO

FLOWSHEET
    BLOCK EVAPORAT IN=1 OUT=2
    BLOCK MIXER IN=2 3 OUT=4
    BLOCK FURNACE IN=4 OUT=5
    BLOCK REACTOR IN=5 OUT=6
    BLOCK BOILER IN=6 OUT=7
    BLOCK PUMP IN=ETHANOL OUT=1
    BLOCK VALVE IN=7 OUT=8
    BLOCK QUENCH IN=8 9 OUT=11 10
    BLOCK SCRUBBER IN=11 12 OUT=14 13
    BLOCK DRYER IN=14 OUT=15 16
PROPERTIES NRTL TRUE-COMPS=YES
    PROPERTIES ELECNRTL / PENG-ROB

STREAM 3
    SUBSTREAM MIXED PRES=3. VFRAC=1. MOLE-FLOW=100.
MASS-FRAC H2O 1.
```

```
STREAM 7B
    SUBSTREAM MIXED TEMP=105. PRES=3.
    MOLE-FLOW ETHANOL 1.98 / ETHYLENE 94.05 / H2O 194.05 /  &
ACETAL 2.97 / HYDROGEN 2.97 / ACETIC 0. / ETHYLACE 0. /
        ACETONE 0. / METHANOL 0. / METHANE 0. /  ETHANE 0. /
        PROPANE 0. / PROPYLEN 0. / N-BUTANE 0. / &
I-BUTANE 0. / CO 0. / CO2 1.

STREAM 9
    SUBSTREAM MIXED TEMP=35. PRES=1.2 MASS-FLOW=30000.
MOLE-FRAC H2O 1.

STREAM 12
    SUBSTREAM MIXED TEMP=25. PRES=1.15 MOLE-FLOW=95.  &
        SOLVENT=H2O FREE-WATER=NO NPHASE=1 PHASE=L
    MOLE-CONC NAOH 1.19 <kmol/cum>

STREAM ETHANOL
    SUBSTREAM MIXED TEMP=25. PRES=1. MOLE-FLOW=100.
    MOLE-FRAC ETHANOL 0.99 / CO2 0.01

BLOCK MIXER MIXER

BLOCK DRYER SEP
    FRAC STREAM=16 SUBSTREAM=MIXED COMPS=ETHANOL ETHYLENE H2O  &
        ACETAL HYDROGEN ACETIC ETHYLACE ACETONE METHANOL  &
        METHANE ETHANE PROPANE PROPYLEN N-BUTANE I-BUTANE CO  &
        CO2 NH3 H2S NAOH NA+ H3O+ NH4+ OH- HCO3- CO3-2 HS-  &
        S-2 NH2COO- FRACS=0. 0. 1. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
        0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.

BLOCK BOILER HEATER
    PARAM PRES=0. DUTY=-0.615275
    HCURVE 1 INDEP-VAR=VFRAC LIST=0. 0.1 0.2 0.3 0.4 0.5  &
0.6 0.7 0.8 0.9 1. PROPERTIES=HXDESIGN
    UTILITY UTILITY-ID=CW

BLOCK EVAPORAT HEATER
    PARAM PRES=0. DUTY=1.16584412
    UTILITY UTILITY-ID=HPSTEAM

BLOCK FURNACE HEATER
    PARAM PRES=0. DUTY=0.73236908
    UTILITY UTILITY-ID=N-GAS

BLOCK QUENCH FLASH2
    PARAM PRES=0. DUTY=0.

BLOCK SCRUBBER FLASH2
    PARAM PRES=0. DUTY=0.
    PROPERTIES ELECNRTL HENRY-COMPS=ESOURO CHEMISTRY=CAUSTIC  &
        FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK REACTOR RSTOIC
    PARAM PRES=0. DUTY=1.10470283
    STOIC 1 MIXED ETHANOL -1. / ETHYLENE 1. / H2O 1.
    STOIC 2 MIXED ETHANOL -1. / ACETAL 1. / HYDROGEN 1.
    CONV 1 MIXED ETHANOL 0.95
    CONV 2 MIXED ETHANOL 0.03
    UTILITY UTILITY-ID=HEAT-OIL
```

```
BLOCK PUMP PUMP
    PARAM PRES=3. NPHASE=2
    PROPERTIES PENG-ROB FREE-WATER=STEAM-TA SOLU-WATER=TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO

BLOCK VALVE VALVE
    PARAM P-OUT=1.1

BLOCK VALVE-B VALVE
    PARAM CALC-CV=YES P-OUT=1. CHECK-CHOKE=NO
    VALVE-DEF VAL-TYPE="GLOBE" MFGR="NELES-JAMESBURY" SERIES= &
        "V500_EQUAL_PERCENT_FLOW" SIZE="10-IN"
    VAL-PARAM VP-DAT=10 CV-DAT=17 XT-DAT=0.79 FL-DAT=0.97 /  &
        VP-DAT=20 CV-DAT=29 XT-DAT=0.79 FL-DAT=0.97 / VP-DAT=30  &
        CV-DAT=42 XT-DAT=0.79 FL-DAT=0.97 / VP-DAT=40 CV-DAT=62  &
        XT-DAT=0.79 FL-DAT=0.97 / VP-DAT=50 CV-DAT=98  &
        XT-DAT=0.78 FL-DAT=0.96 / VP-DAT=60 CV-DAT=170  &
        XT-DAT=0.76 FL-DAT=0.95 / VP-DAT=70 CV-DAT=293  &
        XT-DAT=0.74 FL-DAT=0.94 / VP-DAT=80 CV-DAT=566  &
        XT-DAT=0.71 FL-DAT=0.92 / VP-DAT=90 CV-DAT=840  &
        XT-DAT=0.69 FL-DAT=0.91 / VP-DAT=100 CV-DAT=950  &
        XT-DAT=0.68 FL-DAT=0.9

UTILITY CW GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=WATER PRES=1. PRES-OUT=1. TIN=90. <F>&
        TOUT=120. <F> CALOPT=FLASH

UTILITY HEAT-OIL GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=OIL COOLING-VALU=100.

UTILITY HPSTEAM GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=STEAM PRES=10. PRES-OUT=10. VFRAC=1.  &
        VFR-OUT=0. CALOPT=FLASH

UTILITY N-GAS GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=GAS COOLING-VALU=11000.

EO-CONV-OPTI

CONV-OPTIONS
    PARAM TOL=1E-010

STREAM-REPOR MOLEFLOW MOLEFRAC

PROPERTY-REP NOPARAM-PLUS
```

C.3.2 Oxydehydrogenation process

```
DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' PDROP=bar

DEF-STREAMS CONVEN ALL

SIM-OPTIONS
    IN-UNITS MET MASS-FLOW='tonne/hr' MOLE-FLOW=MMscmh  &
        VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' MASS=tonne PRESSURE=bar  &
        TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter  &
        MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum'  &
        MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg'  &
        MOLE-VOLUME='cum/kmol' MOLES=MMscm HEAT=Gcal  &
        MASS-CONC='kg/cum' MOLE-CONC='kmol/cum' PDROP=bar  &
        VOL-HEAT-CAP='kcal/cum-K'
    SIM-OPTIONS OLD-DATABANK=NO

DESCRIPTION ""

DATABANKS 'APV72 PURE24' / 'APV72 AQUEOUS' / 'APV72 SOLIDS' /  &
        'APV72 INORGANIC' / 'APV72 ASPENPCD' / 'APV72 PURE856'

PROP-SOURCES 'APV72 PURE24' / 'APV72 AQUEOUS' / 'APV72 SOLIDS' &
         / 'APV72 INORGANIC' / 'APV72 ASPENPCD' /  'APV72 PURE856'

COMPONENTS
    C2H6 C2H6 / O2 O2 / CO2 CO2 / C2H4 C2H4 / ACETIC C2H4O2-1 /
    H2O H2O / CO CO / N2 N2 / CH4 CH4 / MDEA C5H13NO2 / H2S H2S /
    HCO3- HCO3- / MDEA+ / CO3-2 CO3-2 / HS- HS- / S-2 S-2 /
    H3O+ H3O+ / OH- OH-

HENRY-COMPS C2 C2H6 C2H4

HENRY-COMPS CO O2 CO

HENRY-COMPS KEMDEA CO2 H2S C2H6 C2H4

CHEMISTRY KEMDEA

FLOWSHEET
    BLOCK COOLER1 IN=PRODUCT1 OUT=FEED2 CONDEN1
    BLOCK SCRUBBER IN=WATER 3 OUT=4 CONDEN3
    BLOCK COMPRESS IN=4 OUT=5
    BLOCK COOLER2 IN=PRODUCT2 OUT=FEED3 CONDEN2
    BLOCK REACTOR1 IN=OXYGEN-1 2 OUT=PRODUCT1
    BLOCK ABSORBER IN=5 7 OUT=9 RICH
    BLOCK COOLER3 IN=PRODUCT3 OUT=3
    BLOCK VALVE-2 IN=RECYCLE OUT=RECYCL-B
    BLOCK STRIPPER IN=RICH-HT OUT=6 8
    BLOCK COOLER4 IN=13 OUT=LEAN-B
    BLOCK FLASH IN=9 OUT=10 11
    BLOCK DEETHANE IN=11 OUT=ETHYLENE RECYCLE
    BLOCK MIXER IN=RECYCL-C ETHANE OUT=1
```

```
    BLOCK REACTOR2 IN=OXYGEN-2 FEED2 OUT=PRODUCT2
    BLOCK REACTOR3 IN=OXYGEN-3 FEED3 OUT=PRODUCT3
    BLOCK VALVE-1 IN=RICH OUT=RICH-LP
    BLOCK PUMP IN=LEAN OUT=7
    BLOCK HEATER IN=1 OUT=2
    BLOCK HX IN=8 RICH-LP OUT=13 RICH-HT

PROPERTIES ELECNRTL HENRY-COMPS=KEMDEA CHEMISTRY=KEMDEA  &
        TRUE-COMPS=YES
    PROPERTIES NRTL / PENG-ROB

PROP-SET XAPP XAPP SUBSTREAM=MIXED COMPS=MDEA CO2 PHASE=L

STREAM ETHANE
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar
    SUBSTREAM MIXED TEMP=25. PRES=10. MOLE-FLOW=162.9
MOLE-FLOW C2H6 140. / CO2 0.37

STREAM LEAN
    SUBSTREAM MIXED TEMP=44. PRES=5. MOLE-FLOW=1679.22357
MOLE-FLOW C2H6 0. / O2 0. / CO2 0.00025556 / C2H4 0. /  &
ACETIC 1.15403682 / H2O 1555.20467 / CO 0. / N2 0. / &
        CH4 0. / MDEA 122.310958 / H2S 0. / HCO3- 0.1515002 / &
        MDEA+ 0.28377867 / CO3-2 0.0139036 / HS- 0. / S-2 0. / &
        H3O+ 6.8626E-009 / OH- 0.10447126

STREAM OXYGEN-1
    SUBSTREAM MIXED TEMP=80. PRES=10. MOLE-FLOW=41.76
    MOLE-FLOW O2 6.6

STREAM OXYGEN-2
    IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr'  &
        HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C  &
        VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum'  &
        MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol'  &
        MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l'  &
        PDROP=bar
    SUBSTREAM MIXED TEMP=80. PRES=10. MOLE-FLOW=41.76
    MOLE-FLOW O2 6.3

STREAM OXYGEN-3
    SUBSTREAM MIXED TEMP=80. PRES=10. MOLE-FLOW=41.76
    MOLE-FLOW O2 6.3

STREAM RECYCL-C
    SUBSTREAM MIXED TEMP=-30.7 PRES=45. MOLE-FLOW=432.4
    MOLE-FRAC C2H6 0.86 / C2H4 0.034 / H2O 0.105

STREAM RICH
    SUBSTREAM MIXED TEMP=36.44 PRES=1.
    MOLE-FLOW C2H6 0.00152307 / O2 0.00083602 / CO2  &
        0.0005689 / C2H4 0.00098885 / ACETIC 0.05490114 /  &
H2O 85.0982413 / CO 0.00650914 / N2 0. / CH4 0. /  &
        MDEA 5.75716338 / H2S 9.3059E-029 / HCO3- 0.75922157 /  &
        MDEA+ 1.17264905 / CO3-2 0.20666536 / HS- 9.3059E-029 / &
        S-2 1.3176E-018 / H3O+ 1.5075E-009 / OH- 9.6746E-005
```

```
STREAM WATER
    SUBSTREAM MIXED TEMP=25. PRES=10. MASS-FLOW=34000.
MOLE-FRAC H2O 1.

BLOCK MIXER MIXER
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK COOLER3 HEATER
    PARAM PRES=0. DUTY=-2.3549519
    UTILITY UTILITY-ID=CW

BLOCK COOLER4 HEATER
    PARAM TEMP=44. PRES=0.
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    UTILITY UTILITY-ID=CW

BLOCK HEATER HEATER
    PARAM PRES=0. DUTY=2.83188741
    UTILITY UTILITY-ID=HPSTEAM

BLOCK COOLER1 FLASH2
    PARAM PRES=0. DUTY=-4.0771789
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    UTILITY UTILITY-ID=CW

BLOCK COOLER2 FLASH2
    PARAM PRES=0. DUTY=-3.5096161
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    UTILITY UTILITY-ID=CW

BLOCK FLASH FLASH2
    PARAM PRES=0. DUTY=-1.3736872
    HCURVE 1 INDEP-VAR=VFRAC LIST=0. 0.1 0.2 0.3 0.4 0.5  &
0.6 0.7 0.8 0.9 1. PROPERTIES=VLE  &
        PRES-PROFILE=CONSTANT
    PROPERTIES NRTL HENRY-COMPS=CO FREE-WATER=STEAM-TA  &
        SOLU-WATER=3 TRUE-COMPS=YES
    UTILITY UTILITY-ID=PROPANE

BLOCK SCRUBBER FLASH2
    PARAM PRES=0. DUTY=0.
    PROPERTIES NRTL HENRY-COMPS=C2 FREE-WATER=STEAM-TA  &
        SOLU-WATER=3 TRUE-COMPS=YES

BLOCK HX HEATX
    PARAM T-COLD=110. U-OPTION=PHASE F-OPTION=CONSTANT  &
        CALC-METHOD=SHORTCUT
    FEEDS HOT=8 COLD=RICH-LP
    PRODUCTS HOT=13 COLD=RICH-HT
    HOT-SIDE DP-OPTION=CONSTANT
    COLD-SIDE DP-OPTION=CONSTANT

BLOCK ABSORBER RADFRAC
    PARAM NSTAGE=21 ABSORBER=NO MAXOL=200
    COL-CONFIG CONDENSER=NONE REBOILER=NONE
    PROP-SECTION 1 21 ELECNRTL HENRY-COMPS=KEMDEA CHEMISTRY=KEMDEA
    FEEDS 5 21 ON-STAGE / 7 1 ON-STAGE
    PRODUCTS 9 1 V / RICH 21 L
P-SPEC 1 650.<psig>
    COL-SPECS
```

```
    REAC-STAGES 1 21 KEMDEA
    HOLD-UP 1 21 MOLE-LHLDP=0.

BLOCK DEETHANE RADFRAC
    PARAM NSTAGE=40
    COL-CONFIG CONDENSER=TOTAL
    RATESEP-ENAB CALC-MODE=EQUILIBRIUM
    FEEDS 11 25
    PRODUCTS ETHYLENE 1 L / RECYCLE 40 L
P-SPEC 1 43.
    COL-SPECS MOLE-B=380. MOLE-L1=704.036282
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK STRIPPER RADFRAC
    PARAM NSTAGE=21 MAXOL=200
    COL-CONFIG CONDENSER=NONE
    FEEDS RICH-HT 1 ON-STAGE
    PRODUCTS 6 1 V / 8 21 L
    P-SPEC 1 18.5 <psig>
    COL-SPECS B:F=0.975
    REAC-STAGES 1 21 KEMDEA
UTILITIES REB-UTIL=LPSTEAM

BLOCK REACTOR1 RSTOIC
    PARAM PRES=10. DUTY=0.
    STOIC 1 MIXED C2H6 -1. / O2 -0.5 / C2H4 1. / H2O 1.
    STOIC 2 MIXED C2H6 -1. / O2 -1.5 / ACETIC 1. / H2O 1.
    STOIC 3 MIXED C2H6 -1. / O2 -2.5 / CO 2. / H2O 3.
    STOIC 4 MIXED C2H6 -1. / O2 -3.5 / CO2 2. / H2O 3.
    EXTENT 1 34.8
    EXTENT 2 6.98
    EXTENT 3 3.336
    EXTENT 4 1.108
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK REACTOR2 RSTOIC
    PARAM PRES=10. DUTY=0.
    STOIC 1 MIXED C2H6 -1. / O2 -0.5 / C2H4 1. / H2O 1.
    STOIC 2 MIXED C2H6 -1. / O2 -1.5 / ACETIC 1. / H2O 1.
    STOIC 3 MIXED C2H6 -1. / O2 -2.5 / CO 2. / H2O 3.
    STOIC 4 MIXED C2H6 -1. / O2 -3.5 / CO2 2. / H2O 3.
    EXTENT 1 34.8
    EXTENT 2 6.98
    EXTENT 3 3.336
    EXTENT 4 1.108
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK REACTOR3 RSTOIC
    PARAM PRES=10. DUTY=0.
    STOIC 1 MIXED C2H6 -1. / O2 -0.5 / C2H4 1. / H2O 1.
    STOIC 2 MIXED C2H6 -1. / O2 -1.5 / ACETIC 1. / H2O1.
    STOIC 3 MIXED C2H6 -1. / O2 -2.5 / CO 2. / H2O 3.
    STOIC 4 MIXED C2H6 -1. / O2 -3.5 / CO2 2. / H2O 3.
    EXTENT 1 34.8
    EXTENT 2 6.98
    EXTENT 3 3.336
    EXTENT 4 1.108
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK PUMP PUMP
    PARAM PRES=45.9 NPHASE=2
```

```
    PROPERTIES ELECNRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO

BLOCK COMPRESS COMPR
    PARAM TYPE=ISENTROPIC POWER=1140.52832
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK VALVE-1 VALVE
    PARAM CALC-CV=YES P-OUT=5.
    VALVE-DEF VAL-TYPE="GLOBE" MFGR="NELES-JAMESBURY" SERIES= &
        "V500_EQUAL_PERCENT_FLOW" SIZE="4-IN"
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

BLOCK VALVE-2 VALVE
    PARAM CALC-CV=YES P-OUT=10.1 CHECK-CHOKE=NO
    VALVE-DEF VAL-TYPE="GLOBE" MFGR="NELES-JAMESBURY" SERIES= &
        "V810_EQUAL_PERCENT_FLOW" SIZE="0.5-IN"
    PROPERTIES NRTL FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES

UTILITY CW GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=WATER PRES=20. PRES-OUT=20. TIN=90. <F>&
        TOUT=120. <F> CALOPT=FLASH

UTILITY HPSTEAM GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=STEAM PRES=30. PRES-OUT=30. VFRAC=1.  &
        VFR-OUT=0. CALOPT=FLASH

UTILITY LPSTEAM GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=STEAM PRES=3. PRES-OUT=3. VFRAC=1.  &
        VFR-OUT=0. CALOPT=FLASH

UTILITY PROPANE GENERAL
    COST PRICE=0. <$/kg>
    PARAM UTILITY-TYPE=REFRIGERATIO COOLING-VALU=10.256 CALOPT=DUTY

EO-CONV-OPTI

CONV-OPTIONS
    PARAM TOL=1E-010

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC PROPERTIES=GASPROPS XAPP

REACTIONS MDEA-ACI REAC-DIST
    IN-UNITS SI MOLE-ENTHALP='cal/mol' VFLOW-RPM='cuft/hr/rpm'  &
        F-FACTOR='(lb-cuft)**.5/hr'
    DESCRIPTION "LIQUID PHASE REACTION"
    REAC-DATA 1 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 2 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 3 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 4 KINETIC PHASE=L CBASIS=MOLAR
    REAC-DATA 5 KINETIC PHASE=L CBASIS=MOLAR
    REAC-DATA 6 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 7 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    K-STOIC 1 A=-9.41650 B=-4234.980 C=0.0 D=0.0
    K-STOIC 2 A=132.8990 B=-13445.90 C=-22.47730 D=0.0
    K-STOIC 3 A=216.0490 B=-12431.70 C=-35.48190 D=0.0
    K-STOIC 6 A=214.5820 B=-12995.40 C=-33.54710 D=0.0
    K-STOIC 7 A=-9.7420 B=-8585.470 C=0.0 D=0.0
```

```
    RATE-CON 4 PRE-EXP=4.31520E+13 ACT-ENERGY=13249.0
    RATE-CON 5 PRE-EXP=3.74860E+14 ACT-ENERGY=25271.560
    STOIC 1 MDEA+ -1.0 / H2O -1.0 / MDEA 1.0 / H3O+ 1.0
    STOIC 2 H2O -2.0 / H3O+ 1.0 / OH- 1.0
    STOIC 3 HCO3- -1.0 / H2O -1.0 / H3O+ 1.0 / CO3-2 1.0
    STOIC 4 CO2 -1.0 / OH- -1.0 / HCO3- 1.0
    STOIC 5 HCO3- -1.0 / CO2 1.0 / OH- 1.0
    STOIC 6 H2O -1.0 / H2S -1.0 / HS- 1.0 / H3O+ 1.0
    STOIC 7 H2O -1.0 / HS- -1.0 / S-2 1.0 / H3O+ 1.0
    POWLAW-EXP 4 CO2 1.0 / OH- 1.0
    POWLAW-EXP 5 HCO3- 1.0

REACTIONS MDEA-CO2 REAC-DIST
    IN-UNITS SI MOLE-ENTHALP='cal/mol' VFLOW-RPM='cuft/hr/rpm'  &
        F-FACTOR='(lb-cuft)**.5/hr'
    DESCRIPTION "LIQUID PHASE REACTION"
    REAC-DATA 1 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 2 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 3 EQUIL PHASE=L KBASIS=MOLE-GAMMA
    REAC-DATA 4 KINETIC PHASE=L CBASIS=MOLAR
    REAC-DATA 5 KINETIC PHASE=L CBASIS=MOLAR
    K-STOIC 1 A=-9.41650 B=-4234.980 C=0.0 D=0.0
    K-STOIC 2 A=132.8990 B=-13445.90 C=-22.47730 D=0.0
    K-STOIC 3 A=216.0490 B=-12431.70 C=-35.48190 D=0.0
    RATE-CON 4 PRE-EXP=4.31520E+13 ACT-ENERGY=13249.0
    RATE-CON 5 PRE-EXP=3.74860E+14 ACT-ENERGY=25271.560
    STOIC 1 MDEA+ -1.0 / H2O -1.0 / MDEA 1.0 / H3O+ 1.0
    STOIC 2 H2O -2.0 / H3O+ 1.0 / OH- 1.0
    STOIC 3 HCO3- -1.0 / H2O -1.0 / H3O+ 1.0 / CO3-2 1.0
    STOIC 4 CO2 -1.0 / OH- -1.0 / HCO3- 1.0
    STOIC 5 HCO3- -1.0 / CO2 1.0 / OH- 1.0
    POWLAW-EXP 4 CO2 1.0 / OH- 1.0
    POWLAW-EXP 5 HCO3- 1.0
```

APPENDIX D

GAIN MATRICES, SINGULAR VALUES

AND CONDITION NUMBERS

Table 32. Singular values and condition numbers of dehydration process with manipulated variable disturbances.

	MVs Changes	-30%	-20%	-10%	-5%	-2%	-1%	-0.5%	-0.2%	-0.1%
Singular Values (SV)	Max SVs	3.736	5.090	9.122	14.293	16.319	16.530	16.619	16.651	16.657
		2.294	2.904	4.264	4.256	4.241	4.236	4.233	4.231	4.230
		0.967	0.856	0.762	0.759	0.758	0.757	0.757	0.757	0.757
		0.589	0.555	0.407	0.409	0.410	0.410	0.410	0.410	0.410
		0.143	0.152	0.158	0.161	0.162	0.162	0.162	0.164	0.164
	Min SVs	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002
	CNs	1167.469	2036.160	3966.130	6806.095	7770.857	8265.000	8309.550	8325.700	8328.400
	MVs Changes	**0.10%**	**0.2%**	**0.5%**	**1%**	**2%**	**5%**	**10%**	**20%**	**30%**
Singular Values (SV)	Max SVs	16.644	16.651	16.651	16.650	16.625	16.406	15.858	14.683	13.624
		6.621	6.584	6.556	6.534	6.500	6.410	6.278	4.091	3.301
		2.859	2.853	2.848	2.844	2.837	2.817	2.787	2.503	1.962
		0.536	0.536	0.536	0.536	0.535	0.535	0.534	0.526	0.490
		0.401	0.401	0.401	0.401	0.401	0.402	0.402	0.395	0.299
	Min SVs	0.178	0.178	0.175	0.175	0.174	0.175	0.176	0.176	0.161
	CNs	100.688	100.731	102.528	102.462	102.310	100.587	96.754	89.040	83.326

Table 33. Singular values and condition numbers of oxydehydrogenation process with manipulated variable disturbances.

	MVs Changes	**-30%**	**-20%**	**-10%**	**-5%**	**-2%**	**-1%**	**-0.5%**	**-0.2%**	**-0.1%**
Singular Values (SVs)	Max SVs	4.718	4.186	4.176	4.232	4.291	4.319	4.331	4.342	4.365
		3.018	3.178	3.371	3.460	3.519	3.541	3.553	3.558	3.561
		1.881	1.954	2.397	2.716	2.948	3.032	3.075	3.102	3.108
		1.637	1.815	1.845	1.850	1.855	1.857	1.858	1.862	1.861
		1.317	1.293	1.354	1.390	1.423	1.438	1.445	1.450	1.455
		1.184	1.195	1.312	1.371	1.399	1.406	1.410	1.412	1.413
		1.146	0.769	0.890	0.960	1.006	1.023	1.031	1.037	1.042
		0.399	0.363	0.361	0.358	0.362	0.361	0.360	0.359	0.359
		0.084	0.074	0.066	0.063	0.061	0.060	0.060	0.060	0.060
	Min SVs	0.009	0.007	0.006	0.005	0.005	0.005	0.005	0.005	0.004
	CNs	512.804	589.549	732.614	829.784	893.938	899.708	941.522	943.935	992.000
	MVs Changes	**0.10%**	**0.2%**	**0.5%**	**1%**	**2%**	**5%**	**10%**	**20%**	**30%**
Singular Values (SVs)	Max SVs	4.356	4.360	4.362	4.359	4.380	4.485	4.711	5.471	4.518
		3.569	3.571	3.577	3.545	3.548	3.594	3.666	3.777	3.726
		3.127	3.135	3.157	2.543	1.862	1.868	1.885	1.962	1.816
		1.861	1.860	1.858	1.859	1.510	1.535	1.612	1.766	1.727
		1.454	1.454	1.460	1.464	1.431	1.454	1.498	1.622	1.438
		1.414	1.415	1.417	1.422	1.369	1.129	1.232	1.354	1.099
		1.041	1.043	1.048	1.056	1.074	0.938	0.866	0.800	1.054
		0.358	0.358	0.353	0.353	0.352	0.349	0.343	0.325	0.292
		0.060	0.060	0.060	0.059	0.059	0.058	0.056	0.052	0.048
	Min SVs	0.003	0.005	0.005	0.006	0.010	0.014	0.013	0.011	0.005
	CNs	1405.194	927.702	948.217	751.517	429.441	327.387	365.186	511.346	982.152

APPENDIX E

SIMULATION RESULTS FOR CALCULATION OF FLEXIBILITY INDICES

Table 34. Simulation results of the dehydration process.

Variable type	Variables and parameters	Unit	Scenarios 1	2	3	4	5	6	7	8	9
Impact variables	Evaporator steam	kg/h	2,425	2,425	2,425	2,425	2,425	2,425	2,425	2,425	2,425
	Reactor heating oil	kg/h	35,578	0	0	0	0	35,578	35,578	35,578	35,578
	Boiler feed water	kg/h	1,136	0	0	1,136	1,136	0	0	1,136	1,136
	Mixer steam	kg/h	1,802	0	1,802	0	1,802	0	1,802	0	1,802
Control variables	Furnace duty	Gcal/h	0.732	0.732	0.732	0.732	0.732	0.732	0.732	0.732	0.732
	Valve opening	%	46.3	46.3	46.3	46.3	46.3	46.3	46.3	46.3	46.3
	Quench water	kg/h	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Specified parameters	Pump temperature	C	25.2	25.2	25.2	25.2	25.2	25.2	25.2	25.2	25.2
	Evaporator outlet temperature	C	108	108	108	108	108	108	108	108	108
	Mixer outlet temperature	C	116	108	116	108	116	108	116	108	116
	Furnace outlet temperature	C	350	418	350	418	350	418	350	418	350
	Reactor temperature	C	350	102	117	102	117	419	350	419	350
	Boiler outlet temperature	C	160	102	117	63	110	419	350	170	160
	Quench outlet temperature	C	83.1	55.9	76.9	39.3	66.2	77.7	**-68.1**	67.0	83.1
	Scrubber outlet temperature	C	81.3	53.2	74.6	39.4	63.3	75.5	**-65.5**	64.2	81.3
	Dryer inlet temperature	C	81.3	53.2	74.6	39.4	63.3	75.5	**-65.5**	64.2	81.3
	Boiler pressure	BAR	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Valve outlet pressure	BAR	1.9	2.7	2.2	2.8	2.5	2.3	0.0	2.6	1.9

Table 34. (Continued)

Variable type	Variables and parameters	Unit	Scenarios 10	11	12	13	14	15	16	17
Impact variables	Evaporator steam	kg/h	0	0	0	0	0	0	0	0
	Reactor heating oil	kg/h	0	0	0	0	35,578	35,578	35,578	35,578
	Boiler feed water	kg/h	0	0	1,136	1,136	0	0	1,136	1,136
	Mixer steam	kg/h	0	1,802	0	1,802	0	1,802	0	1,802
Control variables	Furnace duty	Gcal/h	0.732	0.732	0.732	0.732	0.732	0.732	0.732	0.732
	Valve opening	%	46.3	46.3	46.3	46.3	46.3	46.3	46.3	46.3
	Quench water	kg/h	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Specified parameters	Pump temperature	C	25.2	25.2	25.2	25.2	25.2	25.2	25.2	25.2
	Evaporator outlet temperature	C	20	20	20	20	20	20	20	20
	Mixer outlet temperature	C	20	110	20	110	20	110	20	110
	Furnace outlet temperature	C	108	112	108	112	108	112	108	112
	Reactor temperature	C	-54	97	-54	97	100	117	100	117
	Boiler outlet temperature	C	-54	97	-130	52	100	117	53	109
	Quench outlet temperature	C	22.6	54.0	4.0	37.8	54.4	76.0	37.5	65.0
	Scrubber outlet temperature	C	29.5	51.3	22.8	38.3	51.8	73.6	38.2	62.1
	Dryer inlet temperature	C	29.5	51.3	22.8	38.3	51.8	73.6	38.2	62.1
	Boiler pressure	BAR	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Valve outlet pressure	BAR	2.9	2.6	3.0	2.8	2.7	2.3	2.9	2.5

Table 34. (Continued)

Variable type	Variables and parameters	Unit	Scenarios 18	19	20	21	22	23	24	25
Impact variables	Evaporator steam	kg/h	2,425	2,425	0	0	0	0	659	655
	Reactor heating oil	kg/h	0	35,578	0	0	0	0	9,667	9,606
	Boiler feed water	kg/h	1,136	0	0	0	1,136	1,136	309	829
	Mixer steam	kg/h	0	1,802	0	1,802	0	1,802	490	487
Control variables	Furnace duty	Gcal/h	0.952	0	0.952	0.952	0.952	0.952	0.952	0.952
	Valve opening	%	46.3	46.3	46.3	46.3	46.3	46.3	46.3	46.3
	Quench water	kg/h	30,000	30,000	30,000	30,000	30,000	30,000	30,000	30,000
Specified parameters	Pump temperature	C	25.2	25.2	25.2	25.2	25.2	25.2	25.2	25.2
	Evaporator outlet temperature	C	108	108	20	20	20	20	103	103
	Mixer outlet temperature	C	108	116	20	110	20	110	108	108
	Furnace outlet temperature	C	494	116	108	113	108	113	158	157
	Reactor temperature	C	108	120	-11	104	-11	104	101	100
	Boiler outlet temperature	C	85	120	-11	104	-107	76	94	76
	Quench outlet temperature	C	45.5	81.8	29.4	59.1	9.7	43.9	50.8	43.1
	Scrubber outlet temperature	C	44.1	79.9	33.1	56.2	24.4	42.7	48.6	42.2
	Dryer inlet temperature	C	44.1	79.9	33.1	56.2	24.4	42.7	48.6	42.2
	Boiler pressure	BAR	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Valve outlet pressure	BAR	2.8	2.1	2.9	2.6	3.0	2.7	2.7	2.8

Table 35. Simulation results of the oxydehydrogenation process.

Variable type	Variable and parameter	Unit	Scenarios 1	2	3	4	5	6	7	8
Impact variables	Cooler 1 Cooling water rate	kg/h	245,737	245,737	245,737	245,737	0	0	0	0
	Cooler 2 Cooling water rate	kg/h	211,529	211,529	0	0	211,529	211,529	0	0
	Cooler 4 Cooling water rate	kg/h	161,025	0	161,025	0	161,025	0	161,025	0
Control variables	Heater steam rate	kg/h	6,611	6,611	6,611	6,611	6,611	6,611	6,611	6,611
	Quench water rate	kg/h	34,000	34,000	34,000	34,000	34,000	34,000	34,000	34,000
Specified parameters	Reactor 1 cooler temperature	C	396	396	396	396	396	396	396	396
	Reactor 2 mixed inlet temperature	C	90	90	90	90	396	396	396	396
	Reactor 2 cooler temperature	C	368	368	368	368	586	586	586	586
	Reactor 3 mixed inlet temperature	C	90	90	368	368	343	343	586	586
	Reactor 3 cooler temperature	C	375	375	570	570	538	538	750	750
	Scrubber temperature	C	71	71	122	122	126	126	148	148
	Compressor temperature	C	193	193	223	223	223	223	226	226
	Product concentration	%mol	96.7	96.7	94.1	94.1	90.7	90.7	89.7	89.7
	Production rate	kg/h	3,301	3,301	3,409	3,409	3,550	3,550	3,579	3,579

Table 35. (Continued)

Variable type	Variable and parameter	Unit	Scenarios						
			9	10	11	12	13	14	15
Impact variables	Cooler 1 Cooling water rate	kg/h	245,737	245,737	0	0	0	0	90,925
	Cooler 2 Cooling water rate	kg/h	0	0	211,529	211,529	0	0	78,268
	Cooler 4 Cooling water rate	kg/h	161,025	0	161,025	0	161,025	0	59,578
Control variables	Heater steam rate	kg/h	0	0	0	0	0	0	0
	Quench water rate	kg/h	43,000	43,000	43,000	43,000	43,000	43,000	43,000
Specified parameters	Reactor 1 cooler temperature	C	152	152	152	152	152	152	152
	Reactor 2 mixed inlet temperature	C	-33	-33	152	152	152	152	78
	Reactor 2 cooler temperature	C	1,479	1,479	394	394	394	394	364
	Reactor 3 mixed inlet temperature	C	1,479	1,479	123	123	394	394	251
	Reactor 3 cooler temperature	C	1,244	1,244	374	374	581	581	479
	Scrubber temperature	C	30	30	92	92	132	132	95
	Compressor temperature	C	30	30	92	92	132	132	95
	Product concentration	%mol	0.0	0.0	91.3	91.3	90.7	90.7	95.8
	Production rate	kg/h	10,909	10,971	3,526	3,526	3,551	3,551	3,342

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